Polymers for Electro-optic Applications

A thesis submitted to the Board of the Faculty of Physical Sciences
in partial fulfilment of the requirements for the degree of

Doctor of Philosophy of The University of Oxford

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Hilary Term 2006

ABSTRACT
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Submitted in partial fulfilment of the requirements for the degree of D. Phil.

Polymer based photovoltaic cells are being intensively investigated. In such cells three key processes need to occur; namely light absorption, charge separation of the exciton, and transport of the separated charges to the electrodes. Light absorption is reliant on the optical density of the polymer. In general charge separation is achieved by blending an electron acceptor with the polymer film. However, blending materials gives rise to potentially unreliable manufacturing and lifetime issues. This thesis describes the preparation of poly(1,4-phenylenevinylene) derivatives containing dipoles in which the process of charge separation can be achieved intramolecularly. The dipole was created with the use of electron donating alkoxy groups attached to the polymer backbone, and electron withdrawing nitro group attached to the fluorenyl side chains. These groups are believed to facilitate the dissociation of the photogenerated exciton, and potentially stabilise the holes and electrons that are formed when the exciton is separated. The fluorenyl side chains were attached to the polymer backbone *via* biphenyl or vinyl linkages. The polymers were primarily formed using the Gilch method and the conjugated polymers were obtained either *via* a soluble precursor route or directly from the monomer. The photophysical properties were studied for polymers with the fluorenyl side-chains as they were found to be more easily formed and stable. For poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] it was found that the photoluminescence quantum yield dropped by a factor of eight relative to the polymer without the nitro group. It was further elucidated that this was due to the exciton being separated. Solar cells containing the polymers from this study showed modest performance.

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. P. L. Burn. for allowing me to do D. Phil. in his group, and for his encouragement and advice throughout the project work.

I would also like to thank Dr. Hazel Assender, Department of Materials (University of Oxford), Prof. Ifor Samuel, Department of Physics (University of St. Andrews) and their research groups for the physics and fabrication of devices using my polymers.

I would like to thank the Felix Scholarship for funding my studies and stay at Oxford, without their help I could not even imagine myself here. I would also like to thank UK trains, which made me think of doing my higher studies at Oxford.

My many thanks goes to the Burn group who helped me a lot and made my stay delightful. Especially, Dr. G. R. Webster and Dr. S. -C. Lo for their valuable suggestions, Dr. P. Ferreira and Dr. K. Knights for the proof reading, Dr. S. Sharma, Dr. C. Shipley and Dr. W. Mitchell for their encouragement and moral support, P. Deakin, N. Cumpstey (will soon be Dr.), and Dr. Y. -J. Pu for their general help.

I would like to thank the Dyson Perrins Laboratory (Old Chemistry Building) and the Chemistry Research Laboratory (New Chemistry Building) for the space, allowing access to instruments and the people especially, Dr. N. Oldham and Mr. C. Sparrow for the mass analysis, Dr. T. Claridge (archiving n.m.r) and Dr. B. Odell for the quick n.m.r. analysis, and Levi Dash for the general help.

Above all, I would like to thank my husband, Amit, for always being supportive and encouraging (even in chemistry...ha ha), my mother (and *late* father) for making my dreams, and the love of my family.

TABLE OF CONTENTS

CHAPTER 1

1 INTRODUCTION **1**
1.1 HISTORICAL BACKGROUND 1
1.2 PRINCIPLES OF OPERATION OF ORGANIC SOLAR CELLS 2
1.2.1 Basic steps of photovoltaic energy conversion 2
1.2.2 Photovoltaic cell performance 3
1.3 ORGANIC SOLAR CELLS 6
1.3.1 Dye Sensitised Nanocrystalline Solar Cells (DSSCs) 6
1.3.1.1 Solar Energy Conversion in Nanocrystalline Cells 10
1.3.2 Polymer Based Photovoltaic Cells 13
1.3.2.1 Solar Energy Conversion in Organic Polymer Based Solar Cells 14
1.4 SYNTHETIC ROUTES FOR CONJUGATED POLYMER 20
1.5 PROJECT AIM(S) 22

CHAPTER 2

2 MONO-BI-PHENYL LINKED PPV DERIVATIVES **25**
2.1 INTRODUCTION 25
2.2 POLY[2-(9,9-DIPROPYLFLUORENYL)-5-(2'-ETHYLHEXYLOXY)-1,4-PHENYLENEVINYLENE] 28
2.2.1 Monomer synthesis 28
2.2.1.1 Retrosynthetic analysis of the Fluorenyl monomer 28
2.2.1.2 Synthesis of the Fluorenyl monomer 29
2.2.2 Polymerisation of the Fluorenyl monomer 32
2.2.3 Properties of the Fluorenyl-PPV 34
2.3 POLY[2-(7-NITRO-9,9-DIPROPYLFLUORENYL)-5-ALKOXY-1,4-PHENYLENEVINYLENE] 44
2.3.1 Synthesis of the Nitrofluorenyl monomers 44
2.3.1.1 Retrosynthetic analysis of the Nitrofluorenyl PPV monomers 45
2.3.1.2 Nitrofluorenyl monomer synthesis 47
2.3.2 Poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-methoxy-1,4-phenylenevinylene] 57
2.3.2.1 Synthesis of chloro-precursor of Methoxy-nitrofluorenyl-PPV 57
2.3.2.2 Properties of chloro-precursor polymer and its thermal conversion to conjugated polymer 59
2.3.2.3 Summary 65
2.3.3 Poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] 66
2.3.3.1 Synthesis of the soluble 2-Ethylhexyloxy-nitrofluorenyl-PPV 67
2.3.3.2 Synthesis of chloro-precursor of 2-Ethylhexyloxy-nitrofluorenyl-PPV 68
2.3.3.3 Comparison of the Properties of precursor polymer and conjugated polymers 69

2.3.3.4 Summary 78
2.4 PHOTOPHYSICAL AND DEVICE PROPERTIES 79
2.5 CONCLUSIONS 83

CHAPTER 3

3 *Bis*-BI-PHENYL LINKED PPV DERIVATIVES 84
3.1 INTRODUCTION 84
3.2 POLY{2-[7-(9,9-DIPROPYLFLUORENYL)-9,9-DIPROPYLFLUORENYL]-5-(2'-ETHYLHEXYLOXY)-1,4-PHENYLENEVINYLENE} 85
3.2.1 Retrosynthetic analysis of the *Bis*-fluorenyl monomer 85
3.2.2 Synthesis of the *Bis*-fluorenyl monomer 88
3.2.2.1 Protecting groups 89
3.2.3 Polymerisation 98
3.2.4 Properties of the *Bis*-fluorenyl PPV 99
3.2.5 Summary 105
3.3 POLY{2-[7-(7-NITRO-9,9-DIPROPYLFLUORENYL)-9,9-DIPROPYLFLUORENYL]-5-(2'-ETHYLHEXYLOXY)-1,4-PHENYLENEVINYLENE} 105
3.3.1 Monomer synthesis 105
3.3.2 Polymerisation and properties of the Nitro-*bis*-fluorenyl PPV 108
3.3.3 Summary 113
3.4 CONCLUSIONS 113

CHAPTER 4

4 MONO-VINYL LINKED PPV DERIVATIVES 114
4.1 INTRODUCTION 114
4.2 POLY{2-[(*E*)-2-(9,9-DIPROPYLFLUORENYL)VINYL]-5-(2'-ETHYLHEXYLOXY)-1,4-PHENYLENEVINYLENE} 116
4.2.1 Synthesis of the Fluorenylvinyl monomer 116
4.2.1.1 Retrosynthetic analysis of the Fluorenylvinyl monomer 116
4.2.1.2 Attempted synthesis of the Monomer (X = Cl) *via* the Heck reaction 117
4.2.1.3 Alternative retrosynthetic analysis of the Fluorenylvinyl monomer 123
4.2.1.4 Synthesis of the Monomer *via* the Horner-Emmons-Wadsworth 124
4.2.1.5 Retrosynthetic analysis of the Monomer *via* the protection route 128
4.2.1.6 Synthesis of the Fluorenylvinyl monomer *via* the protection route 130
4.2.1.7 Summary 140
4.2.2 Polymerisation of the Monomer and properties of the Fluorenylvinyl-PPV 141
4.2.3 Attempted synthesis of the Fluorenylvinyl *bis*-xanthate monomer 148
4.2.4 Summary 149
4.3 POLY{2-[(*E*)-2-(7-NITRO-9,9-DIPROPYLFLUORENYL)VINYL]-5-ALKOXY-1,4-PHENYLENEVINYLENE} 150
4.3.1 Synthesis of the Alkoxy-nitrofluorenylvinyl monomers *via* the Heck reaction 151
4.3.1.1 Alternative Heck route 153

4.3.1.2 Alternative route for the synthesis of Ethylhexyloxy-nitrofluorenylvinyl monomer 158
4.3.1.2.1 Attempted de-alkylation and re-alkylation route 158
4.3.1.2.2 Nitration route 160
4.3.1.3 Synthesis of the Ethylhexyloxy-nitrofluorenylvinyl monomer *via* the protection method 161
4.3.1.4 Methoxy-nitrofluorenylvinyl monomer synthesis *via* radical method 165
4.3.2 Polymerisation of the Alkoxy-nitrofluorenylvinyl monomers 167
4.3.2.1 Synthesis and properties of the Methoxy-nitrofluorenylvinyl PPV precursor polymer and the conjugated polymer 167
4.3.2.1.1 Summary 173
4.3.2.2 Attempted synthesis of the Ethylhexyloxy-nitrofluorenylvinyl PPV 174
4.3.3 Attempted synthesis of the Nitrofluorenyl *bis* xanthate monomer 176
4.3.3.1.1 Summary 177
4.4 CONCLUSIONS 177

CHAPTER 5

5 SUMMARY & OUTLOOK 180

CHAPTER 6

6 EXPERIMENTAL 182
6.1 GENERAL PROCEDURES 182
6.2 EXPERIMENTAL FOR CHAPTER 2 184
6.2.1 Synthesis of poly[2-(9,9-dipropylfluorenyl)-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] 184
6.3.1 Synthesis of poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-methoxy-1,4-phenylenevinylene] 192
6.4.1 Synthesis of poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] 204
6.3 EXPERIMENTAL FOR CHAPTER 3 212
6.5.1 Synthesis of poly{2-[7 (9,9-dipropylfluorenyl)-9,9-dipropylfluorenyl]-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene} 212
6.6.1 Synthesis of poly{2-[7 (7-nitro-9,9-dipropylfluorenyl)-9,9-dipropylfluorenyl]-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene} 228
6.4 EXPERIMENTAL FOR CHAPTER 4 237
6.7.1 Synthesis of poly{2-[(*E*)-2-(9,9-dipropylfluorenyl)vinyl]-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene} 237
6.8.1 Synthesis of poly{2-[(*E*)-2-(7-nitro-9,9-dipropylfluorenyl)vinyl]-5-methoxy-1,4-phenylenevinylene} 260
6.9.1 Synthesis of poly{2-[(*E*)-2-(7-nitro-9,9-dipropylfluorenyl)vinyl]-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene} 270

7 REFERENCES 288

ABBREVIATIONS

AIBN	2,2'-Azo*bis*(2-methylpropionitrile)
a.m.u.	Atomic Mass Units
aq	Aqueous
bp	Boiling Point
BuLi	Butyllithium
CI	Chemical Ionisation
CuPc	Copper phthalocyanine
δ	Chemical shifts
Δ	Heat at reflux
DCM	Dichloromethane
DHP	Dihydropyran
DIBAL-H	Diisobutylaluminium hydride
DMAP	4-*N,N*-Dimethylaminopyridine
DMF	*N,N*-dimethylformamide
DSC	Differential Scanning Calorimetry
DSSC	Dye Sensitised Solar Cell
EDG	Electron Donating Group
$\eta_{AM1.5}$	Efficiency at AM1.5 conditions (AM is air mass)
EI	Electron Impact Ionisation
e.s.r.	Electron Spin Resonance
EWG	Electron Withdrawing Group
g.p.c.	Gel Permeation Chromatography
Prep-gpc	Preparatory Gel Permeation Chromatography
HMDS	1,1,1,3,3,3-Hexamethyldisilazane
HOMO	Highest Occupied Molecular Orbital
Hz	Hertz
i-	Iso
IR	Infrared
ITO	Indium Tin Oxide
J	Coupling Constant
λ_{max}	Wavelength at maximum absorption
LUMO	Lowest Unoccupied Molecular Orbital
M	Molar Concentration, mol dm^{-3}
MDMO	Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]
Me	Methyl
MEHPPV	Poly[5-methoxy-2-(2'-ethylhexyloxy)-1,4-phenylenevinylene]
mg	Milligram
MHz	Megahertz
M^+/MH^+	Molecular ion
min	Minute
mol	Moles
mp	Melting Point
m/z	Mass to charge ratio
$\overline{M}_w$	Weight Average Molecular weight
$\overline{M}_n$	Number Average Molecular Weight
n-	Normal
n.m.r.	Nuclear Magnetic resonance

OLED	Organic Light Emitting Diode
PCBM	1-(3-Methoxycarbonylpropyl)-1-phenyl-[6.6]C_{61}
PD	Polydispersity
PEDOT	Poly[3,4-(ethylenedioxy)-thiophene]
P3HT	Poly(3-hexylthiophene-2,5-diyl)
PL	Photoluminescence
PPV	Poly(1,4-phenylenevinylene)
PSS	Poly(styrenesulphonate)
PV	Photovoltaics
Py	Pyridine
r.p.m.	Revolutions per Minute
r.t.	Room Temperature
TBAB	Tetra-*n*-butylammonium bromide
TBDMS	*t*-Butyldimethylsilyl
TEA	Triethylamine
TGA	Thermogravimetric analysis
T_g	Glass Transition Temperature
THF	Tetrahydrofuran
THP	Tetrahydropyranyl
TMS	Trimethylsilyl
t.l.c.	Thin Layer Chromatography
U.V.	Ultraviolet

INTRODUCTION

Chapter 1

1 INTRODUCTION

1.1 Historical Background

The first example of a rudimentary solar cell was discovered in 1839 when Becquerel showed that a voltage was formed when light was shone onto a metal electrode in an electrolyte solution. In 1906, Pochettino discovered that anthracene showed photoconductivity[1] Semiconducting properties of some organic dyes such as methylene blue came into the picture in the early 1960s. After the discovery of dyes, many other naturally occurring biological classes were explored for the photovoltaic (PV) effect. The scientific community was attracted towards the photosynthetic processes of plants and some microorganisms. They found that carotenes, chlorophyll and phthalocyanines also show a PV effect. Simultaneously there was progress recorded in solar cells based on inorganic compounds. In 1954 a leap in the production of more efficient solar cells took place when single crystals of silicon were used as the active layer and efficiencies of 6% were achieved by Bell Laboratories. Since then there has been ongoing research on methods for the improvement and commercialisation of solar energy harvesting. Throughout the later half of the twentieth century significant improvement in solar cells was seen with the use of amorphous silicon and increased purity of silicon wafers allowing the preparation of solar cells with efficiencies of up to 35% in research laboratories and 19% in commercial cells[2] Other inorganic materials that have been used in solar cells include copper indium gallium selenide (CIGS) and cadmium telluride (CdTe) with efficiencies ranging between 15 to 20%. However, there are several

problems associated with these materials in large-scale production including high cost and toxicity, and in addition they tend to be brittle, thus limiting their general applications[3].

As a consequence solar cells based on organic materials (plastic solar cells) have come to the fore as an important area of research and development. Grätzel, in 1991, discovered the first organic photovoltaic cell based on a dye sensitised nanocrystalline material[4], and in the early 1990s scientists began to explore conjugated polymers for PV[5-6] Since then there has been a surge in the development of organic solar cells as they could provide a better a prospective than their inorganic competitors. Organic based solar cells have the potential to be used in thin, lightweight and inexpensive cells, which can be flexible and manufactured on a large-scale. The physical flexibility associated with plastic solar cells will allow them to be used in applications in which brittle inorganic solar cells cannot be used.

1.2 Principles of operation of organic solar cells

1.2.1 Basic steps of photovoltaic energy conversion

For organic photovoltaic devices to work, three key processes need to occur: namely, light absorption, charge separation, charge transport and charge collection at the electrodes. All the steps are important and optimisation of each step is required to create the best PV devices. The physical or chemical processes behind these principal steps vary between different types of solar cells and photovoltaic materials. In the standard

inorganic pn-junction solar cell, light absorption occurs *via* band gap excitation of electrons in the bulk of the semiconductor, charge separation caused by the internal electric field occurs at the pn-junction, and charge is collected by transport of electrons and holes (electric current) through the bulk of the semiconductor to the electrical contacts. An ideal light absorbing material is one which absorbs all the wavelengths of the sunlight, that is, follows the solar spectrum. The peak intensity in the solar spectrum appears in the visible just below 500 nm, and the spectrum extends well into the near-infrared region. The light absorption characteristics of the material depend upon its structure and needs to be considered when designing organic materials for solar cells. Over the last decade, advances in organic solar cells have been steady and improvements have been achieved by changing either the cell geometry of the device, or the material selection, or both.

1.2.2 Photovoltaic cell performance

The efficiency by which a light absorbing material converts photons to electrons is called the incident photon:converted electron (IPCE) efficiency and is defined by Equation **1-1**. Sometimes IPCE is also referred to the external quantum efficiency (EQE). The IPCE of a cell is dependant on the quantum yield for charge injection (Φ), and the efficiency of electron collection (η) in the external circuit and both these correspond to kinetic parameters.

$$\text{IPCE}, \eta_c = \text{LHE} \cdot \Phi \cdot \eta$$

Equation 1- 1: Calculation of IPCE efficiency

The IPCE is a function of light harvesting efficiency (LHE) of the dye and therefore dependant upon surface area of the semiconductor and the absorption cross-section of the molecular sensitiser.

This is a complicated method for calculation of the IPCE efficiency and in practice the IPCE efficiency is calculated by use of Equation **1-2**. This involves the use of monochromatic light of wavelength λ and power P_{in}, with I_{sc}, the short circuit current which is the output current of a solar cell when the voltage is zero, determined from photocurrent spectra.

$$\text{IPCE}, \eta_c = \frac{1240 \cdot I_{sc}}{\lambda \cdot P_{in}}$$

I_{sc} = Short circuit current ($mAcm^{-2}$)
λ = Wavelength (nm)
P_{in} = Photon flux (Wm^{-2})

Equation 1- 2: Calculation of IPCE efficiency by spectral methods

A correction of the IPCE has to be made to take into account the reflection and absorption losses due to the semiconductor and glass to show the efficiency of the dye at absorbing all photons incident upon the dye. Incident Photon to Conducted Electron (IPCE) measurement is wavelength dependent and hence it is relatively simple to determine how efficient a material is at converting light into electrons. In the literature IPCE are often quoted at a particular wavelength giving what seem to be excellent efficiencies. However, the IPCEs tend to be reported at the absorption maxima of the material and, not from the effect of the complete solar spectrum. Therefore, IPCE is not a good parameter to compare with different materials that absorb at different wavelengths.

The overall efficiency or global efficiency of a solar device (η_e) is the correct value for comparing device performance, and is obtained from Equation **1-3**. η_e combines the effect of every factor, which influences the photovoltaic device performance.

$$\eta_e = \frac{V_{oc} \cdot I_{sc} \cdot FF}{P_{in}}$$

V_{oc} = Open circuit voltage
I_{sc} = Short circuit current
FF = Fill factor
P_{in} = Incident light power

$$\text{where, } FF = \frac{I_{pp} \cdot V_{pp}}{V_{oc} \cdot I_{sc}}$$

I_{pp} = Current at peak power
V_{pp} = Voltage at peak power

Equation 1- 3: Calculation of overall solar cell efficiency[7]

The open circuit voltage, V_{oc}, is the voltage when the current flow in the device is zero. The fill factor of a photovoltaic device is the maximum output of the device at peak power. Theoretically the maximum value of FF value is 1.0; values of 0.6-0.7 (dyes) and 0.4-0.5 (conjugated polymers) have been achieved.

The efficiency of the solar cell depends on the temperature of the cell, and which is even more important, on the quality of the illumination, that is the total light intensity and the spectral distribution of the intensity. For this reason, a standard measurement condition has been developed to facilitate comparable testing of solar cells between different laboratories. The standard conditions used for testing of terrestrial solar cells require the light intensity to have a power at 1000 Wm^{-2}, a spectral distribution of AM1.5 global standard solar spectrum [AM 1.5 (AM is air mass) ≡ 1 Sun], and a temperature of the cell at 25 °C. The power output of the solar cell at these conditions is the nominal power of the cell, or module, and is reported in *peak* watts, Wp. In practice, special solar

simulator light sources are used for the standard measurements and these do not exactly match the solar spectrum. Hence, Equation **1-3** has been modified to Equation **1-4** to take into account the mismatch factor (M) between the solar simulator and sun spectra.

$$\eta_{AM\,1.5} = \eta_e \cdot M \qquad M = \text{Spectra mismatch factor}$$

Equation 1- 4: Efficiency at AM1.5[7]

The device efficiencies can only be compared if the measurements are performed under AM1.5 conditions. However, the efficiencies are not always quoted at standard conditions and sometimes it is only possible to compare IPCE at specific wavelengths.

1.3 Organic solar cells

Organic solar cells can be broadly classified depending on the nature of the light absorbing material as either dye sensitised or polymer based cells.

1.3.1 Dye Sensitised Nanocrystalline Solar Cells (DSSCs)

Nanocrystalline dye-sensitised solar cells are promising candidates for low-cost and efficient photovoltaic devices[8-9]. These devices are based on the successful combination of nanostructured electrodes and efficient charge injection dyes. These devices consist of a wide band-gap semiconductor material with a large internal surface area. Onto this surface a dye is chemically adsorbed and upon excitation of the dye by light, the excited dye is oxidised (giving up an electron to the circuit), and a redox system

is used to regenerate the dye back to the neutral ground state before excitation can take place again. The first significant progress made in the preparation of an efficient dye sensitised nanocrystalline solar cell was achieved by Grätzel *et al.* in 1991[4]. This solar cell is called the dye sensitised nanocrystalline solar cell or the Grätzel cell after its inventor.

The simple dye sensitised solar cell consists of five important components, as highlighted in Figure **1-1**. The device architecture is comprised of cathode/metal oxide/dye/anode/transparent substrate. There are two conducting electrodes between which there is a metal oxide layer onto which a dye is chemisorbed with either a redox electrolyte solution or the hole transport layer.

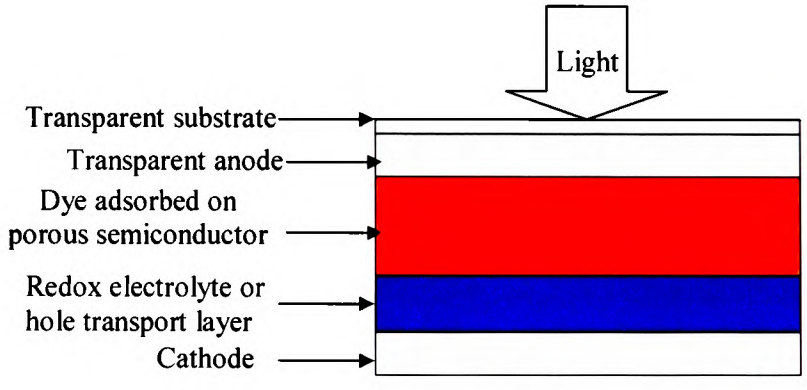


Figure 1- 1: Simple Nanocrystalline Solar Cell

The anode must be transparent to allow light into the device. The material used for the anode is usually tin oxide:fluoride (SnO_2:F). Onto the anode a wide band gap oxide mesoporous semiconductor layer, usually TiO_2, is deposited. Titanium dioxide, TiO_2, has several advantages over other metal oxides. It is cheap to produce in high purity, non-toxic, abundant, good transparency and environmentally safe. Alternatively

other wide band gap oxides such as ZnO, CdSe, WO_3 and SnO_2, and Nb_2O_5 have also been investigated with varying degrees of success[8] but have generally given lower efficiencies due to mismatch of energy levels of dye and semiconductor, and aggregation problem. The factor which generally determines the choice of semiconductor is that the band edge of the band gap must be below the LUMO of the dye used, otherwise injection of the electron into the conduction band of the semiconductor will not occur. TiO_2 is deposited from a colloidal solution, and electronic contact between the particles is achieved by sintering at high temperature. This produces a porous layer with a large surface area and allows a high loading of a monolayer of the sensitising dye. The formation of a chemisorbed monolayer of dye molecules upon the surface of the TiO_2 occurs by placing the semiconductor in a solution containing the dye. Many of the dyes used in nanocrystalline solar cells are based on inorganic transition metal complexes and in particular $Ru(bipy)_2X_2$[4,10-13] based materials and more recently small organic chromophores have been used[14-17] The best $\eta_{AM1.5}$ reported for ruthenium dye **1.1**, Figure **1-2** (ITO/TiO_2/dye**1.1**/LiI:I_2:guanidinium thiocyanate:organic solvent/Pt) is 11%[13]. Organic dyes offer three advantages: *(i)* they are a cheaper alternative to produce than complexes containing rare transition metals; and *(ii)* allow an easier tuning of the wavelength of light absorbed; *(iii)* they do not suffer from recycling problems associated with heavy metals. However, the organic dyes suffer from the problem of oxidative degradation on metal-oxide[14]. A common characteristic of organic dyes is the presence of Donor-pi-acceptor (D-π-A) structure, which can produce a large dipole moment favourable for charge separation. The π-network between the donor and acceptor groups could be varied affecting the conjugation length and thereby controlling the light

absorption characteristics of the dye. The most efficient DSSC (ITO/TiO_2/dye**1.2**/LiI:I_2:organic solvent/Pt) with a small organic molecule, indoline dye **1.2** (Figure **1-2**) has a $\eta_{AM1.5}$ of 6.5%[17].

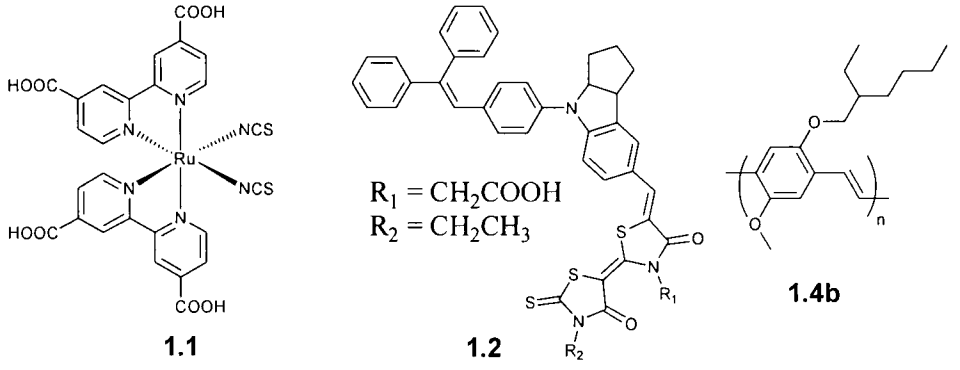


Figure 1- 2: Inorganic dye (N3) **1.1**, Organic dye (Indoline) **1.2**, and MEHPPV **1.4b**

Conjugated polymers[18-22] have also been used as the sensitiser in DSSCs but have been significantly less efficient, at best $\eta_{AM1.5}$ of 0.5% for (SnO_2:F/TiO_2/MEHPPV**1.4b**:electron acceptor(1:1.6 w/w)/Au)[22] {poly[5-methoxy-2-(2'-ethylhexyloxy)-1,4-phenylenevinylene] **1.4b**, **Figure 1-2**, (MEHPPV)}. The main reasons for the lower efficiency is incomplete pore filling by the polymer into the TiO_2 matrix resulting in a poor polymer semiconductor interface and the fact that the polymer, which generally has a low hole mobility, also acts as the hole transport layer. That is, the oxidised polymer at the interface is only slowly reduced back into its neutral ground state. The redox electrolyte or hole transport layer system used is crucial to the function of the solar cell as this allows reduction of the dye/conjugated polymer back into the neutral electronic configuration[9]. The reduction process must be fast, otherwise the overall cycle of the solar cell is slowed, affecting the device performance[8]. The best electrolyte thus far

has been the iodide/triiodide (I^-/I_3^-) couple but the disadvantage of this is that it is a solution based system and prone to leakage. The use of non-volatile ionic liquids, such as imidazolium iodides improves the stability but decreases $\eta_{AM1.5}$ to 6%[13]. Other ways to solve the instability and leakage problem of the regenerative layer have been to use quasi-solid-state[23-25]or solid-state hole transporting semiconductors, including inorganic materials such as CuI[26], CuSCN[27] and conjugated small molecules[28-30] or polymers[31-34]. The problems with all these materials is poor intimate contact, charge mobility, and thermal stability through them is generally less efficient as compared to liquid electrolytes resulted in significantly lower device efficiencies. Polymer electrolytes have provided a $\eta_{AM1.5}$ of up to 2.6%[23] but recently 8.1%[24] has been reported. Both devices involved *in-situ* polymerisation of monomers to form a cross-linked polymer allowing a better interface between TiO_2 and the solid electrolyte. The metal cathode used is normally a metal, chosen so that catalysis of the cathodic reduction of the redox system can occur easily[10] such as platinum. Finally, cell was encapsulated as a protection against aerial oxidation of the dye and electrodes.

1.3.1.1 Solar Energy Conversion in Nanocrystalline Cells

The working cycle of a typical DSSC with a TiO_2 semiconductor layer and I^-/I_3^- couple as an electrolyte regeneration layer is depicted in Figure **1-3**. When the nanocrystalline cell absorbs light, excitation of the dye occurs. This causes an electron to be promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in the dye. Charge separation occurs by injection

of the excited electron into the conduction band of titanium dioxide and a hole transport process from thereby oxidised dye to the electrolyte. The electron transfer mechanism is strongly dependent on the electronic structure of the adsorbed dye molecule and the energy level matching between the excited state of the dye and the conduction band of the TiO_2.

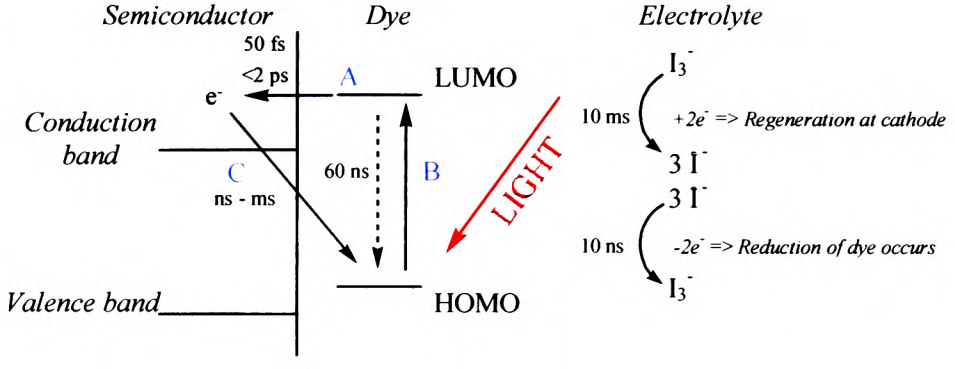


Figure 1- 3: Principle of operation and kinetics of TiO_2/Ru dye/electrolyte interfaces

It is best if the LUMO level of the dye is above the conduction band edge of the TiO_2 and the dye's HOMO level is below the chemical potential of the I^-/I_3^- redox pair in the electrolyte, both presenting an energetic driving force for the electron and hole separation. The neutral ground state of the dye is subsequently restored by electron donation from the electrolyte. The charge transport occurs with electrons moving through the nanostructured TiO_2 electrode and "hole" transport in the electrolyte. Finally, the I^- is regenerated by the reduction of the I_3^- at the counter electrode and this process allows charge to flow from the cathode and thus the circuit is completed. In principle, the operation of the cell is regenerative in nature, since no chemical substances are consumed or produced during the working cycle. The efficiency of DSSCs is affected by a number

of factors[35]. First electron traps in the TiO_2 can reduce the current. Second, the kinetics of each step of the pathway needs to be optimised and there is a need of each step to occur concurrently to allow its smooth functioning in the desired fashion. For example, the nanocrystalline photovoltaic cell with titanium dioxide as the semiconductor, a ruthenium based dye and an I^-/I_3^- redox system, studies have shown that the injection of an electron from the LUMO of the dye into the conduction band of the semiconductor is an extremely fast process, even though it occurs in two stages (Process A), Figure **1-3**. The first stage, which corresponds to the bulk of electron injection (84%), takes place in about 50 fs, with the second stage (16%) taking place at a slower time of about 2 ps[36]. The slower component is very sensitive to the condition of the sample, for example the purity of the dye. Relaxation of the excited dye back to the ground state is a much slower process, which occurs in about 60 ns, Process B, Figure **1-3**. Reduction of the oxidised dye (in its excited state) can occur either by electron injection from the semiconductor, which is unfavourable, or by use of a suitable redox system. Reduction of the dye from TiO_2 can occur, but is at least three orders of magnitude slower, Process C, Figure **1-3**. The most crucial aspect of the nanocrystalline solar cell is the rate of reduction of the oxidised dye by the redox system, in this instance iodide. This process has to be fast otherwise poor collection yields and low life cycle of the sensitiser occurs. It has been shown that reduction of the dye occurs in about 10 ns, with the redox system regenerated at the cathode in ~10 ms[37] The regeneration of the dye by I^- is also a very fast reaction occurring in 10 ns in the normal conditions in the DSSC. This is important for obtaining high cycle life for the dye, since lack of adequate conditions for the regeneration leads to dye degradation[9,38]. In general, the kinetics of each step in a DSSC is affected by the

nature of the dye and the semiconductor, and the redox couple and these have to be selected to best match the various rates.

1.3.2 Polymer Based Photovoltaic Cells

Photovoltaic cells based upon polymeric materials are an alternative for the preparation of low cost, efficient and flexible solar cells. In their simplest form[39] they consist of an organic photoactive material sandwiched between an anode and a cathode, Figure **1-4**.

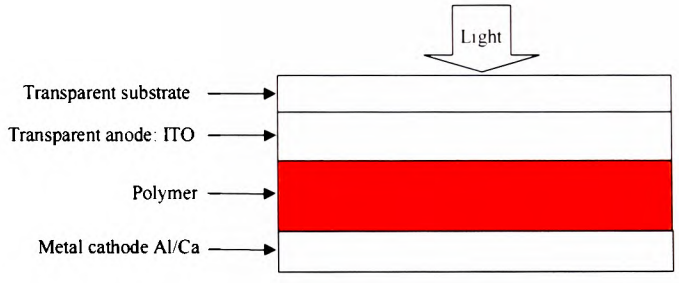


Figure 1- 4: Simple organic polymer based photovoltaic cell

One of the electrodes, usually the anode, must be transparent to allow light into the device. The most commonly used anode material is indium tin oxide (ITO) onto which the conjugated polymer is deposited by spin-coating from solution. The cathode is normally a low work function metal such as aluminium or calcium, which are deposited by vapour deposition. As these metals are reactive to atmospheric oxygen, efficient encapsulation of the solar cell is essential[40].

1.3.2.1 Solar Energy Conversion in Organic Polymer Based Solar Cells

Conjugated polymers can act as semiconductors due to delocalisation of the π-bonds along the polymer backbone[41-42]. The difference in energy between HOMO and LUMO generally lies in the range of 1.5-3 eV (830-400 nm) for conjugated polymers. When light is absorbed by the conjugated polymer based solar cell, an electron is excited from the HOMO into the LUMO of the conjugated polymer to form an exciton, Figure **1-5**.

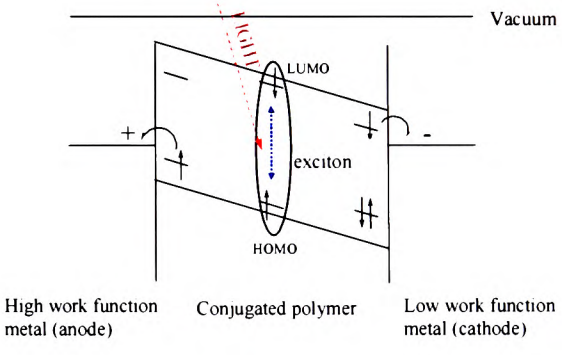


Figure 1- 5: Mechanism of electricity generation

However, unlike the mechanism for inorganic semiconductors where the electron is free to migrate to opposite electrodes, the electron is not free to move rapidly to the cathode because the excited electron is bound to the hole with an energy of ~100 meV[42-43, 45]. In addition, when the exciton is separated the charge transport proceeds by hopping mechanism between localised states, rather than by transport within a band which results in low charge mobilities. Although the electron is fixed in this bound state, extraction of the electron can take place at an interface, completing the circuit[44]. Therefore, the key steps are again light absorption, charge separation, and charge transport. Conjugated

polymers have been designed to absorb across a broad range of wavelengths across the visible spectrum (Figure **1-6**) and in general, a film thickness of ~100 nm[45] will absorb all the incident photons.

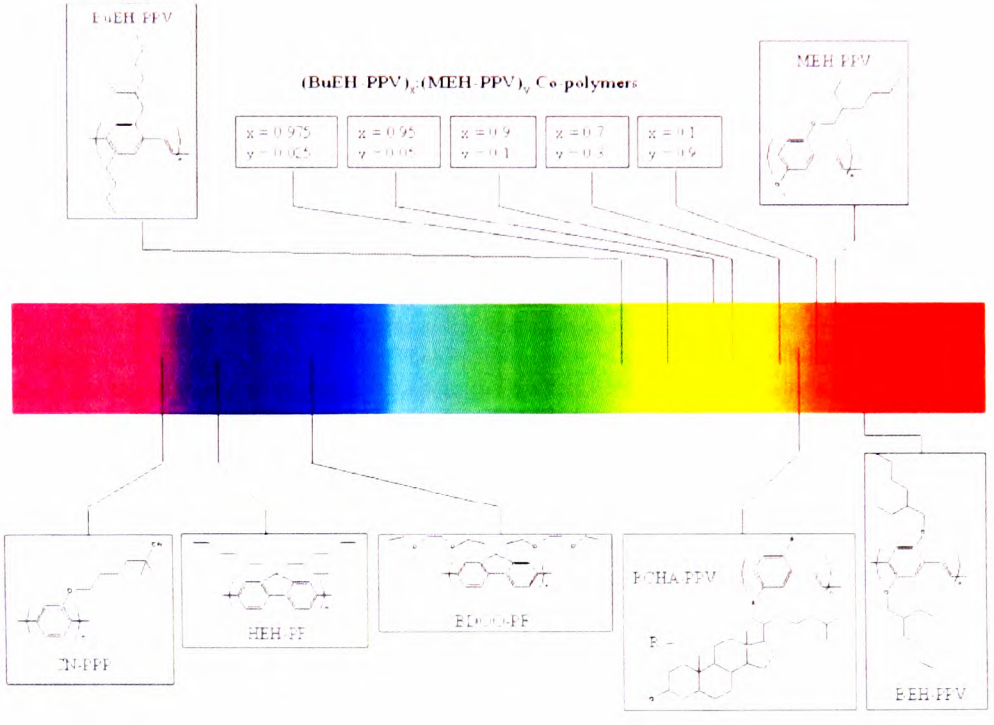


Figure 1- 6: Band gap engineering of semiconducting polymers[46]

The polymers explored were poly(arylene)s such as poly(thiophene)[47-51] and poly(fluorene) copolymers[52-56], poly(arylenevinylene) such as poly(1,4-phenylenevinylene) (PPV) derivatives[57-60], and poly(aryleneacetylene) derivatives[61-62] or their copolymers[63-64] to maximise their sunlight absorption regime. In single layer devices containing a neat polymer film exciton dissociation mainly occurs at an interface to form charges that can migrate to the electrodes to complete the circuit. Hence, photoexcitation

normally leads to decay of the exciton directly back to the ground state by photoluminescence or other non-radiative decay pathways. Therefore, solar cells with neat single homopolymer layer devices all show very poor efficiencies typically of 10^{-3}-10^{-2}%[65]. This is clearly too low to be used for practical applications.

There have been various strategies used to induce charge separation. The first strategy studied is a bilayer heterojunction device[66] in which the light absorbing material is deposited on to a layer of opposite electron affinity material. For example, many conjugated polymers are easily oxidised if deposited on a higher electron affinity material such as TiO_2[67], C_{60} **1.5a** [68-69] (Figure **1-8**) and its derivatives or another polymer[70]. The mechanism for the PV process in a bilayer heterojunction device is depicted in Figure **1-7**; the donor material absorbs the light and as a result electron is promoted from HOMO to LUMO, forming a singlet exciton.

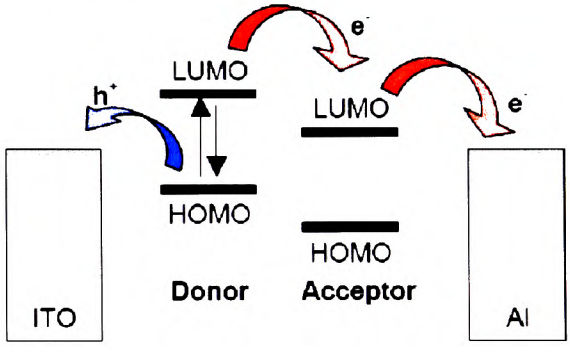
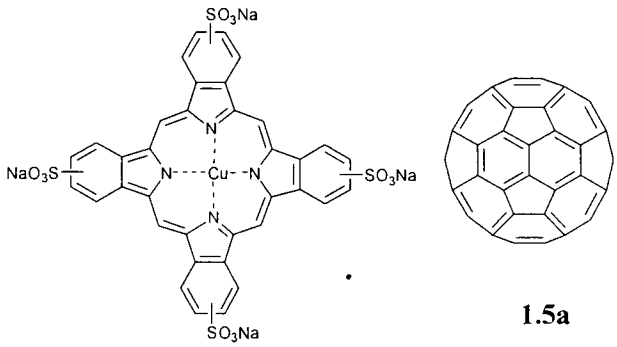


Figure 1- 7: Exciton dissociation at the interface[1]

The excited electron can then either hop to the available low-lying orbital of acceptor material or recombine with the hole giving out luminescence. Thus the concentration and dispersity of the acceptor material is essential for the efficient dissociation of the exciton.

The preparation of bilayer devices suffered from two drawbacks. First, physical limitations imposed during casting of materials namely solubility, evaporation and thermal degradation. Second, it was found that charge separation is only facilitated at the interface of donor and acceptor material and hence the effective light-harvesting layer is limited by the diffusion lengths of the exciton, which are typically in the range of 10 nm (less than the film thickness ~100 nm). This implied that the charges that are formed at the interface have a long way to travel to the electrodes giving a higher probability of them being quenched. It might be thought that the nanoporous TiO_2 would provide a large interface and efficient devices. However, the device efficiencies were found to be low due to poor infiltration of the rigid conjugated polymers into the pores of electron acceptor material, TiO_2 accounting for poor film morphology[71] The best efficiency of a bilayer device reported so far is 4.2%[72] ($\eta_{AM1.5}$) with copper phthalocyanine (CuPc) **1.3** and C_{60} **1.5a** (Figure **1-8**) in device configuration of ITO/**1.3**/**1.5a**/electron-blocking layer/Ag.



1.3

1.5a

Figure 1- 8: Copper phthalocyanine (CuPc) **1.3**, and C_{60} **1.5a**

The most common and thus far most efficient method for separating charges has been bulk heterojunction devices[73] in which the electron donating and accepting components are intimately mixed giving a large surface area. Formation of heterojunctions have been achieved by two methods, either by the blending of two polymers with different electron affinities[74-76] or by the mixing of a conjugated polymer with a molecular material with the desired electron acceptor properties[58,77-83]. The enhancement in surface area of the donor/acceptor interface results in the higher rate of electron transfer between the donor and acceptor and more efficient charge separation can be achieved. However, once the charges are separated they have to be able to move to the opposite electrodes (Figure **1-9**) without recombination and other quenching mechanisms.

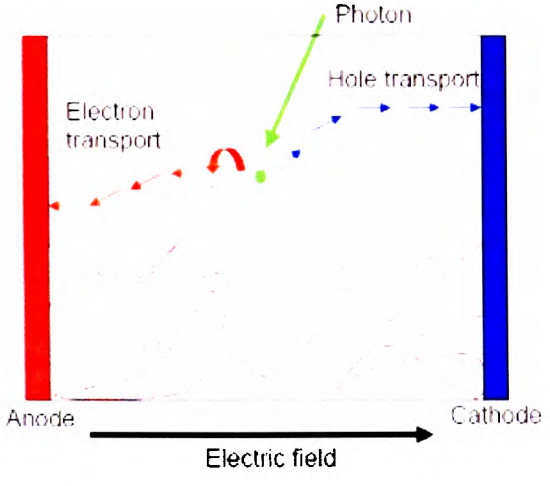
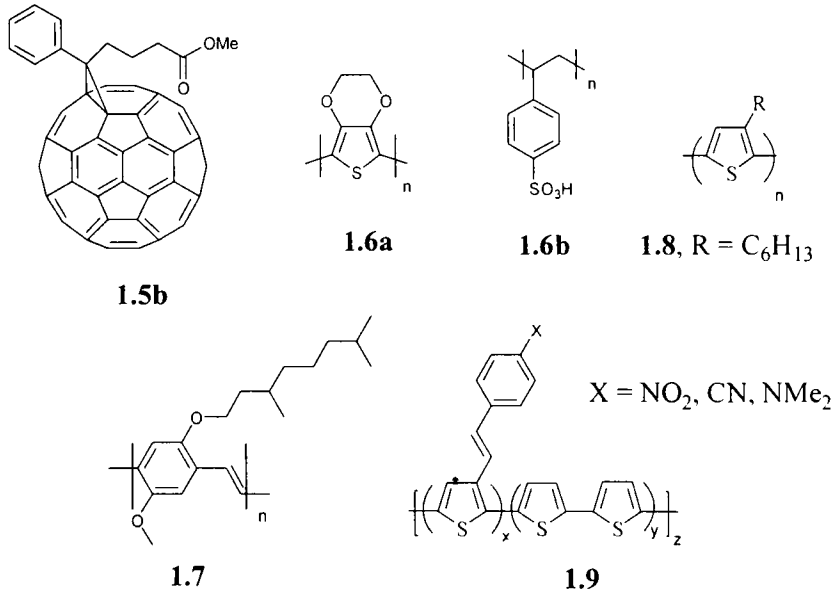


Figure 1- 9: Transport of holes and electrons in bulk heterojunction device[84]

This means that there has to be a percolation pathway for the two opposite charges and is critically dependant on the concentration of the electron donor and acceptor and how they are arranged in the polymer film, that is the film morphology of the blend. Ideally, the

network should be a bicontinuous interpenetrating network to channel the opposite charge carriers to the required electrodes. Sometimes due to random diffusion processes, the electrons and holes will also travel to the wrong electrode due to mischanneling and recombine there, contributing to loss mechanisms. Although some phase segregation is desirable, too much segregation can decrease device efficiency[84]. The most efficient devices reported so far for the materials (Figure **1-10**) is 3.3%[47] for ITO/PEDOT:PSS/**1.7**:**1.5b**(1:4)/LiF/Au {poly[3,4-(ethylenedioxy)-thiophene] **1.6a** :poly(styrenesulphonate) **1.6b** (PEDOT:PSS); poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] **1.7** (MDMOPPV); C_{60} adduct, 1-(3-methoxycarbonylpropyl)-1-phenyl-[6.6]C_{61} (PCBM) **1.5b**} and ~4% for ITO/PEDOT:PSS/**1.8**:**1.5b**/LiF/Al[7,48]{poly(3-hexylthiophene-2,5-diyl) P3HT **1.8**}.



1.5b **1.6a** **1.6b** **1.8**, R = C_6H_{13}

1.7 **1.9**

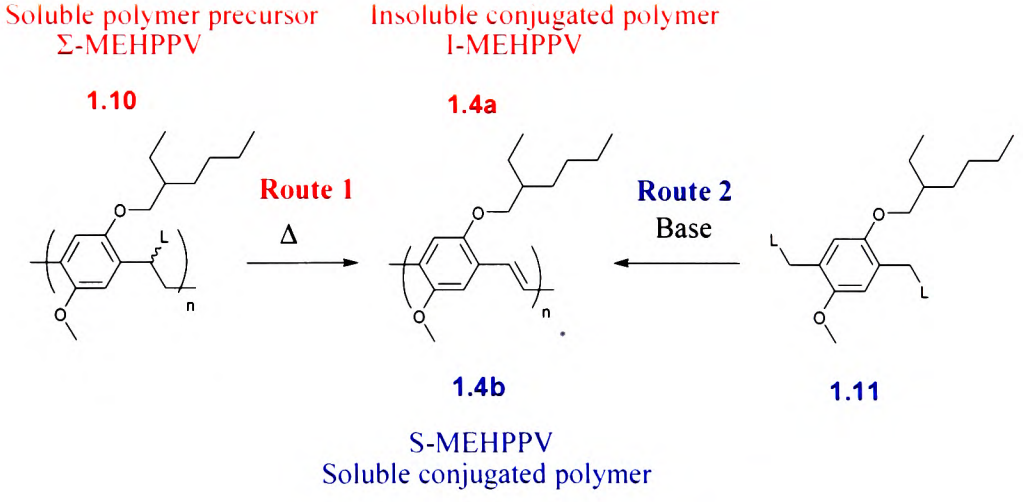
Figure 1- 10: PCBM **1.5b**, PEDOT **1.6a**, PSS **1.6b**, MDMOPPV **1.7**, P3HT **1.8**, and Donor-acceptor polymer **1.9**

Recently an efficiency of approaching to 5%[7] has been overcome for poly(alkylthiophene) and **1.5b** bulk heterojunction solar cell. An alternative approach to charge separation is to design polymers that have components with different electron affinities. The main effort in this area has been to tether the electron-accepting units onto a conjugated polymer. This involved attachment of C_{60} derivatives on to the oligomer units or a polymer backbone[85-86]. In addition, the problem of phase segregation at higher loading of PCBM **1.5b** in the polymer:**1.5b** blend in a bulk heterojunction device has also been solved as tethered structure would allow a higher loading of C_{60} units in the blends necessary to achieve higher efficiency. This is however an "intermolecular" charge separation process. In contrast there has been little effort in designing materials that can have intramolecular charge separation in a similar manner to the dyes that have dipoles. One report on this latter strategy has involved devices that contain electropolymerised poly(thiophene)s[87] with electron withdrawing groups (EWG) **1.9** (Figure **1-10**) attached to the conjugated polymer backbone. These devices worked very poorly although whether this was due to the polymer design or the fact that electropolymerised materials tend to be impure and contain lots of defects. Nevertheless, it is this last approach of intramolecular charge separation that forms the basis of this project and involved the synthesis of charge-separation polymers.

1.4 Synthetic routes for conjugated polymer

Conjugated polymers are designed so that they are either soluble in the conjugated form or are produced in an insoluble form *via* a precursor polymer using the Gilch

method[88]. The former route has the advantage that the synthesis are generally easier and processing straightforward whilst the latter route has the advantage that multilayer devices can be easily produced as the polymer can be rendered in the insoluble form in the last step. However, multilayer devices can also be fabricated with the soluble conjugated polymers by solution processing with the use of orthogonal solvents to prevent washing off an already deposited polymer when applying the next layer. This problem can also be solved by preparing polymer films *via* alternate routes i.e. precursor route. For example, MEHPPV **1.4** can be prepared in an insoluble form **1.4a** (I-MEHPPV) and a soluble form **1.4b** (S-MEHPPV). The insoluble form **1.4a** is prepared *via* a soluble precursor polymer Σ-MEHPPV **1.10** (Route 1) and the soluble form **1.4b** directly from the monomer **1.11** (Route 2) as shown in Scheme **1-1**. In the soluble precursor route, insoluble conjugated polymer **1.4a** was obtained after thermal conversion of soluble precursor **1.10**.



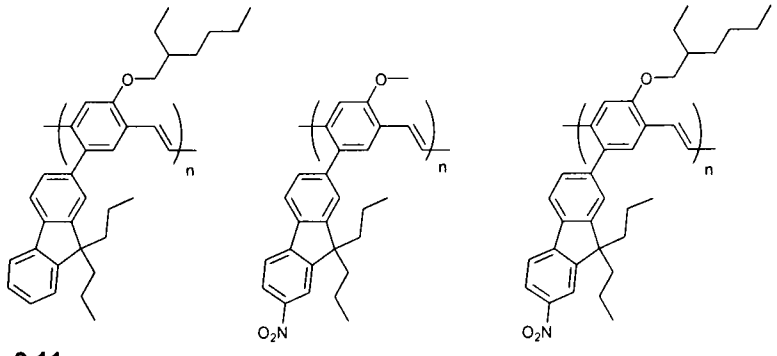
Scheme 1-1: MEHPPV synthetic route

The insolubility is thought to be due to the entanglement of polymer chains or crosslinking of the polymer. Other layers are then deposited without interfering with the previously deposited polymer layer. A layer of soluble polymer can then be applied as soluble conjugated polymer. Solubility of the conjugated polymer is due to the longer alkyl chains. Both the synthetic routes were used for the formation of conjugated polymers in this project.

1.5 Project aim(s):

The aim of my project was to develop a family of poly(1,4-phenylenevinylene) derivatives with pendant fluorene moieties for photovoltaic applications. The polymers developed have an electron donating alkoxy group directly attached to the PPV backbone and electron withdrawing nitro group attached to the fluorenyl side groups. The presence of such groups in the polymers creates a dipole and the aim was to observe whether the dipole would assist in intramolecular charge separation of the generated exciton after photoexcitation of the polymer backbone. Three main factors were investigated; the type of link between the fluorenyl group and the polymer backbone (biphenyl or vinyl), the distance between the electron withdrawing and donating group, and conjugated polymers prepared via a precursor polymer route versus soluble fully conjugated polymers.

Chapter 2 is concerned with the synthesis and characterisation of mono-fluorenyl-biphenyl-linked PPV derivatives, Figure **1-11**.



2.11 **2.28** **2.30**

Figure 1- 11: Mono-biphenyl-linked PPV derivatives

The polymers have a fluorenyl unit linked directly to the polymer backbone. Polymer **2.11** is the basic structure while **2.28** and **2.30** have the nitro group attached. Polymers **2.28** and **2.30** differ by the length of alkyl chain of the alkoxy group with the former being processed via a precursor polymer. The photophysical and device properties of **2.11** and **2.30** were studied in collaboration with Dr. H. Assender, Department of Materials, University of Oxford and Prof. I. Samuel, Organic Semiconductor Centre, University of St. Andrews.

Chapter 3 describes the synthesis and characterisation of polymers **3.18** and **3.24** (Figure **1-12**), which differ from the polymers in Chapter 2 by the addition of an extra fluorene moiety.

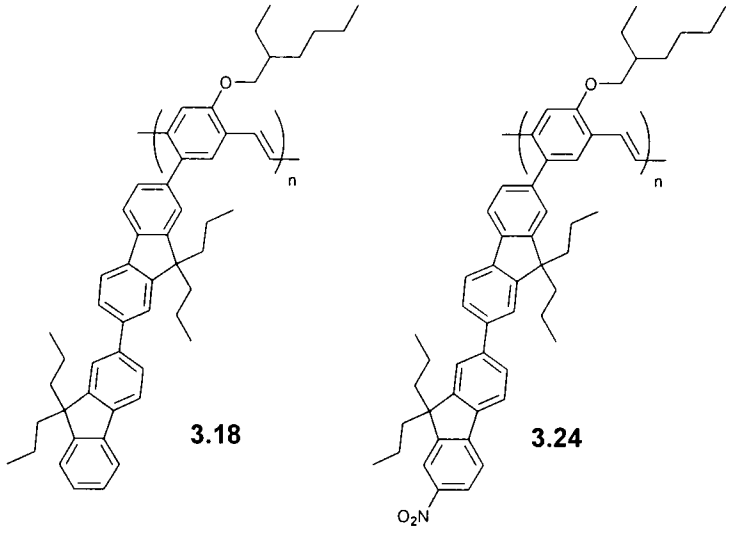


Figure 1- 12: *Bis*(biphenyl)-linked PPV derivatives

Chapter 4 explores the possibility of introducing a vinyl linkage between the polymer backbone and pendant fluorenyl moieties, Figure **1-13**. The aim was to determine the effect of the more planar vinyl linkage and hence the photophysical properties of the materials.

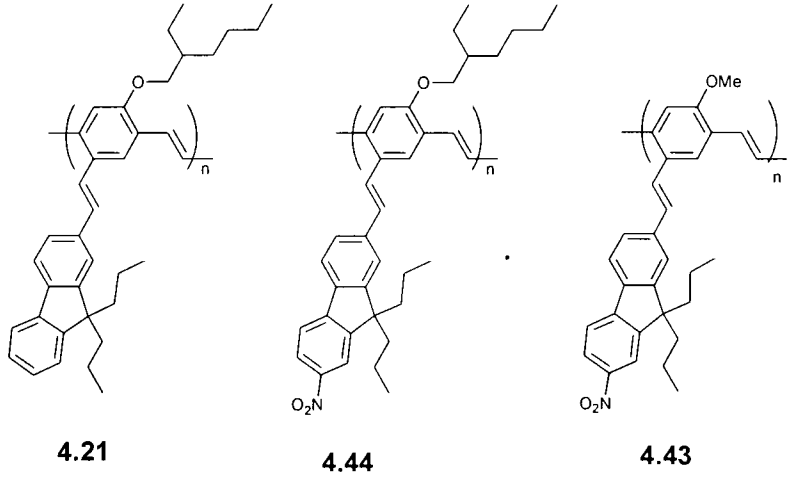


Figure 1- 13: Mono-vinyl-linked PPV derivatives

MONO-BI-PHENYL LINKED PPV DERIVATIVES

Chapter 2

2 MONO-BI-PHENYL LINKED PPV DERIVATIVES

2.1 Introduction

Poly(1,4-phenylenevinylene) (PPV) and its derivatives have been explored for light emitting diodes (LED)[89-93], and photovoltaics (PV)[94-95] because of their interesting opto-electronic properties. Although research in the organic photovoltaic area is still in its infancy, different approaches to polymer design have been attempted to improve the efficiency, stability and processability of the device. There are three main processes in PV devices; namely, photoexcitation of the polymer to give an exciton, exciton dissociation, and charge collection at electrodes. In the context of this work polymers are designed and prepared to study the dissociation of the exciton to form a free electron and hole thereby preventing loss of efficiency arising from recombination. This approach is different to the attempts made to prevent the same loss by device design. Bulk heterojunction solar cell devices are normally used to encourage charge separation and prevent recombination, leading to tremendous improvement in device efficiencies. Polymer bulk heterojunction solar cells are obtained by blending the polymer with another semiconductor, either inorganic, e.g., TiO_2[18-21], or organic, e.g., PCBM[48,57,60] or another polymer[75]. In these devices the polymer acts as a light harvester and charge separation occurs intermolecularly at the interface with the second semiconductor. The question that therefore arose was whether or not device efficiencies could also be improved if the charge separation process occurs intramolecularly, within the polymer itself. This involved designing a polymer with the following properties: processability,

high optical density, good charge mobility, and importantly a dipole, which could aid in charge separation. The charge separation polymers are designed so as to have electron donating groups (EDG) and withdrawing groups (EWG) that would give rise to a dipole and potentially stabilise the holes and electrons that are formed from a charge separated exciton. The generalised structure of the charge separation polymer and the mono-bi-phenyl linked polymers synthesised is shown in Figure **2-1**. In this work, the EDG was an alkoxy group, whereas for the EWG a nitro group was used. The polymers in this family of materials has the alkoxy group attached to the phenyl ring that becomes part of the polymer backbone and the electron withdrawing nitro group attached to a fluorenyl moiety, which itself is attached to the polymer backbone. Fluorene was chosen as the side group because poly(fluorene)s have liquid crystalline behavior and have good charge mobility[96]. The fluorene moiety acts as a spacer (linker group) between the ED and EW groups.

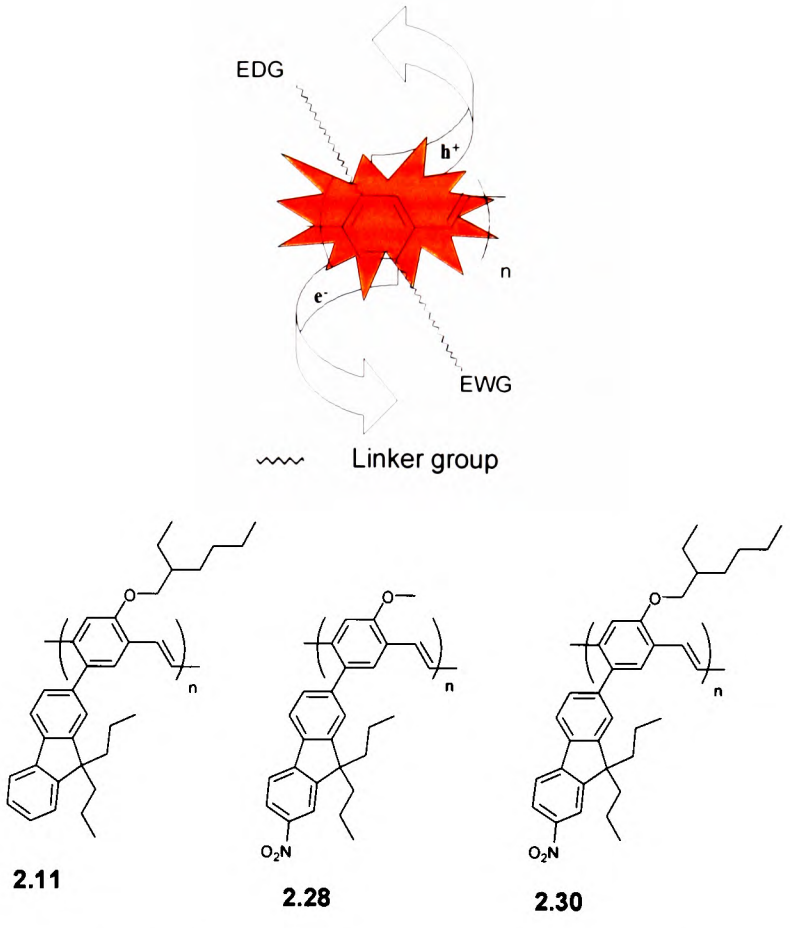


Figure 2-1: Schematic representation of charge separation polymers

This chapter describes the synthesis and study on PPV derivatives with side groups comprised of a single fluorene moiety. The soluble poly[2-(9,9-dipropylfluorenyl)-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] **2.11** (S-EH-FPPV) is the parent polymer and was prepared so the effect of the nitro group in soluble poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] **2.30** (S-EH-NO_2FPPV) could be understood. The 2-ethylhexyl and *n*-propyl side chains were attached to ensure that **2.11** and **2.30** were soluble in their conjugated forms. Polymer **2.30** differs from **2.28** in the

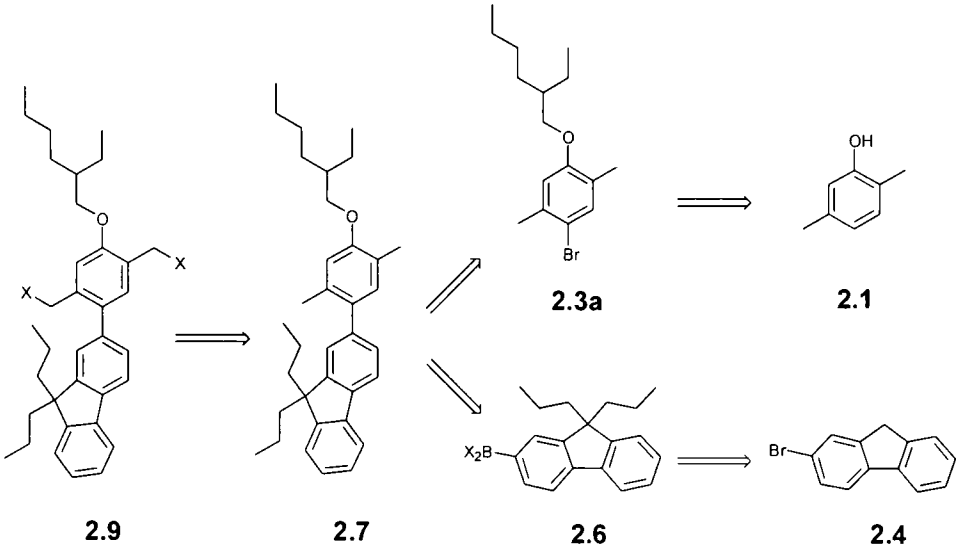
length of the alkoxy group. With only a methoxy group the conjugated polymer poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-methoxy-1,4-phenylenevinylene] **2.28** (I-M-NO_2FPPV) would not be expected to be soluble in its conjugated form and hence the insoluble form would have to be prepared *via* a precursor polymer.

2.2 Poly[2-(9,9-dipropylfluorenyl)-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene]

2.2.1 Monomer synthesis

2.2.1.1 Retrosynthetic analysis of the fluorenyl monomer

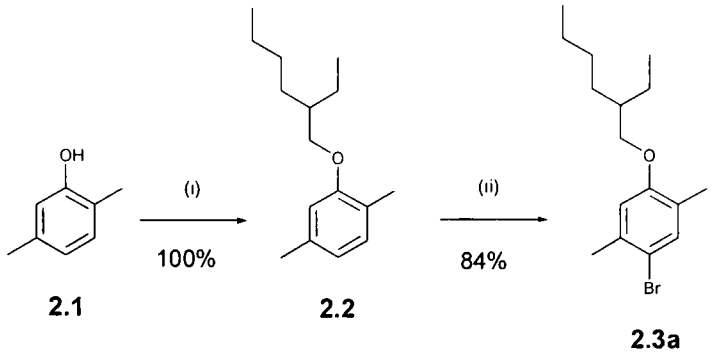
The retrosynthetic strategy pursued for the preparation of S-EH-FPPV monomer **2.9** is illustrated in Scheme **2-1**. A key step for the synthesis of ethylhexyloxy-fluorenyl monomer **2.9** is the C-C coupling of 1-bromo-4-(2′-ethylhexyloxy)-*p*-xylene **2.3a** with fluorenylboronic acid **2.6** to give biphenyl linked *bis*-methyl monomer precursor **2.7**. The dimethyl-ethylhexyloxy-fluorene **2.7** would then be transformed to the *bis*(halomethyl) monomer **2.9** by utilising methodology developed by the group.



Scheme 2- 1: Retrosynthetic analysis of S-EH-FPPV monomer **2.9**

2.2.1.2 Synthesis of the Fluorenyl monomer

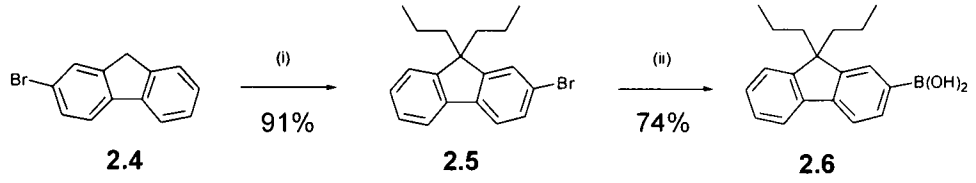
The initial steps in the pathway involved the conversion of commercially available 2,5-dimethylphenol **2.1** to 1-bromo-4-(2′-ethylhexyloxy)-*p*-xylene **2.3a**, Scheme **2-2**. The branched 2-ethylhexyl group was chosen as it acts as a solubilising group for the conjugated polymer, S-EH-FPPV **2.11**. A solution of 2,5-dimethylphenol **2.1** in acetonitrile was deprotonated with potassium *t*-butoxide at 0 °C and the alkoxide ion formed was reacted with a slight excess amount of 2-ethylhexyl bromide. This gave 2-(2′-ethylhexyloxy)-*p*-xylene **2.2** in a quantitative yield after removal of unreacted 2-ethylhexyl bromide from the crude reaction mixture by distillation. The next step was the bromination of 2-(2′-ethylhexyloxy)-*p*-xylene **2.2** with bromine in glacial acetic acid, which gave 1-bromo-4-(2′-ethylhexyloxy)-*p*-xylene **2.3a** in an 84% yield.



Scheme 2- 2. *Reagents and conditions*: (i). a. $KOBu^t$, CH_3CN, 0 °C;

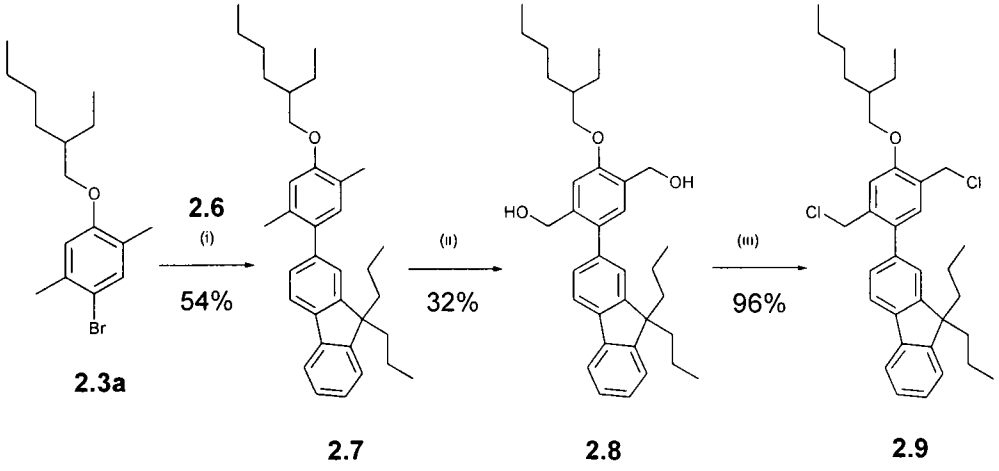
b. 2-Ethylhexyl bromide, r.t.; (ii). Br_2, MeOH, AcOH

Commercially available 2-bromofluorene **2.4** was modified to form the side group of the polymer, Scheme **2-3** by di-alkylation at the 9-position. Di-alkylation at the 9-position will give improved solubility to the polymer, and also prevent fluorenone formation by oxidation of fluorene. Di-alkylation of 2-bromofluorene **2.4** was achieved using 1-bromopropane, sodium hydroxide and tetra-*n*-butylammonium bromide as the phase transfer agent in a toluene and water mixture at 60 °C. This gave dipropylbromofluorene **2.5** in a 91% yield after work-up and purification. The next step on the synthesis was the transformation of the bromine group of dipropylbromofluorene **2.5** to the corresponding boronic acid **2.6**. The synthesis of fluorenylboronic acid **2.6** from dipropylbromofluorene **2.5** was carried out by metallation with *n*-butyllithium in tetrahydrofuran at -78 °C and followed by quenching the anion with trimethyl borate. The trimethyl borate ester was hydrolysed under acidic medium and purification of the crude material gave fluorenylboronic acid **2.6** as a mixture of free acid and anhydrides in an overall yield of 74%.



Scheme 2- 3. *Reactions and conditions*: (i). *n*-PrBr, PhMe, $NaOH_{(aq)}$, TBAB, 60 °C; (ii). a. THF, *n*-BuLi, -78 °C; b. $B(OMe)_3$, -78 °C → 0 °C; c. $H^+_{(aq)}$.

Suzuki coupling of 1-bromo-4-(2′-ethylhexyloxy)-*p*-xylene **2.3a** with fluorenylboronic acid **2.6** was achieved with *tetrakis*(triphenylphosphine)palladium (0) and aqueous sodium carbonate in toluene, Scheme **2-4**.



Scheme 2- 4. *Reagents and conditions*: (i). **2.6**, $Pd(PPh_3)_4$, PhMe, $Na_2CO_{3(aq)}$, Δ; (ii) a. NBS, AIBN, CCl_4, Δ; b. NaOAc, AcOH, Δ; c. $LiAlH_4$, THF; (iii) $SOCl_2$, DCM

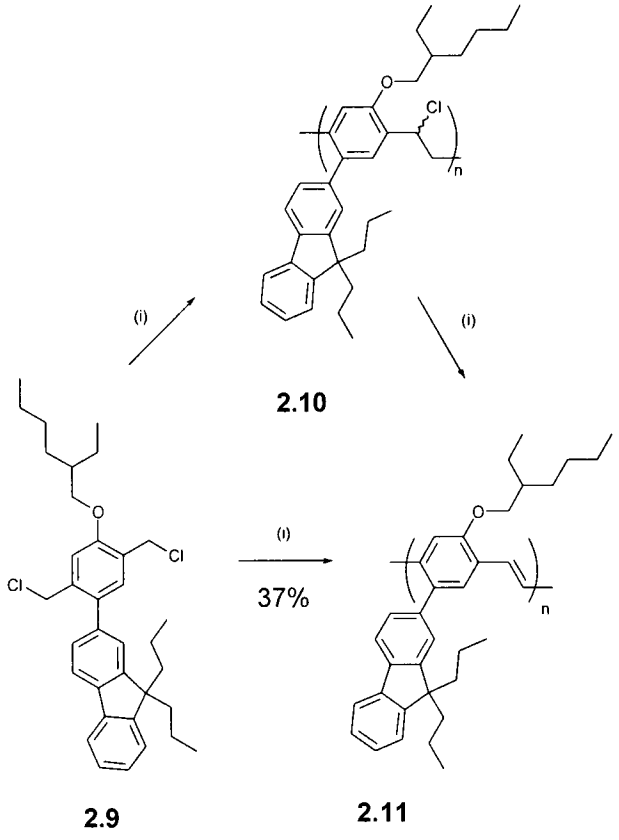
The mixture was heated at reflux for 15 hours to give dimethyl-ethylhexyloxy-fluorene **2.7** in a 54% yield after work-up and purification. The radical bromination of dimethyl-ethylhexyloxy-fluorene **2.7** occurred using *N*-bromosuccinimide and

2,2'-azo-*bis*(isobutyronitrile) as the free radical initiator in carbon tetrachloride heated at reflux. This reaction yielded an inseparable mixture of mono-, di-, tri-, tetra-brominated compounds. Previous work within the group had shown that to gain pure *bis*-chloro monomers similar to **2.9** from a brominated mixture usually required a several step procedure. The brominated mixture was partly purified by a silica-plug using dichloromethane as an eluent before acetylation. The mixture was acetylated by reaction with sodium acetate in glacial acetic acid heated at reflux. The acetylation reaction yielded a mixture of inseparable *mono*- and *bis*-acetate containing compounds as well as *mono*- and *bis*-aldehyde compounds. Thereafter, reduction of this mixture using lithium aluminium hydride in tetrahydrofuran at -15 °C allowed the isolation of diol **2.8** in an overall yield of 32% for the three steps. The *bis*(hydroxymethyl) groups of compound **2.8** are transformed to the *bis*(chloromethyl) groups of monomer **2.9** on treatment with thionyl chloride in anhydrous dichloromethane at room temperature. The ethylhexyloxy-fluorenyl monomer **2.9** was purified and isolated in a 96% yield.

2.2.2 Polymerisation of the Fluorenyl monomer

The polymerisation of monomer **2.9** was carried out using the Gilch method[88] Base induced polymerisation of the monomer **2.9** was carried out using 5.0 equivalent of potassium *t*-butoxide in tetrahydrofuran to form the fully conjugated soluble polymer, poly{2-[(9,9-dipropylfluorenyl)-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene]} **2.11** (S-EH-FPPV), Scheme **2-5**. The formation of **2.11** goes *via* the precursor polymer **2.10** but in the presence of the excess base hydrogen chloride is eliminated and **2.10** is not

isolated. If desired the precursor polymer **2.10** could be isolated if less than 1.0 equivalent of base was used during polymerisation step.



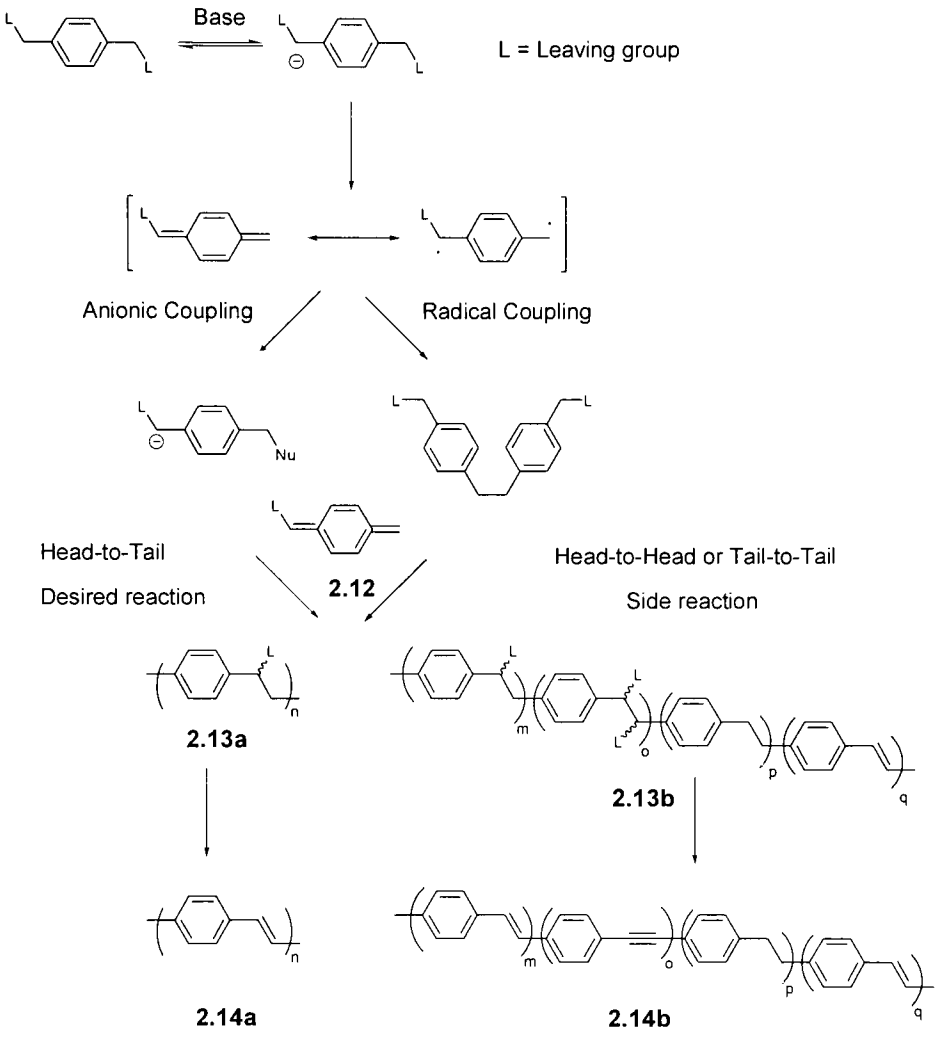
Scheme 2- 5. *Reagents and conditions*: (i). KOBu^t, THF

A 0.2 M solution of potassium *t*-butoxide in anhydrous tetrahydrofuran was added to the 0.2 M solution of **2.9** in tetrahydrofuran at room temperature under a nitrogen atmosphere. The reaction mixture was allowed to stir for 3 hours before purification. The polymer was purified from unreacted monomer, oligomers, and the potassium chloride by-product in several steps. First, the reaction mixture was filtered through a cotton-wool plug to remove any large insoluble particulates. The polymer was then precipitated from

the filtrate by being poured into ice-cold methanol, a non-solvent for the polymer. The polymer was isolated from the supernatant by centrifugation with the residue taken up in tetrahydrofuran. The process was repeated two times before the polymer was dried under vacuum to give S-EH-FPPV **2.11** in a ~37% yield as a yellow solid.

2.2.3 Properties of the Fluorenyl-PPV

The weight average molecular weight ($\overline{M}_w$) and polydispersity index (PD) of the S-EH-FPPV **2.11** was determined by gel permeation chromatography (GPC) using polystyrene as standards and found to be $\overline{M}_w = 4.3 \times 10^6$ g/mol and PD 2.3. Polymer **2.11** had good solubility in chloroform and tetrahydrofuran. The conjugated structure of the polymer **2.11** was confirmed by ^{1}H n.m.r., spectroscopy. In analysing the ^{1}H n.m.r. spectrum, it is important to understand how the mechanism for the polymerisation proceeded. The generalised mechanism to form the conjugated PPV by polymerisation of the PPV monomers and its derivatives is not fully understood, and several processes have been suggested. However, it is generally agreed that the polymerisation proceeds through a reactive quinodimethane **2.12** intermediate, the "true monomer". However, the nature of the propagating species, whether radical[97-99] or anionic[100-101], is still debated and may be substrate and/or leaving group dependent, Scheme **2-6**.

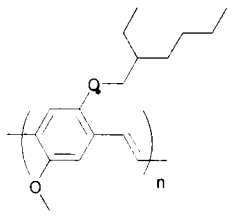


Scheme 2- 6. Possible defects introduced during Gilch polymerisation

Several reports have suggested a radical polymerisation due to a decrease in molecular weight of the PPV polymer with the addition of radical scavengers and chain transfer agents such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)[97], carbon tetrabromide[98], and oxygen[99] In contrast, the addition of 4-*t*-butylbenzyl chloride[100-101]

and 4-methoxyphenol[102] resulted in an inverse relationship between the amount of benzyl chloride and molecular weight, suggesting an anionic polymerisation.

Independent of whether the polymerisation is anionic or radical the desired polymerisation pathway is head-to-tail coupling from quinoidal intermediate **2.12** to form the regular precursor polymer **2.13a**. The head-to-tail arrangement means that every ethylene units will have a leaving group that can be eliminated *in situ* to form the conjugated polymer **2.14a** with vinylene linkages. However, if head-to-head and tail-to-tail couplings occur then on elimination there will be ethylene and acetylene linkages were introduced along the backbone of the polymer **2.14b**. These defects affect the delocalisation of the conjugated backbone and have been postulated to shorten the lifetime of Organic Light Emitting Diode (OLED) devices[103-104] The ^{1}H n.m.r. spectrum (Figure **2-3)** of poly[5-methoxy-2-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (S-MEHPPV) **1.4b** (Figure **2-2**) shows the signals associated with the ethylene units arising from H-H couplings at ~2.9 p.p.m.[105]. It is also important to note that the halo precursor polymer to PPV have the CHX methine is normally observed at ~5.7 p.p.m.[106] Therefore, the absence of this signal in the ^{1}H n.m.r. spectrum of S-EH-FPPV **2.11** indicates that the conversion has gone to completion.



1.4b

Figure 2- 2: Structure of S-MEHPPV **1.4b** (prepared *via* direct route)

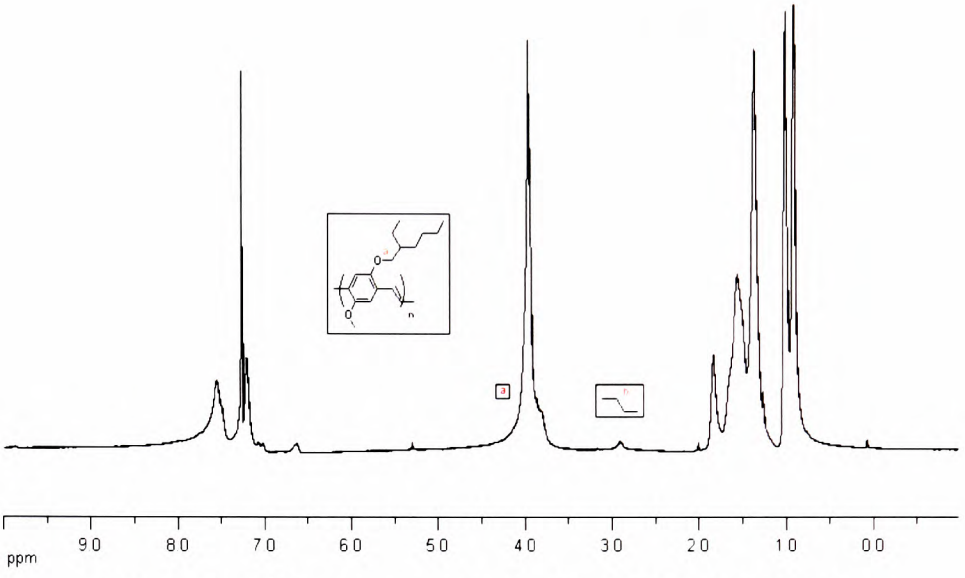


Figure 2- 3: ^{1}H n.m.r. spectrum of S-MEHPPV **1.4b** in $CDCl_3$

The formation of S-EH-FPPV **2.11** goes *via* precursor **2.10** in a similar way to the formation of MEHPPV. The ^{1}H n.m.r. spectrum of **2.11** is shown in Figure **2-4** and it can be seen there are no methine protons in the region of ~5.8 p.p.m.

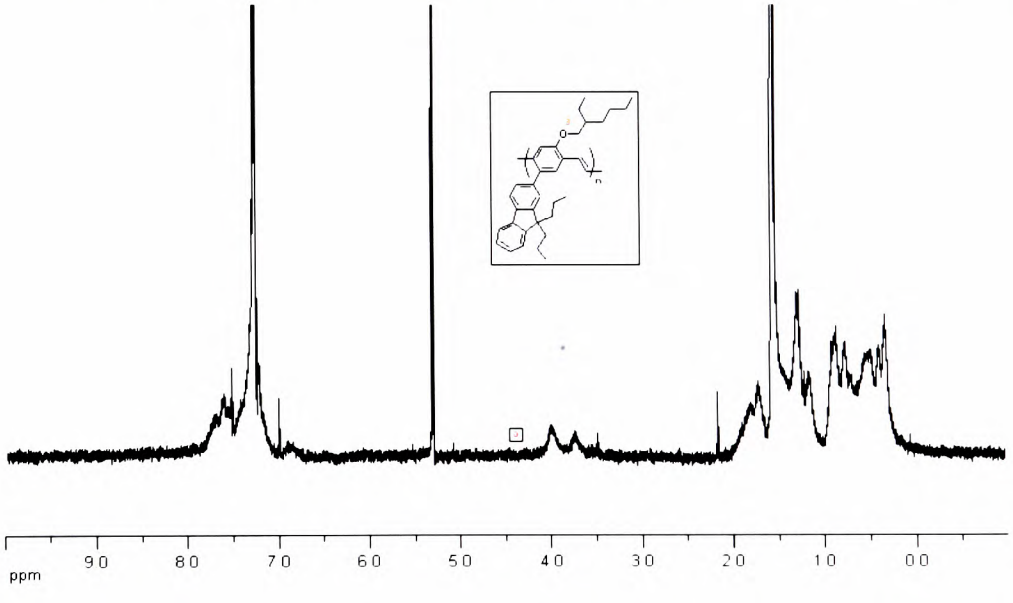
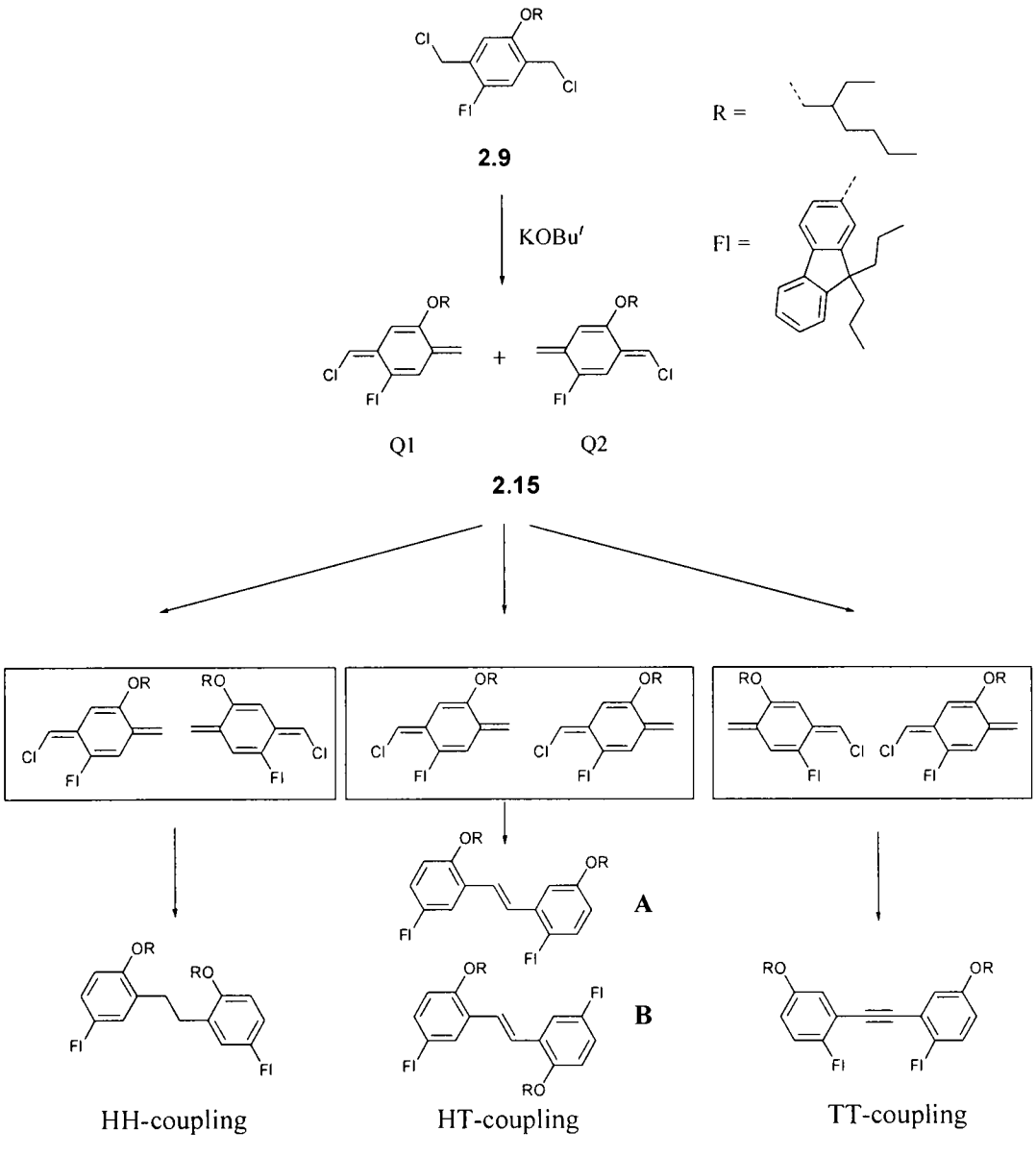


Figure 2- 4: ^{1}H n.m.r. spectrum of S-EH-FPPV **2.11** in $CDCl_3$

Furthermore, the ratio of the integrals for OCH_2 protons at 3.6-4.1 p.p.m. to the aromatic protons between 6.7-7.9 p.p.m. was consistent with the polymer being fully conjugated. Importantly, the absence of the ethylene protons (benzylic nature) at ~2.8 p.p.m.[105, 107] in the ^1H n.m.r. of **2.11** indicated the absence of head-to-head defects in the polymer indicating regioregularity of the polymer backbone. The regioregularity of the polymer could arise from both electronic and steric effects in the monomer determining the percentage of formation amongst *p*-quinodimethane derivatives[104, 108-109]. The formation of *p*-quinodimethane derivatives (Q1 and Q2) **2.15** (Scheme **2-7**) from the fluorenyl monomer **2.9** is controlled by both electronic and steric effects due to difference in the acidity of the two chloromethyl groups. The formation of quinoidal intermediate Q1 is favoured electronically while the formation of Q2 is favoured because of the sterically encumbered chloromethyl group due to the fluorenyl substituent at position-2. The ^1H n.m.r. of **2.11** showed absence of the *bis*-benzyl moiety suggested either the predominance of one quinoidal intermediate and propagation occurred in head-to-tail fashion resulted in a high selectivity to from the regioregular polymer (**A**, Scheme **2-7**) or the formation of both Q1 and Q2 which lead to the formation of regioisomers (**B**, Scheme **2-7**) in the polymer backbone.



Scheme 2- 7: Differences in the polymerisation mechanism leading to HH, HT, and TT couplings

The OCH_2 protons of 2-ethylhexyloxy group appeared as two broad singlets unlike in the ^1H n.m.r. spectrum (Figure **2-3**) of S-MEHPPV **1.4b**. However OCH_2 protons signal in

similar environment were reported both as a broad singlet[108, 110] or multiplet [108-109] in the literature. Drury et al.[111] assigned the OCH_2 signals at 3.5 p.p.m. and 4.1 p.p.m. due to *cis*-and *trans*-linkages respectively in the polymer backbone of poly(*m*-phenylenevinylene-*co*-2,5-dioctyloxy-*p*-phenylenevinylene). The ratio of OCH_2 signals at 3.5 p.p.m to 4.1 p.p.m. were found to decrease on treatment with iodine mediated *cis-trans* isomerisation. Moreover, the signal at ~6.7 p.p.m. in the ^1H n.m.r. spectrum of **2.11** initially suggested the presence of *cis*-double bonds in the polymer backbone. In order to confirm the absence of any *cis*-isomer, the polymer **2.11** was treated with catalytic amount of iodine in toluene and heated at reflux for 3 hours under nitrogen to allow *cis-trans* isomerism. The ^1H n.m.r. spectrum of the purified polymer **2.11** was found to be unaffected after treatment indicating the absence of such impurity. The absence of *cis*-impurity in **2.11** is in agreement with the work of Becker et al. on PPVs synthesised *via* Gilch route[107]

The thermal stability of S-EH-FPPV **2.11** was determined by thermogravimetric analysis (TGA) at a heating rate of 2 °C/min under a nitrogen atmosphere, Figure **2-5**. Polymer **2.11** exhibits good thermal stability with the onset temperature of degradation at 380 °C. The lack of significant weight loss at lower temperatures indicated that the polymerisation conditions had led to a fully conjugated polymer. For halo precursors generally hydrogen halide elimination occurs between 150-200 °C[112-113] Differential scanning calorimetry (DSC) of **2.11** showed that it did not have a glass transition temperature (T_g).

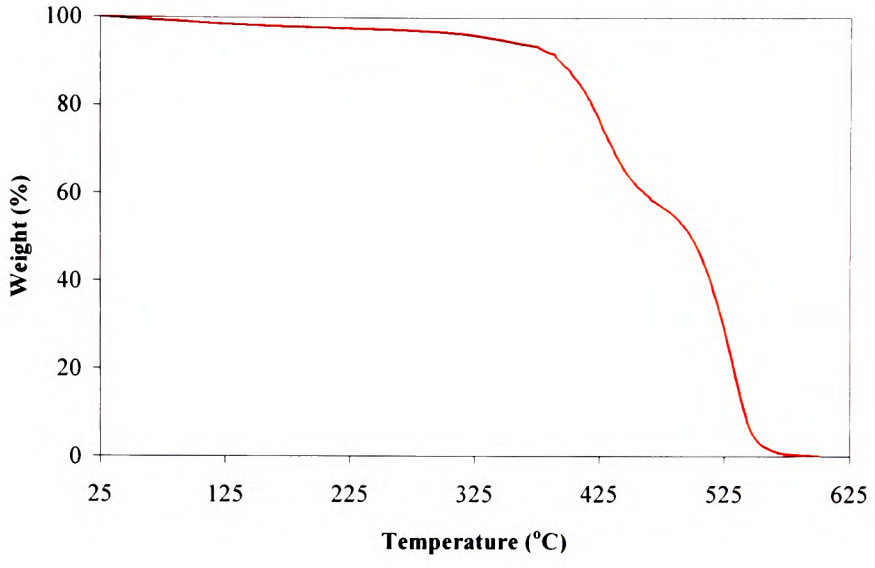


Figure 2-5: TGA of S-EH-FPPV **2.11**

Films of S-EH-FPPV **2.11** were studied by infrared and U.V.-visible spectroscopy. For the infrared study the polymer **2.11** was drop cast from tetrahydrofuran onto a freshly prepared KBr disc. The spectrum (Figure **2-6**) showed a relatively strong absorption peak at 965 cm^{-1} which corresponds to the C=C-H *trans*-vinylene C-H out-of-plane bend indicating **2.11** has predominantly *trans* configuration of vinylene units in the backbone. In order to investigate further the presence of any *cis*-linkages in the polymer **2.11**. The assignment of the *cis*-vinylene modes was investigated in the literature and found different quoted values for *cis*-vinylene out-of-plane bend. Pang et al.[114] and Huang et al.[115] attributed the peak at 873 cm^{-1} to the *cis*-vinylene out-of-plane mode, while Dalton and co-workers[116] assigned the peak occurring at 691 cm^{-1} to *cis*-vibration. No peak corresponding to *cis*-vinylene out-of-plane was observed both in the region ~873

cm^{-1} and at ~691 cm^{-1} in the infrared spectrum of **2.11** suggesting absence of the *cis*-linkages.

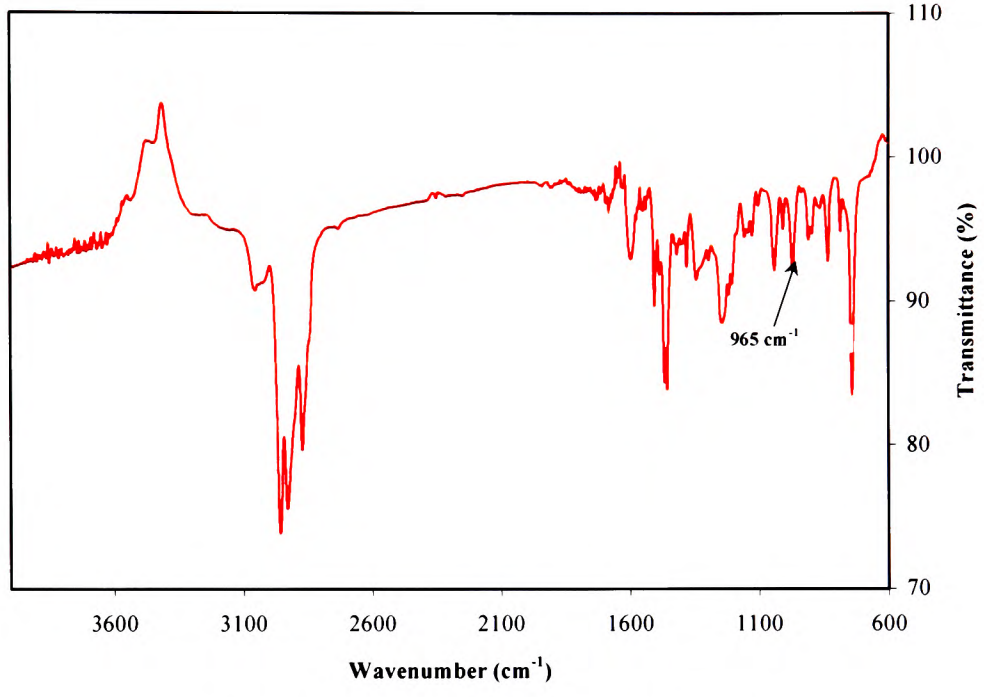


Figure 2-6: Infrared spectrum of S-EH-FPPV **2.11**

The U.V.-visible absorption spectra of PPVs can be divided into two regions. This is illustrated with the U.V.-visible spectrum of S-MEHPPV **1.4b**, Figure **2-7**. A short wavelength, around ~200 nm there are the localised π–π^* transitions whilst at longer wavelengths the delocalised π–π^* transitions are observed. In general conjugated polymers, such as PPV, a good degree of π–backbone delocalisation was observed when the ratio of the intensity of delocalised to localised π–π^* transitions is high. For **1.4b** it can be seen in Figure **2-7** that the delocalised π–π^* transitions are much stronger than the localised π–π^* transitions indicating a good level of delocalisation along the polymer backbone.

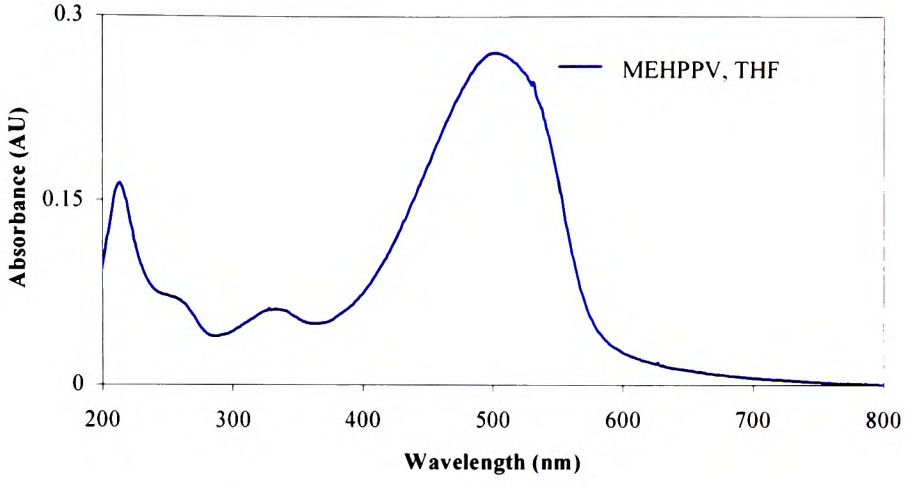


Figure 2-7:U.V.-visible spectrum of S-MEHPPV **1.4b** on quartz

The thin film U.V.-visible spectrum of S-EH-FPPV **2.11** and its monomer precursor, **2.7** are shown in Figure **2-8**.

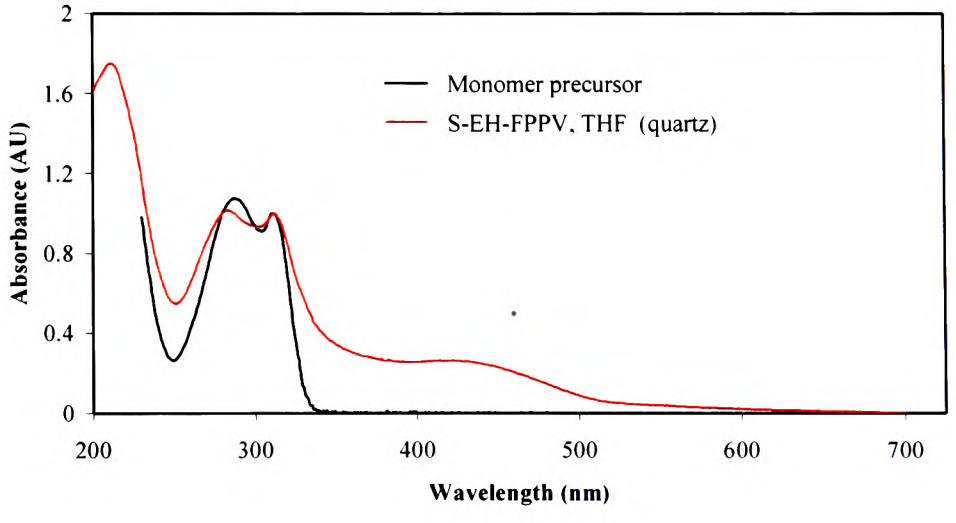


Figure 2- 8: U.V.-visible spectrum of monomer precursor **2.7** and S-EH-FPPV **2.11**

The film was formed by spin-coating **2.11** from tetrahydrofuran onto a quartz substrate and was of good quality. The U.V.-visible spectrum of polymer **2.11** showed that it absorbed in the wavelength range from 200-525 nm. The absorption around ~211 nm was due to the localised $\pi-\pi^*$ transitions. The relatively strong absorptions at 283 and 312 nm are similar to that observed for the monomer chromophore and hence can be assigned to those units in the polymer. However, a key difference between the spectra of S-MEHPPV **1.4b** and S-EH-FPPV **2.11** is that the ratio of the absorption at the longer wavelengths > 400 nm due to the delocalised $\pi-\pi*$ transitions of the polymer backbone is significantly smaller for **2.11**. The relatively weak intensity of the delocalised $\pi-\pi*$ absorption might at first sight suggest that an incomplete conversion to the fully conjugated polymer had occurred in the synthesis. However, both the ^{1}H n.m.r. and the TGA indicated that the polymer backbone of **2.11** is fully conjugated. Therefore the low intensity of the delocalised $\pi-\pi*$ transition must be due to conformational disorder of the polymer backbone. The conformational disorder is due to the steric hindrance at the "biphenyl" link of the fluorenyl unit twisting the polymer backbone and on average shortening the effective conjugation length of the polymer.

2.3 Poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-alkoxy-1,4-phenylenevinylene]

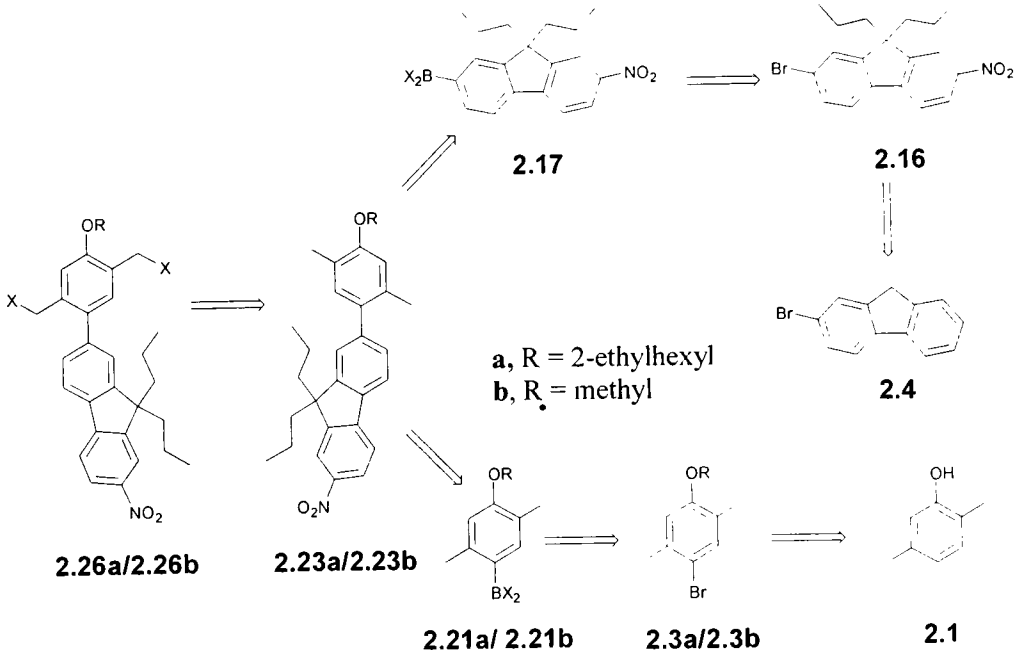
2.3.1 Synthesis of the Nitrofluorenyl monomers

Two nitrofluorenyl monomers that differed in the alkoxy group chosen (methyl and 2-ethylhexyl) were synthesised and polymerised to form nitrofluorenyl-PPV

polymers. In the case of the methoxy side group the nitrofluorenyl-PPV was prepared *via* a precursor polymer as the methoxy group did not provide enough lipophilicity to solubilise the conjugated polymer. The nitrofluorenyl-PPV with the 2-ethylhexyloxy side group is the direct analogue of the fluorenyl-PPV polymer **2.11** described in section **2.2.2** and is key to the study. It was hoped that if the methoxy derivative could be easily formed then films of it would have better charge transport than the 2-ethylhexyloxy derivative as it contains less insulating material.

2.3.1.1 Retrosynthetic analysis of the Nitrofluorenyl-PPV monomers

The strategy for the preparation of nitrofluorenyl monomers is shown in Scheme **2-8.**



Scheme 2- 8: Retrosynthetic analysis of nitrofluorenyl-PPV monomers **2.26a** and **2.26b**

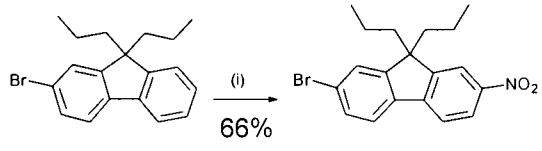
The nitrofluorenyl monomers **2.26a** and **2.26b** were structurally analogous to fluorenyl monomer **2.9** apart from the fact that **2.26a** has a 2-ethylhexyloxy and **2.26b** has a methoxy group and both **2.26a** and **2.26b** have a nitro EWG at the 7-position on the fluorenyl side chain.

The earlier successful coupling of fluorenylboronic acid **2.6** with 1-bromo-4-(2′-ethylhexyloxy)-*p*-xylene **2.3a** to form dimethyl-ethylhexyloxy-fluorene **2.7** (Scheme **2-4**) suggested a straightforward pathway for the synthesis of nitrofluorenyl monomers **2.26a** and **2.26b**. The reaction between nitrofluorenylboronic acid **2.17** with 1-bromo-4-(2′-ethylhexyloxy)-*p*-xylene **2.3a** or 1-bromo-4-methoxy-*p*-xylene **2.3b** should lead directly to the corresponding dimethyl-ethylhexyloxy-nitrofluorene **2.23a** and dimethyl-methoxy-nitrofluorene **2.23b** respectively. It might be thought that a faster route to the desired material would be to simply nitrate earlier synthesised dimethyl-ethylhexyloxy-fluorene **2.7**. However, previous work in the group had shown that because the phenyl ring is heavily substituted with electron donating groups means that it would be more susceptible to electrophilic substitution during nitration than a fluorene ring. Therefore, the nitration of dipropylbromofluorene **2.5** with subsequent formation of nitrofluorenylboronic acid **2.17** was the preferred route, as it would allow the formation of **2.23a** and **2.23b** from the same intermediate. However, if the coupling reaction between the nitrofluorenylboronic acid **2.17** with the 1-bromo-4-(2′-ethylhexyloxy)-*p*-xylene **2.3a** or 1-bromo-4-methoxy-*p*-xylene **2.3b** did not work as predicted then the reactive groups (halide or boronic acid) could be reversibly introduced to allow the reaction to proceed, that is, coupling of nitrobromofluorene **2.16** with the ethylhexyloxy-*p*-xylene-boronate ester **2.21a** or methoxy-*p*-xylene-boronate ester **2.21b**.

Once the *bis*-methyl monomer precursor, namely dimethyl-ethylhexyloxy-nitrofluorene **2.23a** and dimethyl-methoxy-nitrofluorene **2.23b**, was synthesised then it would be transformed to the corresponding ethylhexyloxy-nitrofluorenyl monomer **2.26a** and methoxy-nitrofluorenyl monomer **2.26b** following the general strategy utilised for the synthesis of ethylhexyloxy-fluorenyl monomer **2.9** (Scheme **2-4**).

2.3.1.2 Nitrofluorenyl monomer synthesis

The strategy investigated involved the attempted formation of nitrofluorenylboronic acid **2.17** in the first step. The dipropylbromofluorene **2.5** compound was derivatised with a nitro group at the 7-position, Scheme **2-9**.



2.5 **2.16**

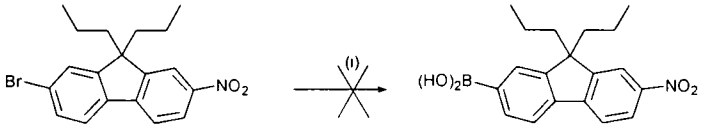
Scheme 2- 9: *Reactions and conditions*: (i). SiO_2/H_2SO_4, HNO_3, DCM

or conc.HNO_3, AcOH, Δ

The nitration of dipropylbromofluorene **2.5** was achieved with a heterogeneous catalyst using the method reported by Riego and co-workers[117] utilising a silica gel catalyst saturated with sulphuric acid. The catalyst was prepared by the absorption of 60% sulphuric acid onto silica, and this was added to a solution of concentrated nitric acid and **2.5** in dichloromethane at room temperature for 24 hours to give nitrobromofluorene **2.16** in a yield of 66%, similar to that reported in the literature[118].

However preparation of the silica catalyst was tedious for large-scale nitration reactions as this involved working with a large volume of concentrated sulphuric acid and silica. In addition, problems were incurred during stirring of the reaction mixture even with a mechanical stirrer and drying of a large volume of catalyst was awkward. It was also found that the catalytic activity of silica catalyst deteriorated with time even though when stored under dry conditions. Therefore the nitration of **2.5** was investigated using a second method. It was found that dipropylbromofluorene **2.5** in glacial acetic acid could be nitrated at 7-position by treatment with concentrated nitric acid when the nitration mixture was heated at reflux for 1.5 hours. Similar yields of the nitrobromofluorene **2.16** were obtained using both methods.

The next synthetic step involved the formation of nitrofluorenylboronic acid **2.17**, Scheme **2-10**. A solution of nitrobromofluorene **2.16** was lithiated with *n*-butyllithium at -78 °C and nitrofluorenyl anion was quenched with trimethyl borate. After an acidic hydrolysis and work-up, several compounds were observed by t.l.c. analysis.



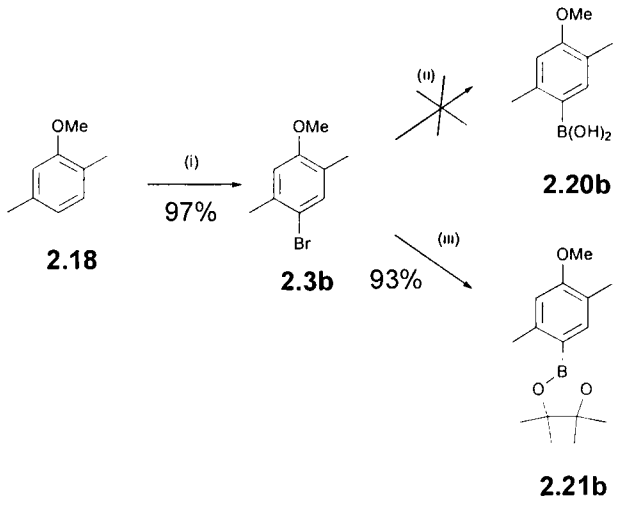
2.16 **2.17**

Scheme 2- 10: *Reactions and conditions*: (i).a. THF, *n*-BuLi, -78 °C; b. $B(OMe)_3$; c. -78 °C → r.t.; c. H^+_{aq}

Isolation of nitrofluorenylboronic acid **2.17** was attempted by column chromatography but none of the fractions showed a ^1H n.m.r. spectrum that corresponded to the desired compound. Neither the starting material nor the protonated starting material were

obtained. Clearly the presence of nitro group at 7-position in nitrobromofluorene **2.16** changes the reactivity of the substrate **2.16** towards metallation reaction using butyllithium as fluorenylboronic acid **2.6** was successfully synthesised from dipropylbromofluorene **2.5** under similar conditions. Problems were reported in the literature for the formation of nitro substituted boronic acid derivatives and this is attributed to the preference of organolithium reagents to react with a nitro group rather a halo group[119-121]

Due to the failure in the synthesis of nitrofluorenylboronic acid **2.17** from nitrobromofluorene **2.16**, the alternative route illustrated in the retrosynthetic strategy had to be followed. That is, the synthesis of two boron derivatives namely, ethylhexyloxy-*p*-xylene and methoxy-*p*-xylene-boronic acid **2.20a/2.20b** or boronate ester **2.21a/2.21b** respectively had to be prepared. The ethylhexyloxy-*p*-xylene-boronate ester **2.21a** could be performed from the earlier synthesised 1-bromo-4-(2'-ethylhexyloxy)-*p*-xylene **2.3a** and 1-bromo-4-methoxy-*p*-xylene **2.3b** was used for the synthesis of methoxy-*p*-xylene-boronate ester **2.21b**. The synthesis of methoxy-nitrofluorenyl monomer precursor **2.23b** required boron derivative **2.21b**. The first step in the formation of boronic acid **2.20b** was the bromination of commercially available 2,5-dimethylanisole **2.18** to form 1-bromo-4-methoxy-*p*-xylene **2.3b**, Scheme **2-11**.

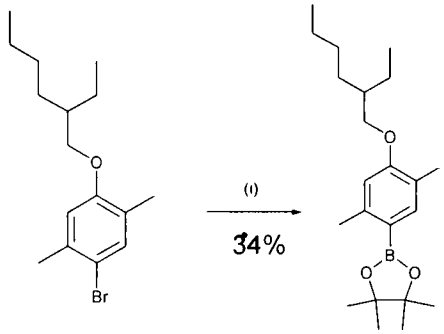


Scheme 2- 11: *Reactions and conditions*: (i). Br_2, MeOH, AcOH; (ii). a. THF, *n*-BuLi or *t*-BuLi, -78 °C; b. $B(OMe)_3$, -78 °C → r.t.; c. H^+_{aq}; (iii). a. THF, *t*-BuLi, -78 °C; b. *i*-PrOB($OC(CH_3)_2$), -78 °C → r.t.

The bromination of 2,5-dimethylanisole **2.18** with bromine was carried out in methanol/glacial acetic acid mixture at 0 °C to give 1-bromo-4-methoxy-*p*-xylene **2.3b** in a 97% yield. The synthesis of methoxy-*p*-xylene-boronic acid **2.20b** from 1-bromo-4-methoxy-*p*-xylene **2.3b** was attempted using lithiation with *n*-butyllithium or *t*-butyllithium at -78 °C in tetrahydrofuran. The anion was quenched and the intermediate ester was hydrolysed under acidic conditions. The t.l.c. analysis of the crude reaction mixture indicated that a more polar compound had formed, possibly the methoxy-*p*-xylene-boronic acid **2.20b**, but attempts to purify the crude product under the conditions normally used to isolate boronic acids were unsuccessful. Instead there was a significant mass loss and a small quantity of unidentifiable compound was recovered. Given the difficulty in isolating the boronic acid it was decided to react the anisole anion with

2-*iso*propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to increase the stability of the anisole boron derivative and decrease its polarity. In a test reaction, lithiation of 1-bromo-4-methoxy-*p*-xylene **2.3b** with *t*-butyllithium in tetrahydrofuran at -78 °C and trapping the resultant anion with 2-*iso*propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane gave methoxy-*p*-xylene-boronate ester **2.21b**, which could be easily purified over silica gel, as a white solid in a 93% yield.

2-Ethylhexyloxy-*p*-xylene-boronate ester **2.21a** was synthesised under similar reaction conditions from the corresponding 1-bromo-4-(2′-ethylhexyloxy)-*p*-xylene **2.3a**. Lithium-halogen exchange of **2.3a** and reaction with 2-*iso*propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane gave ethylhexyloxy-*p*-xylene-boronate ester **2.21a** in a 34% yield, Scheme **2-12**. In addition, the 1-bromo-4-(2′-ethylhexyloxy)-*p*-xylene **2.3a** was recovered in a 60% yield, indicating the poor quality of the *t*-butyllithium that was used. The compound **2.21a** was synthesised in a sufficient quantity therefore metallation reaction of **2.3a** was not repeated with a fresh batch of *t*-butyllithium at this stage.

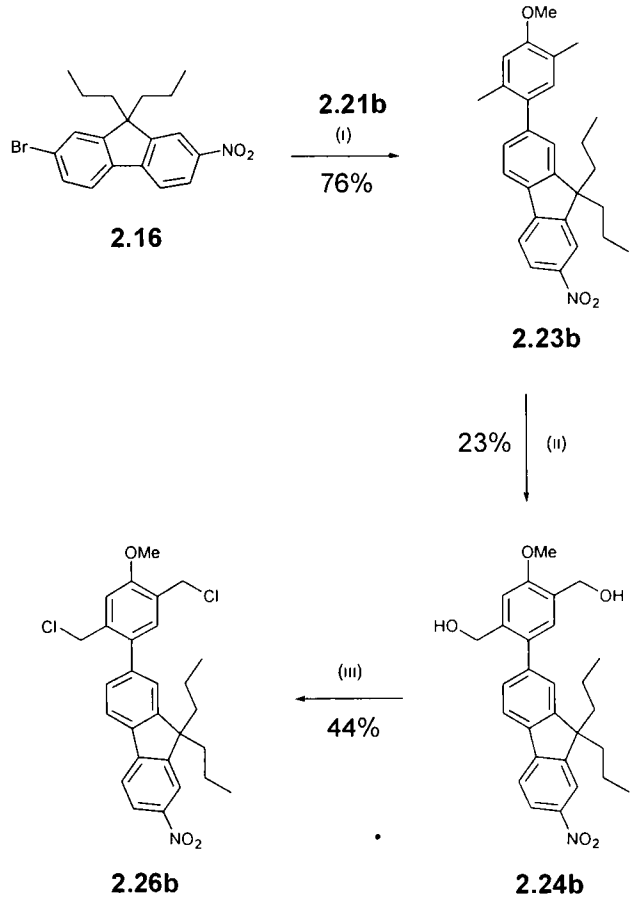


2.3a **2.21a**

Scheme 2- 12: *Reactions and conditions*: (i). a. THF, *t*-BuLi, -78 °C;

b. *i*-PrOB(OC(CH$_3$)$_2$), -78 °C → r.t.

The synthesis of methoxy-nitrofluorenyl monomer **2.26b** was performed earlier than ethylhexyloxy-nitrofluorenyl monomer **2.26a** to understand the reaction pathway. The carbon-carbon coupling reaction of nitrobromofluorene **2.16** with the methoxy-*p*-xylene-boronate ester **2.21b** was carried out under Suzuki conditions, with *tetrakis*(triphenylphosphine)palladium (0), aqueous sodium carbonate and toluene heated at reflux, Scheme **2-13**.



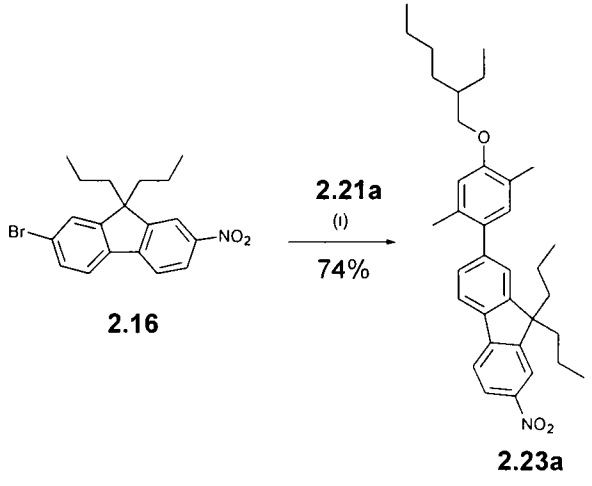
Scheme 2- 13: *Reactions and conditions*: (i). **2.21b**, $Pd(PPh_3)_4$, PhMe, $Na_2CO_{3(aq)}$, Δ; (ii) a. NBS, AIBN, CCl_4, Δ; b. NaOAc, AcOH, Δ; c. $LiAlH_4$, THF (iii) $SOCl_2$, DCM

The monomer precursor, dimethyl-methoxy-nitrofluorenyl **2.23b** was obtained in a 76% yield. The next step towards the synthesis of monomer **2.26b** from the monomer precursor **2.23b** was based on the strategy utilised for the preparation of ethylhexyloxy-fluorenyl monomer **2.9**, that is free radical bromination followed by acetylation, reduction, and chlorination. In a test reaction, benzylic bromination of the methoxy-dimethyl compound **2.23b** was achieved using *N*-bromosuccinimide and 2,2'-azo-*bis*(isobutyronitrile) in carbon tetrachloride heated at reflux and the usual inseparable mixture of bromomethyl compounds was formed. The mixture of brominated compounds was acetylated with sodium acetate in glacial acetic mixture heated at reflux to give *mono*- and *bis*-acetates and *mono*- and *bis*-aldehydes. This mixture was then reduced with lithium aluminium hydride to give methoxy-*bis*-hydroxy **2.24b** in an overall 23% yield for the three steps. Methoxy-*bis*-hydroxy **2.24b** was treated with thionyl chloride in dichloromethane to form methoxy-*bis*(chloromethyl) monomer **2.26b** in 44% yield. When the reaction for the synthesis of monomer **2.26b** was scaled up, radical bromination and acetylation of dimethyl-methoxy-nitrofluorenyl **2.23b** proceeded as per expectations, however reduction of the mixture of acetates and aldehydes with lithium aluminium hydride in tetrahydrofuran at -18 °C gave a poorly soluble compound. Not much structural information could be gathered, as the unknown compound was highly insoluble in common solvents. A small amount of the reduced compound was filtered through a plug of silica to remove any inorganic impurities and the fraction obtained was carried over to the final synthetic step, that is, halogenation towards monomer synthesis. The reduced compound was treated with thionyl chloride in dichloromethane. Surprisingly, after three hours of stirring the reaction mixture was found to be soluble and

t.l.c. of the crude indicated the formation of a new spot of similar R_f to the monomer **2.26b**. The halogenated compound was purified using general purification methods. The colour of the halogenated compound was bright yellow as compared to dull yellow colour of the earlier synthesised batch of the monomer **2.26b**. The ^{1}H n.m.r. and ^{13}C n.m.r. spectrum of the halogenated compound was recorded and compared with the corresponding spectrum of the monomer **2.26b**. Both ^{1}H n.m.r. and ^{13}C n.m.r. spectrum of the halogenated compound showed the presence of additional signals in the aromatic region but no effect on aliphatic signals was observed. The integration of protons in aromatic and aliphatic region along with ^{13}C n.m.r. spectrum suggested a dimeric structure of the halogenated compound. It has been reported in the literature that reaction of nitro compounds with lithium aluminium hydride can lead to the formation of azo or azoxy compounds[122] *via in-situ* generated nitroso, hydroxylamine and amino compounds. The infrared spectrum showed N—O stretch[123] (azoxy) at 1600 cm^{-1} and the mass analysis of the halogenated compound indicated the molecular ion peaks of 930 and 946 (MALDI carried out at EPSRC National Mass Spectrometry Service, University of Wales, Swansea) suggesting the formation of *bis*(chloromethyl) azo- and azoxy- compounds respectively. The dimerisation reaction most probably occurred during the reduction of mixture of acetates and aldehydes using lithium aluminium hydride as the solubility of the reduced product obtained was fairly different from previously synthesised methoxy-*bis*-hydroxy **2.24b**. This suggested that the reduction of nitro group occurred along with the acetate and aldehyde groups present in the acetylated mixture with lithium aluminium hydride, and resulted in the formation of a dimeric *bis*(hydroxy) azo- and azoxy- compounds instead of methoxy-*bis*-hydroxy **2.24b**. Halogenation of the dimeric

bis(hydroxy) azo- and azoxy- compounds gave dimeric *bis*(chloromethyl) monomer with azo- and azoxy-linkage. It was therefore decided to try and isolate *bis*-acetates for the synthesis of ethylhexyloxy-nitrofluorenyl monomer **2.26a** and methoxy-nitrofluorenyl monomer **2.26b**.

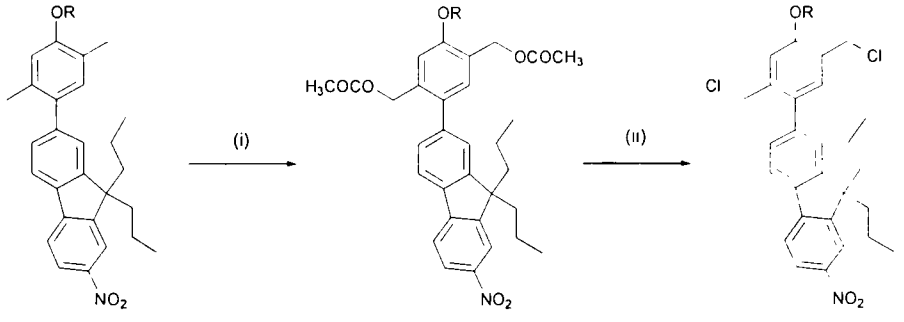
The monomer precursor, dimethyl-ethylhexyloxy-nitrofluorenyl **2.23a** was synthesised under the similar conditions as were used for the formation of dimethyl-methoxy-nitrofluorenyl **2.23a**. The reaction of nitrobromofluorene **2.16** with the ethylhexyloxy-*p*-xylene-boronate ester **2.21a** was carried out under Suzuki conditions, with *tetrakis*(triphenylphosphine)palladium (0) in toluene, Scheme **2-14**. This gave **2.23a** in a 74% yield.



Scheme 2- 14: *Reactions and conditions*: (i). **2.21a**, $Pd(PPh_3)_4$, PhMe, $Na_2CO_{3(aq)}$, Δ

The dimethyl groups of ethylhexyloxy-monomer precursor **2.23a** and methoxy-monomer precursor **2.23b** were modified under similar reaction conditions, Scheme **2-15**. The compound **2.23a** or **2.23b** were first brominated with *N*-bromosuccinimide and 2,2'-azo-*bis*(isobutyronitrile) in carbon tetrachloride heated at reflux to give a mixture of

benzylic brominated compounds then acetylated in sodium acetate and glacial acetic mixture. After aqueous work-up, the crude acetylation mixtures was purified by column chromatography and recrystallisation gave the ethylhexyloxy-*bis*-acetate **2.25a** and methoxy-*bis*-acetate **2.25b** in 42% and 53% yields respectively for the two reaction steps.



2.23a/2.23b **2.25** **2.26**

a, R = 2-ethylhexyl, 42% **a**, R = 2-ethylhexyl, 83%
b, R = methyl, 53% **b**, R = methyl, 80%

Scheme 2- 15: *Reactions and conditions*: (i). a. NBS, AIBN, CCl_4, Δ; b. NaOAc, AcOH, Δ; (ii) HCl, 1,4-dioxane, Δ

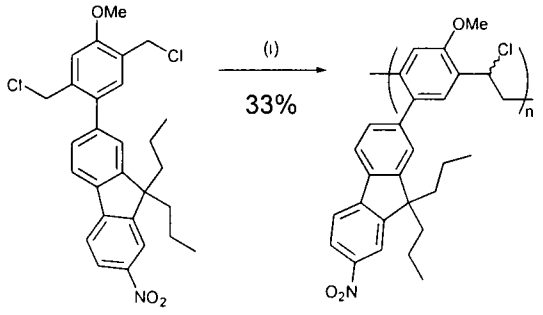
The *bis*(acetoxymethyl) groups of compound **2.25a** and **2.25b** were transformed to the corresponding *bis*(chloromethyl) monomers, namely ethylhexyloxy-nitrofluorenyl **2.26a** and methoxy-nitrofluorenyl **2.26b** by treatment with concentrated hydrochloric acid in 1,4-dioxane heated at reflux. The monomers **2.26a** and **2.26b** were obtained in 83% and 80% yields respectively.

2.3.2 Poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-methoxy-1,4-phenylenevinylene]

Polymerisation of both the nitrofluorenyl monomers **2.26a** and **2.26b** was carried out with different equivalents of base. The polymers would be obtained *via* different synthetic routes. It was anticipitated that the methoxy-nitrofluorenyl monomer **2.26b** would not give a soluble conjugated polymer. This meant that the precursor polymer would have to be isolated. In contrast the ethylhexyloxy-nitrofluorenyl monomer **2.26a** should give rise to a soluble conjugated polymer. It was decided to pursue the synthesis and polymerisation of nitrofluorenyl monomer with the methyl group first to determine whether the polymerisation, solubility, and/or the properties of the resultant precursor polymer poly{2-[(7-nitro-9,9-dipropylfluorenyl)-5-methoxyphenyl]-1-chloroethylene}**2.28** (I-M-NO_2FPPV) is affected by the nitro group before the synthesis of polymer poly{2-[2-(7-nitro-9,9-dipropylfluorenyl)]-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene} **2.30** (S-EH-NO_2FPPV) with the longer 2-ethylhexyl group was attempted.

2.3.2.1 Synthesis of chloro-precursor of Methoxy-nitrofluorenyl-PPV (Σ-M-NO_2FPPV)

The synthesis of precursor polymer **2.27** (Σ-M-NO_2FPPV) from *bis*-chloromethylated methoxy-nitrofluorenyl monomer **2.26b** is shown in Scheme **2-16**.



2.26b **2.27**

Scheme 2- 16: *Reactions and conditions*: (i) KOBu^t, THF

The polymerisation of monomer **2.26b** was carried out by adding 0.9 equivalents of potassium *t*-butoxide as a 0.2 M solution in tetrahydrofuran to a 0.2 M monomer solution in tetrahydrofuran at room temperature under argon. After stirring for two hours, the reaction mixture had gelled. In an attempt to disperse the polymer network, extra solvent was added and the reaction mixture was put on an ultrasonic bath for an hour. However, this did not break the polymer network. The formation of physically entangled, and/or chemically linked polymer networks may be prevented by diluting the reaction mixture. The polymerisation reaction was attempted with a lower monomer and base concentration, 0.05 M and 0.1 M respectively and after two hours no gelation was observed.

The purification of Σ-M-NO_2FPPV **2.27** from oligomers and unpolymerised monomer was carried out in several steps. First the reaction mixture was filtered through a cotton-wool plug to remove any insoluble particles and then the polymer was precipitated into ice-cold methanol. The polymer **2.27** was isolated by centrifugation and decanting the supernatant. The polymeric residue was redissolved in tetrahydrofuran. The

process was repeated three times, before being dried briefly under vacuum to give Σ-M-NO_2FPPV **2.27** in a ~33% yield. The precursor polymer **2.27** was then dissolved in dry tetrahydrofuran and stored at low temperature in the dark to prevent elimination of hydrogen chloride leading to the formation of an insoluble conjugated polymer **2.28**.

2.3.2.2 Properties of chloro-precursor polymer and its thermal conversion to conjugated polymer

The chloro-precursor polymer Σ-M-NO_2FPPV **2.27** was characterised by g.p.c., TGA, DSC, ^{1}H n.m.r., infrared and U.V.-visible spectroscopy. G.p.c. analysis showed that the precursor polymer **2.27** had a molecular weight, $\overline{M}_w$ of 6.5 × 10^5 g/mol (relative to polystyrene standards) and a polydispersity, PD of 6.2. The ^{1}H n.m.r. (Figure **2-9**) of Σ-M-NO_2FPPV **2.27** showed broad signals consistent with the formation of polymer **2.27** structure.

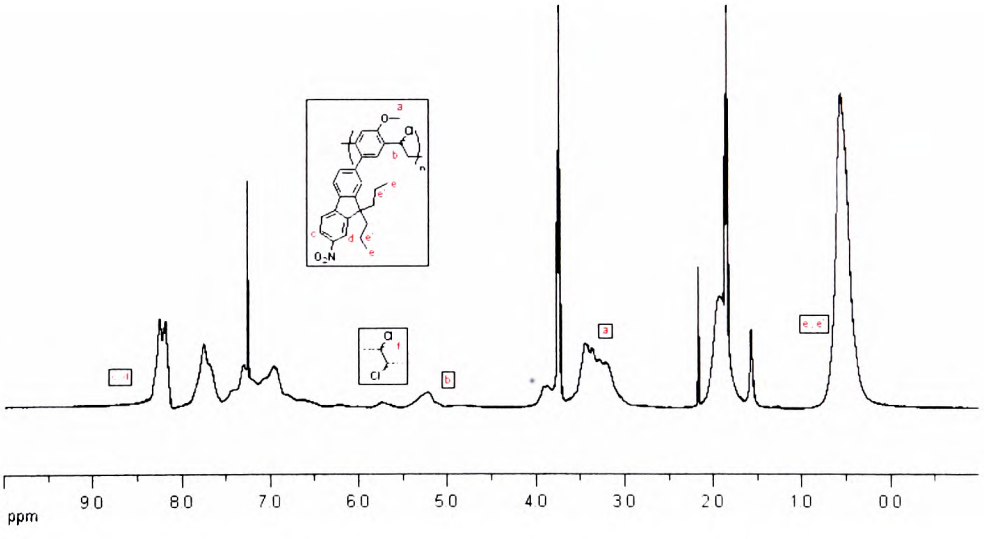


Figure 2- 9: ^{1}H n.m.r. spectrum of Σ-M-NO_2FPPV **2.27** in $CDCl_3$

In this case the fact that it was a precursor polymer rather than a fully conjugated polymer could be seen by the presence of signal at 5.0-5.5 p.p.m. corresponding to the methine proton of the CHCl moiety. Comparison of the integration of the CHCl signal with CH_2CH_3 signals of the two-propyl groups at 0.3-1.1 p.p.m. showed that the precursor polymer contained ~20% of other arrangement units. The precursor polymers can often contain some conjugation arising from base-promoted elimination during polymerisation. In addition, the polymerisation mechanism can give rise to the possibility of head-to-head and tail-to-tail arrangements of the monomer units in the polymer. A small degree of tail-to-tail arrangement was observed as indicated by the formation of 1,2-dichloroethylene units at 5.5-5.9 p.p.m.[105]. This was further visualised for the slight offset in the integration of aromatic protons namely, 6-H and 8-H (2 H, 8.1-8.4 p.p.m.) to the CHCl moiety. No ethylene protons (benzylic nature) at ~2.8 p.p.m. in the ^{1}H n.m.r. of **2.27** were observed indicating absence of head-to-head defects.

The thermal characteristics of the Σ-M-NO_2FPPV **2.27** were studied by DSC and TGA. DSC analysis of precursor polymer **2.27** indicated the presence of a glass transition temperature (T_g) at 68 °C suggesting that the precursor polymer could be annealed before it was locked in place by the conversion to the conjugated polymer **2.28**. It has been reported that the annealed polymer films show an improvement in their optical properties over non-annealed films[124]. The temperature at which hydrogen chloride was eliminated from the precursor polymer to form the conjugated polymer **2.28** and stability of the conjugated polymer was determined by TGA studies. Polymer Σ-M-NO_2FPPV **2.27** showed a steady weight loss on heating at a rate of 10 °C per minute before three significant weight losses at 210 °C, 300 °C and, 400 °C were observed (Figure **2-10**). The

initial steady weight loss, < 5%, was due to the trapped solvent within the polymer network as the solid polymer was obtained by briefly drying from the its solution in tetrahydrofuran. A mass loss of ~7% (calculated by drawing tangents at 150 and 230 °C) at 210 °C, was attributed to the elimination of hydrogen chloride to form the conjugated polymer **2.28**. The theoretical mass loss for dehydrochlorination was calculated to be 8%. This implies that the precursor polymer contains around 12% of conjugated units, which is consistent with the ^{1}H-n.m.r (Figure **2-9**). The second major mass loss occurred at 300 °C, which was the start of the polymer degradation. At 410 °C the polymer started to completely breakdown.

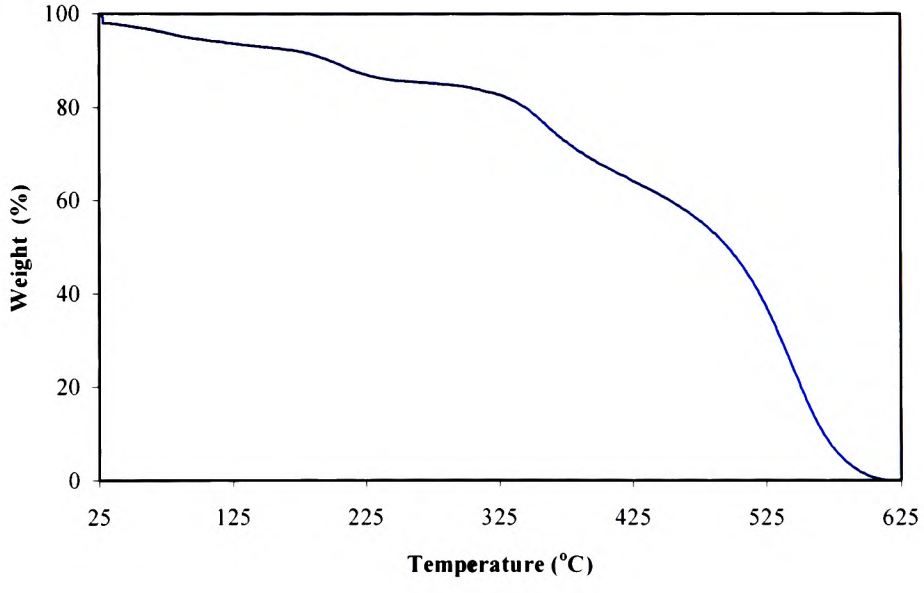
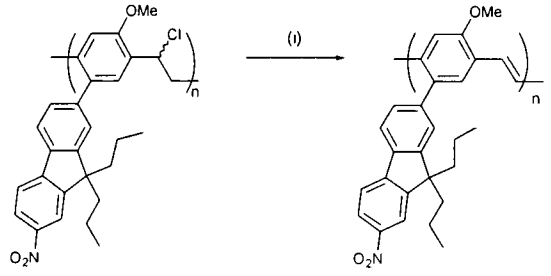


Figure 2- 10: TGA of Σ-M-NO_2FPPV **2.27**

Once the temperature for elimination of hydrogen chloride from precursor polymer, Σ-M-NO_2FPPV **2.27** was determined from the TGA then its thermal conversion to form the insoluble conjugated polymer **2.28** (I-M-NO_2FPPV) was carried out. The conversion of precursor polymer **2.27** to conjugated polymer **2.28** was followed by infrared and U.V.-visible spectroscopy. For the infrared study, the Σ-M-NO_2FPPV **2.27** was drop cast onto a KBr disc and residual solvent was allowed to evaporate under ambient conditions. For the U.V.-visible study, a solution of **2.27** was spin-coated on to both quartz and ITO coated glass substrates. The infrared and U.V.-visible spectra were recorded before and after thermal conversion of the precursor polymer **2.27**. Thermal conversion of the precursor polymer **2.27**, to form the I-M-NO_2FPPV **2.28**, Scheme **2-17**, was achieved by heating the films at 215 °C, under a dynamic vacuum for 17 hours.



2.27 **2.28**

Scheme 2- 17: *Reactions and conditions*: (i) 215 °C, Vacuum

The infrared spectrum of the Σ-M-NO_2FPPV **2.27** and I-M-NO_2FPPV **2.28** films are shown in Figure **2-11**. The film of **2.28** showed a new absorption peak at 970 cm^{-1} due to the C=C-H *trans*-vinylene C-H out of plane bend, indicating that the thermal conversion has taken place to form the conjugated backbone. Importantly, the absorptions at 1520 cm^{-1} and 1333 cm^{-1} corresponding to the antisymmetric and symmetric stretch of

the nitro group in the Σ-M-NO_2FPPV **2.27** were also observed in the spectrum of the I-M-NO_2FPPV **2.28** respectively indicating that the nitro group is not eliminated during thermal conversion at 215 °C and both the polymers were stable to the thermal conversion.

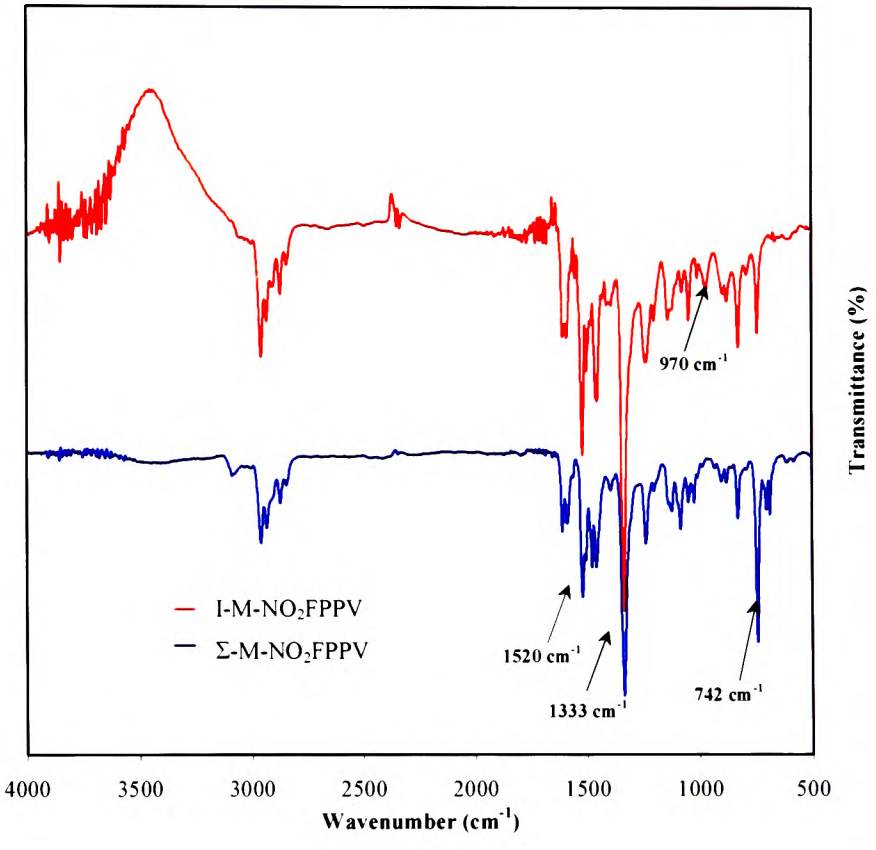


Figure 2- 11: Infrared spectra of Σ-M-NO_2FPPV **2.27** and I-M-NO_2FPPV **2.28**

The films of Σ-M-NO_2FPPV **2.27** spin-coated from a tetrahydrofuran solution, were all found to be hazy, patchy and of poor quality, suggesting that aggregation of the polymer had occurred. To overcome this aggregation of polymer film, chloroform was

used. The chloroform solutions were prepared by removing the tetrahydrofuran under vacuum and then redissolving the polymer in chloroform, which was then spin-coated immediately. Halo precursor polymers are unstable in chloroform with hydrogen chloride being eliminated. Good quality films of **2.27** were prepared from chloroform solution (Figure **2-12**).

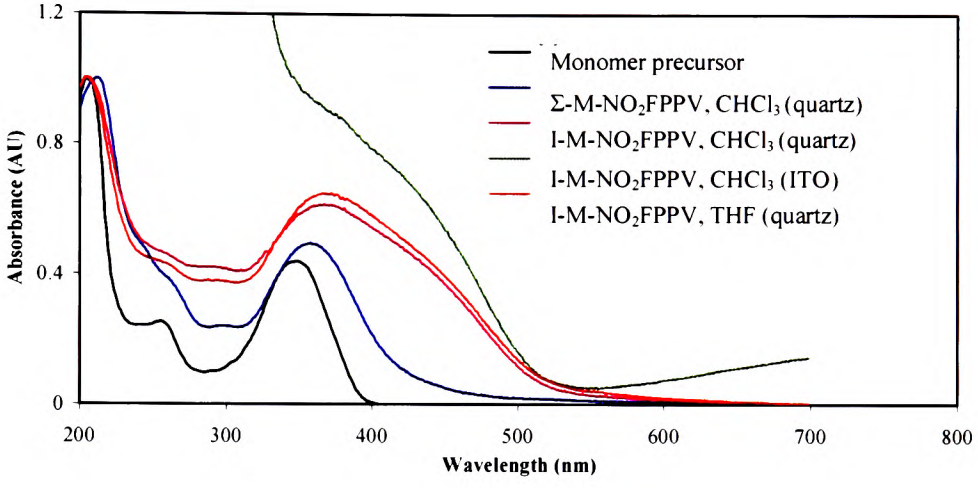


Figure 2- 12: U.V.-visible spectra of monomer precursor **2.23b**, Σ-M-NO_2FPPV **2.27** and I-M-NO_2FPPV **2.28**

The spectra of the monomer precursor **2.23b** (*n*-pentane) and films of Σ-M-NO_2FPPV **2.27** were similar with peaks at ~349 nm and ~357 nm corresponding to the localised π-π* transitions and the absorption of the "nitrofluorenylphenyl" chromophore respectively. On thermal conversion a broad absorption above 400 nm was observed corresponding to the delocalised π-π* transitions of the backbone. The change in absorption wavelength was mirrored by the pale yellow film of the precursor polymer being transformed into a bright yellow film after thermal treatment. After thermal conversion the shape of U.V.-

visible spectrum of I-M-NO_2FPPV **2.28** was found to be similar irrespective of the nature of solvent used for spin-coating the precursor polymer film. It is interesting to note that thermal conversion of the Σ-M-NO_2FPPV **2.27** film (spin-coated from tetrahydrofuran) to I-M-NO_2FPPV **2.28** at 215 °C, the films obtained were of good quality indicating that as the conversion temperature was above the T_g ($T > T_g$ of the polymer), the polymer flowed into an annealed state during the conversion. The Σ-M-NO_2FPPV **2.27** film was also coated onto ITO glass and converted to give a film in a similar long wavelength absorption suggesting that there may be minimal chemical interaction of the eliminated hydrogen chloride with the ITO. The degree of conjugation obtained for the conjugated polymer can be understood by comparison of the ratios of the localised to the delocalised π-π* transitions, the smaller the ratio the better the delocalisation.

2.3.2.3 Summary

In summary, the methoxy-nitrofluorenyl monomer **2.26b** to fully conjugated polymer, I-M-NO_2FPPV **2.28** has been successfully synthesised and polymerised from precursor polymer, Σ-M-NO_2FPPV **2.27**. Good quality thin films were obtained by spin-coating **2.27** from chloroform and on thermal conversion the fully conjugated polymer **2.28** was formed. However, the U.V.-visible spectrum of **2.28** showed that the longer wavelength associated with the delocalised π–π* transitions was still weaker as when compared with the localised π–π* transitions. The ^{1}H n.m.r. of Σ-M-NO_2FPPV **2.27** showed no saturated unit defects which could account for the shortening of the effective conjugation length available for delocalisation and hence lower ratio value of

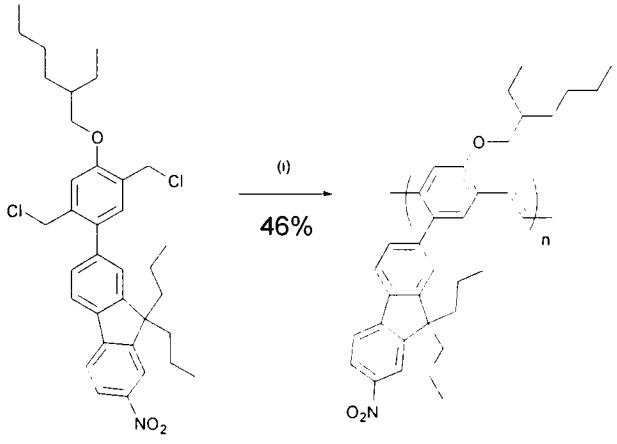
delocalised to localised π–π* transitions observed after its thermal conversion to I-M-NO_2FPPV **2.28**. This could be again accounted by twisting of the polymer backbone by the biphenyl linkage. However, the ratio of delocalised π–π* transitions to the localised π–π* transitions was higher than S-FEH-PPV **2.11** (without nitro as EWG).

2.3.3 Poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene]

In general, there are two approaches towards the synthesis of conjugated polymer has involved *(i)* polymers that are insoluble in their final conjugated form and are prepared *via* processable precursor polymers, *(ii)* or materials that are soluble in their conjugated form. The latter polymers are comparatively easy to synthesise and processible in single layer devices, but problems were incurred during their use in multilayer devices because of the problems of their co-solubility with the other materials. Hence, former method for the synthesis of the conjugated polymers is more in use in multilayer devices. The synthesis of the conjugated polymer, ethylhexyloxy-nitrofluorenyl-PPV **2.30** (EH-NO_2FPPV) with 2-ethylhexyloxy as the electron-donating group was pursued through two routes, the soluble precursor route and directly to the conjugated polymer. The different routes were investigated in order to study the affect of the different synthetic routes on the optical properties of the conjugated polymer.

2.3.3.1 Synthesis of soluble 2-Ethylhexyloxy-nitrofluorenyl-PPV

The synthesis of the soluble conjugated polymer S-EH-NO_2FPPV **2.30a** was carried out by treatment of the ethylhexyloxy-nitrofluorenyl monomer **2.26a** with 5.0 equivalents of the potassium *t*-butoxide in anhydrous tetrahydrofuran, Scheme **2-18**. A 0.1 M solution of monomer **2.26a** was reacted with 0.05 M solution of potassium *t*-butoxide. After 3.5 hours, the reaction mixture was quenched by precipitation into an ice-cold methanol.



2.26a **2.30a**

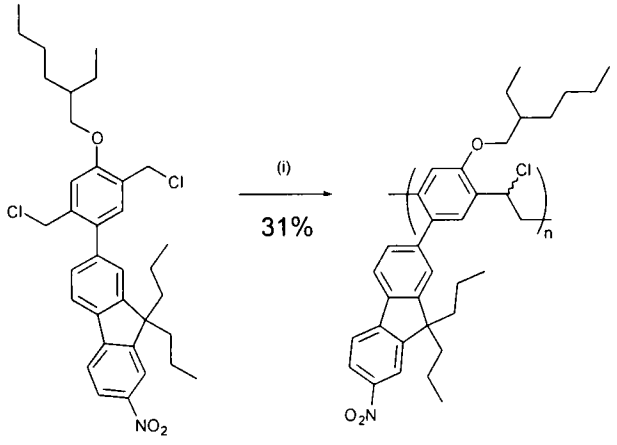
Scheme 2- 18: *Reagents and conditions*: (i). 5.0 equiv. $KOBu^t$, THF

The purification of the polymer was achieved by centrifugation and dissolving the precipitate obtained in tetrahydrofuran. The polymer solution was precipitated again by pouring into ice-cold methanol. The process was repeated until no oligomer and, monomer impurities were detected in the g.p.c. trace. The precipitate obtained was dried

under vacuum in dark to give the soluble conjugated polymer **2.30a** (S-EH-NO_2FPPV) as a dark yellow solid in a 46% yield.

2.3.3.2 Synthesis of chloro-precursor of 2-Ethylhexyloxy-nitrofluorenyl-PPV

In the soluble precursor route, the soluble precursor polymer (Σ-EH-NO_2FPPV) **2.29** is synthesised from the ethylhexyloxy-nitrofluorenyl monomer **2.26a**, Scheme **2-19**.



2.26a **2.29**

Scheme 2- 19: *Reagents and conditions*: (i). 0.9 equiv. $KOBu^t$, THF

A 0.1 M solution of monomer **2.26a** in anhydrous tetrahydrofuran was reacted with 0.9 equivalents of 0.1 M solution of potassium *t*-butoxide in tetrahydrofuran. After 3.5 hours the reaction mixture was filtered through a cotton-wool plug to remove insoluble particles and the filtrate was added drop-wise to ice-cold methanol. The precursor polymer precipitate was isolated by centrifugation followed by decantation of the supernatant. Further purification of the precursor polymer involved its dissolution in a minimum

volume of tetrahydrofuran and precipitated again in ice-cold methanol. The process was repeated one more time and the precipitate was briefly dried *in vacuo* to give the precursor polymer in ~31% yield as a light-yellow precipitate. The precursor polymer **2.29** (Σ-EH-NO_2FPPV) was stored as a solution in anhydrous tetrahydrofuran at low temperature in the dark.

2.3.3.3 Comparison of the Properties of precursor polymer and conjugated polymers

The soluble conjugated polymer S-EH-NO_2FPPV **2.30a** and chloro-precursor polymer Σ-EH-NO_2FPPV **2.29** were characterised by g.p.c., TGA, DSC, ^{1}H n.m.r., infrared and U.V.-visible spectroscopy. G.p.c. analysis of S-EH-NO_2FPPV **2.30a** and Σ-EH-NO_2FPPV **2.29** and showed they had an $\overline{M}_w$ = 2.9 x 10^5 and 6.0 x 10^5 g/mol, and PD = 3.3 and 8.1. The ^{1}H n.m.r. spectroscopy was used to characterise the structure of Σ-EH-NO_2FPPV **2.29** and S-EH-NO_2FPPV **2.30a** in deuterated chloroform. The ^{1}H n.m.r. (Figure **2-13**) of S-EH-NO_2FPPV **2.30a** showed a broad doublet signals at 3.2-4.0 p.p.m. due to OCH_2 protons. The absence of signal at 5.0-5.5 p.p.m. due to CHCl proton indicated the formation of fully conjugated backbone of the polymer. The integration of aromatic protons at 8.0-8.5 p.p.m. (2 H) region is consistent with the OCH_2 protons at 3.2-4.0 p.p.m. (2 H). Interestingly, unlike the ^{1}H n.m.r. of S-MEHPPV **1.4b** (Figure **2-3**) but similar to the ^{1}H n.m.r. of S-EH-FPPV **2.11** (Figure **2-4**) there was no signal due to benzylic protons at ~2.8 p.p.m. suggesting absence of head-to-head defects in the polymer backbone. The polymerisation of monomer **2.26a** proceeded in a regioregular fashion *via* predominantly more favoured quinoidal intermediate.

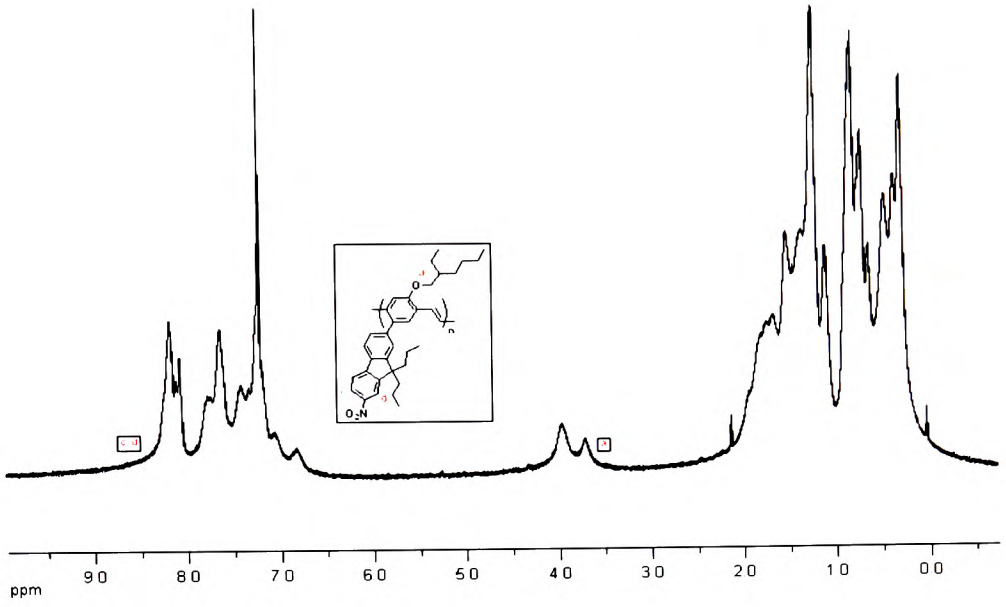


Figure 2- 13: ^{1}H n.m.r. spectrum of S-EH-NO_2FPPV **2.30a** in $CDCl_3$

The ^{1}H n.m.r. spectrum (Figure **2-14**) of Σ-NO_2EH-FPPV **2.29** showed broad signals at 0.2-2.1, 3.0-4.0 p.p.m. and 4.7-5.5 p.p.m. due to alkyl, OCH_2 and CHCl protons respectively and were consistent with the formation of precursor polymer backbone structure. The spectrum showed a small percentage of tail-to-tail defects in the precursor polymer at ~5.7 p.p.m. due to the formation of 1,2-dichloroethylene units. This accounted for the discrepancy in the integration of aromatic protons at 8.1-8.5 p.p.m. (2 H) with CHCl proton (0.7 H) at 4.7-5.5 p.p.m.. Some signals were seen at ~2.5 p.p.m. suggesting *bis*-benzyl moieties in the polymer backbone.

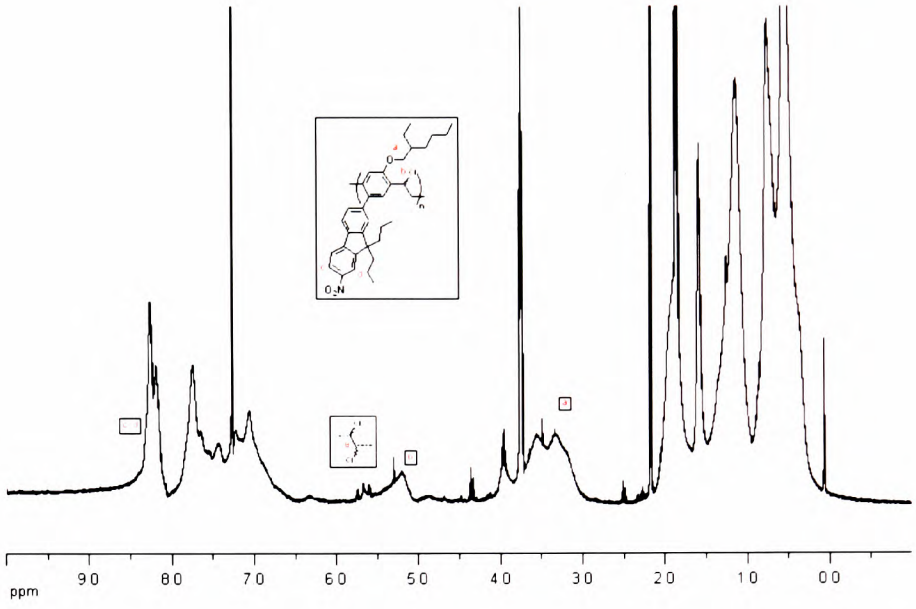


Figure 2- 14: ^{1}H n.m.r. spectrum of Σ-NO_2EH-FPPV **2.29** in $CDCl_3$

The thermal behaviour of the polymers Σ-EH-NO_2FPPV **2.29**, and S-EH-NO_2FPPV **2.30a** were studied, Figure **2-15**.

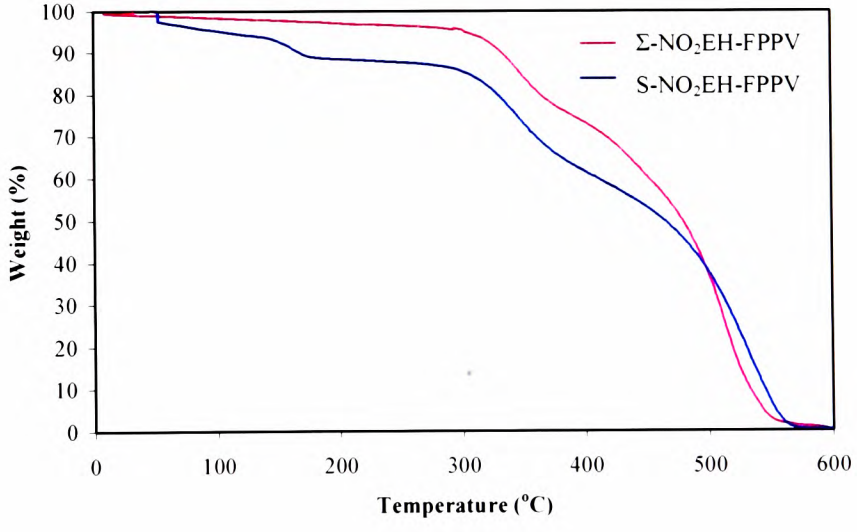
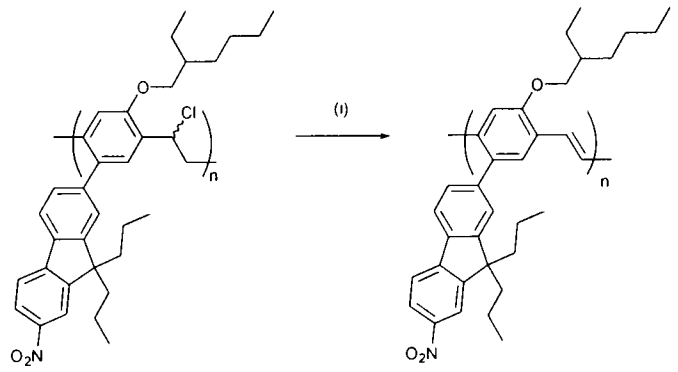


Figure 2- 15: TGA of Σ-NO_2EH-FPPV **2.29** and S-NO_2EH-FPPV **2.30a**

Thermogravimetric analysis of **2.29** and **2.30a** was determined at a heating rate of 2 °C/min. The precursor polymer **2.29** indicated four weight losses namely, initial steady weight loss was due to the volatilisation of low molecular weight species such as solvent; dehydrochlorination at 143 °C (experimental weight loss 6%, theoretical weight loss 7%) to form insoluble conjugated polymer (I-EH-NO_2FPPV) **2.30b** followed by initiation of polymer degradation at 310 °C and finally at 410 °C a complete polymer decomposition occurred. This weight loss of ~6% at 143 °C implies that the precursor polymer contains around 14% of conjugated units, which is consistent with the ^{1}H-n.m.r of **2.29**. The TGA curve of **2.30a** showed its thermally stability up to 310 °C thereafter it degrades completely in two stages. The thermal stability and degradation of polymers **2.30a** and **2.30b** (formed after dehydrochlorination) prepared from two different routes showed similar behaviour. No T_g was detected by DSC analysis of the polymer **2.30a**. Polymer **2.29** quantity was not sufficient to perform DSC studies.

After the determination of temperature for the dehydrochlorination by TGA of Σ-EH-NO_2FPPV **2.29**, it was then thermally converted to insoluble conjugated polymer, I-EH-NO_2FPPV **2.30b** (Scheme **2-20**). The infrared and U.V.-visible spectroscopy was used to study the thermal conversion. A thin film of Σ-EH-NO_2FPPV **2.29** was drop-cast on to a freshly prepared KBr disc, whilst for the U.V -visible study polymer was spin-coated on to quartz substrate. The infrared and U.V.-visible spectra of thin films of **2.29** were pre-recorded on KBr and quartz substrate before thermal conversion. The polymer **2.29** coated substrates were heated at 160 °C under vacuum to dehydrochlorinate Σ-EH-NO_2FPPV **2.29** to form I-EH-NO_2FPPV **2.30b**. The infrared and U.V.-visible spectra of the thermally treated polymer coated substrates were again recorded.



2.29 **2.30b**

Scheme 2- 20: *Reagents and conditions*: (i). 160 °C, Vacuum

The infrared study of films of the conjugated polymers prepared *via* different synthetic routes, S-EH-NO_2FPPV **2.30a** (directly from the monomer **2.26a**) and I-EH-NO_2FPPV **2.30b** (from the precursor **2.29**), and the precursor polymer Σ-EH-NO_2FPPV **2.29** are shown in Figure **2-16**.

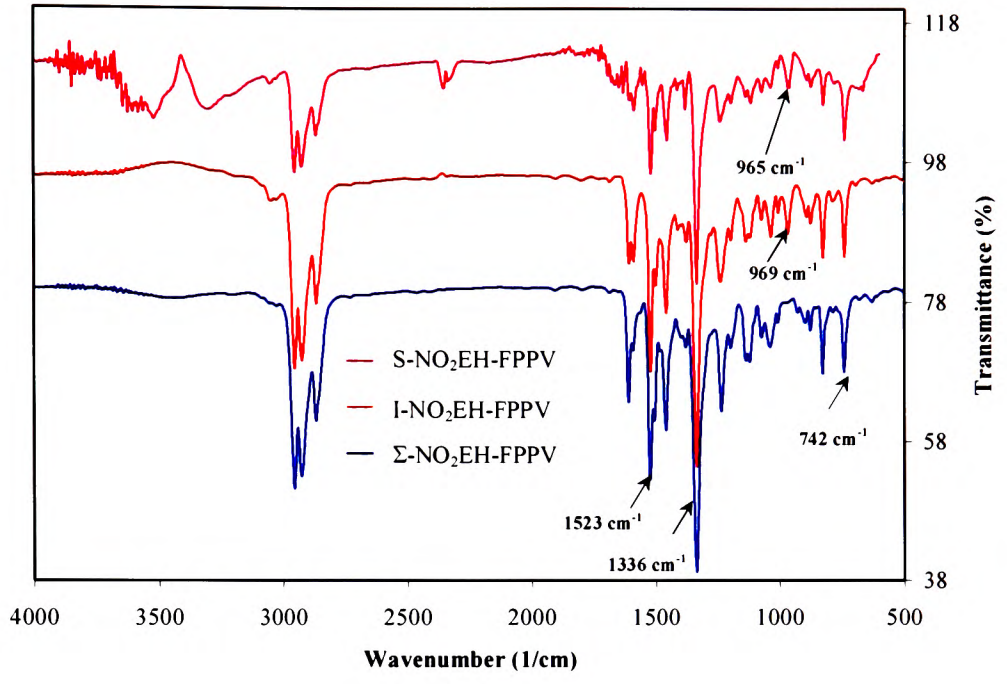


Figure 2- 16: Infrared spectra of Σ-EH-NO_2FPPV **2.29,** S-EH-NO_2FPPV **2.30a** and I-EH-NO_2FPPV **2.30b**

Thermal conversion of Σ-EH-NO_2FPPV **2.29** to I-EH-NO_2FPPV **2.30b** led to the formation of C=C-H *trans*-vinylene C-H out of plane bend at 969 cm^{-1}. The S-EH-NO_2FPPV **2.30a** also showed C=C-H *trans*-vinylene C-H out of plane bend at 965 cm^{-1} indicating the presence of *trans* configuration of the double bond in the conjugated polymer backbone. All the three polymers **2.29**, **2.30a**, and **2.30b** showed characteristic absorption peak due to the antisymmetric and symmetric stretch of the nitro group around 1523 cm^{-1} and 1336 cm^{-1} respectively. The presence of nitro group in **2.30b** indicated it is not eliminated from the polymer **2.29** during thermal conversion.

The U.V.-visible spectra of monomer precursor **2.23a** in solution, polymer films of Σ-EH-NO_2FPPV **2.29**, I-EH-NO_2FPPV **2.30b** and S-EH-NO_2FPPV **2.30a** are shown in Figure **2-17**.

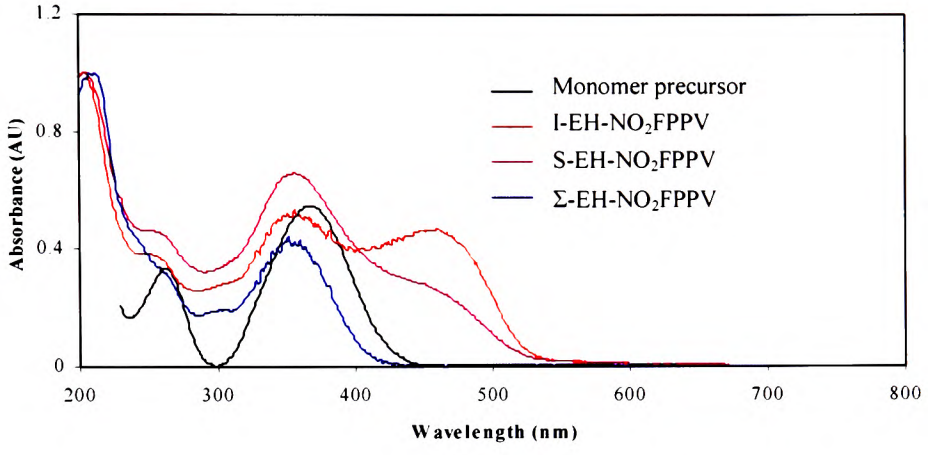


Figure 2- 17: U.V.-visible spectra of monomer precursor **2.23a**, Σ-EH-NO_2FPPV **2.29**, S-EH-NO_2FPPV **2.30a**, I-EH-NO_2FPPV **2.30b**, and S-EH-FPPV **2.11** on quartz

The film of **2.29** and **2.30a** was prepared by spin-coating tetrahydrofuran solution on to quartz substrate and dried under ambient conditions. The spectrum of Σ-EH-NO_2FPPV **2.29** was similar to that of the monomer precursor **2.23a** with the localised π–π* transitions at ~210 nm and a relatively strong absorption at ~350 nm due to the "dipole" chromophore. After thermal conversion of **2.29** to I-NO_2EH-FPPV **2.30b** another maximum at ~460 nm due to the delocalised π–π* transitions was observed. A significant difference was observed in the U.V.-visible absorption characteristics of conjugated polymers prepared from two different routes. When conjugated polymer **2.30a** was prepared directly from the monomer the delocalised π–π* transitions appeared as a shoulder at ~420 nm. However when **2.30b** was prepared by thermal conversion

there is a distinct peak and the optical density is relatively greater. This can be qualitatively seen in comparing the ratio of the π–π* localised and delocalised transitions. The smaller the ratio of localised to delocalised transitions the better the delocalisation along the polymer backbone. For **2.30a** prepared directly from the monomer the ratio found is 3.7 while polymer **2.30b** prepared from the precursor **2.29** has a ratio of 2.1. This implied the existence of more coplanar domains in polymer **2.30b** resulting in longer effective conjugation length than **2.30a** and thereby allowing a better charge delocalisation across the backbone. Moreover a drastic change in the colour of polymer **2.29** film was observed upon thermal conversion to **2.30b**. The colour changed from light-yellow to dark-yellow indicates the conversion of un-conjugated backbone to a fully conjugated backbone of the polymer. S-EH-NO_2FPPV **2.30a** film was of similar colour to I-EH-NO_2FPPV **2.30b** film. The only difference between polymer **2.30a** and **2.30b** is the processing temperature apart from the synthetic method. Polymer film **2.30b** was obtained by thermal treatment while **2.30a** was prepared under ambient conditions. In order to assign the reason for their optical property difference, that is the appearance of delocalised π–π* transitions as a peak in **2.30b** and as a shoulder in **2.30a**. Polymer **2.30a** film was heated at similar conditions, that is, at 160 °C under vacuum. No significant difference was noticed after thermal treatment of polymer film **2.30a**.

U.V.-visible spectra of S-EH-NO_2FPPV **2.30b**, S-EH-FPPV **2.11**, I-EH-NO_2FPPV **2.30b** and I-M-NO_2FPPV **2.28** were compared after normalisation the spectra at localised π-π* transitions, Figure **2-18**.

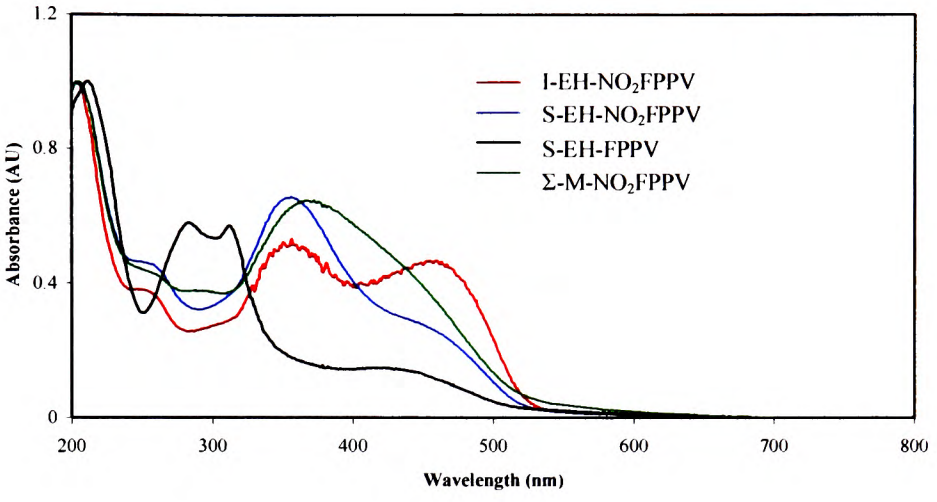


Figure 2- 18: U.V.-visible spectra of S-EH-NO_2FPPV **2.30a**, S-EH-FPPV **2.11**, I-EH-NO_2FPPV **2.30b**, and I-M-NO_2FPPV **2.28** on quartz

The ratio of delocalised to localised π-π* transitions of the S-EH-NO_2FPPV **2.30a** was found to be two-fold higher than the S-EH-FPPV **2.11**, without the nitro group prepared using excessive equivalents of base. Moreover there is a red shift in both the monomer chromophore and delocalised π-π* transitions. This is attributed to the more delocalised backbone and the presence of nitro group in the fluorene ring resulting in extension of π-electron delocalisation in the former. In case of polymers prepared *via* precursor route the intensity of delocalised π-π* transitions was higher for I-M-NO_2FPPV **2.28** than I-EH-NO_2FPPV **2.30b** indicating there are more chromophores with the same transition in **2.28**.

2.3.3.4 Summary

In summary, the 2-ethylhexyloxy-nitrofluorenyl-PPVs were synthesised successfully *via* two routes as a soluble conjugated polymer, S-EH-NO_2FPPV **2.30a** directly from the monomer **2.26a**, and as an insoluble conjugated polymer, I-EH-NO_2FPPV **2.30b** *via* precursor polymer **2.29**. The polymers **2.29** and **2.30a** were obtained in high molecular weight. The thermal behaviour of **2.30a** and **2.30b** (formed after dehydrochlorination of **2.29**) was found to be similar. Interestingly, the ^{1}H-n.m.r spectrum of **2.30a** showed no synthetic defects but precursor polymer **2.29** showed tail-to-tail defects. The U.V.-visible absorption characteristics were found to be dependent on the nature of synthetic route. The precursor route for the formation of **2.30b** showed stronger delocalised π–π^* transitions than **2.30a** prepared from the monomer. The delocalised π–π^* transitions appeared as a shoulder in **2.30a** and as a maximum in **2.30b**. This could be attributed to the presence of more planarity in the adjacent units of polymer **2.30b**. For 2-ethylhexyloxy-nitrofluorenyl-PPVs the ratio of delocalised π–π^* transitions to the localised π–π^* transitions was higher than its structural analogue S-FEH-PPV **2.11** (without nitro as EWG) but the ratio is still lower than 1 as compared to S-MEHPPV **1.4b**. The value should be ≥ 1 for a good level of delocalisation, suggesting a shorter average conjugation length available for delocalisation. In general, the longer wavelength delocalised transitions of 2-ethylhexyloxy-nitrofluorenyl-PPVs are still weak as compared with the localised π–π^* transitions and mainly attributed to the twisting of the polymer backbone by the biphenyl linkage.

2.4 Photophysical and device properties

The photophysical properties and device performance of polymers S-EH-FPPV **2.11** and S-EH-NO_2FPPV **2.30a** were studied in the Department of Physics (University of St. Andrews) and the Department of Materials (University of Oxford). The choice of the polymers amongst other biphenyl-linked PPVs was based on the fact that both **2.11** and **2.30a** were prepared directly from the monomer and were structurally analogous apart from **2.30a** which had an EW nitro group attached. The first question that had to be answered was whether the chromophore with the dipole reduced the recombination of the excitons upon photoexcitation. This can be determined by measuring the Photoluminescence Quantum Yield (PLQY) of the material and the results are summarised in Table **2-1**.

Table 2-1: PLQY of S-EH-FPPV **2.11** and S-EH-NO_2FPPV **2.30a**

Polymer	PLQY (%)	
	ITO	**Solution**[†]
2.11	6.4	19.1
2.30a	0.8	2.8

[†] Chlorobenzene

The PLQY is a measure of luminescence observed by electron-hole recombination, a competitive pathway to the desired electron-hole separation pathway in solar-energy harvesting devices. A PLQY of 100% would indicate that for every photon absorbed a photon would be released. The PLQY of S-EH-NO_2FPPV **2.30a**, which has the dipole due to the nitro group was decreased by a factor of 8 relative to S-EH-FPPV

2.11 both in solution and as a film on ITO. This clearly indicates that the attachment of the nitro group reduces radiative charge recombination although the measurement does not indicate whether this is due to charge separation or some other mechanism. The decrease in PLQY of **2.30a** could be either due to the non-radiative decay of the bound exciton to the ground state or by the charge separation process aided by the presence of ED and EW groups attached to the polymer. To determine whether charge separation was occurring Light-induced Electron Spin Resonance (LESR) studies[125-126] of the polymers **2.11** and **2.30a** were carried out by Dr. J. -C. Ribierre (St. Andrews). The e.s.r. trace of polymers **2.11** and **2.30a** as films coated from chlorobenzene are shown in Figure **2-19**. The light-induced e.s.r. spectrum is recorded at 20 K and obtained by subtraction of the dark e.s.r. signal and the signal under illumination.

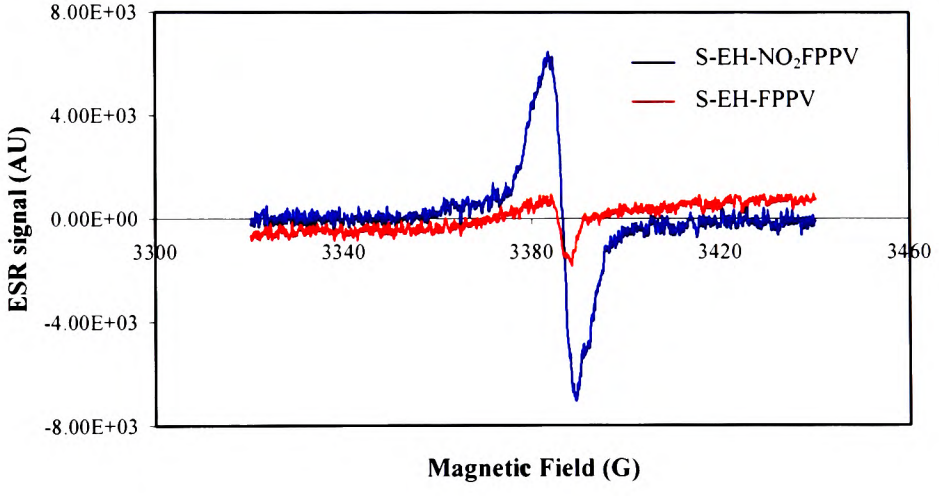


Figure 2- 19: LESR spectra of S-EH-FPPV **2.11** and S-EH-NO_2FPPV **2.30a**

A larger e.s.r. signal was observed for polymer **2.30a** than **2.11** under identical conditions, indicating the presence of more radical species in the polymer **2.30a** as

compared to **2.11**. This therefore suggests that decrease of the PLQY in the polymer with the dipole, **2.30a**, is due to a charge separation process.

The device performance of the polymers S-EH-FPPV **2.11** and S-EH-NO_2FPPV **2.30a** were also studied, Table **2-2**.

Table 2-2: Device results of single layer and bulk-heterojunction devices

Polymer	**ITO/PEDOT:PSS/Polymer†/Al**			
	V_{oc} (V)	**I_{sc} (mA/cm^2)**	**FF**	**Efficiency (%)**
2.11	1.21	1.4E-03	0.28	6.3E-04
2.30a	1.20	8.6E-03	0.18	2.1E-03
	ITO/PEDOT:PSS/{Polymer:PCBM 1.5b}†(1:3)/Al			
2.11	0.92	2.42	0.32	0.95
2.30a	1.01	1.20	0.25	0.52

† Film thickness 50 ± 5 nm

Neat polymer single layer devices as well as devices with a blend of the polymers and PCBM **1.5b** were fabricated. The device configuration of neat polymer layer solar cell was ITO/PEDOT:PSS/Polymer/Al while for a bulk heterojuction cell a 1:3, polymer:**1.5b**, blend was used. The ITO surface was modified by deposition of an interfacial hole transporting layer of poly[3,4-(ethylenedioxy)-thiophene]**1.6a**:poly(styrenesulphonate) **1.6b** (PEDOT:PSS) (Figure **1-10**, Chapter 1) between ITO and the active polymer material. This molecularly doped conjugated polymer serves two functions: *(i)* modification of work-function of

ITO, and *(ii)* it also smooth out the uneven surface of ITO[1] Single layer devices were prepared by spin-coating **2.29** or **2.30a** from tetrahydrofuran solution onto PEDOT**1.6a**:PSS**1.6b** modified ITO-coated glass substrate. The aluminium cathode was then evaporated onto the polymer layer. Both neat single layer devices performed poorly although the efficiency of the device based on **2.30a** was 30 times higher than the device containing polymer **2.11**. This could be accounted on the basis of esr studies indicating a better charge separation process in the polymer **2.30a** as compared to **2.11**. The open circuit voltage (V_{oc}) and short circuit current (I_{sc}) showed opposite trends in their values. The V_{oc} was found to be similar whilst I_{sc} was found to be higher for **2.30a** (dipole containing polymer) as compared to **2.11**. The low I_{sc} values of the devices containing **2.11** and **2.30a** indicate that for both the polymers at least one of the charge carriers has poor mobility. Interestingly, the efficiencies of the devices are similar to other single layer neat polymer cells reported in the literature[65, 87] The poor mobility of charge carriers is one reason accounting for the low efficiency of the single layer neat polymer devices. The mobility of charge carriers could be improved by blending the devices with PCBM **1.5b**[127-128]. Bulk heterojunction devices were fabricated by blending the polymers **2.11** and **2.30a** with 75% (w/w) of PCBM **1.5b**. A good improvement in the I_{sc} values were reflected in a several fold improvement in device efficiencies of both polymers over the neat single layer devices. However the efficiencies of the blended polymer (**2.11** or **2.30a**) devices with PCBM **1.5b** are still lower than the reported efficiencies (3-5%)[7,48,60] for other polymer:PCBM **1.5b** bulk heterojunction devices in similar configuration. Further optimisation of the device structures could lead to even higher efficiencies.

2.5 Conclusions

A new family of polymers specifically designed for photovoltaic applications has been developed. The polymers have a high average molecular weight and good thermal stability. However, the U.V.-visible spectra of these polymers showed only weak absorption at the longer wavelengths associated with delocalised π–π^* transitions. The lower absorbance of delocalised π–π^* transitions to the localised π–π^* transitions in the biphenyl-linked PPV polymers was due to the twisting of polymer backbone by the "biphenyl linkage" formed from joining of the fluorene unit to the polymer backbone thereby shortening the effective conjugation length of the polymer. This would be affected to give a more disordered film with poorer charge mobility leading to lower device efficiencies. The polymers prepared *via* thermal conversion of precursor polymers tended to give relatively strong delocalised π–π^* transitions. To avoid this effect it was decided to introduce a vinyl linkage between the fluorene moiety and the backbone of the polymer (as discussed in Chapter 4).

The attachment of an electron withdrawing nitro moiety caused a quenching of the luminescence with LESR studies indicating that this is due to the charge separation process. However neat devices performed poorly and in a similar manner to other neat devices indicating that charge transport needs to be improved. Nonetheless, the fact that the EWG does have an effect on the properties of the polymers suggests that polymers containing a dipole might be an important step forward in materials development for organic PV.

Bis-BI-PHENYL LINKED PPV DERIVATIVES

Chapter 3

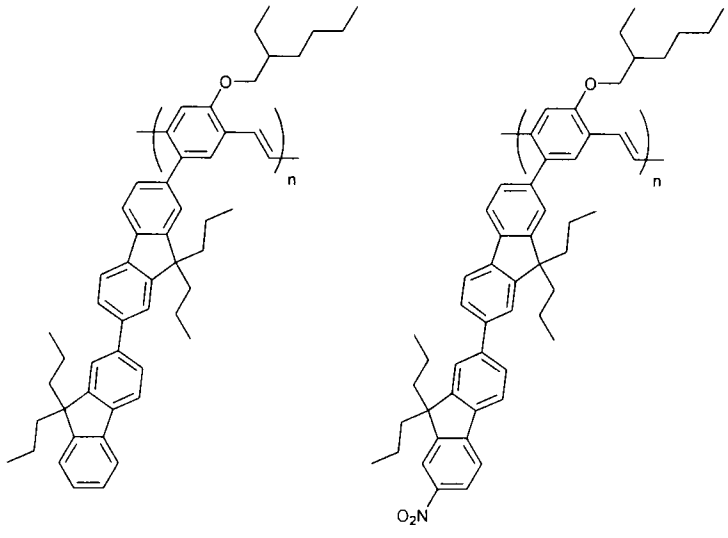
3 *Bis*-BI-PHENYL LINKED PPV DERIVATIVES

3.1 Introduction

A series of mono-biphenyl-linked fluorenyl-PPV polymers have been synthesised and characterised successfully (Chapter 2). In order to study how the increase in dipole length between electron donating (ED) alkoxy group and electron withdrawing (EW) nitro group would affect the charge separation properties of the polymer, an additional fluorene moiety was introduced into the side chain of the fluorenyl-PPV *via* another biphenyl linkage. This would enable a direct comparison of the properties of mono-fluorenyl and *bis*-fluorenyl biphenyl-linked PPVs. In addition, a polymer without the nitro group was also synthesised to compare how the presence of a nitro group would affect the properties of the polymer.

This chapter describes the synthesis and properties of PPV derivatives comprised of *bis*-fluorenyl side groups attached to the PPV backbone *via* a bi-phenyl linkage. The parent soluble (s) conjugated polymer is poly{2-[7-(9,9-dipropylfluorenyl)-9,9-dipropylfluorenyl]-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene} **3.18** (S-EH-F_2PPV), which has 2-ethylhexyloxy as the EDG. The second polymer with the nitro group attached synthesised was poly{2-[7-(7-nitro-9,9-dipropylfluorenyl)-9,9-dipropylfluorenyl]-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene} **3.24** (S-EH-NO_2F_2PPV). The structures of **3.18** and **3.24** are shown in Figure **3-1**. S-EH-NO_2F_2PPV **3.24** has a dipole consisting of 2-ethylhexyloxy as the EDG and nitro as the EWG across the phenyl *bis*-fluorene group. The 2-ethylhexyloxy and propyl

groups at the 9-position of the fluorenyl moieties were introduced to ensure solubility for both **3.18** and **3.24** in their conjugated form.



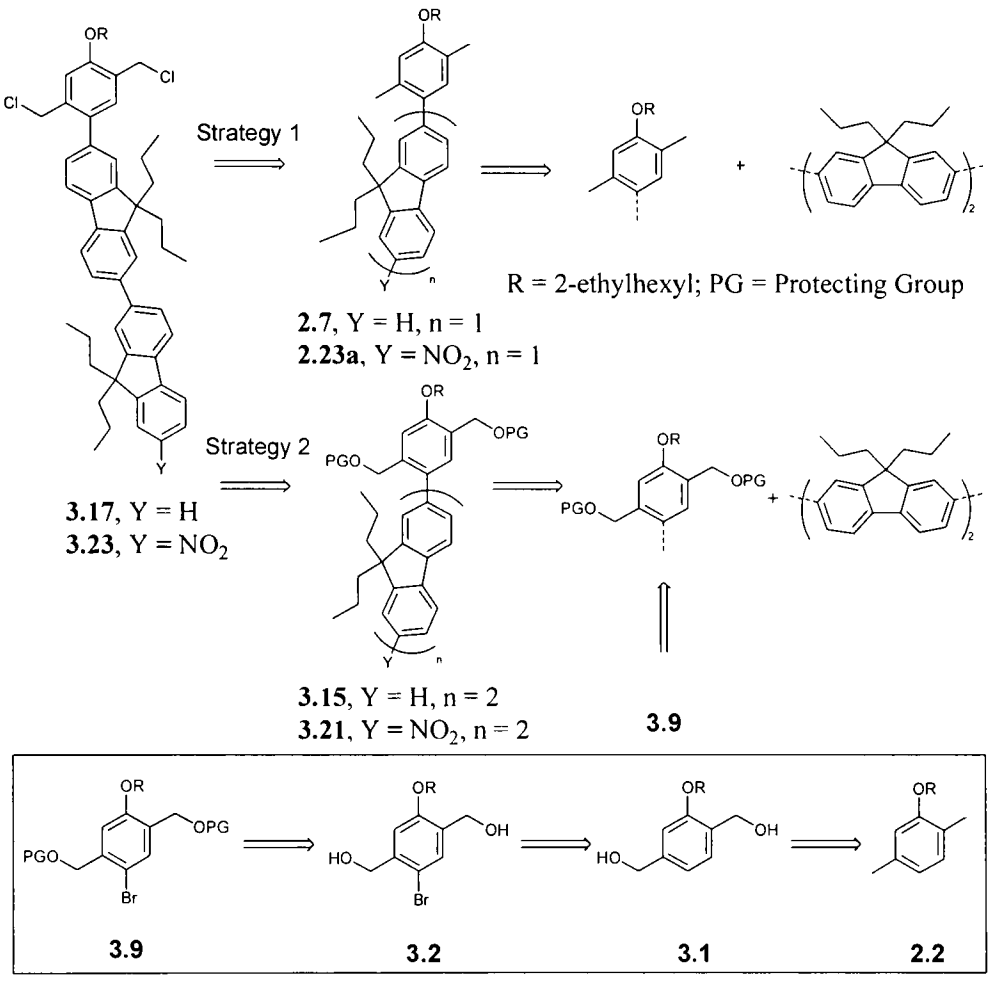
3.18 **3.24**

Figure 3- 1: Polymers: S-EH-F_2PPV **3.18** and S-EH-NO_2F_2PPV **3.24**

3.2 Poly{2-[7-(9,9-dipropylfluorenyl)-9,9-dipropylfluorenyl]-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene}

3.2.1 Retrosynthetic analysis of the *Bis*-fluorenyl monomer

The retrosynthetic analysis of the *bis*-fluorenyl monomers that are required for the formation of **3.18** and **3.24** is shown in Scheme **3-1**. It was initially thought that the synthesis of *bis*-fluorenyl monomers could be achieved following the strategy used for the preparation of the mono-fluorenyl PPVs (Strategy 1, Chapter 2).



Scheme 3- 1: Strategies for the synthesis of *bis*-fluorenyl monomers **3.17** (Y = H) and **3.23** (Y = NO_2). Strategy 1 adds the fluorenyl units first before activation of the methyl groups while strategy 2 reverses the process.

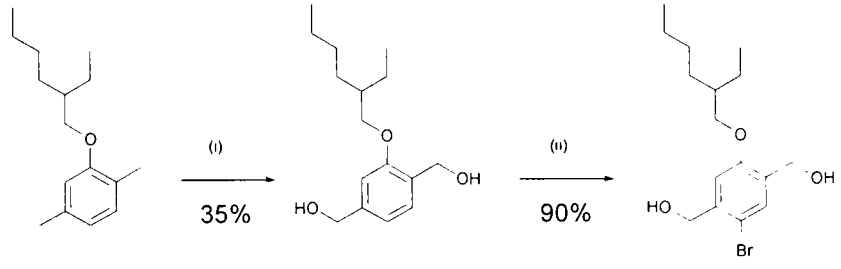
However, while the early steps in the route for the synthesis of mono-fluorenyl PPVs monomers (Chapter 2), proceeded satisfactorily but poor overall yield was obtained during activation of methyl groups of monomer precursor to chloromethyl groups. The

weaker steps were where the dimethyl groups had to be transformed to *bis*(chloromethyl) groups *via* a series of steps (benzylic bromination, acetylation, reduction, and halogenation). This multistep procedure resulted in difficult purification of intermediates and resulted in only moderate overall yields late in the synthesis of the monomer. It was anticipitated that, if the same procedure was followed after the addition of a second fluorenyl group, then the purification of the monomers would be more difficult and the low yielding steps late on the longer synthetic pathway would be unacceptable. Therefore an alternative method for the synthesis *bis*-fluorenyl monomers **3.17** and **3.23** was envisaged (Strategy 2). The approach involves activating the methyl groups first before coupling the fluorenyl units. The advantages of this route are that the lower yielding steps are in the early part of the synthesis. This second strategy should be more versatile as it would enable the synthesis of a family of polymers by the simple addition of the modified fluorenyl moieties. For strategy 1 or 2 the fluorenyl groups can be added sequentially or the fluorenyl units could be linked before addition to the phenyl moiety that forms the backbone of the polymer. The key intermediate in strategy 2 is the protected 4-(2′-ethylhexyloxy)bromobenzene **3.9**. The hydroxyl groups of 2,5-*bis*(hydroxymethyl)-4-(2′-ethylhexyloxy)bromobenzene **3.2**, which can be converted to the halides ready for polymerisation, must be masked before performing the Suzuki coupling to prevent undesired side reactions. The choice of the protecting group is important, as it should be able to withstand the alkaline reaction conditions of Suzuki reaction and also allow the formation of boronic acid derivatives if stepwise fluorenyl side-chain extension is used.

3.2.2 Synthesis of the *Bis*-fluorenyl monomer

The synthesis of monomer to S-EH-F_2PPV **3.18** was divided in two halves. One half involved the preparation of the THP-protected 4-(2′-ethylhexyloxy)bromobenzene **3.9** with the second half comprising the development of the *bis*-fluorenyl compound **3.14**.

The first step in the synthesis of THP-protected 4-(2′-ethylhexyloxy)bromobenzene **3.9** required the previously synthesised 2-(2′-ethylhexyloxy)-*p*-xylene **2.2**. The transformation of **2.2** to 1,4-*bis*(hydroxymethyl)-2-(2′-ethylhexyloxy)benzene **3.1** was carried out by our standard procedure, Scheme **3-2**.



2.2 **3.1** **3.2**

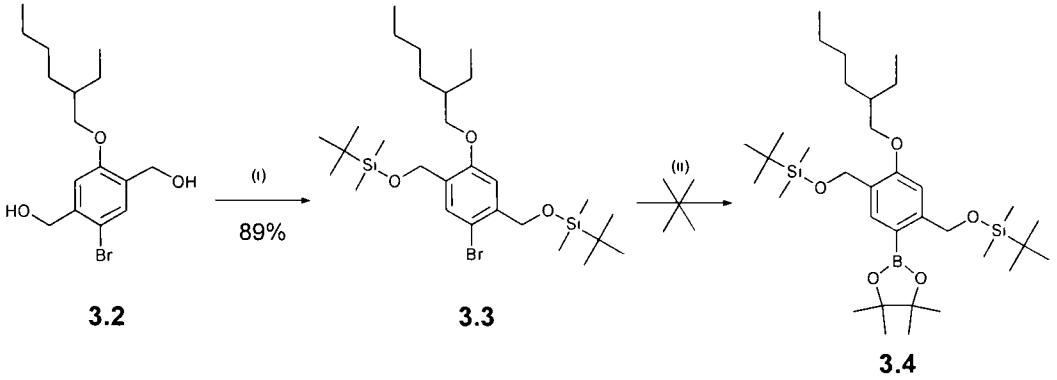
Scheme 3- 2: *Reactions and conditions*: (i). a. NBS, AIBN, CCl_4, Δ; b. NaOAc, AcOH, Δ; c. KOH_{aq}, MeOH; (ii) NBS, DMF, dark or Br_2, MeOH, AcOH

A mixture of **2.2**, 2.2 equivalents of *N*-bromosuccinimide, and 2,2′-azo-*bis*(isobutyronitrile) in carbon tetrachloride was heated at reflux. After aqueous work-up and a preliminary purification of the crude mixture was performed by filtering the crude mixture solution in dichloromethane through a plug of silica. The mixture of brominated compounds obtained was acetylated by treatment with sodium acetate in glacial acetic acid heated at reflux for 5 hours. The acetates were then hydrolysed in alkaline medium utilising potassium hydroxide in aqueous methanol to give a mixture of crude benzyl

alcohols, which on purification gave 1,4-*bis*(hydroxymethyl)-2-(2'-ethylhexyloxy)benzene **3.1** in an overall 35% yield. This yield was similar to that reported in the literature[129] Electrophilic bromination of **3.1** was achieved with *N*-bromosuccinimide[130] in *N,N*-dimethylformamide at room temperature in the dark and gave 2,5-*bis*(hydroxymethyl)-4-(2'-ethylhexyloxy)bromobenzene **3.2** (*bis*-diol bromide) in a 66% yield. Alternatively, bromination of **3.1** could be achieved with bromine in a glacial acetic acid/methanol mixture to give **3.2** in a 90% yield.

3.2.2.1 Protecting groups

The next step in making the generalised monomer was the protection of two alcohol moieties of *bis*-diol bromide **3.2**. Silylating agents were initially chosen to protect the hydroxyl groups. The choice was based on the fact that bulky silyl derivatives require mild protecting and de-protecting conditions and are known to be stable. The hydroxyl groups of *bis*-diol bromide **3.2** were silylated on treatment with a slight excess of *t*-butyldimethylsilyl trifluoromethanesulphonate (TBDMS-OTf) and imidazole in *N,N*-dimethylformamide, Scheme **3-3**.



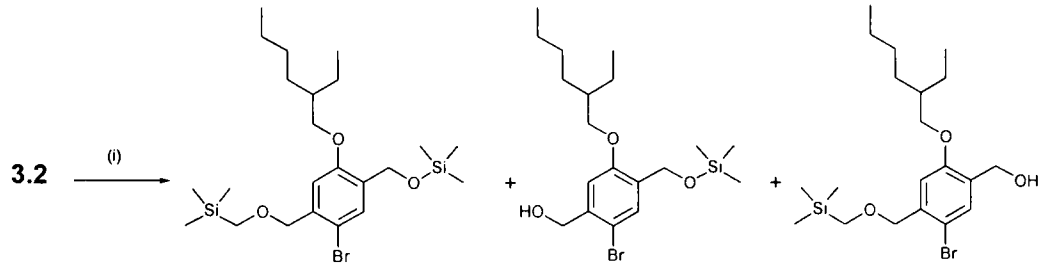
3.2 **3.3** **3.4**

Scheme 3- 3. *Reactions and conditions:* (i). TBDMS-OTf, Imidazole, DMF; (ii) a. THF, *t*-BuLi, -78 °C; b. i-PrOB(OC(CH_3)$_2$); c. -78 °C → r.t.

The reaction proceeded in a 89% yield to give 1-bromo-2,5-*bis*-(*t*-butyl-dimethyl-silanyloxymethyl)-4-(2'-ethylhexyloxy)-benzene **3.3** (TBDMS-bromide). The synthesis of the corresponding borolane derivative **3.4** (TBDMS-borolane) of TBDMS-bromide **3.3** was the next goal. Preparation of TBDMS-borolane **3.4** from **3.3** was attempted using *t*-butyllithium in tetrahydrofuran at -78 °C to form the carbanion. The solution of **3.3** in tetrahydrofuran was pre-cooled at -78 °C then treated with 1.2 equivalents of *t*-butyllithium. The solution turned yellow suggesting anion formation but the yellow colour faded gradually over 10 minutes before the addition of 2-*iso*propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. ^{1}H n.m.r. spectrum of the "purified" material revealed the presence of starting material mixture with 5% of protonated compound. The reaction was carried out again using 2.0 equivalents of *t*-butyllithium but upon purification of the crude material, only starting material was recovered. The lack of carbanion formation with *t*-butyllithium suggested that it was too bulky to react with the sterically encumbered substrate.

It was therefore decided to try and metallate TBDMS-bromide **3.3** using *n*-butyllithium in freshly distilled tetrahydrofuran solution (over sodium) under similar conditions. Interestingly, the reaction mixture turned yellow on addition of *n*-butyllithium and soon decolourised. 2-*Iso*propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added, and aqueous work-up and purification of the crude gave the starting material in a 98% yield. Clearly *n*-butyllithium was too sterically demanding to metallate the bulky substrate. Therefore, it was decided to protect the hydroxyl groups of **3.2** with the less bulky trimethylsilyl moiety. In the first attempt to form the 1-bromo-4-(2'-ethylhexyloxy)-2,5-*bis*-trimethylsilanyloxymethyl-benzene **3.5** (TMS-bromide), **3.2** was treated with chlorotrimethylsilane in presence of imidazole, and 4-*N,N*-dimethylaminopyridine as a catalyst in a dichloromethane/tetrahydrofuran mixture at room temperature. After 24 hours, t.l.c. indicated that only starting material was present. In a second reaction the same conditions were used except that the reaction mixture was heated at reflux for 15 hours under nitrogen. On purification of the crude material, 2% of 1-bromo-4-(2'-ethylhexyloxy)-2,5-*bis*-trimethylsilanyloxymethyl-benzene **3.5** (TMS-bromide) of the desired compound was obtained, with majority of the remaining material being unprotected **3.2** recovered in a 89% yield. In an effort to improve the yield, stronger basic conditions were utilised. A solution of **3.2** in tetrahydrofuran was treated with sodium hydride and then chlorotrimethylsilane was added drop-wise but only starting material (97%) was recovered. The lack of reactivity of **3.2** with chlorotrimethylsilane was surprising given the ease of formation of more sterically encumbered TBDMS-OTf. Finally, 1,1,1,3,3,3-hexamethyldisilazane (HMDS) was used as the silylating agent. A solution of **3.2** in dichloromethane/tetrahydrofuran mixture was

treated with the slight excess of HMDS with iodine added as the catalyst at room temperature using the literature procedure[131], Scheme **3-4**.

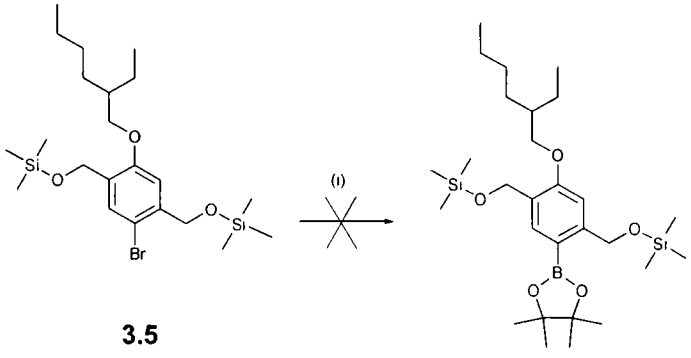


3.5 **3.6** **3.7**

Scheme 3- 4: *Reactions and conditions*: (i). HMDS, I_2, DCM, THF, r.t.

Even after the very long reaction time of 45 hours only 31% of the desired disilyl derivative of **3.2** and a mixture of regio-isomers of monosilyl compounds **3.6** and **3.7** in a combined yield of 64% were formed. HMDS was better than chlorotrimethylsilane. In a final effort to improve the yield of **3.5** the reaction mixture of compound **3.2** and iodine was heated at reflux after the drop-wise addition of HMDS. The yield of **3.5** was significantly improved and formed in a 92% yield.

The next step in the synthesis was the transformation of TMS-bromide **3.5** into the corresponding borolane compound **3.8**, Scheme **3-5**. Experience gained during the attempted synthesis of borolane from TBDMS-bromide **3.3** (Scheme **3-3**), showed that *n*-butyllithium base could be used safely for the lithium-halogen exchange reaction of silyl derivatives.



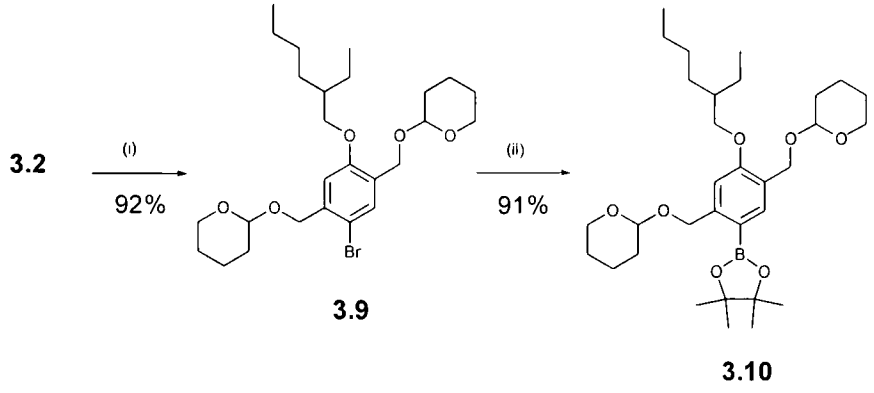
3.5 **3.8**

Scheme 3- 5. *Reactions and conditions*: (i). a. THF, *t*-BuLi, -78 °C; b. *i*-PrOB(OC(CH$_3$)$_2$); c. -78 °C → r.t.

On treatment of TMS-bromide **3.5** solution in tetrahydrofuran with *n*-butyllithium at -78 °C, the solution turned yellow suggesting anion formation. However, the colour of the anion vanished far rapidly before the addition of the 2-*iso*propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. ^{1}H n.m.r. and t.l.c. analysis of the crude obtained after aqueous work up showed mainly the presence of unconverted TMS-bromide **3.5**. The failure of the butyllithium reaction to metallate TBDMS-bromide **3.3** and TMS-bromide **3.5**, may be attributed to the steric hindrance created by the bulk of the silyl protecting groups.

The inability to form the borolane compound with the silyl protecting groups meant that both the nature and size of the protecting group was crucial. The new protecting group needed to fulfil four requirements: *(i)* the groups should not prevent the attack of butyllithium in the metal-halogen exchange either sterically or electronically; *(ii)* avoid making the benzylic protons susceptible to deprotonation by butyllithium; *(iii)* should be stable enough to withstand both alkaline and reflux conditions of the Suzuki; *(iv)* and finally the groups should be cleanly removed and in good yields.

The tetrahydropyranyl (THP) ether was therefore chosen to protect the hydroxyl groups of **3.2**, Scheme **3-6**.

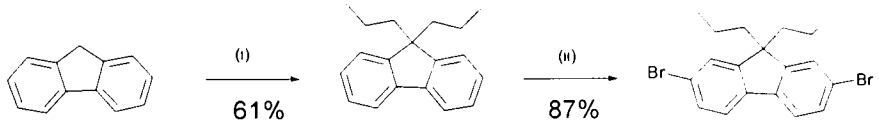


Scheme 3- 6. *Reactions and conditions*: (i). DHP, PPTS or *p*-TSA, THF;(ii) a. THF, *t*-BuLi, -78 °C; b. *i*-PrOB(OC(CH$_3$)$_2$); c. -78 °C → r.t.

The synthesis of 2-[5-bromo-2-(2′-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxy]tetrahydro-2*H*-pyran **3.9** (THP-bromide) was initially carried out with 3,4-dihydropyran (DHP) and hydrogen chloride in ether at room temperature to give **3.9** in a 40% yield. To improve the yield of **3.9** *p*-toluenesulphonic acid monohydrate (*p*-TSA) and pyridinium *p*-toluene sulphonate (PPTS) were tried as catalysts. Solutions of **3.2**, DHP and catalyst in anhydrous tetrahydrofuran were reacted at room temperature. The reaction with *p*-TSA gave THP-bromide **3.9** in an 82% yield while that with PPTS gave **3.9** in a 92% yield. Although PPTS is a milder catalyst than *p*-TSA it generally results in higher yields and cleaner reaction mixtures as it promotes the tetrahydropyranylation of alcohols under non-reversible conditions[132] The next step was to focus upon the formation of borolane derivative **3.10** (THP-borolane). THP-bromide **3.9** was treated with *t*-butyllithium in tetrahydrofuran at -78 °C.

Interestingly, this time the yellow colour of the anion persisted in the solution unlike when the protecting group was silyl ether. The anion was trapped with 2-*iso*propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to form THP-borolane **3.10** in an excellent 91% yield.

After the successful synthesis of THP-borolane **3.10** the other half required for the coupling reaction was *bis*-fluorenyl bromide **3.14**. Fluorene **3.11** was di-alkylated using a slight excess of potassium *t*-butoxide and *n*-propyl bromide, Scheme **3-7**. The reaction was performed at 45 °C to minimise the formation of mono-alkylated fluorene. The crude product was purified by recrystallisation and di-propylfluorene **3.12** was obtained in a 61% yield.



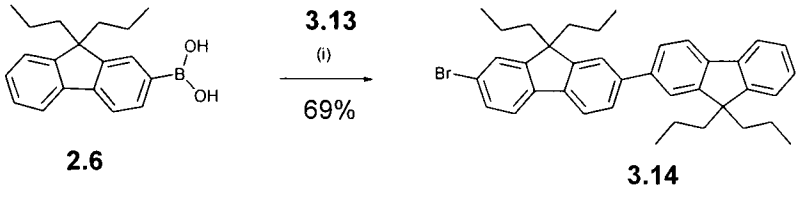
3.11 **3.12** **3.13**

Scheme 3- 7. *Reactions and conditions*: (i). a. KOBu^t, *n*-PrBr, DMSO, 45 °C;

(ii). Br_2, $CHCl_3$

Bromination of di-propylfluorene **3.12** at the 2- and 7-positions was achieved by treatment of **3.12** with 2.2 equivalents of bromine in chloroform at room temperature in dark. After 4 hours the excess bromine was reduced to bromide with a saturated solution of sodium metabisulphite and the fluorene di-bromide **3.13** was obtained in 87% yield after purification.

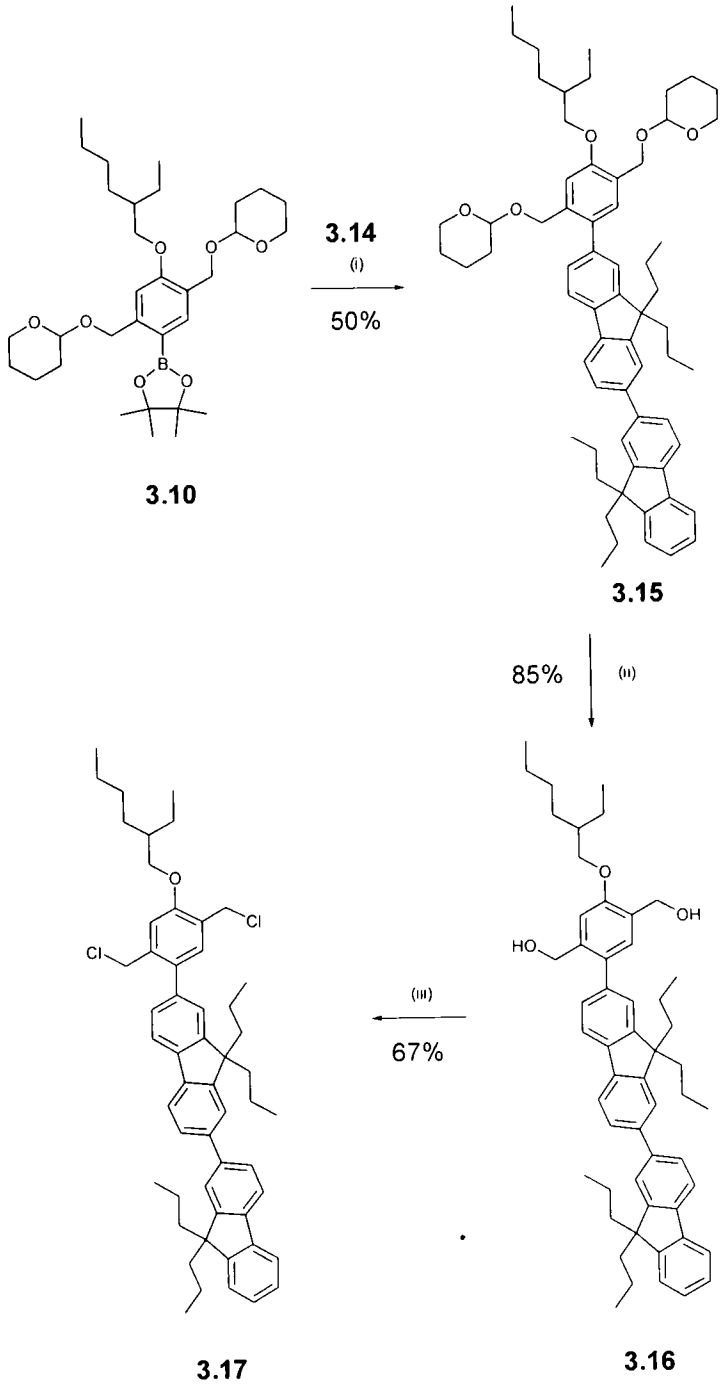
A Suzuki coupling of fluorene di-bromide **3.13** with fluorenylboronic acid **2.6** was performed, Scheme **3-8** using 1.7 equivalents of **3.13** gave the mono-coupled product, *bis*-fluorenyl bromide **3.14** as a white crystalline solid in a 69% yield.



2.6 **3.14**

Scheme 3- 8. *Reactions and conditions*: (i). **3.13**, $Pd(PPh_3)_4$, PhMe, $Na_2CO_{3(aq)}$, Δ

The next step in the synthesis of *bis*-fluorenyl monomer **3.17** required the formation of the *bis*-fluorene diol **3.16**, Scheme **3-9** by coupling THP-borolane **3.10** with *bis*-fluorenyl bromide **3.14**. The compound **3.10** was reacted with 1.2 equivalents of **3.14** in aqueous sodium carbonate and toluene mixture heated at reflux with *tetrakis*(triphenylphosphine) palladium (0) as catalyst. The yield of *bis*(THPfluorene) ether **3.15** obtained was in the range of 40-50% irrespective of whether either substrate was in excess or the length of the reaction time. The moderate yields of the coupled product **3.15** may be due to a poor batch of palladium catalyst. However the reaction was not performed with a fresh batch of palladium catalyst as **3.15** was synthesised in a sufficient quantity. The conversion of *bis*(THPfluorene) ether **3.15** to *bis*-fluorene diol **3.16** with the use of weak acid-mediated deprotection conditions. The deprotection of **3.15** with catalytic amount of *p*-TSA in methanol/dichloromethane mixture resulted in the formation of *bis*-fluorene diol **3.16** as a white solid in an 85% yield.

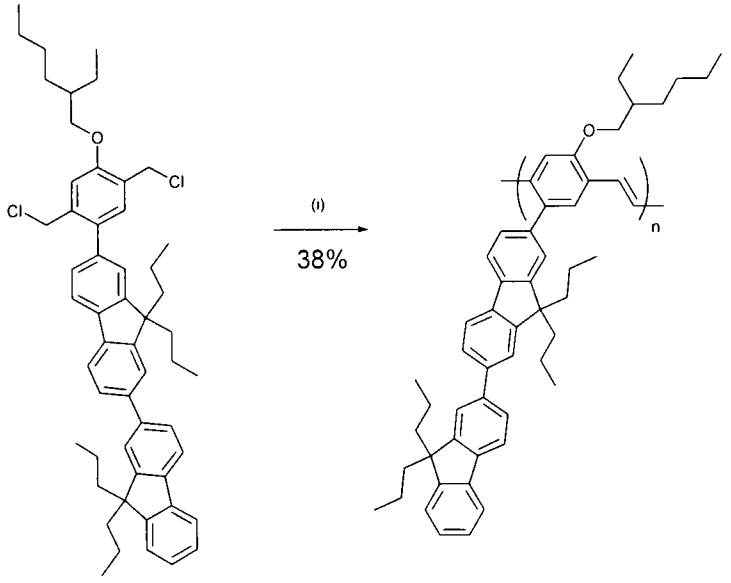


Scheme 3- 9. *Reactions and conditions*: (i). **3.14**, $Pd(PPh_3)_4$, PhMe, $Na_2CO_{3(aq)}$, Δ; (ii). *p*-TsOH, DCM, MeOH; (iii) $SOCl_2$, DCM

The final step to monomer **3.17** was the chlorination of *bis*-fluorene diol **3.16**. The *bis*(hydroxymethyl) groups of **3.16** were converted to *bis*(chloromethyl) moieties of **3.17** with thionyl chloride in dichloromethane in a 67% yield.

3.2.3 Polymerisation

The *bis*-fluorenyl monomer **3.17** was polymerised under the standard conditions, Scheme **3-11**.



3.17 **3.18**

Scheme 3- 10. *Reactions and conditions*: (i) KOBu^t, THF

A 0.2 M solution of monomer **3.17** in tetrahydrofuran was treated with 5.0 equivalents of a 0.2 M tetrahydrofuran solution of potassium *t*-butoxide at room temperature. The colour of the reaction mixture changed from colourless to yellow, and eventually to green. After 3 hours, ice-cold methanol was added to quench the polymerisation reaction. The

polymer was purified from remaining monomer and oligomers by several precipitations from tetrahydrofuran/ice-cold methanol mixture. The polymer obtained was dried under vacuum to remove trapped solvent and *bis*-fluorenyl-PPV (S-EH-F_2PPV) **3.18** was obtained as a yellow solid in a 38% yield.

3.2.4 Properties of the *Bis*-fluorenyl-PPV

Bis-fluorenyl-PPV (S-EH-F_2PPV) **3.18** was characterised using g.p.c., ^{1}H n.m.r., TGA, and infrared and U.V.-visible spectroscopy. G.p.c. analysis showed S-EH-F_2PPV **3.18** had a $\overline{M}_w$ of 1.9×10^6 g/mol, relative to polystyrene standards with a polydispersity, PD of 12.2. Polymer **3.18** had good solubility in tetrahydrofuran, toluene, chloroform, and dichloromethane. The ^{1}H n.m.r. spectrum of S-EH-F_2PPV **3.18** is shown in Figure **3-1** and gives a strong evidence that the polymer is fully conjugated.

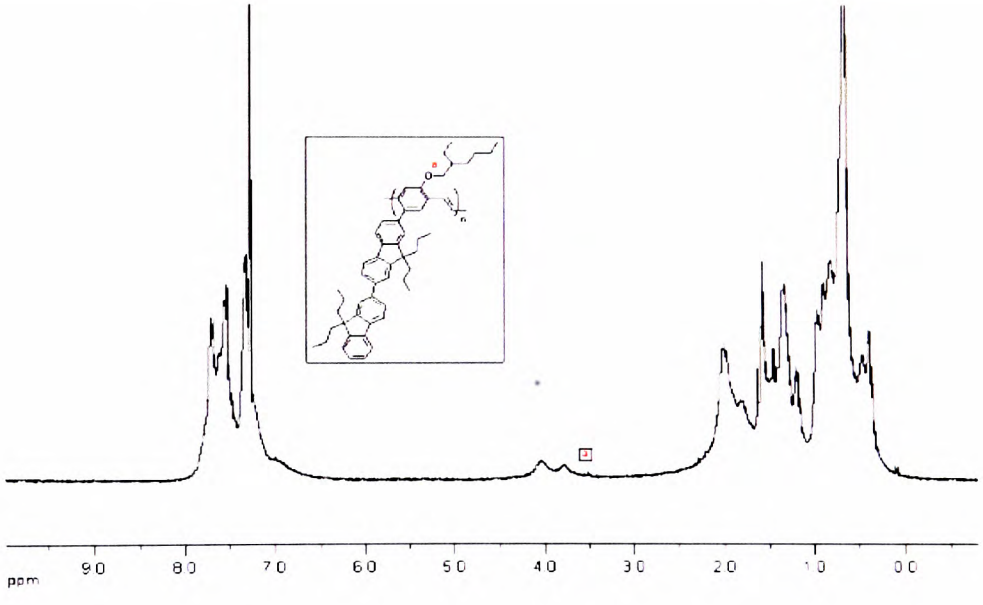


Figure 3- 1: ^{1}H n.m.r. spectrum of S-EH-F_2PPV **3.18** in $CDCl_3$

While the formation of the fully conjugated polymer proceeded *via* precursor polymer having CHCl protons. The ^{1}H n.m.r. clearly shows no signals at ~5.8 p.p.m. indicating the absence of CHCl protons and hence non-eliminated linkages. Interestingly unlike the ^{1}H n.m.r. of S-MEHPPV **1.4b** (Figure **2-3**) there was no signal corresponding to benzylic protons of backbone observed at ~2.8 p.p.m. This strongly suggests the absence head-to-head defects in the polymer backbone. The regioregularity of the polymer could arise from both electronic and steric effects[104, 108-109] The steric and electronic effect of *bis*-fluorenyl moiety at position-2 believed to control the formation of one *p*-quinodimethane derivative preferentially from the proton abstraction of chloromethyl group of the monomer **3.17** and propagation occurred in head-to-tail fashion resulted in the absence of *bis*-benzyl defects. The behaviour of *bis*-fluorenyl monomer **3.17** towards polymerisation was found similar to the fluorenyl monomer **2.9** as discussed in Scheme **2-7** (Chapter 2).

The thermal properties of S-EH-F_2PPV **3.18** were determined by analysing change in weight loss with temperature under a nitrogen atmosphere. The TGA curve of **3.18** is shown in Figure **3-2**. The TGA was carried out at a heating rate 2 °C /min. There was no significant weight loss up to 400 °C indicating that there were no leaving groups on the polymer backbone. Above 400 °C, decomposition of the polymer occurred. The first weight reduction of ~32% corresponds to the loss the propyl and 2-ethylhexyl side-chains (theoretical mass loss 37%). At ~500 °C the polymer backbone starts to degrade.

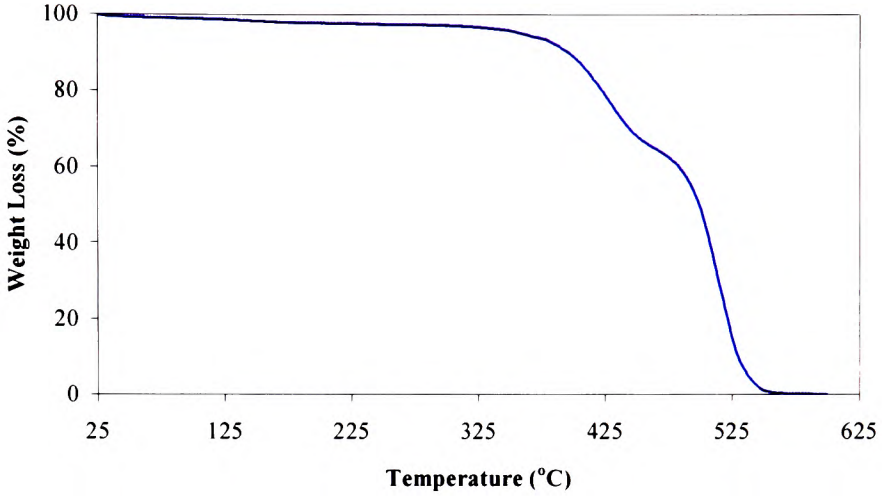


Figure 3- 2: TGA of S-EH-F_2PPV **3.18**

The infrared spectrum (Figure **3-3**) of a drop-cast film (tetrahydrofuran) S-EH-F_2PPV **3.18** on KBr had an absorption at 968 cm^{-1} corresponding to the C=C-H *trans*-vinylene out of plane bend of the conjugated polymer and indicating that the conjugated polymer backbone had mostly *trans*-linkages.

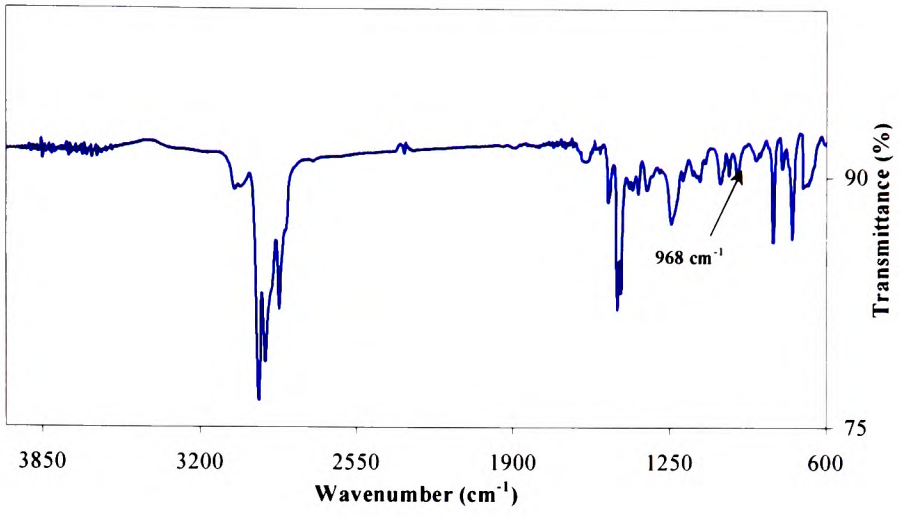


Figure 3- 3: Infrared spectrum of S-EH-F_2PPV **3.18**

The U.V.-visible spectra of monomer **3.17** in solution (dichloromethane), polymer films of S-EH-F_2PPV **3.18** are shown in Figure **3-4**.

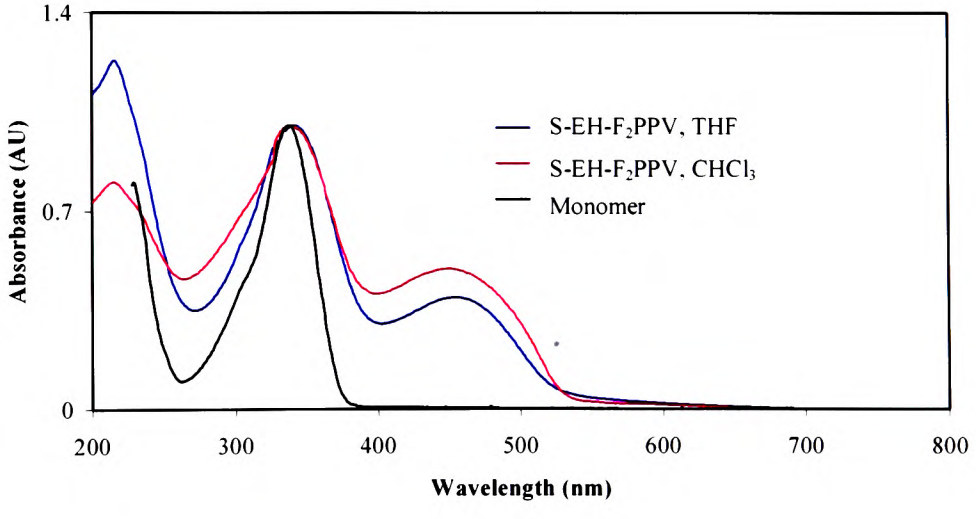


Figure 3- 4: U.V.-visible spectra of monomer **3.17** and S-EH-F_2PPV **3.18**

The films of S-EH-F_2PPV **3.18** were prepared on quartz by spin-coating from chloroform or tetrahydrofuran solutions. S-EH-F_2PPV **3.18** showed good solubility in chloroform and tetrahydrofuran. For the polymer films, the absorption at 210 nm is due to the localised π-π* transitions and the maximum centered at ~450 nm is due the delocalised π-π* transition of the PPV backbone. The relatively strong absorption at 340 nm is assigned to the presence of *bis*(fluorenyl)phenyl chromophore as it appears at a similar wavelength to that of the monomer **3.17**. It is interesting to note that the ratio of the intensity of the localised to delocalised π-π* transitions in the spectra of **3.18** is different when the films were prepared from different solvents. When the films are spin-coated from tetrahydrofuran the ratio of localised to delocalised π-π* transitions is higher indicating that the backbone of the polymer is more twisted with poorer delocalisation. This strongly suggests that whilst the polymer is soluble in tetrahydrofuran it is a poor solvent for the polymer backbone. Such effect of nature of solvent was not observed in the previous fluorenyl-PPVs synthesised (Chapter- 2).

The U.V.-visible spectra (Figure **3-5**) of films of S-EH-F_2PPV **3.18** and S-EH-FPPV **2.11** were compared to study the effect of longer pendant groups, two fluorenyl units as compared to the one fluorenyl unit respectively. The spectra were normalised at localised π-π* transitions (216 nm) for the comparison. Chloroform and tetrahydrofuran were used to prepare the films of **3.18** and **2.11**.

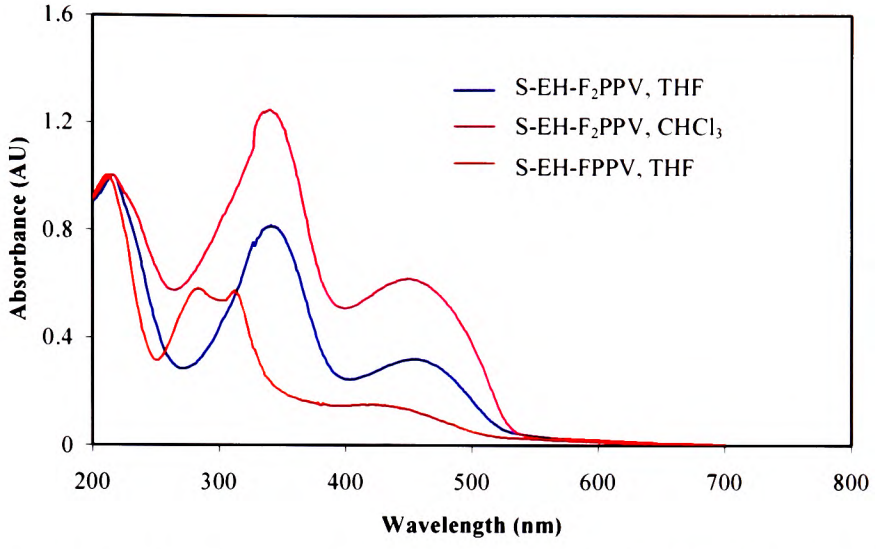


Figure 3- 5: U.V.-visible spectra of S-EH-F_2PPV **3.18** and S-EH-FPPV **2.11** on quartz

The films of S-EH-F_2PPV **3.18** showed a red shift in both the side-chain chromophore and delocalised π-π* absorptions when compared with the film of S-EH-FPPV **2.11**. The former red shift is logical as the side-chain of **3.18** has an extra fluorene unit. However the red shift on the delocalised π-π* transitions for **3.18** than in **2.11** is more difficult to understand. Both **2.11** and **3.18** have similar steric demands close to the polymer backbone with each having a fluorenyl moiety attached to the phenyl ring. The fact that there is a red shift and increased intensity in the delocalised π-π* transitions for **3.18** when compared to **2.11** for films prepared from the same solvent indicates that the polymer backbone of **3.18** is more delocalised and there are more chromophores with the same transition. With the delocalised π-π* transitions strengthened when the film of **3.18** is formed from chloroform solution. This strongly suggests that the morphology of the polymer **3.18** in chloroform solution is different to that in tetrahydrofuran assuming the

morphology is dependent on the solution[133]. This increase in order on the solid state could also be due to the interleaving of the *bis*-fluorene units. The propyl chains at fluorene units in the monomer unit embrace a neighbouring backbone and serves to keep backbones from direct close contact between parallel arrays of fluorene segments[134] The behaviour of interleaving is also observed in other aromatic polymers accounting for crystallinity[135].

3.2.5 Summary

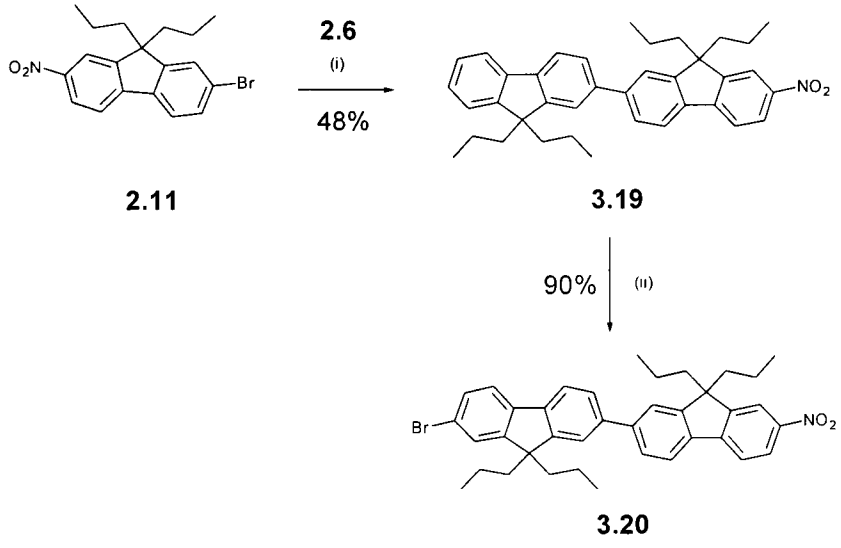
In summary, a successful strategy for the preparation of a generalised activated monomer precursor was prepared. This was used to synthesise *bis*-fluorenyl monomer **3.17**, which was polymerised to give a high molecular weight *bis*-fluorenyl-PPV **3.18** (S-EH-F_2PPV). The polymer had good thermal stability and films prepared from chloroform solution had a higher ratio of delocalised to localised π-π^* transitions on the U.V.-visible absorption spectrum than films prepared from tetrahydrofuran or with one fluorenyl unit in the side-chain.

3.3 Poly{2-[7-(7-nitro-9,9-dipropylfluorenyl)-9,9-dipropylfluorenyl]-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene}

3.3.1 Monomer synthesis

With the THP-borolane **3.10** in hand it was only necessary to prepare nitro-*bis*-fluorenyl bromide **3.20** with a nitro group and the bromide of **3.20** ready for the

coupling reaction. From the earlier work on the synthesis of nitro-fluorenyl-PPVs (Chapter 2), it was known that a borolane derivative could not be easily formed in the presence of a nitro group. It was therefore envisaged that nitrobromofluorene **2.16** could be coupled to fluorenylboronic acid **2.6** with the *bis*-fluorene moiety subsequently being brominated. Palladium catalysed coupling of nitrobromofluorene **2.16** with fluorenylboronic acid **2.6** (Scheme **3-11**) afforded nitro-*bis*-fluorene **3.19** in a 48% yield after purification.



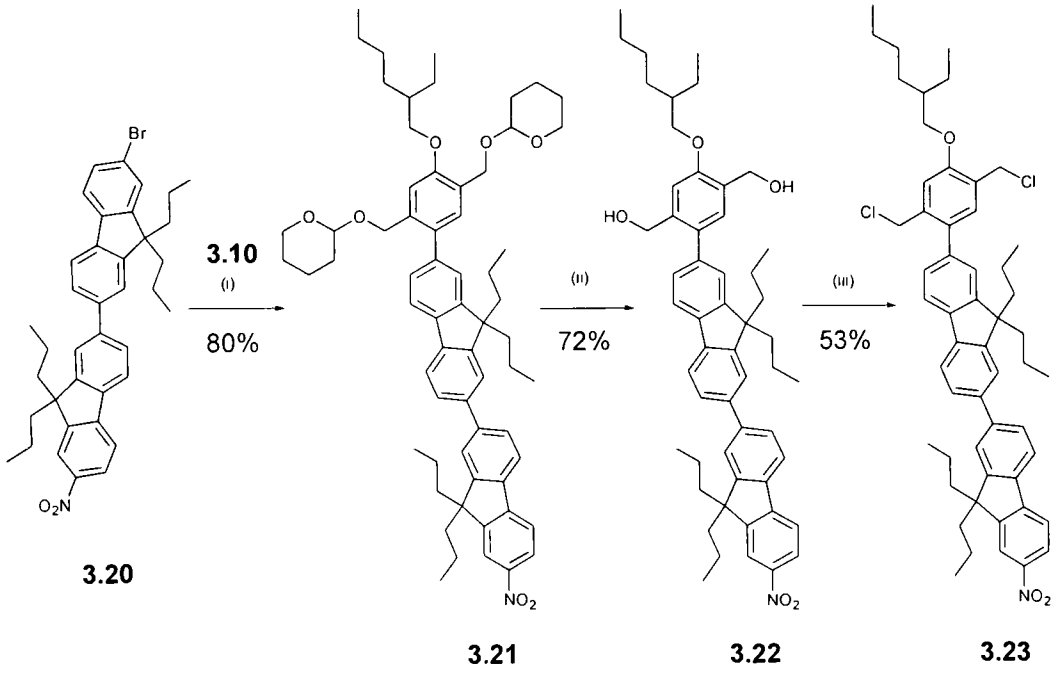
Scheme 3- 11. *Reactions and conditions*: (i). **2.6**, $Pd(PPh_3)_4$, PhMe, $Na_2CO_{3(aq)}$, Δ;

(ii). Br_2, $CHCl_3$

The introduction of the bromine moiety onto the 7'-position of nitro-*bis*-fluorene **3.19** was the next step in the synthesis. This was achieved by treating a solution of **3.19** in chloroform with bromine. Nitro-*bis*-fluorene bromide **3.20** was afforded in a 90% yield after aqueous work-up and purification. The fact that bromination went onto the fluorenyl

moiety without the nitro group can be understood in terms of the electron withdrawing nature of nitro group deactivating the fluorenyl group to which it is attached towards electrophilic substitution.

C-C coupling of nitro-*bis*-fluorene bromide **3.20** with THP-borolane **3.10** under Suzuki conditions using *tetrakis*(triphenylphosphine) palladium (0) as a catalyst proceeded in an 80% yield to give nitro-*bis*(THPfluorene) ether **3.21**. The deprotection of **3.21** using *p*-TSA in dichloromethane/methanol mixture gave nitro-*bis*-fluorene diol **3.22** in a 72% yield (Scheme **3-12**).



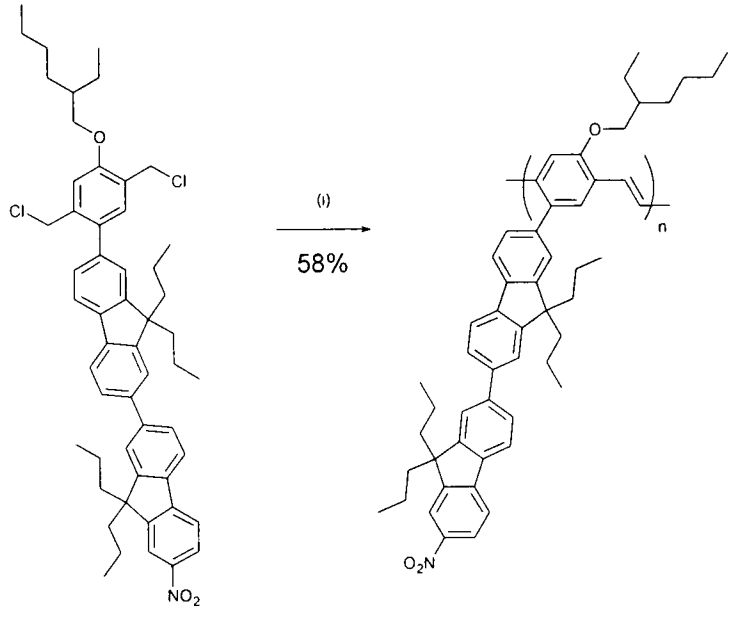
Scheme 3- 12. *Reactions and conditions*: (i). **3.10**, $Pd(PPh_3)_4$, PhMe, $Na_2CO_{3(aq)}$, Δ; (ii). *p*-TsOH, DCM, MeOH; (iii) $SOCl_2$, DCM

The final step in the synthesis of monomer **3.23** was the conversion of the hydroxyl groups in nitro-*bis*-fluorene diol **3.22** to chlorides. Treatment of **3.22** with an excess of

thionyl chloride for 3 hours resulted in the formation of nitro*bis*(chloromethyl) monomer **3.23** in a 53% yield. Efforts to improve the yield of monomer **3.23** by changing the reaction time or adding further equivalents of thionyl chloride during the reaction did not improve the yields.

3.3.2 Polymerisation and properties of the Nitro-*bis*-fluorenyl-PPV

Polymerisation reaction of nitro*bis*(chloromethyl) monomer **3.23** in tetrahydrofuran was carried out, Scheme **3-13**.



3.23 **3.24**

Scheme 3- 13. *Reactions and conditions*: (i). KOBu^t, THF

An equimolar (0.2 M) solution of potassium *t*-butoxide in tetrahydrofuran was added to the monomer **3.23** solution in tetrahydrofuran at room temperature. The reaction was monitored by g.p.c. and it was found that after 3.5 hours polymer of sufficiently high

molecular weight had been formed. The polymerisation reaction was quenched by pouring into ice-cold methanol and the mixture was centrifuged. The precipitate obtained was dissolved in a minimum amount of tetrahydrofuran before being filtered through cotton-wool to remove insoluble particles. The polymer was purified by two precipitations into ice-cold methanol from which it was collected by centrifugation. This process removed the low molecular weight impurities. The polymer obtained was vacuum dried to give nitro-*bis*-fluorenyl-PPV **3.24** (S-EH-NO_2F_2PPV) as a yellow solid in a 58% yield.

G.p.c. analysis against polystyrene standards showed that S-EH-NO_2F_2PPV **3.24** had a $\overline{M}_w$ of 3.2×10^5 g/mol and a PD of 7.2. The ^{1}H n.m.r of S-EH-NO_2F_2PPV **3.24**, Figure **3-6**, shows that there are no CHCl signals indicating the polymer is fully conjugated.

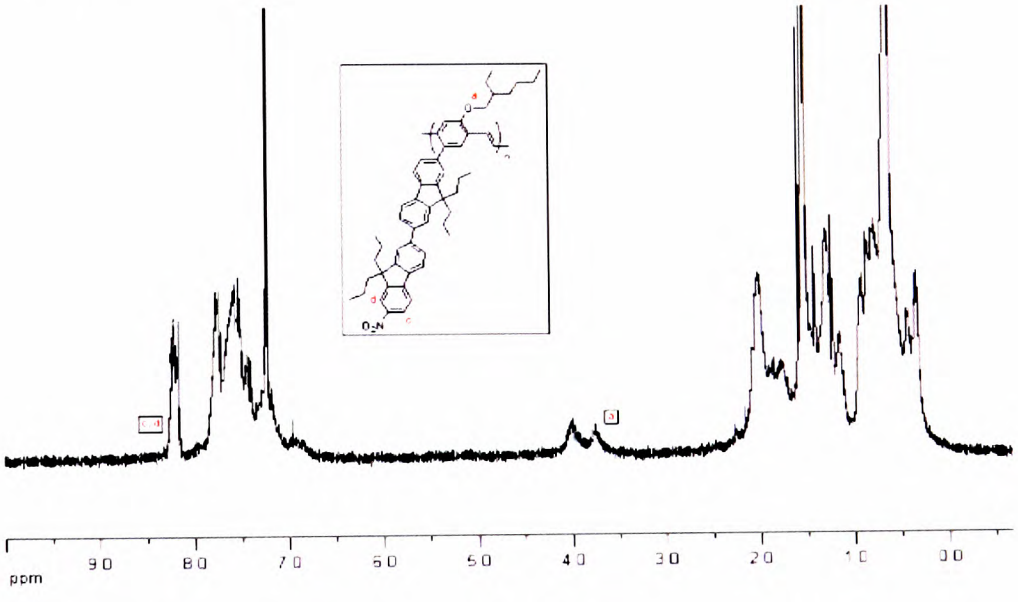


Figure 3- 6: ^{1}H n.m.r. of S-EH-NO_2F_2PPV **3.24** in $CDCl_3$

All the signals are broad as expected for a polymer spectrum. In addition, there are no signals due to benzylic protons of ethylene units in the polymer backbone at ~2.8 p.p.m. indicating that the polymer was regioregular.

Thermogravimetry analysis (Figure **3-7**) further confirmed the structure of S-EH-NO_2F_2PPV **3.24**. TGA was carried out at a heating rate 2 °C/min. and no weight loss due to dehydrochlorination at around 150-200 °C was observed also indicating that the polymer had a full conjugated backbone. Polymer **3.24** showed good thermal stability up to 345 °C after which it steadily degraded.

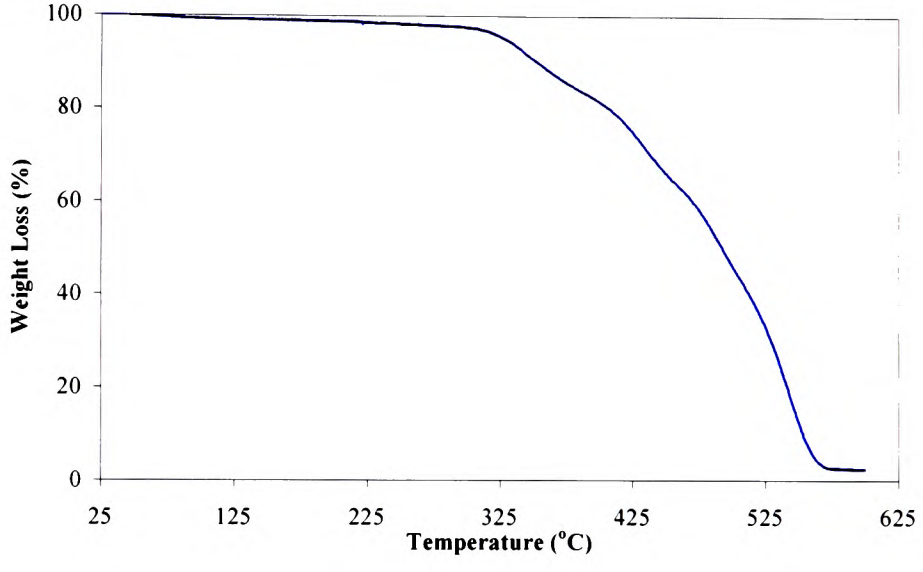


Figure 3- 7: TGA of S-EH-NO_2F_2PPV **3.24**

The infrared spectrum (Figure **3-8**) of S-EH-NO_2F_2PPV **3.24** was obtained as a film drop-cast from chloroform solution on a freshly prepared KBr disc. The absorption peak at 970 cm^{-1} was attributed to the C-H stretch of *trans*-vinylene bond indicating that the conjugation along the backbone of the polymer was predominantly *trans*. The

absorptions at 1522 cm^{-1} and 1337 cm^{-1} correspond to the antisymmetric and symmetric stretch of the nitro groups in **3.24**.

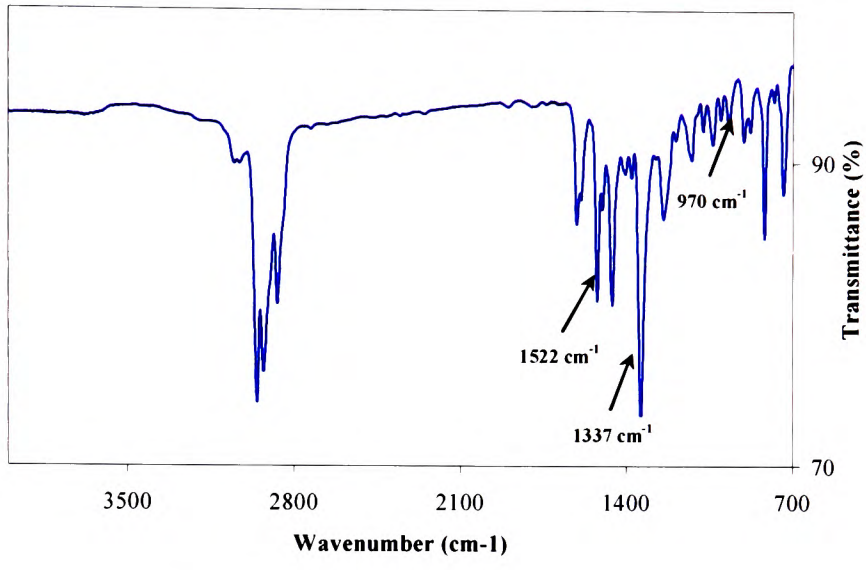


Figure 3- 8: Infrared spectrum of S-EH-NO_2F_2PPV **3.24**

Thin films of S-EH-NO_2F_2PPV **3.24** for U.V.-visible analysis were obtained by spin-coating the polymer from chloroform or tetrahydrofuran solutions onto quartz. The U.V.-visible spectra of the films were recorded and compared with the spectrum of the monomer **3.23** in solution and polymer films of S-EH-F_2PPV **3.18**, S-EH-NO_2FPPV **2.30a**, Figure **3-9**. The spectra of the films of polymer **3.24** showed absorption at similar wavelengths as the monomer **3.23** with peaks at 300 and 380 nm. The polymer **3.24** showed broad absorption in the 260-540 nm. The strong absorption at 380 nm was due to the "dipole" chromophore and absorptions at 210 nm and >450 nm were due to the localised and delocalised π-π^* transitions respectively.

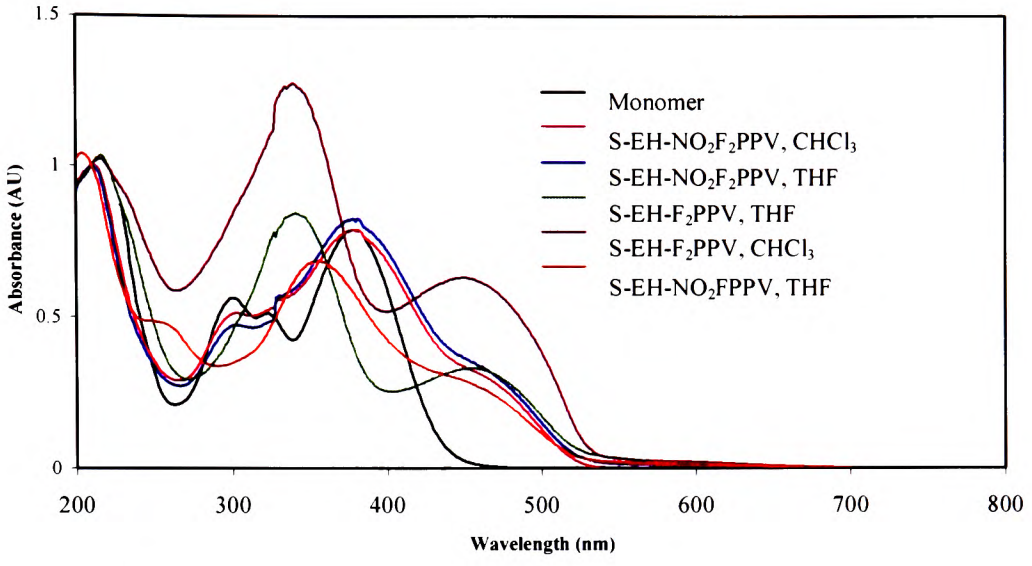


Figure 3- 9: U.V.-visible spectra of monomer **3.23** (dichloromethane), and films of S-EH-NO_2FPPV **2.30a**, S-EH-F_2PPV **3.18** and S-EH-NO_2F_2PPV **3.24**

The ratio of delocalised to localised π-π* transitions is lower than 1 (desired value is greater than 1) and also found lower to S-EH-F_2PPV **3.18**, indicating conformational disorder is responsible for the lower ratio. No synthetic disorder (*bis*-benzyl signals) in the polymer backbone structure was noticed in the ^{1}H n.m.r. of the polymer **3.24** which could account for shortening of the effective conjugation length available for delocalisation. The nature of solvent used for polymer film formation had no effect on the spectra of the **3.24** films. No difference in the absorption wavelength of the delocalised π-π* transitions was noticed in nitro-*bis*-fluorenyl PPV **3.24** film in comparison to the nitro-fluorenyl PPV **2.30a** (S-EH-NO_2FPPV) film apart from a bathochromic shift of 30 nm in the "dipole" chromophore absorption. This is attributed to the presence of one additional fluorenyl unit long linker, that is, nitro-*bis*-fluorenylphenyl unit as compared to

the nitro-fluorenylphenyl unit respectively. However, the ratio of delocalised to localised π-π^* transitions in **3.24** was slightly higher (6%) than **2.30a**.

3.3.3 Summary

In summary, nitro-*bis*-fluorenyl monomer **3.23** was synthesised *via* more versatile protection de-protection route. Gilch conditions were used to polymerise the monomer to form S-EH-NO_2F_2PPV **3.24**. Polymer was characterised and optical properties were studied.

3.4 Conclusions

A new versatile monomer precursor was synthesised and the monomers were successfully synthesised in good yields. The monomers were polymerised to give high molecular weight polymers.

A new class of soluble conjugated polymers, *bis*-fluorenyl biphenyl linked PPV, with and without an electron withdrawing nitro group have been prepared. The addition of the second fluorenyl group between the electron-donating and electron-withdrawing group extended the dipole when compared with the earlier family of mono-fluorenyl-PPV. The U.V.-visible absorption spectra of *bis*-fluorenyl PPV displayed more delocalised backbone compared to the corresponding mono-fluorenyl equivalents. The polymers have good thermal stability and good solubility in commonly used solvents.

MONO-VINYL LINKED PPV DERIVATIVES

Chapter 4

4 MONO-VINYL LINKED PPV DERIVATIVES

4.1 Introduction

In chapters 2 and 3 the side groups were directly attached to the polymer backbone with the biphenyl link causing steric hindrance and twisting of the polymer backbone and chromophores leading to decreased π-delocalisation. It would therefore be advantageous if the PPV backbone and the side-groups could be coplanar. Therefore, a new series of poly(2-alkoxy-1,4-phenylenevinylene)s with fluorenyl side-groups linked to polymer backbone *via* a vinylene linkage were designed (Figure **4-1**). Planarity between the poly(1,4-phenylenevinylene) (PPV) backbone and side-groups should give an improved dipole moment and the lack of steric constraint will allow the polymer backbone to be more delocalised.

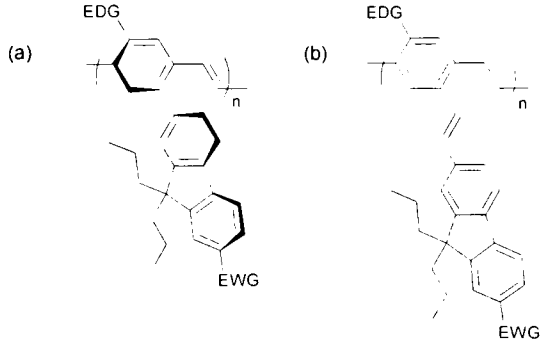
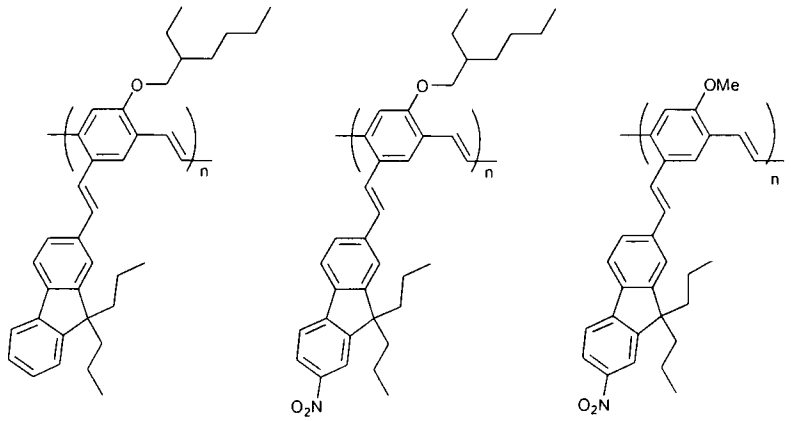


Figure 4 - 1: Generalised view of torsion angles in fluorenyl-PPV (a). biphenyl-linked and (b).vinyl-linked

The target fluorenylvinyl PPVs are shown in Figure **4-2**. The parent conjugated polymer designed is soluble poly{2-[(*E*)-2-(9,9-dipropylfluorenyl)vinyl]-5-(2′-

ethylhexyloxy)-1,4-phenylenevinylene} **4.21** (S-EH-FVPPV) which has no electron withdrawing group (EWG). The two other polymers have the EW nitro group attached to the fluorenyl moiety and are soluble poly{2-[(*E*)-2-(7-nitro-9,9-dipropylfluorenyl)vinyl]-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene} **4.44** (S-EH-NO_2FVPPV) and poly{2-[(*E*)-2-(7-nitro-9,9-dipropylfluorenyl)vinyl]-5-methoxy-1,4-phenylenevinylene} **4.43** (I-M-NO_2FVPPV).



4.21 **4.44** **4.43**

Figure 4 - 2: Mono-vinyl linked PPV derivatives: S-EH-FVPPV **4.21**, S-EH-NO_2FVPPV **4.44**, and S-M-NO_2FVPPV **4.43**

The difference between **4.44** and **4.43** is the length of the alkoxy side-chain with them having 2-ethylhexyloxy and methoxy moieties respectively. This series of fluorenylvinyl PPV derivatives will allow a direct comparison of the effect of the nitro group in this family of materials and the effect of vinyl moiety on the properties of the polymers relative to those discussed in the previous chapters. As S-EH-FVPPV **4.21** and S-EH-NO_2FVPPV **4.44** have the longer EDG, 2-ethylhexyloxy, this would give rise to

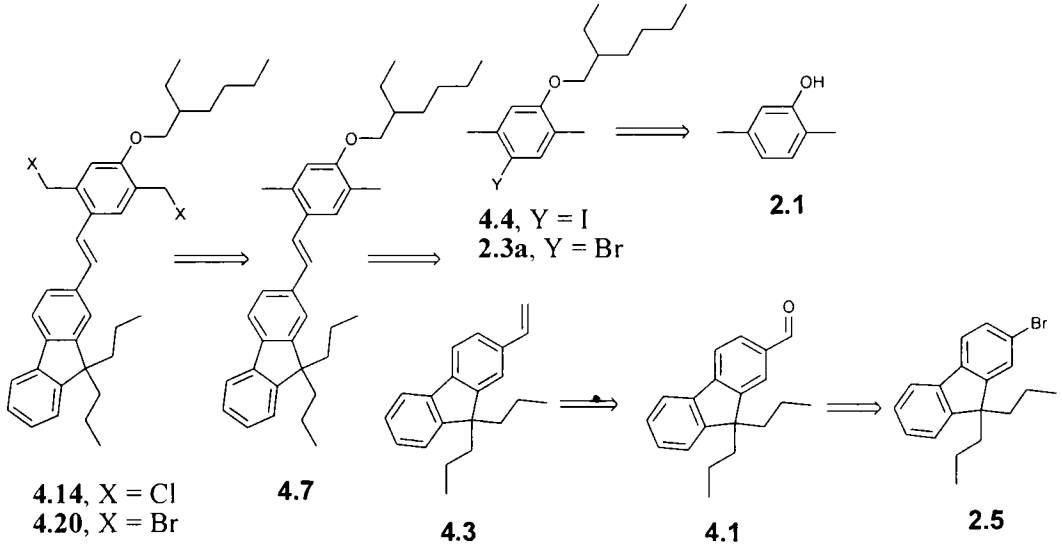
soluble conjugated polymers. I-M-NO_2FVPPV **4.43** with the methoxy side-chain would not be expected to be soluble in its conjugated form and hence needs to be prepared *via* a precursor polymer.

4.2 Poly{2-[(*E*)-2-(9,9-dipropylfluorenyl)vinyl]-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene}

4.2.1 Synthesis of the Fluorenylvinyl monomer

4.2.1.1 Retrosynthetic analysis of the Fluorenylvinyl monomer

The retrosynthetic analysis for the fluorenylvinyl monomer **4.14** required for the formation of S-EH-FVPPV **4.21** is shown in Scheme **4-1**.

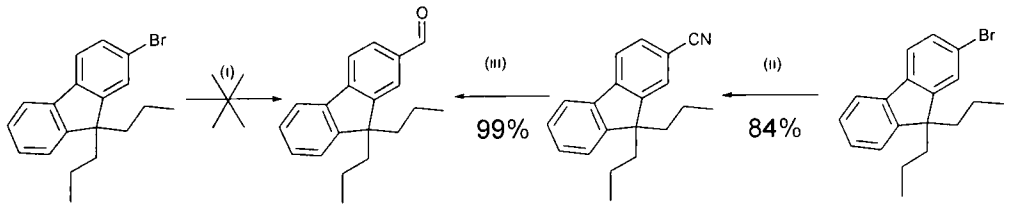


Scheme 4- 1: Retrosynthetic approach for the fluorenylvinyl monomer **4.14** or **4.20**

The vital step in the synthesis of monomer **4.14** is the formation of the (*E*)-dimethylvinylfluorene **4.7**. The approach requires the Heck coupling of vinylfluorene **4.3** with the 1-halo-4-(2'-ethylhexyloxy)-*p*-xylene **2.3a** (Y = Br) or **4.4** (Y = I). It was anticipitated that **4.3** could be formed from fluorenylaldehyde **4.1** which in turn could be synthesised from commercially available 2-bromofluorene after di-alkylation at the 9-position to form dipropylbromofluorene **2.5** (Scheme **2-3**, Chapter 2). The transformation of (*E*)-dimethylvinylfluorene **4.7** to monomer **4.14** (X = Cl) or **4.20** (X = Br) could be carried out in the standard four steps namely, bromination at the benzylic position, acetylation, reduction and halogenation.

4.2.1.2 Attempted synthesis of the Monomer (X = Cl) via the Heck reaction

The first step in the synthesis of vinylfluorene **4.3** was the preparation of fluorenylaldehyde **4.1**, Scheme **4-2**.



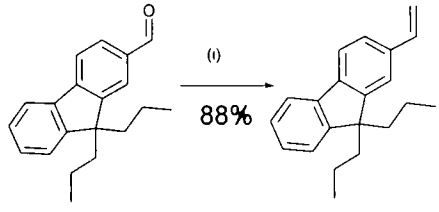
Scheme 4- 2. *Reactions and conditions*: (i). a. THF, *n*-BuLi, -78 °C; b. DMF;

c. -78 °C → r.t.; (ii). a. CuCN, DMF, Δ; b. $FeCl_3.6H_2O$, H_3O^+

(iii). a. DIBAL-H, DCM, PhMe, -78 °C; b. r.t.; c. H_3O^+

The synthesis of fluorenylaldehyde **4.1** was attempted by lithiation of dipropylbromofluorene **2.5** (Chapter 2) in tetrahydrofuran at -78 °C followed by quenching of the fluorenyl anion with *N,N*-dimethylformamide. After purification no fluorenylaldehyde **4.1** was recovered and majority of the product formed was a mixture of unidentifiable compounds. Alternatively, the fluorenylaldehyde **4.1** was synthesised *via* an indirect route that first involved replacement of the bromine in dipropylbromofluorene **2.5**, with a nitrile group by treatment with 4 equivalents of copper cyanide in *N,N*-dimethylformamide heated at reflux to give the cyanofluorene **4.2** in a 84% yield. Cyanofluorene **4.2** was reduced with diisobutylaluminium hydride (DIBAL-H) in a dichloromethane/toluene mixture with the DIBAL-H being added with the reaction temperature at -78 °C then allowing it to warm to room temperature. The imine intermediate was then hydrolysed to afford the fluorenylaldehyde **4.1** in a 99% yield. This gave fluorenylaldehyde **4.1** in two simple steps in an overall yield of 92%.

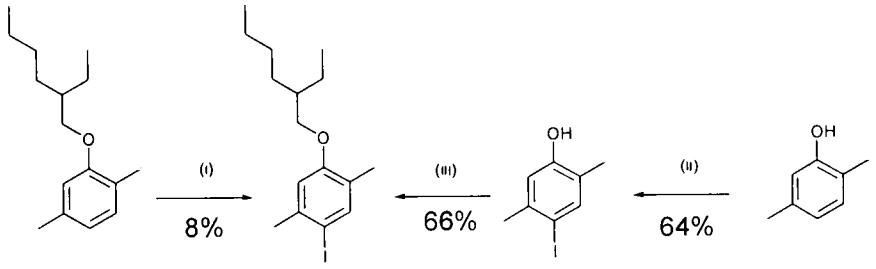
The Wittig reaction of **4.1** in *N,N*-dimethylformamide with triphenylphosphoniummethyl iodide in the presence of potassium *t*-butoxide at room temperature gave vinylfluorene **4.3** in an 88% yield, Scheme **4-3**.



4.1 **4.3**

Scheme 4- 3. *Reactions and conditions*: (i). $Ph_3P^+CH_3I^-$, $KOBu^t$, THF

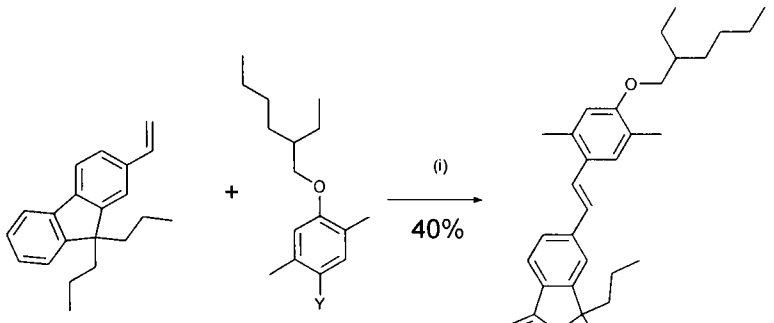
The 1-iodo-4-(2′-ethylhexyloxy)-*p*-xylene **4.4** required for the Heck coupling with **4.3**, was synthesised from 2-(2′-ethylhexyloxy)-*p*-xylene **2.2** in a very poor yield (8%) using a silver acetate mediated iodination, Scheme **4-4**.



Scheme 4- 4. *Reactions and conditions*: (i). AgOAc, I_2, $CHCl_3$, dark (ii). BTMA.ICl_2 (**4.6**), CH_2Cl_2, $CaCO_3$; (iii). 2-Ethylhexyl bromide, $KOBu^t$, CH_3CN

A more efficient route was found which involved iodination of 2,5-dimethylphenol **2.1** using benzyltrimethylammonium dichloroiodate (BTMA.ICl_2) **4.6** and calcium carbonate in dichloromethane. The 4-iodo-2,5-dimethyl-phenol **4.5** could be purified by recrystallisation and was isolated in a 64% yield. Etherification of **4.5** with potassium *t*-butoxide and 2-ethylhexyl bromide afforded the required 1-iodo-4-(2′-ethylhexyloxy)-*p*-xylene **4.4** in a 66% yield.

Heck coupling of 1-halo-4-(2′-ethylhexyloxy)-*p*-xylene **2.3a** (Y = Br, Chapter 2)/ **4.4** (Y = I) and vinylfluorene **4.3** (Scheme **4-5**) was investigated under a range of conditions that are summarised in Table **4-1**.



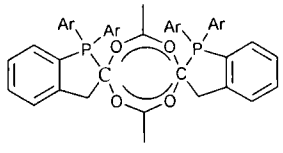
4.3 **4.4**, Y = I; **2.3**, Y = Br **4.7**

Scheme 4- 5. *Reactions and conditions*: (i). Herrmann's catalyst (**4.8**), 2,6-di-*t*-butylcresol, Na_2CO_3, DMA, Δ or Pd $(OAc)_2$, K_3PO_4, DMA, 144 °C

Table 4-1: Reagents and conditions used for the Heck reaction

Halo anisole	Pd catalyst	Base	Temp. (°C)	Time (days)	4.7 (%)
2.3a (Y = Br)	Pd(II) acetate	K_3PO_4	144	4	19
	Herrmann's catalyst **4.8**	Na_2CO_3	166	4	40
4.4 (Y = I)	Pd(II) acetate	K_3PO_4	144	4	34
	Herrmann's catalyst **4.8**	Na_2CO_3	166	4	30

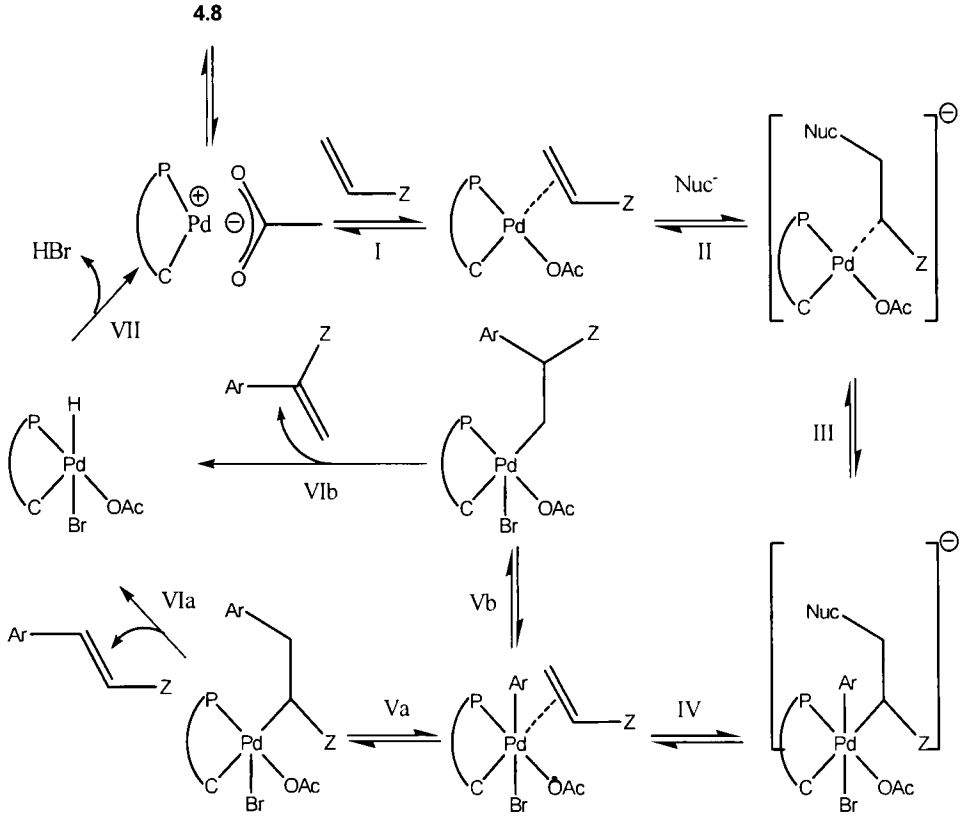
The Heck reaction was carried out between **4.3** and **2.3a** (Y = Br)/**4.4** (Y = I) using two different catalysts, namely palladium (II) acetate and Herrmann's catalyst **4.8**, Figure **4-2**.



4.8 Ar = *o*-tolyl

Figure 4- 2: Structure of Herrmann's catalyst

Herrmann's catalyst **4.8** was prepared using literature procedure[136] by reaction of commercially available palladium (II) acetate with *tri*(*o*-tolylphosphine) in toluene at 60 °C and obtained as a yellow solid in a 82% yield. The activity of the catalyst was not affected after several months even though stored at room temperature. Herrmann's catalyst **4.8** is thermally stable and is used for sluggish reactions that require high temperatures. The proposed mechanism[137] for the Heck reaction using a Pd (II)-Pd (IV) catalytic cycle is shown in Scheme **4-6**.



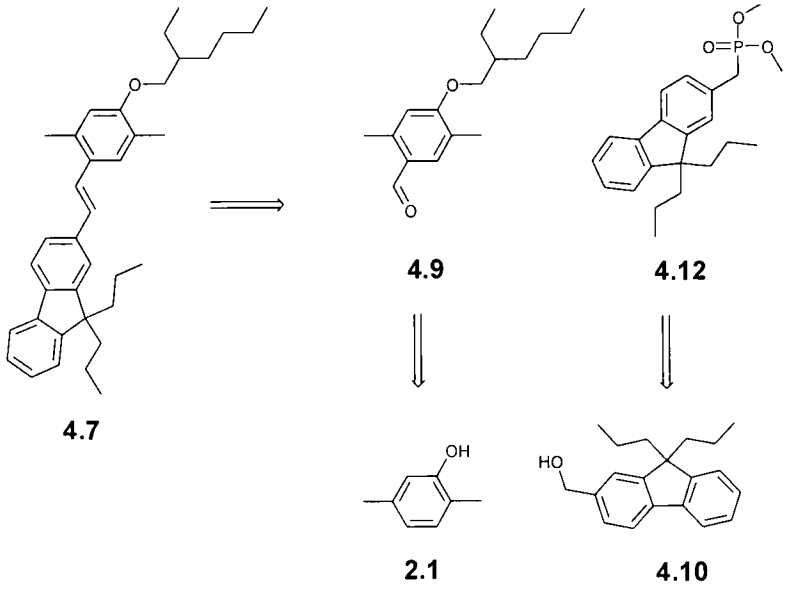
Scheme 4- 6: Proposed mechanism[137] for the Heck reaction using a Herrmann's catalyst **4.8**: I. CH_2=CHZ; II. Reversible attack by nucleophile (OAc , Br^- or OH^-) (attack is shown on the terminal carbon atom but it could be on the internal carbon); III. Oxidative addition of ArBr; IV. Loss of nucleophile; Va/b. Migration of Ar to terminal/internal carbon; VIa/b. β-Hydrogen elimination; VII. Removal of HBr by base.

The reaction conditions used for the Heck coupling of **4.3** and 1-halo-4-(2'-ethylhexyloxy)-*p*-xylene **2.3a** (Y = Br)/**4.4** (Y = I) with the catalysts were different and based on the literature methods. Herrmann's catalyst **4.8** was used in presence of a free radical inhibitor, 2,6-di-*t*-butyl-*p*-cresol and anhydrous sodium carbonate in *N,N*-dimethylacetamide heated at reflux. Polymerisation of 3,5-di-*t*-butylstyrene was observed under similar reaction conditions at 130 °C[138] Therefore, free radical inhibitor was used to prevent any polymerisation of the vinylfluorene **4.3** at 166 °C. On the other hand, with palladium (II) acetate the reaction was performed at 144 °C in absence of free radical inhibitor and potassium phosphate was used as a base[139]. No polymerisation of **4.3** was observed at 144 °C by ^{1}H n.m.r spectroscopy. The yield of the desired Heck product, (*E*)-dimethylvinylfluorene **4.7** ranged between 19-40%. When 1-bromo-4-(2'-ethylhexyloxy)-*p*-xylene **2.3a** was used, Herrmann's catalyst **4.8** gave a much better yield of **4.7** than when palladium (II) acetate was the catalyst as the former has a higher turnover number at high temperatures[140]. In Heck reactions, if the rate-determining step is the insertion of the palladium to the C-X bond then the iodides should couple with vinyl compounds in better yields as compared to the bromides due to the weak C–I bond. However, in the current work no improvement in the yield of (*E*)-dimethylvinylfluorene **4.7** was observed for the iodides when Herrmann's catalyst **4.8** was used. Although there was a modest improvement in the yield of iodides over bromides when palladium (II) acetate was the catalyst. The behaviour of palladium (II) acetate and **4.8** are in accordance with the reported mechanism where oxidative addition of the aryl halide has been found to be rate-determining step[141-142] to palladium but alkene addition in the latter[143-144].

As (*E*)-dimethylvinylfluorene **4.7** is an early intermediate for the synthesis of fluorenylvinyl monomer **4.14** (X = Cl) or **4.20** (X = Br) and the benzylic bromination, acetylation, reduction, and halogenation in general give a low overall yield. Therefore, an alternative methodology was sought for the preparation of **4.7**.

4.2.1.3 Alternative retrosynthetic analysis of the Fluorenylvinyl monomer

The second retrosynthetic strategy considered for the preparation of (*E*)-dimethylvinylfluorene **4.7** is illustrated in Scheme **4-7**.



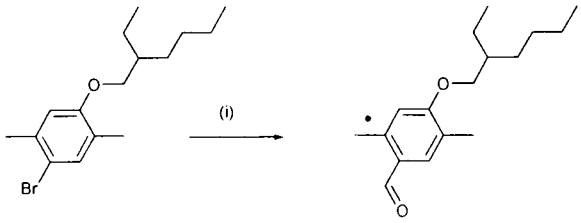
Scheme 4- 7: Horner-Emmons-Wadsworth approach for the synthesis of (*E*)-dimethylvinylfluorene **4.7**

Horner-Emmons-Wadsworth reaction was chosen for the introduction of the double bond between substituted fluorene and alkoxy-*p*-xylene to form the desired

(*E*)-dimethylvinylfluorene **4.7**. The choice of Horner-Emmons-Wadsworth reaction over Wittig reaction was based on the fact that the by-product of the former reaction is a phosphate ester and hence soluble in water, unlike the triphenylphosphine oxide by-product of the Wittig reaction, which facilitates the easy separation of the olefin product. This route involved reaction between the 4-(2′-ethylhexyloxy)-2,5-dimethylbenzaldehyde **4.9** (ethylhexyloxy-benzaldehyde) and the fluorenylphosphonate ester **4.12** with the stereo-selectivity of the olefin product **4.7** being governed by the stability of phosphorus ylide. Thus the formation of *E*-isomer would be favoured when the phosphonate functionality is attached to the fluorene rather than the phenyl ring with the electron-donating alkoxy group. The synthesis of fluorenylphosphonate ester **4.12** and ethylhexyloxy-benzaldehyde **4.9** could be pursued from fluorenylaldehyde **4.1** and 1-bromo-4-(2′-ethylhexyloxy)-*p*-xylene **2.3a** respectively.

4.2.1.4 Synthesis of the Monomer via the Horner-Emmons-Wadsworth

The synthesis of ethylhexyloxy-benzaldehyde **4.9** from 1-bromo-4-(2′-ethylhexyloxy)-*p*-xylene **2.3a** is shown in Scheme **4-8**.

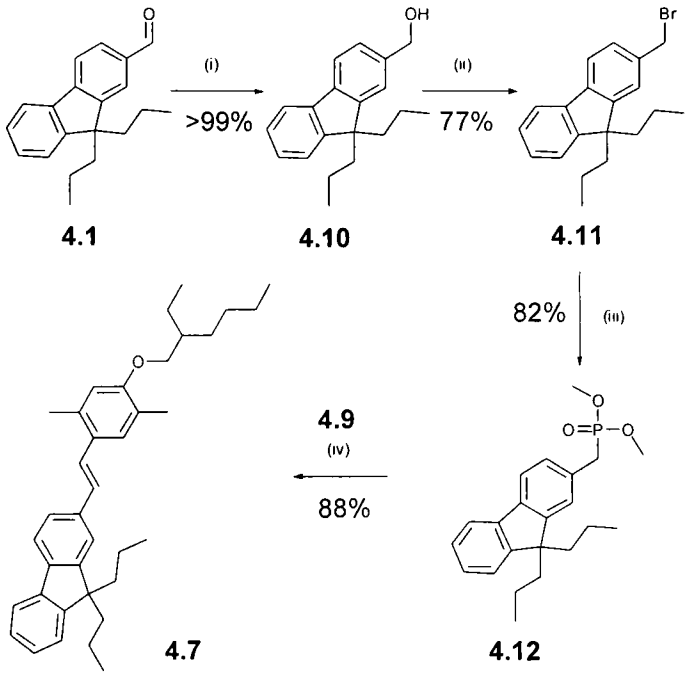


2.3a **4.9**

Scheme 4- 8. *Reactions and conditions*: (i) a. THF, *t*-BuLi, -78 °C; b. DMF; c.-78 °C → r.t.

Formylation of **2.3a** was achieved by treatment with *t*-butylithium in tetrahydrofuran at -78 °C followed by addition of *N,N*-dimethylformamide and hydrolysis to afford ethylhexyloxy-benzaldehyde **4.9** in a 71% yield.

The next part in the synthesis of **4.7** was the formation of fluorenylphosphonate ester **4.12** required for the coupling with **4.9**. The ester **4.12** was obtained from fluorenylaldehyde **4.1** in three steps as shown in Scheme **4-9**.



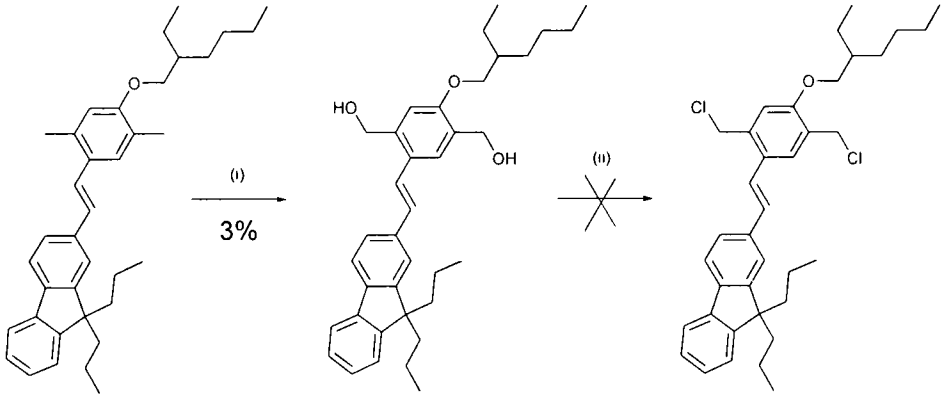
Scheme 4- 9. *Reactions and conditions*: (i) a. $NaBH_4$, EtOH, *i*-PrOH; (ii) PBr_3, -10 °C; -10 °C → 100 °C; (iii). $P(OMe)_3$, 80 °C; (iv). **4.9**, $KOBu^t$, THF

Reduction of fluorenylaldehyde **4.1** to fluorenylalcohol **4.10** was performed by treatment with sodium borohydride in an ethanol/*i*-propanol mixture and **4.10** was obtained in a quantitative yield. Methanol could not be used as the solvent for the sodium borohydride reduction reaction as the fluorenylaldehyde **4.1** was found to react spontaneously with

methanol at room temperature to form acetals as indicated by the formation of OCH_3 signals and absence of C=O stretch in the ^1H n.m.r and infrared spectroscopy respectively. Bromination of fluorenylalcohol **4.10** was carried out using phosphorous tribromide both as a reactant and solvent at 100 °C. The excess phosphorous tribromide in the reaction mixture was decomposed and purification of the crude gave the fluorenylbromide **4.11** in a 77% yield. The Arbuzov reaction of **4.11** with trimethyl phosphite was carried out at 80 °C to give fluorenylphosphonate ester **4.12** in an 82% yield. The Horner-Emmons-Wadsworth coupling reaction of **4.12** with ethylhexyloxy-benzaldehyde **4.9** was carried out using potassium *t*-butoxide in tetrahydrofuran at room temperature. The phosphonate **4.12** solution showed an instantaneous colour change from colourless to red suggested the formation of fluorenyl carbanion on addition of the base. The progress of the reaction was monitored by t.l.c. and it was found that the reaction colour faded to colourless, as the carbanion was consumed up by the ethylhexyloxy-benzaldehyde **4.9**.The dimethylvinylfluorene **4.7** was obtained as the *E*-isomer in a 88% yield as a white solid.

The standard strategy for the activation of the methyl groups was studied for (Scheme **4-1**) the synthesis of the monomer **4.14** (X = Cl) from (*E*)-dimethylvinylfluorene **4.7**, Scheme **4-10**. The first step was the free-radical bromination of the benzylic hydrogens of (*E*)-dimethylvinylfluorene **4.7** with *N*-bromosuccinimide using 2,2'-azo-*bis*(isobutyronitrile) as an initiator in carbon tetrachloride heated at reflux. This procedure gave an inseparable mixture of mono-, di-, tri-, tetra-brominated compounds. The succinimide by product was removed from the crude brominated compounds by filtering through a plug of silica. In the second step,

acetylation of the bromomethyl compounds was carried out using sodium acetate in glacial acetic acid to afford the corresponding esters and aldehydes, which were then reduced to the alcohol functionality with lithium aluminium hydride in tetrahydrofuran. However, even after exhaustive attempts to purify the impure fluorenyl-*bis*-alcohol **4.13** by column chromatography, using a wide variety of solvent mixtures as eluents only a small amount of almost pure (~7%) fluorenyl-*bis*-alcohol **4.13** was recovered.



4.7 **4.13** **4.14**

Scheme 4- 10. *Reactions and conditions*: (i). a. NBS, AIBN, CCl_4, Δ; b. NaOAc, AcOH, Δ; c. $LiAlH_4$, THF; (ii) $SOCl_2$, DCM, 0 °C

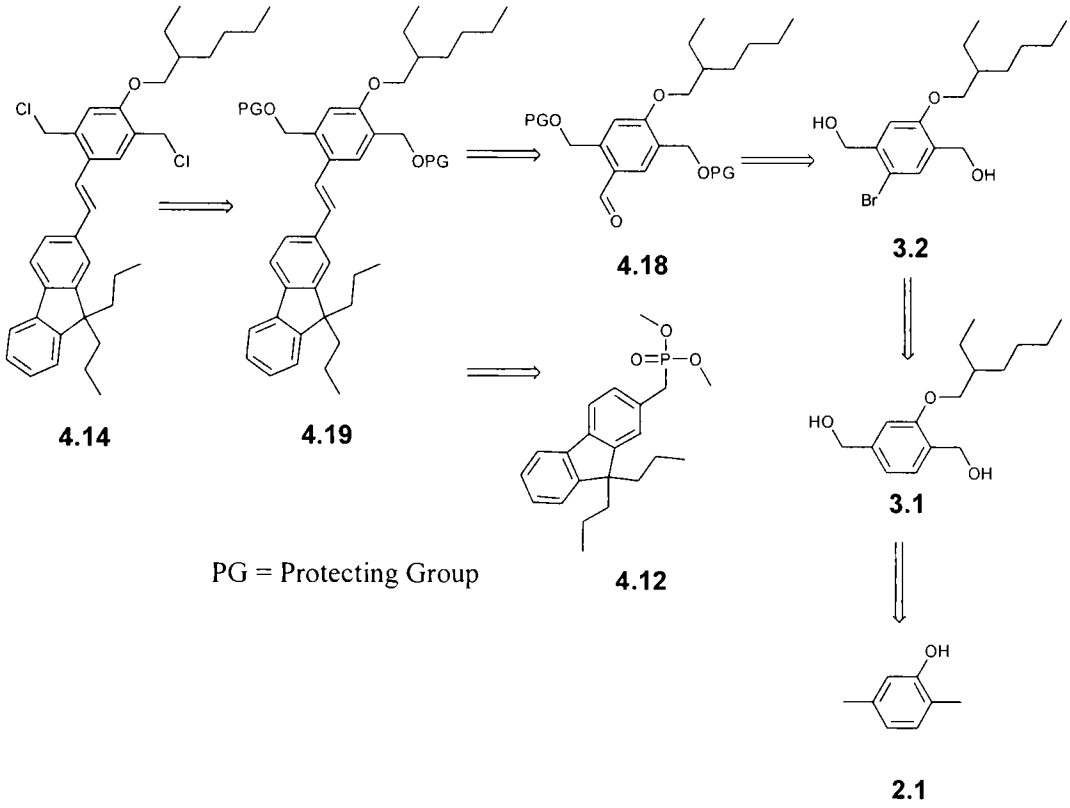
Further purification of the fluorenyl-*bis*-alcohol **4.13** was accomplished by recrystallisation from a dichloromethane/light petroleum mixture at 0 °C to give **4.13** as a white solid in a very low overall yield of 3% after three steps. Compound **4.13** seemed to be unstable in both solid and solution form turning to a yellow colour when stored in a vial at room temperature. This was further confirmed by ^1H n.m.r. analysis of the yellow solid indicated by the appearance of aldehyde and several unidentifiable signals. **4.13** also undergoes decomposition even in the n.m.r. tube when a recorded sample kept for a day

and ^{1}H n.m.r. was re-recorded. At this stage, a test reaction to form *bis*-chloro fluorenylvinyl monomer **4.14** from fluorenyl-*bis*-alcohol **4.13** was tried using thionyl chloride in anhydrous dichloromethane at 0 °C. Although *bis*(chloromethyl) monomer **4.14** was formed it could not be purified by column or chromatotron chromatography. It was not clear why the reaction failed but given the procedure to form the *bis*-diol **4.13** was low yielding a new synthetic strategy for the synthesis of fluorenylvinyl monomer **4.14** (X = Cl) was required.

4.2.1.5 Retrosynthetic analysis of the Monomer via the protection route

As a result of the shortcomings encountered in the final stage of the synthesis of the fluorenylvinyl monomer **4.14**, a new synthetic strategy was devised. Since the method of introduction of double bond between fluorene and alkoxybenzene moieties was understood, the introduction of functionality that could allow polymerisation was the next challenge. This meant a rethink of the chemistry already used and the order in which certain key steps should take place. The method proposed to achieve the required functionality is shown in Scheme **4-11**. It was decided to carry out as much chemistry as possible before the formation of vinylene linkage. The synthesis of 2,5-*bis*(hydroxymethyl)-4-(2′-ethylhexyloxy)bromobenzene **3.2** (*bis*-diol bromide) from commercially available 2,5-dimethyl phenol **2.1** was described in Chapter 3. Thus, **3.2** was used as a starting point for the synthesis of the fluorenylvinyl monomer **4.14**. Protection of the hydroxyl functionality of **3.2** with trimethylsilanyloxymethyl (TMS),

and tetrahydropyranyl (THP) ether had been carried out earlier and both the compounds were available to explore the new route.



Scheme 4- 11: An alternative approach for the synthesis of fluorenylvinyl monomer **4.14**

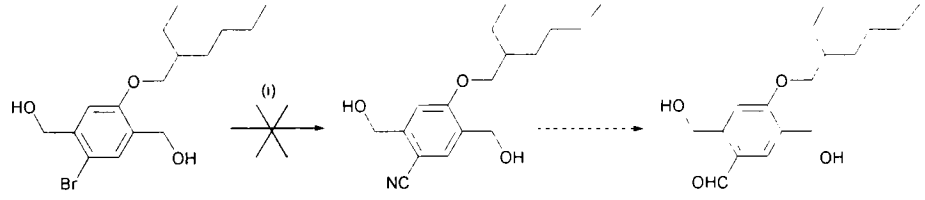
Conversion of the bromide to the corresponding formyl group of either TMS-bromide **3.5** or THP-bromide **3.9** would afford 2,5-diprotected-4-(2'-ethylhexyloxy)benzaldehyde **4.18a** (Protecting group, PG = TMS) or **4.18b** (PG = THP). The Horners-Emmons-Wadsworth reaction of the protected aldehyde **4.18a** or **4.18b** with fluorenylphosphonate ester **4.12** could then be utilised to introduce the alkene linkage

between the two to form the protected alkene **4.19** before deprotection and activation to form the monomer **4.14**.

4.2.1.6 Synthesis of the Fluorenylvinyl monomer via the protection route

The first target towards the synthesis of fluorenylvinyl monomer **4.14** (X = Cl) required the protected aldehyde **4.18** (Scheme **4-11**) that could be prepared from 2,5-*bis*(hydroxymethyl)-4-(2'-ethylhexyloxy)bromobenzene **3.2** (*bis*-diol bromide) directly or from its THP- (**3.9**) or TMS- (**3.5**) protected derivatives.

In a first attempt, cyanation of *bis*-diol bromide **3.2** to afford **4.15** was tried using copper cyanide and *N,N*-dimethylformamide heated at reflux, which led to an unidentifiable mixture of oxidised products as detected by several aldehyde signals in the ^{1}H n.m.r. spectra of the fractions collected after separation by column chromatography (Scheme **4-12**).

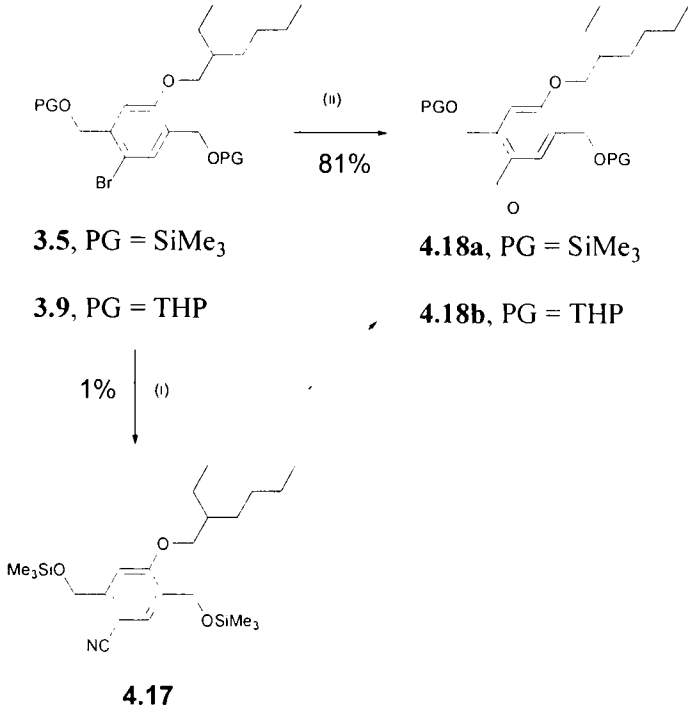


3.2 **4.15** **4.16**

Scheme 4- 12. *Reactions and conditions*: (i). CuCN, DMF, Δ

This result indicated that the hydroxyl groups needed to be protected before the introduction of the aldehyde functionality and the two main strategies used for the

preparation of protected aldehyde **4.18a** (PG = TMS) or **4.18b** (PG = THP) are shown in Scheme **4-13**.



Scheme 4- 13. *Reactions and conditions*: (i). and (ii). cf. Table **4-2**

Although Scheme **4-13** shows the successful reactions a large number of reactions were carried out in an attempt to achieve the required transformation and these are outlined in Table **4-2**.

Table **4-2:** Reagents and reaction conditions studied for the formation of TMS-CN **4.17** and aldehyde **4.18a** (PG = TMS) and **4.18b** (PG = THP) from protected compound **3.5** and **3.9** respectively

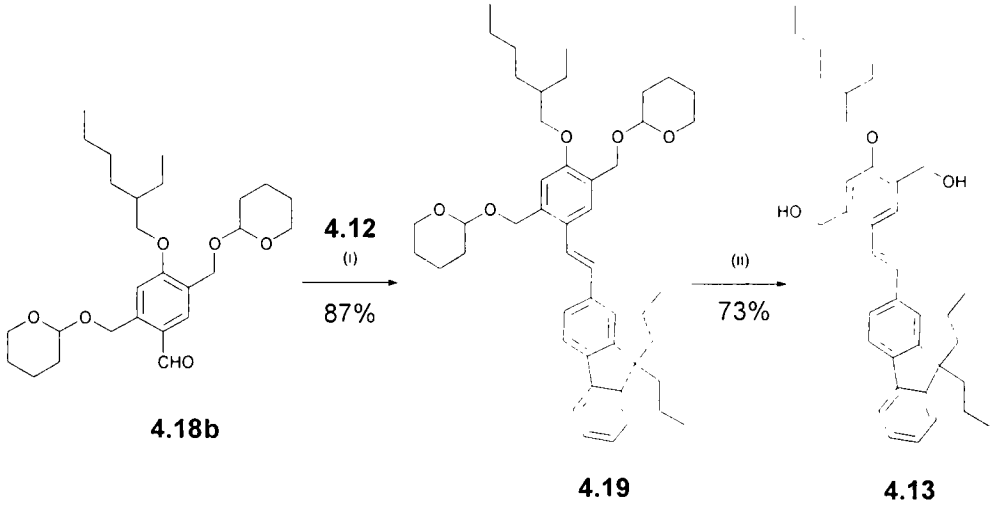
		Reagents used to introduce			
Compound	**Entry**	**CN**	**4.17**	**CHO**	**4.18a/b**
		4.17	**(%)**	**4.18a/b**	**(%)**
	1	CuCN, DMF, Δ			-
	2	$Pd(Ph_3)_4$, TMSiCN, TEA, Δ	~ 1		
	3	$Pd(Ph_3)_4$, TMSiCN, CuI, TEA, Δ			
3.5 (X = TMS)	4	$Pd(Ph_3)_4$, CuI, Bu_3P, TMSiCN, TMDA, PhMe, Δ			
	5	$K_4[Fe(CN)_6]$, $Pd(OAc)_2$, dppf, Na_2CO_3, NMP, Δ			
3.9 (X = THP)	6	•		*t*-BuLi, THF, DMF	81

As described in Chapter 3 the metallation of TMS-bromide **3.5** using alkyllithiums was unsuccessful. Earlier work had shown that the nitrile group could be

introduced smoothly using copper cyanide therefore; cyanation of TMS-bromide **3.5** using copper cyanide in *N,N*-dimethylformamide was attempted (Entry 1). This failed to produce the desired compound **4.17** but an unidentifiable mixture of compounds was obtained. Palladium (0) catalysed cyanation of **3.5** (Entry 2) with trimethylsilylcyanide[145] (TMSiCN) and triethylamine (TEA) led to the formation of TMS-cyanide **4.17** but in a low yield (~1%) and starting material was recovered (80%). The formation of TMS-cyanide **4.17** was confirmed by ^{1}H n.m.r. and infrared spectroscopy. The infrared spectrum of **4.17** showed the C≡N stretching vibration at 2100 cm^{-1} In order to improve the yield of **4.17** a catalytic amount of copper iodide[146] was added to the reaction mixture of **3.5**, palladium (0) catalyst and TMSiCN (Entry 3), but no TMS-cyanide **4.17** was formed and starting material was recovered (90%). In another attempt to improve the yield (Entry 4), TEA was replaced with tetramethylenediamine (TMDA)[147] a stronger base, and auxiliary ligand *t*-butylphosphine was added but again no desired nitrile was isolated and starting material was recovered (92%). It has been reported that potassium hexacyanoferrate(II)[148] can also be used as the cyanide source in palladium catalysed cyanation reactions (Entry 5) but this also failed to produce the desired **4.17**. The failure of cyanation reaction of the TMS-bromide **3.5** could be attributed to the large size of trimethylsilyl groups at *o*- and *m*-position to the bromide preventing the attack of cyanating reagents. This stopped further investigation in the synthesis of TMS-cyanide **4.17** from TMS-bromide **3.5**. At this stage it was decided to use another protecting compound THP-bromide **3.9** for the synthesis of THP-aldehyde **4.18b**, as it was known to undergo facile lithium-halogen exchange (Chapter 3). Lithiation of THP-bromide **3.9** with *t*-butyllithium in tetrahydrofuran was carried out at -78 °C and the anion formed was

quenched with *N,N*-dimethylformamide (Entry 6). After hydrolysis THP-aldehyde **4.18b** was obtained in a 81% yield.

The next step was the Horner-Wadsworth-Emmons reaction of the THP-aldehyde **4.18b** with the fluorenylphosphonate ester **4.12** (Scheme **4-14**) and a summary of the different reaction conditions investigated are in Table **4-3**.



Scheme 4- 14. *Reactions and conditions*: (i). **4.12**, cf. Table **4-3**;

(ii). *p*-TsOH, DCM, MeOH

The reaction to form the vinyl link was first carried out using potassium *t*-butoxide as it had been used successfully to couple ethylhexyloxy-benzaldehyde **4.9** with fluorenylphosphonate ester **4.12** previously (Scheme **4-9**). A solution of THP-aldehyde **4.18b** with the fluorenylphosphonate ester **4.12** in tetrahydrofuran was treated with potassium *t*-butoxide at room temperature (Entry 1). Purification of the crude by column chromatography over silica gel gave a small amount of the impure THP-alkene **4.19** (~10%) along with an inseparable impurity. The other fractions collected contained several unidentifiable compounds.

Table **4-3**: Reaction conditions used to form THP-alkene **4.19**

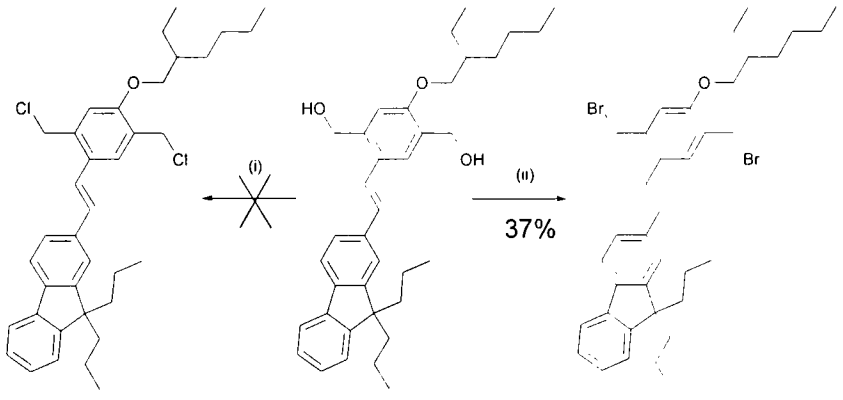
Entry	Base	Temperature (°C)	Solvent	**4.19** (%)
1	KOBu^t	r.t.	THF	Impure, ~ 10
2	KOBu^t	0	THF	Impure, ~ 5
3	KOBu^t	-18	THF	Impure, ~ 5
4	NaH	r.t.	THF	Impure, ~ 4
5	*n*-BuLi	-78 → 0	THF	Impure, ~ 13
6	*t*-BuLi	-78 → 0	THF	Impure, ~ 15
7	LDA	-78	THF	27
8	LDA	0 → r.t.	THF	87

The most likely impurity from the Horner-Wadsworth-Emmons reaction is the presence of the *cis*-isomer and the ^{1}H n.m.r. indicated that this could be the case. Therefore, an attempt at a *cis-trans* isomerisation of the impure THP-alkene **4.19** was carried out. A mixture of THP-alkene **4.19** and catalytic amount of iodine in toluene was heated at reflux for three hours. T.l.c. analysis showed the presence of a very small amount of THP-alkene **4.19** along with several new spots. Purification of the crude was attempted by column chromatography but only impure **4.19** was recovered in an overall yield of ~1% for two steps. This indicated that the impurity was not a *cis*-isomer. The coupling reaction was carried out with potassium *t*-butoxide in tetrahydrofuran at lower temperatures 0 °C (Entry 2) and -18 °C (Entry 3) to allow the formation of THP-alkene

4.19 in good yields. But neither reaction gave an improvement in purity nor in yield of the product **4.19**. It was decided to explore other bases for the formation of alkene as the nature of base can play an important role in the Horner-Wadsworth-Emmons reaction. The different bases used were sodium hydride (Entry 4), *n*-butylithium (Entry 5), and *t*-butyllithium (Entry 6), but none gave the desired pure alkene **4.19** instead a mixture of unidentifiable oxidised species was recovered. Finally lithium di-iso-propylamide (LDA) was investigated. A methylene proton of fluorenylphosphonate ester **4.12** was abstracted with LDA in tetrahydrofuran at -78 °C and the anion formed allowed to react with THP-aldehyde **4.18b** (Entry 7). After purification, THP-alkene **4.19** was successfully obtained in a 27% yield. The yield of the reaction was further improved when a solution of **4.12** and **4.18b** in tetrahydrofuran was treated with LDA at 0 °C. After the addition, the reaction temperature was allowed to gradually rise to room temperature. The THP-alkene **4.19** was obtained in an excellent 87% yield. The penultimate step to the monomer was then the acid-catalysed deprotection of THP-alkene **4.19** to form the fluorenyl-*bis*-alcohol **4.13**. A solution of THP-alkene **4.19** and catalytic amount of *p*-toluenesulphonic acid in a methanol/dichloromethane mixture gave fluorenyl-*bis*-alcohol **4.13** in a 73% yield after purification. Fluorenyl-*bis*-alcohol **4.13** was stored at low temperature in the dark to prevent degradation. There was a significant improvement in the yield of the fluorenyl-*bis*-alcohol **4.13** obtained *via* the protection route (73%) over the yield obtained *via* the free-radical halogenation (3%, cf. Scheme **4-10**).

The final conversion was the formation of *bis*-halomethyl monomer **4.14** (X = Cl) or **4.20** (X = Br) from fluorenyl-*bis*-alcohol **4.13**, Scheme **4-15**. The different reagents

and reaction conditions used for the conversion of **4.13** to **4.14** and **4.20** are summarised in Table **4-4**.



4.14 **4.13** **4.20**

Scheme 4- 15. *Reactions and conditions*: (i). $SOCl_2$, Py, DCM, 0 °C;

(ii). PBr_3, DCM, 40 °C (cf. Table **4-4**)

The earlier failure in the synthesis of *bis*-chloromethyl monomer **4.14** from *bis*(hydroxymethyl) **4.13** using thionyl chloride (Scheme **4-10**, Entry 1) suggested that the reaction medium might be too acidic to affect the double bond of **4.13**. Therefore, the halogenation reaction was carried out in the presence of 2.5 equivalents of pyridine (Py) (Entry 2), but no pure monomer **4.14** was obtained upon purification.

Table 4-4 Reagents and reaction conditions utilised for the formation of *bis*-halides **4.14** (X = Cl) or **4.20** (X = Br) from fluorenyl-*bis*-alcohol **4.13**

Entry	Reagents	Solvent	Temperature	Time (h)	4.14/4.20 (%)
1	$SOCl_2$	DCM	0 °C	2	
2	$SOCl_2$, Py	DCM	0 °C	2	
3	*p*-TsCl, Py, DMAP	THF	0 °C to r.t.	19	
4	CCl_4, PPh_3	PhMe	r.t. to reflux	15	
5	HBr, AcOH	AcOH	r.t.	1.5	
6	HBr, AcOH	AcOH	60 °C	0.6	
7	PBr_3	ether	0 °C	1	11
8	PBr_3	ether	r.t.	2	34
9	PBr_3	DCM	r.t.	1.5	32
10	PBr_3	DCM	40 °C	1.5	37

Several other reaction methods were explored to synthesise the *bis*-chloro monomer **4.14** but all led to the formation of an impure monomer **4.14**. These include treatment of **4.13** with *p*-toluenesulphonyl chloride (*p*-TsCl) in pyridine and 4-*N*,*N*-dimethylaminopyridine (DMAP) (Entry 3) and **4.13** was also reacted with carbon tetrachloride and triphenylphosphine (Entry 4)[149]. Hence a number reaction conditions ranging from acidic to neutral and basic were tried for the chlorination reaction of fluorenyl-*bis*-alcohol **4.13**

but in all the cases neither **4.13** was recovered nor pure *bis*-chloride **4.14** was obtained. It was therefore decided to attempt to synthesise the *bis*-bromide **4.20** from fluorenyl-*bis*-alcohol **4.13** instead. Attempts to brominate the hydroxyl groups of fluorenyl-*bis*-alcohol **4.13** under strong acidic mixture of hydrobromic acid in glacial acetic acid at r.t. (Entry 5)[150], and 60 °C (Entry 6) were used but again no starting material or desired product was isolated. The only halogenation method that gave nearly acceptable yields was the reaction of **4.13** with phosphorous tribromide (Entries 7-10). The earlier assumption for the failure of formation of pure monomer under acidic reaction conditions was therefore erroneous as halogenation reaction proceeded satisfactorily with phosphorous tribromide. The initial reaction involved the treatment of **4.13** with phosphorous tribromide at 0 °C for 1 hour and this gave **4.20** in an 11% yield (Entry 7). A three-fold improvement in the yield of *bis*-bromide **4.20** was achieved when reaction was carried out in ether at room temperature and the reaction left for 2 hours (Entry 8). Changing the solvent from ether to dichloromethane (Entry 9) did not result in an improved yield of **4.20** and there was only slight improvement in the yield when reaction was carried out at 40 °C in dichloromethane (Entry 10). Under these latter conditions the *bis*-bromide **4.20** was obtained in 37% yield. It is important to note that prolonged reaction time and excess of phosphorous tribromide reagent led to the formation of several unidentified by-products. Also during purification of the *bis*-bromide **4.20**, it was found to decompose on silica gel to give a number of unidentified by-products. Compound **4.20** also decomposed when stored at room temperature in the dark indicated by the development of several spots on a t.l.c. plate and unidentified signals in the ^{1}H n.m.r. along with aldehyde signals. This indicated **4.20** was susceptible to oxidation both

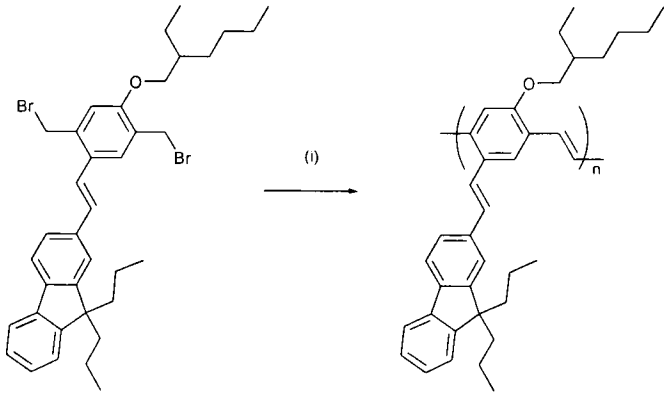
in solution and the solid state. However, providing the *bis*-bromide monomer **4.20** was stored at - 18 °C under an inert atmosphere in dark conditions it was relatively stable over longer periods of time.

4.2.1.7 Summary

In summary, alteration of the synthetic pathway from Heck to Horner-Emmons-Wadsworth route for the introduction of vinyl moiety led to a significant improvement in the yield of the crucial intermediate, dimethylvinylfluorene **4.7** for the synthesis of monomer. The general method for the synthesis of monomer from (*E*)-dimethylvinylfluorene **4.7** *via* radical method involving activation of methyl groups at the later stage of the synthesis was attempted but found not to be useful. However the activation of methyl groups *via* the protection route at earlier stage before the introduction of vinyl moiety was proved to be a better synthetic strategy for the formation of monomer. Notably the transformation of *bis*-alcohol fluorenylvinyl **4.13** to *bis*-halide **4.14** (X= Cl) and **4.20** (X= Br) was proved to be critical and strongly dependent on the nature of halogenating agents and purification strategy. The synthesis and reaction conditions for the formation of the *bis*-bromide fluorenylvinyl monomer **4.20** was optimised.

4.2.2 Polymerisation of monomer and properties of the Fluorenylvinyl-PPV

Base-induced polymerisation of *bis*-bromide monomer **4.20** was carried out using the standard conditions, Scheme **4-16**.



4.20 **4.21**

Scheme 4- 16. *Reactions and conditions*: (i) KOBu^t, THF, r.t. → reflux

A 0.1 M solution of *bis*-bromide monomer **4.20** in freshly distilled tetrahydrofuran was treated with 5.0 equivalents of potassium *t*-butoxide as a 0.2 M solution in tetrahydrofuran at room temperature under nitrogen. The reaction showed a colour change from colourless to yellow on addition of the solution of base. The progress of the reaction was monitored by g.p.c. analysis by taking aliquots from the reaction mixture at different time intervals. After 2 hours only oligomeric material was observed, so the reaction was allowed to proceed for a longer time. However no polymer was detected by g.p.c. analysis even after 24 hours. In another attempts, two test polymerisation reactions were performed, one at 0 °C and another heated at reflux after addition of the solution of base while keeping the other conditions identical. After 3 hours of stirring, g.p.c. analysis

showed un-polymerised monomer for the reaction performed at 0 °C, while a mixture of oligomers and monomer was detected from the reaction carried out under reflux.

Finally, when the polymerisation was performed at room temperature for 3 hours then heated at reflux for 24 hours under nitrogen, a small amount of polymer **4.21** ($\overline{M}_w$ of 1.4×10^5 g/mol; PD 1.7) along with oligomeric material ($\overline{M}_w$ of 3.2×10^3 g/mol; PD 1.1) was detected in the g.p.c. trace, Figure **4-3**.

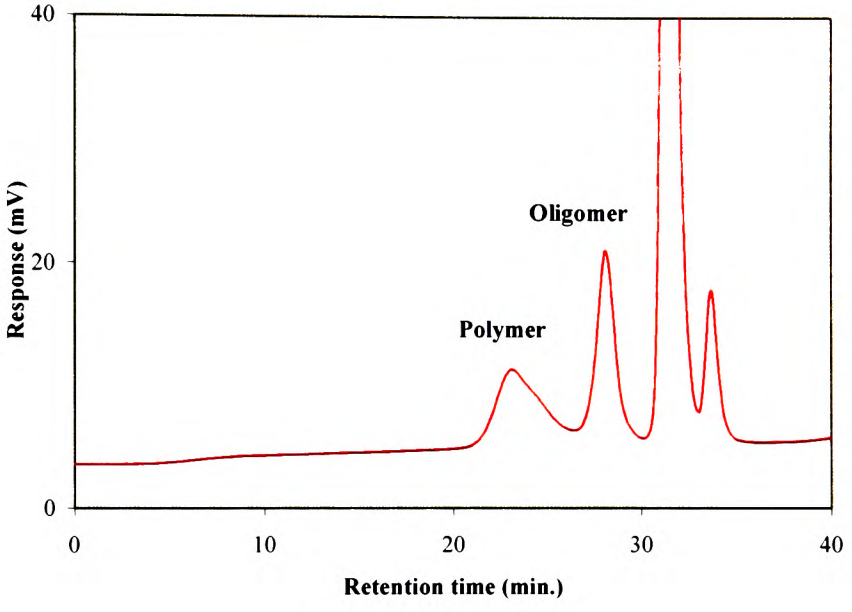


Figure 4 - 3: G.p.c. trace of the aliquot taken from polymerisation reaction heated at reflux for 24 hours

The purification of the resultant polymer from oligomeric material was attempted initially using the normal precipitation-dissolution technique. The reaction mixture was added into ice-cold methanol and the precipitate was isolated by centrifugation and decantation of the supernatant. The residue was then redissolved in tetrahydrofuran and

the process repeated three times, before the remaining solid was dried under vacuum. However the oligomeric material remained and but no pure polymer **4.21** was isolated. In another purification attempt, column chromatography over BIO-beads® using tetrahydrofuran as eluent was attempted. This also failed to remove the oligomeric material from the polymer **4.21**. Finally, purification of a small amount of polymer was achieved on a small amount of an impure polymer **4.21** with preparatory g.p.c. (PREP-gpc). The g.p.c. analysis of the polymer after purification showed S-EH-FVPPV **4.21** had a $\overline{M}_w$ of 3.1 × 10^4 g/mol, relative to polystyrene standards with a PD of 3.5 (Figure **4-4**). The relatively low molecular weight of the polymer suggests that even when the monomer **4.20** is stored carefully there is still some degradation leading to impurities that inhibit the polymerisation.

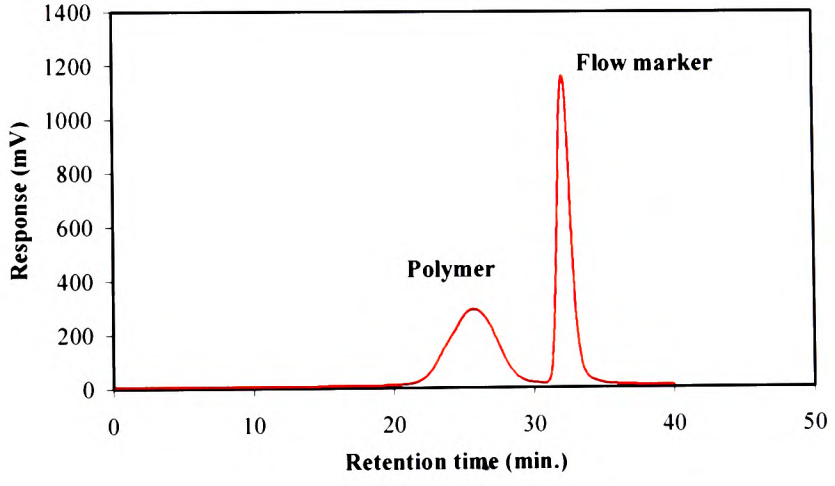


Figure 4 - 4: G.p.c. trace of S-EH-FVPPV **4.21** after PREP-gpc

^{1}H n.m.r. spectra of S-EH-FVPPV **4.21** before and after PREP-gpc are shown in Figure **4-5**. While the g.p.c. indicated that oligomeric material had been removed from

the polymer the ^{1}H n.m.r. indicated that it had introduced some other impurity and defects as seen with the unaccountable signals at 5.5 and 8.3 p.p.m. and aldehyde signals at around 10 p.p.m.

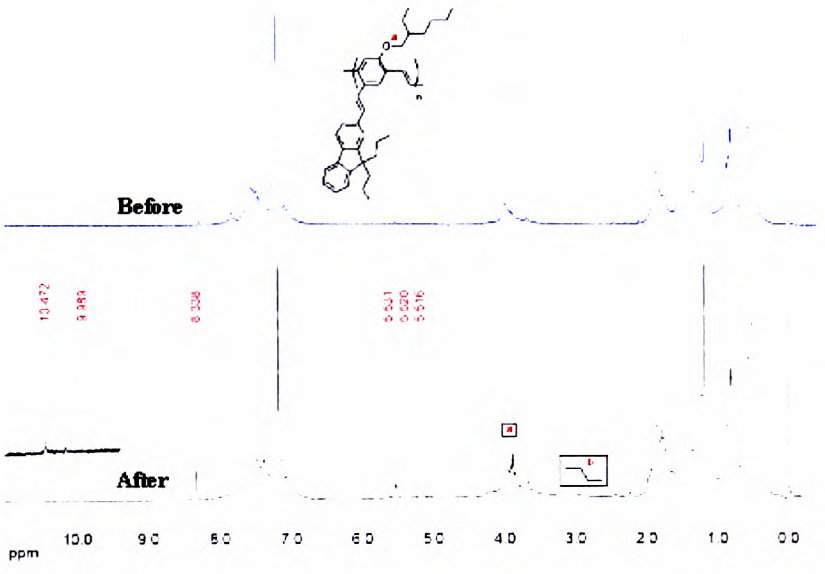


Figure 4 - 5: ^{1}H-n.m.r. spectra of S-EH-FVPPV **4.21** in $CDCl_3$ before and after PREP-gpc

Nevertheless, the ^{1}H n.m.r. showed that **4.21** was a conjugated polymer rather than a precursor polymer as there was no signal at 5.5 p.p.m. corresponding to the methine proton of a CHCl moiety. This was not unexpected as 5.0 equivalents of potassium *t*-butoxide was used during polymerisation reaction. Unlike the polymerisation of the biphenyl linked monomers in Chapter 2 and 3 a small signal at ~3.0 p.p.m. due to ethylene protons (benzylic) after PREP-gpc purification arose from a head-to-head arrangement of the monomer units. Interestingly the OCH_2 signal centered around 3.9 p.p.m. of **4.21** is essentially a single broad signal. This is also different from the polymers in Chapter 2 and 3 that showed two signals for these protons. In those latter

polymers the presence of second peak was initially believed to be the *cis*-isomer in the polymer backbone caused by the steric encumbrance of the fluorenyl side groups but no change was observed in the appearance of OCH_2 signals by iodine mediated *cis-trans* isomerisation. This ruled out the possibility of *cis* and *trans* linkages in the polymer. However, the broad OCH_2 signal for **4.21** (before purification) developed a moderate small signal at 3.7 p.p.m. suggests that the polymer backbone is affected during purification.

Thermal behaviour of S-EH-FVPPV **4.21** was not studied due to insufficient quantity of the purified polymer and its general instability.

The infrared spectra of S-EH-FVPPV **4.21** before and after PREP-gpc are shown in Figure **4-6**.

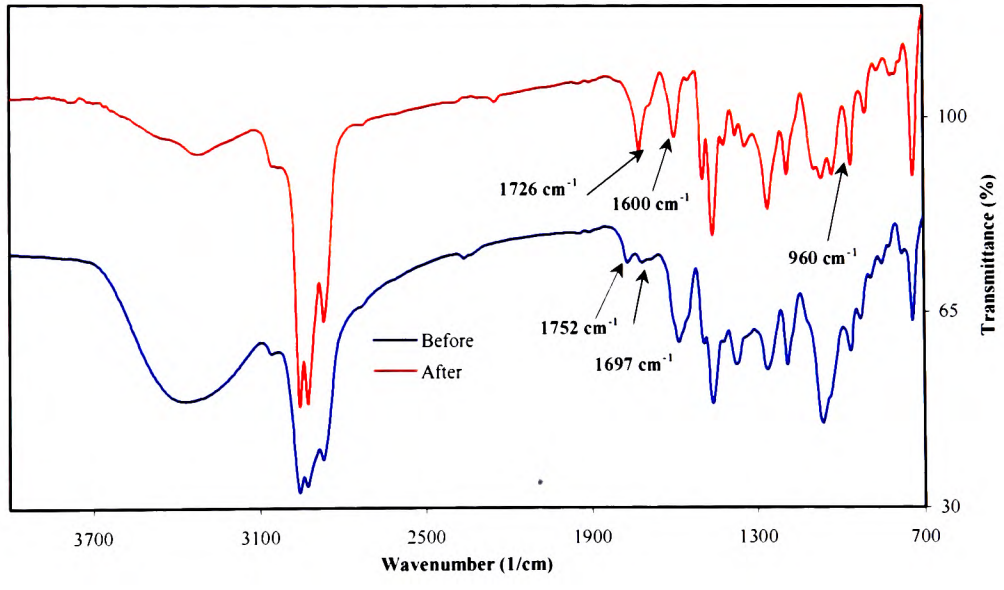
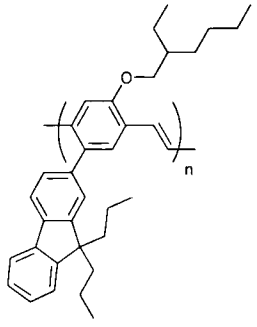


Figure 4 - 6: Infrared spectra of S-EH-FVPPV **4.21** before and after PREP-gpc

Thin films of the polymer were obtained by drop-casting a solution of polymer in tetrahydrofuran on to freshly prepared KBr disc. The absorption due to the C=C-H *trans*-vinylene C-H out-of-plane-bend at 960 cm^{-1} was observed. After PREP-gpc a well defined carbonyl stretch peak at 1726 cm^{-1} was observed indicating that partial oxidation of the polymer **4.21** had occurred during purification and was confirmed by the aldehyde signals in the ^1H n.m.r. spectrum (Figure **4-5**).

The U.V.-visible spectra of S-EH-FVPPV **4.21** (before and after PREP-gpc purification) and S-EH-FPPV **2.10** (Figure **4-8**) as films and their respective monomers in dichloromethane are shown in Figure **4-7**. The films were obtained by spin-coating the polymer from tetrahydrofuran solution onto quartz substrates.



2.10

Figure 4 - 7. Biphenyl-linked polymer: S-EH-FPPV **2.10**

The first point to note from the U.V.-visible spectra is that the absorption maximum of monomer **4.20** is red shifted when compared to **2.7**. This indicates that the introduction of the vinyl moiety between the polymer backbone and fluorenyl side-groups improves the delocalisation. S-EH-FVPPV **4.21** showed localised π–π^* transitions at ~210 nm and delocalised π–π^* transitions was observed > 415 nm.

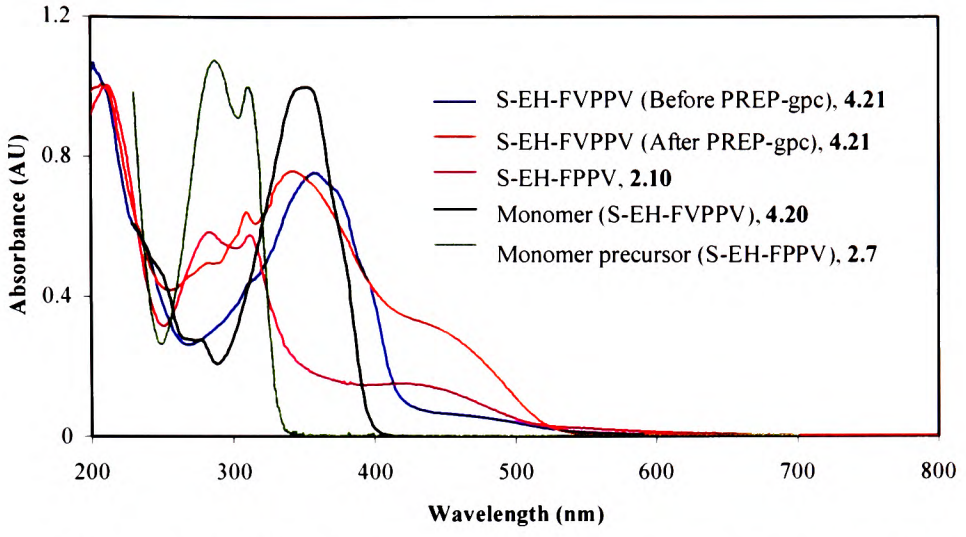


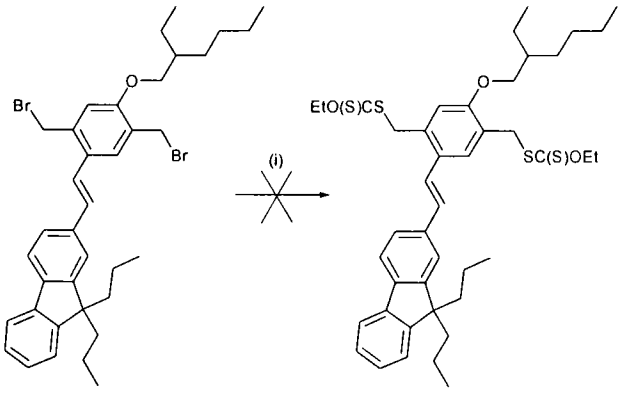
Figure 4 - 8: U.V.-visible spectra of fluorenylvinyl monomer **4.20**, fluorenyl monomer precursor **2.7**, S-EH-FVPPV **4.21** and S-EH-FPPV **2.10**

In addition **4.21** exhibits another transition centred at ~345 nm which is due to the "fluorenylvinylphenyl" chromophore of the monomer as it is at similar wavelength to that observed for **4.20**. After purification of **4.21** the delocalised π–π^* transitions became stronger and the ratio of delocalised π–π^* transitions to localised π–π^* transitions was improved 5 times (0.07: before and 0.37: after PREP-gpc purification). This indicated more delocalisation of π–network after purification although it is not clear why this should be the case. An interesting comparison is between the vinyl-linked polymer S-EH-FVPPV **4.21** and biphenyl-linked polymer S-EH-FPPV **2.10**. S-EH-FPPV **2.10** without the vinyl linkage between fluorenyl side chain and PPV backbone exhibited a weak delocalised π–π^* transition and a lower ratio of localised to delocalised π–π^* transition (0.15), which was attributed to the steric hindrance at the "biphenyl" link of the fluorenyl unit twisting the polymer backbone and on average shortening the effective

conjugation length of the polymer. However the introduction of "vinyl" link appears to have improved the coplanarity between the polymer backbone and side chains as indicated by the improved ratio of delocalised to localised π–π^* transitions in the purified **4.21**. The delocalised π–π^* transitions tails off at similar maximum wavelength in both the polymers **2.10** and **4.21** suggesting that the π–network delocalisation along the PPV backbone was not extended when the vinyl linked side-chain was present.

4.2.3 Attempted synthesis of the Fluorenylvinyl *bis*-xanthate monomer

There are several synthetic advantages of *bis*-xanthates over *bis*-halide monomers for the formation of conjugated PPVs, which include: *(i)* the xanthate groups impart solubility, so the intermediate oligomers and polymers had to be more soluble in tetrahydrofuran, toluene and chlorinated solvents; *(ii)* xanthate leaving groups are less reactive and less susceptible to substitution and elimination during polymerisation and purification; *(iii)* xanthate precursor polymers require high conversion temperatures to form the conjugated polymer and hence it is possible to carry out polymerisation reaction at high temperature; (iv) the *bis*-xanthate monomers tend to be more stable monomer when compared to the halogenated counterparts, which can facilitate storage and handling of the monomer. It was therefore decided to see whether **4.20** could be converted to *bis*-xanthate monomer **4.22**, Scheme **4-17**.



4.20 **4.22**

Scheme 4- 17. *Reactions and conditions*: (i) KS(CS)OEt, TBAB, DCM, 0 °C or r.t. or Δ

Thus, reaction of the *bis*-bromide **4.20** with potassium *O*-ethylxanthate and tetra-*n*-butylammonium bromide in dichloromethane was carried out at 0 °C then slowly warmed to room temperature. However, after 5 hours, no material with an R_f consistent with the structure of the product was observed by t.l.c. analysis, and only starting material **4.20** was recovered in a ~45% yield as a slightly impure compound upon separation of the crude reaction mixture. The reaction to form the xanthate could, however, be thermally driven and heating the reaction mixture at reflux for 12 hours afforded complete consumption of the *bis*-bromide **4.20** and *bis*-xanthate **4.22**, which could not be purified was obtained along with several unidentifiable compounds.

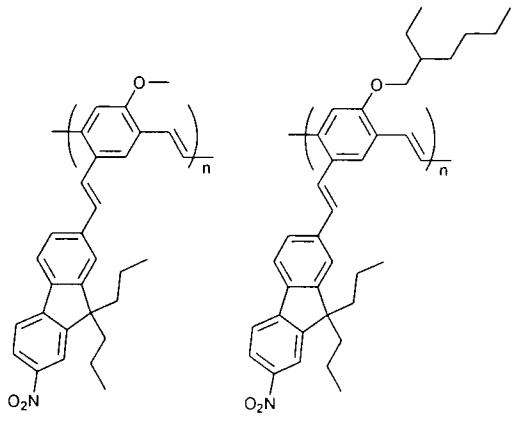
4.2.4 Summary

The fluorenylvinyl-PPV, S-EH-FVPPV **4.21**, was synthesised from the *bis*-bromide monomer **4.20**. Although the polymer **4.21** was found to be susceptible to

oxidation, but a strong effect on U.V.-visible spectrum of **4.21** was observed due to the presence of vinyl linkage between fluorenyl side chain and PPV backbone. This effect was explained in terms of extended conjugation between the polymer backbone and the co-planar fluorenyl side groups. The synthesis of *bis*-bromide **4.20**, fluorenylvinyl monomer, was successful *via* the protection route over the free-radical route. The substitution reaction of bromo groups of the *bis*-bromide **4.20** with xanthate groups was not successful. This might be due to the instability of **4.20** under the reaction conditions as indicated by its consumption in the attempted formation of the xanthate.

4.3 Poly{2-[(*E*)-2-(7-nitro-9,9-dipropylfluorenyl)vinyl]-5-alkoxy-1,4-phenylenevinylene}

As in the case of the polymers described in Chapter 2 and 3, the aim of the work was to compare the properties of the polymers with and without the electron-withdrawing (EW) nitro group. Therefore, two new polymers were designed with the same basic architecture as the fluorenylvinyl polymer **4.21** with a nitro group at the 7-position in the fluorene ring, Figure **4-8**. The two polymers, namely poly{2-[(*E*)-2-(7-nitro-9,9-dipropylfluorenyl)vinyl]-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene} S-EH-NO_2FVPPV **4.44** and poly{2-[(*E*)-2-(7-nitro-9,9-dipropylfluorenyl)vinyl]-5-methoxy-1,4-phenylenevinylene} **4.43** (I-M-NO_2FVPPV), differ only in the length of the alkyl chain of the electron donating group. The presence of a longer alkoxy chain in **4.44** allowed the formation of a soluble conjugated polymer while the shorter methoxy group led to an insoluble conjugated polymer.



4.43 **4.44**

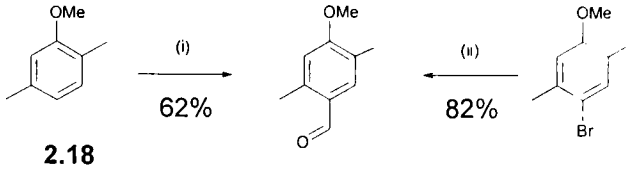
Figure 4- 8: Structure of nitrofluorenyl-PPVs: I-M-NO_2FVPPV **4.43** and S-EH-NO_2FVPPV **4.44**

4.3.1 Synthesis of the Alkoxy-nitrofluorenylvinyl monomers *via* the Heck reaction

The synthesis of the nitrofluorenylvinyl monomers was performed along similar lines as for fluorenylvinyl monomer **4.14** (X = Cl) and **4.20** (X = Br). Monomer **4.41**, with the methoxy group was the first to be studied and this was followed by the synthesis of ethylhexyloxy-substituted nitrofluorenylvinyl monomer **4.37** (X = Cl) and **4.39** (X = Br).

As this work was being carried out in parallel to that described earlier in the Chapter the first strategy to be studied for the introduction of the vinyl unit in the monomer was the Heck reaction. Hence, the formation of important intermediate for methoxy-nitrofluorenylvinyl monomer is methoxy-dimethylphenylvinylnitrofluorene **4.25b** which required 4-methoxy-2,5-dimethylstyrene **4.24** (methoxystyrene) and

nitrobromofluorene **2.16** (Chapter 2). For the synthesis of **4.25b** the first step involved the formylation of 2,5-dimethylanisole **2.18** to form formylanisole **4.23**, Scheme **4-18**.



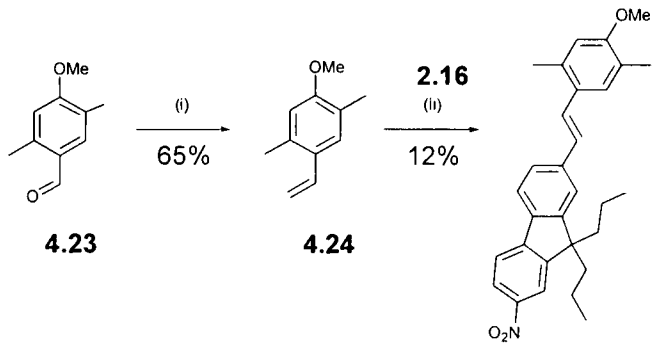
2.18 **4.23** **2.3b**

Scheme 4- 18. *Reactions and conditions*: (i) $POCl_3$, DMF;

(ii). a. THF, *t*-BuLi, -78 °C; b. DMF, -78 °C → r.t

This was carried out by treatment of 2,5-dimethylanisole **2.18** with phosphorous oxychloride in *N,N*-dimethylformamide under Vilsmeyer-Haack conditions. After the addition of reactants at 0 °C the reaction temperature was raised steadily to 124 °C (initiation temperature) and thereafter stirred at 100 °C for 3 hours to afford the 4-methoxy-2,5-dimethylbenzaldehyde **4.23** (formylanisole) in a 62% yield. However, problems were faced during scale up of the reaction as once the reaction was initiated it required careful control to avoid a thermal runaway. Therefore, **4.23** was also synthesised *via* an alternate two-step pathway. The previously synthesised 1-bromo-4-methoxy-*p*-xylene **2.3b** was treated with *t*-butyllithium and reacted with *N,N*-dimethylformamide followed by hydrolysis to give **4.23** in an 82% yield.

The next steps involved the conversion of the aldehyde to a vinyl group and its coupling under Heck conditions to **2.16**, Scheme **4-19**. The Wittig reaction of **4.23** with methyltriphenylphosphonium iodide in tetrahydrofuran using potassium *t*-butoxide gave 1-methoxy-2,5-dimethyl-4-vinylbenzene **4.24** (methoxy-styrene) in a 65% yield.



4.23 **4.24** **4.25b**

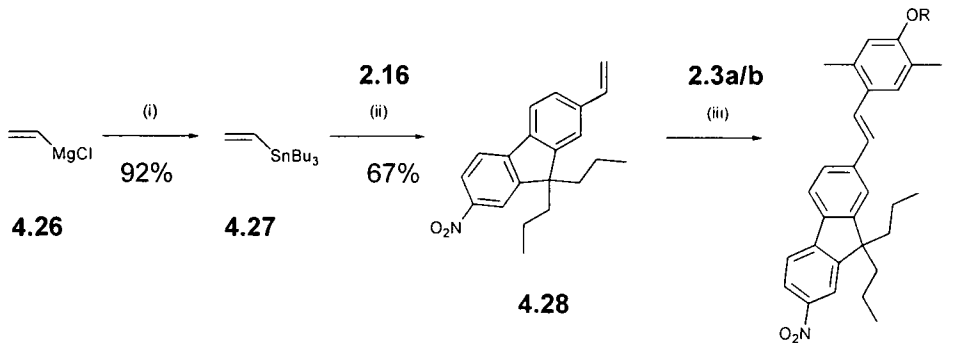
Scheme 4- 19. *Reactions and conditions:* (i). a. $PH_3P^+CH_3I^-$, $KOBu^t$, THF; (ii) **2.16**, Herrmann's catalyst **4.8**, 2,6-di-*t*-butylcresol, Na_2CO_3, DMA, Δ.

Heck reaction of methoxy-styrene **4.24** with nitrobromofluorene **2.16** was carried out using Herrmann's catalyst **4.8** and 2,6-di-*t*-butyl-*p*-cresol as a free radical inhibitor in *N,N*-dimethylacetamide heated at 130 °C for 4 days, no product **4.25b** was indicated by ^{1}H n.m.r. analysis. When the Heck reaction was performed at reflux for 4 days *(E)*-methoxy-dimethylphenylvinylnitrofluorene **4.25b** was obtained in a 12% yield. A poor yield of **4.25b** was obtained because of its low solubility and due to the presence of a number of impurities, which were generated during the reaction, and hard to remove during purification. Therefore, an alternative method for the synthesis of ethylhexyloxy analogue **4.25a** was attempted.

4.3.1.1 Alternative Heck route

An alternative route for the synthesis of methoxy-dimethylphenylvinylnitrofluorene **4.25b** was carried out where the reversal in

functionality of vinyl and bromo group was used, that is, the vinyl group was introduced on the nitrobromofluorene **2.16** instead of 2-alkoxy-*p*-xylene units, Scheme **4-20**.



4.26 **4.27** **4.28**

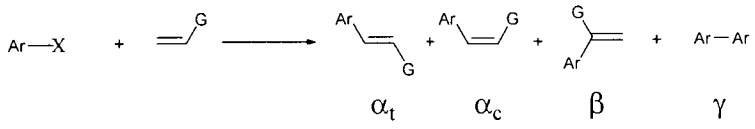
4.28a, R = 2-ethylhexyl, ~28 %
4.28b, R = methyl, 52 %

Scheme 4- 20. *Reactions and conditions:* (i). $SnBu_3Cl$, Δ; (ii) **2.16**, $Pd(PPh_3)_4$, PhMe, Δ; (iii) **2.3a** or **2.3b**, Herrmann's catalyst **4.8**, 2,6-di-*t*-butylcresol, Na_2CO_3, DMA, Δ.

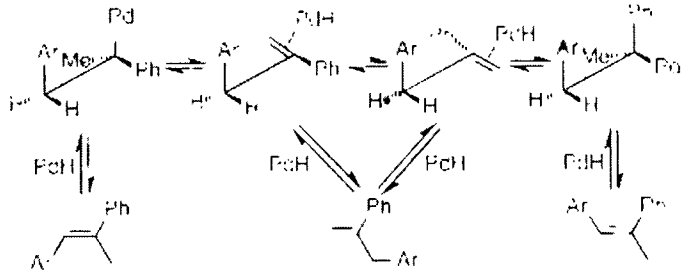
Trans-metallation of vinylmagnesium chloride **4.26** with tri-*n*-butyltin chloride formed the tri-*n*-butylvinyl stannane **4.27** in a 92% yield. Stille coupling of alkyltin reagent **4.27** with nitrobromofluorene **2.16** was carried out using *tetrakis*(triphenylphosphine)palladium(0) in toluene. The corresponding vinylnitrofluorene **4.28** was obtained in a 67% yield. Palladium coupling of **4.28** with 1-bromo-4-(2'-ethylhexyloxy)-*p*-xylene **2.3a** or 1-bromo-4-methoxy-*p*-xylene **2.3b** was achieved with Herrmann's catalyst **4.8** in *N,N*-dimethylacetamide in presence of sodium carbonate and 2,6-di-*t*-butylcresol as a radical scavenger, heated at reflux for 4 days. Methoxy-dimethylphenylvinylnitrofluorene **4.25b** was obtained in an improved yield of 52% but ethylhexyloxy-dimethylphenylvinylnitrofluorene **4.25a** was slightly impure and obtained in only a ~28% yield. This suggests that the presence of a vinyl group on the fluorene component, vinylnitrofluorene **4.28**, provided a better reagent for the synthesis

of **4.25b** as compared to the methoxy-styrene **4.24** route (Scheme **4-18**). The Heck reaction for the formation of **4.25a** was revisited with a different choice of catalyst and base to improve the purity. The reaction was catalysed by palladium (II) acetate and potassium phosphate in *N,N*-dimethylacetamide at 144 °C. No improvement in the yield and purity of **4.25a** was observed. However, the ethylhexyloxy-dimethylphenylvinylnitrofluorene **4.25a** was obtained with an inseparable impurity (~2-5%). The impurity was of similar polarity and high boiling point as **4.25a** and similar type of impurity was observed during the synthesis of methoxy-dimethylphenylvinylnitrofluorene **4.25b** using the previous route (Scheme **4-18**) which, could also not be isolated by either chromatographic or distillation techniques. Several research groups[151-154] reported the formation of 1,1-disubstituted alkenes (β), 1,2-disubstituted *cis*-alkenes (α_c), and C–C coupled (γ) by-products along with the desired *trans*-alkene (α_t) in Heck reaction, Scheme **4-21**.

a)

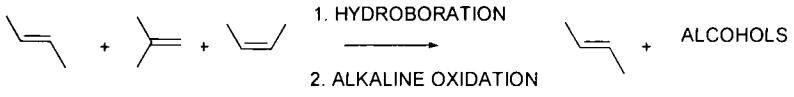


b)



Scheme 4- 21: Heck reaction a). products isolated; b). isomerisation[152] of intermediates: reaction of ArBr with prop-1-ene-2-ylbenzene

The formation of 1,1-disubstituted alkene (β) as a side product along with the desired alkene is shown in the proposed mechanism of the Heck reaction (Scheme **4-6**, and **4-21**) and dictated by the migration of the aryl group. The formation of α and β alkenes proceeded via isomerisation process and different conformations of the intermediate is shown in Scheme **4-21**. Although the formation of γ product is cited in the literature but its formation is not mechanistically registered. It has been observed the regioselectivity of the Heck product depends upon several factors[154] and in general, the formation of 1,2-disubstituted alkenes (α_t and α_c) is favoured with olefins bearing electron-withdrawing substituents, and electron-donating groups favored 1,1-disubstituted alkene (β). This accounted for the improvement in the yield of methoxy-dimethylphenylvinylnitrofluorene **4.25b** when alkene moiety was attached to the electron deficient reacting centre in an alternative methodology (Scheme **4-20**). Though the impurity in compound **4.25a** was not isolated the ^{1}H n.m.r. of the Heck product suggested the presence of the *cis*-isomer and some 1,1-disubstituted alkene. The presence of such isomers along with the desired *trans*-isomer would affect the degree of electron delocalisation of the dipole chromophore in the resultant polymer and thereby affecting the opto-electronic properties of the materials. A first step towards the purification of **4.25a** was to isomerise the *cis*-double bonds with catalytic iodine in toluene heated at reflux. However no significant change in the ^{1}H n.m.r. of **4.25a** was observed after this thermal treatment suggesting that the *cis*-isomer was not perhaps an impurity. Another chemical strategy used in an attempt to purify **4.25a** and was based on the difference in reactivity of alkenes towards hydroboration reagents, Scheme **4-22**.



Scheme 4- 22: Hydroboration-oxidation of alkenes

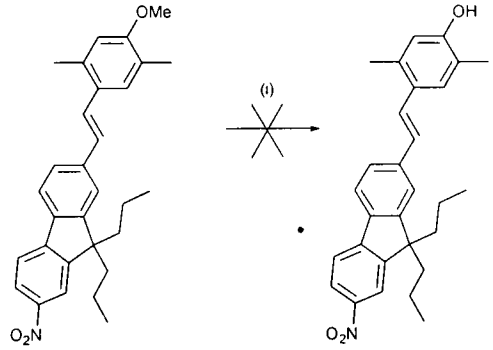
Since 9-borabicyclo[3.3.1]nonane (9-BBN) is known for its selectivity to attack the less-hindered side and more reactive double bond of an alkene it was thought that if the impurity was the 1,1-disubstituted alkenes in **4.25a** then it might be possible to hydroborate and oxidise the terminal alkene, leaving the *trans*-isomer unaffected. In a test reaction the **4.25a** obtained after *cis-trans* isomerisation was reacted with 9-BBN in tetrahydrofuran and the reaction monitored by t.l.c. The hydroboration reaction proceeded to a very small extent when carried out at room temperature as indicated by the light yellow colouration of reaction mixture and t.l.c. However, when the reaction heated at reflux for 3 hours a dark yellow coloured solution was obtained. Oxidation of the hydroborated compound **4.25a** with hydrogen peroxide in alkaline medium led to some improvement in the purity of **4.25a** as confirmed by ^{1}H n.m.r. analysis. It was considered that the sluggish reaction was due to the bulky nature of 1,1-disubstituted alkene and therefore, diborane, a less hindered reagent was used instead. In this case, a yellow coloured solution was obtained in 15 minutes after the peroxide oxidation under alkaline medium gave *(E)*-ethylhexyloxy-dimethylphenylvinylnitrofluorene **4.25a** was isolated in an overall 5% yield for three steps with no alcohol being recovered after alkaline hydrolysis. The low overall yield may be attributed to the high reactivity of diborane, which reacted with the alkenes in an unselective fashion. The use of hydroboration-oxidation methodology for purification of **4.25a** was stopped at this point and instead a more selective route for the formation of the *trans*-isomer was sought.

4.3.1.2 Alternative route for the synthesis of ethylhexyloxy-nitrofluorenylvinyl monomer

The complications in the synthesis of ethylhexyloxy-dimethylphenylvinylnitrofluorene **4.25a** could be solved either by *(i)* removal of the methyl group of methoxy-dimethylphenylvinylnitrofluorene **4.25b** and re-alkylation, or *(ii)* nitration of (*E*)-dimethylvinylfluorene **4.7** or *(iii)* forming nitro-substituted phosphonate ester **4.34** and coupling it with THP-aldehyde **4.18b**, followed by deprotection and halogenation. The first two routes use existing materials and were studied first.

4.3.1.2.1 Attempted de-alkylation and re-alkylation route

The de-alkylation of methoxy-dimethylphenylvinylnitrofluorene **4.25b** was attempted with several different reagents Scheme **4-23**, with the reaction conditions summarised in Table **4-4**.



4.25b **4.29**

Scheme 4- 23. *Reactions and conditions*: (i). cf. Table **4-4**

Methoxy-dimethylphenylvinylnitrofluorene **4.25b** has a double bond therefore a less stringent condition was used in an initial attempt to cleave the aryl methyl ether bond to form **4.29**. Demethylation of 4-isopropenylanisole[155] and *p*-nitroanisole[156] has been reported utilising sodium ethanethiolate (NaSEt) in *N,N*-dimethylformamide indicating success of the reaction in presence of both double bond and nitro group. A mixture of **4.25b** and 1.5 equivalents of NaSEt in *N,N*-dimethylformamide was heated at 85 °C (Entry 1).

Table 4-4: De-alkylating reagents used for methoxy-dimethylphenylvinylnitrofluorene **4.25b**

Entry	Reagent	Solvent	Temp. (°C)	Inference
1	$NaSC_2H_5$	DMF	85 → 100	**4.25b** recovered (95%)
2	$NaSC_2H_5$	Ethylene glycol	190	**4.25b** recovered (89%)
3	BBr_3	DCM	0	Unknown compounds
4	BBr_3	DCM	0 °C→ r.t.	Unknown compounds
5	BBr_3	DCM	40	Unknown compounds
6	HBr (48%), TBAB	Toluene	111	**4.25b** recovered (97%)

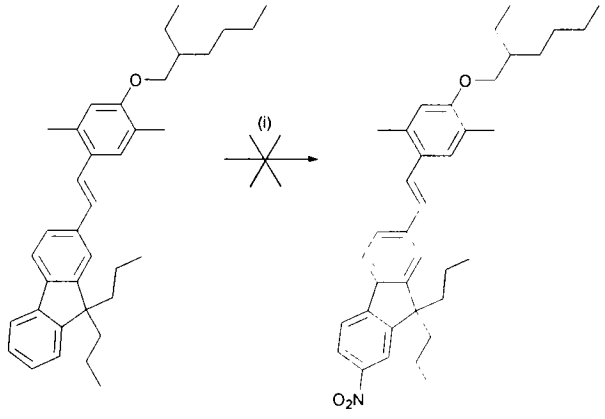
After 3 hours no product was detected by t.l.c. analysis. The reaction mixture was heated at 100 °C for 48 hours to affect demethylation. No product **4.29** was obtained but starting material was recovered in a 95% yield upon purification. In another attempt, reaction was performed with NaSEt in ethylene glycol at a higher reaction temperature of 190 °C

(Entry 2). However, starting material was recovered in an 89% yield. Boron tribromide (BBr_3) mediated dealkylation of **4.25b** was attempted at three different temperatures 0 °C (Entry 3), after addition of BBr_3 at 0 °C reaction was allowed to warm to room temperature (Entry 4), and 40 °C (Entry 5). In all the cases (entries 3-5) an unidentifiable mixture of compounds was obtained. In a final attempt, **4.25b** was treated with hydrogen bromide and phase transfer agent, tetra-*n*-butylammonium bromide in toluene heated at reflux (Entry 6). This also resulted in no reaction and **4.25b** was recovered in a 97% yield.

Failure to de-alkylate methoxy-dimethylphenylvinylnitrofluorene **4.25b** under both strong and mild conditions prevented the synthesis of ethylhexyloxy-dimethylphenylvinylnitrofluorene **4.25a** and hence the other alternative synthetic pathways were investigated.

4.3.1.2.2 Nitration route

Nitration of (*E*)-dimethylvinylfluorene **4.7** was attempted by treating a suspension of **4.7** in glacial acetic acid with conc. nitric acid heated at reflux (Scheme **4-24**). Although the phenyl ring was activated with EDG it was hoped that since it was sterically encumbered nitration would occur on the fluorenyl moiety. However, several unidentified oxidised species were recovered instead of the desired compound **4.25a**. The failure of nitration reaction of the **4.7** is likely to be due to either the presence of vinyl linkage or activated benzene ring.



4.7 **4.25a**

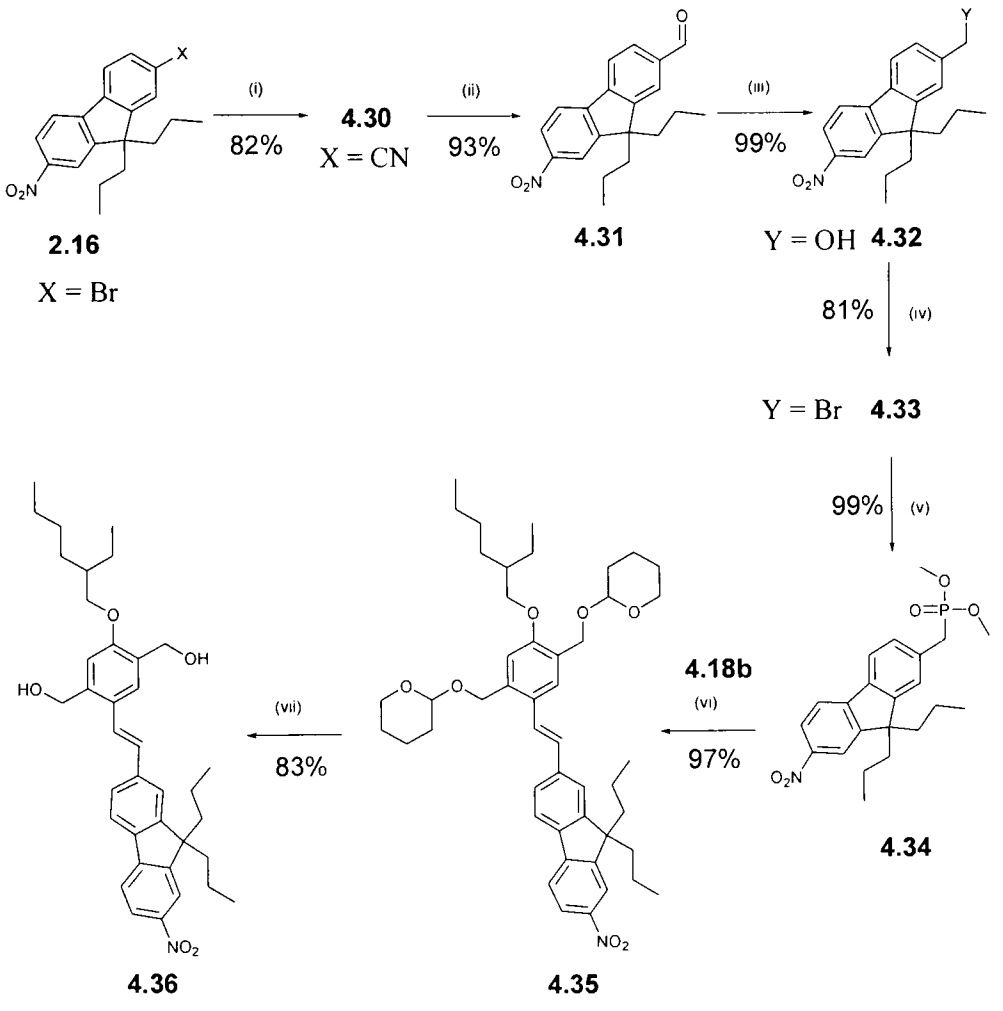
Scheme 4- 24. *Reactions and conditions*: (i). HNO_3, AcOH, Δ

Having exhausted the shorter synthetic routes for the synthesis of ethylhexyloxy-dimethylphenylvinylnitrofluorene **4.25a** an intermediate for ethylhexyloxy-nitrofluorenylvinyl monomer **4.37** (X = Cl) or **4.39** (X = Br), the longer route involving the use of nitrofluorenylphosphonate **4.34** was investigated.

4.3.1.3 Synthesis of the Ethylhexyloxy-nitrofluorenylvinyl monomer via the protection method

Synthesis of ethylhexyloxy-nitrofluorenylvinyl monomer **4.39** was pursued using the THP-aldehyde **4.18b** developed for the formation of fluorenylvinyl monomer **4.20**, Scheme **4-25**. Rosenmund-von Braun reaction of nitrobromofluorene **2.16** with copper cyanide in *N,N*-dimethylformamide heated at reflux gave nitrofluorenylcarbonitrile **4.30** in a 93% yield. Reduction of nitrofluorenylcarbonitrile **4.30** with DIBAL-H in of

toluene/dichloromethane mixture at -78 °C followed by hydrolysis gave nitrofluorenylaldehyde **4.31** in an 82% yield.

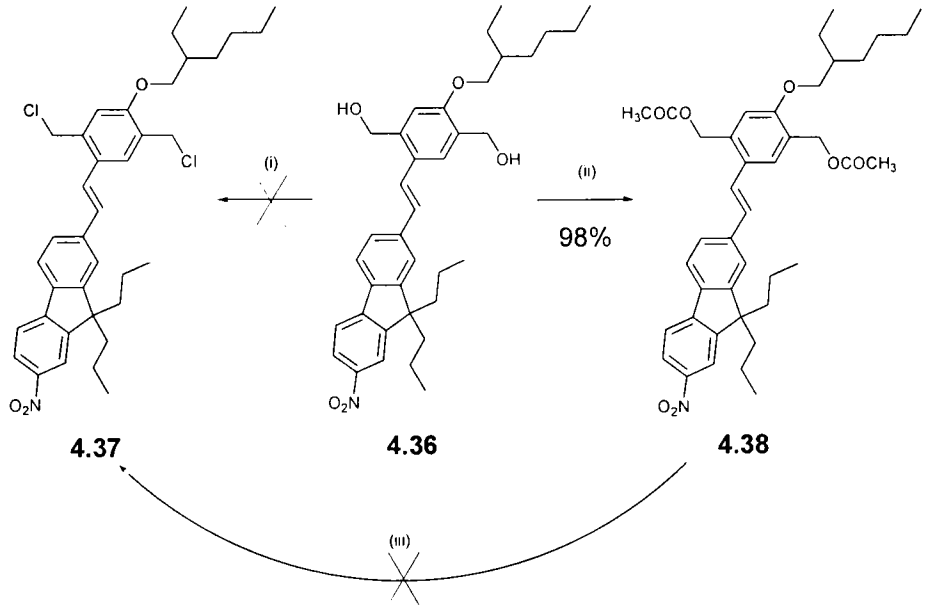


Scheme 4- 25. *Reactions and conditions*: (i) a. CuCN, DMF, Δ; b. $FeCl_3.6H_2O$, H_3O^+; (ii). a. DIBAL-H, DCM, PhMe, -78 °C; b. r.t.; c. H_3O^+; (iii). $NaBH_4$, EtOH, *i*-PrOH; (iv) PBr_3, 100 °C; (v). $P(OMe)_3$, 80 °C; (vi). **4.18b**, LDA, THF; (vii). *p*-TsOH, DCM, MeOH

It was observed that both the rate of addition of DIBAL-H to the solution of nitrofluorenylcarbonitrile **4.30** and the temperature had to be controlled precisely in order to prevent unwanted side reactions. Nitro group reduction of **4.30** was observed when reaction temperature exceeded -78 °C during the addition of DIBAL-H. The nitrofluorenylaldehyde **4.31** was further reduced to alcohol **4.32** with sodium borohydride in an *i*-propanol/ethanol mixture at room temperature. The reaction was accomplished in 2 hours and nitrofluorenylalcohol **4.32** was obtained in a 99% yield. Bromination of nitrofluorenylalcohol **4.32** was carried out with phosphorous tribromide at 100°C to afford nitrofluorenylbromide **4.33** in an 81% yield. The nitrofluorenylphosphonate ester **4.34** was obtained in a 96% yield on treatment of **4.33** with trimethyl phosphite at 80 °C. The coupling reaction of nitrofluorenylphosphonate ester **4.34** with THP-aldehyde **4.18b** proceeded successfully with LDA and the (*E*)-nitroTHP-alkene **4.35** was obtained in a 97% yield. The formation of nitroTHP-alkene **4.35** was unsuccessful when potassium *t*-butoxide was used as the base. (*E*)-nitroTHP-alkene **4.35** was deprotected with a catalytic quantity of *p*-toluenesulphonic acid monohydrate in a dichloromethane/methanol mixture at room temperature and the resulting nitrofluorenyl-*bis*-alcohol **4.36** was obtained as a yellow solid in an 83% yield.

It was anticipated the presence of inductively and mesomerically electron withdrawing nitro group in nitrofluorenyl-*bis*-alcohol **4.36** would impart some chemical stability to the double bond as compared to the fluorenyl-*bis*-alcohol **4.13**, which does not have the nitro group. Halogenation of the nitrofluorenyl-*bis*-alcohol **4.36** (Scheme **4-26**) was attempted with a variety of chlorinating and brominating reagents under acidic, neutral, or basic conditions in a similar manner to the study on the halogenation of the

fluorenyl-*bis*-alcohol **4.13**. The synthesis of nitrofluorenyl *bis*(chloromethyl) monomer **4.37** was attempted using all the reagents mentioned in Table **4-4**. The inability to convert the nitrofluorenyl-*bis*-alcohol **4.36** to the corresponding *bis*-chloride **4.37** suggested that both **4.36** and fluorenyl-*bis*-alcohol **4.13** have similar reactivity. An alternative route for the synthesis of nitrofluorenyl-*bis*-chloride **4.37** monomer from nitrofluorenyl-*bis*-acetate **4.38** was therefore attempted, which involved the preparation of the nitrofluorenyl-*bis*-acetate **4.38**.

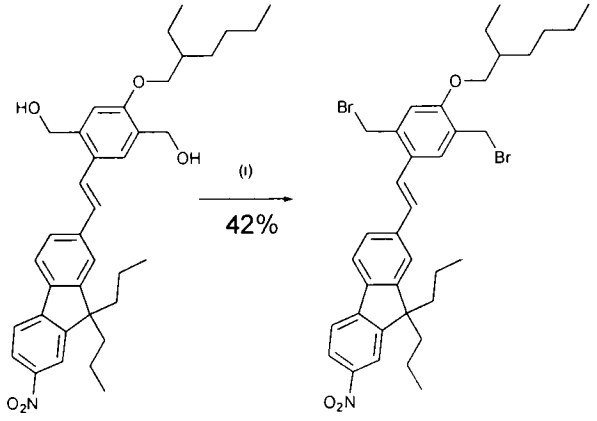


Scheme 4- 26. *Reactions and conditions*: (i). $SOCl_2$, DCM, dark, (cf. Table **4-4**); (ii) DMAP, TEA, Ac_2O; (iii). conc. HCl, 1,4-dioxane, Δ

The acetate moieties of the methoxy analogue to **4.38** were stable and had been successfully transformed to the *bis*-chloride **4.41** monomer (See Scheme **4-28**). Treatment of nitrofluorenyl-*bis*-hydroxy **4.36** with DMAP, triethylamine, and acetic

anhydride gave nitrofluorenyl-*bis*-acetate **4.38** in a 98% yield. The transformation of acetate groups to chloro groups was attempted with concentrated hydrochloric acid and 1,4-dioxane heated at reflux but only impure nitrofluorenyl-*bis*-chloride **4.37** was recovered from the reaction mixture in a ~35% yield.

The final halogenation reaction tried was bromination of nitrofluorenyl-*bis*-alcohol **4.36** with phosphorous tribromide in diethyl ether at 0 °C at room temperature, Scheme **4-27**.



4.36 **4.39**

Scheme 4- 27. *Reactions and conditions*: (i). a. PBr_3, DCM, 0 °C, dark; b. 0 °C → r.t.

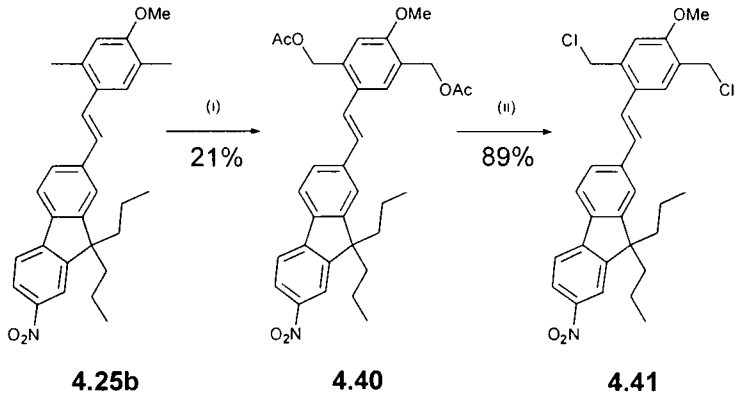
After an hour, nitrofluorenyl-*bis*-bromide **4.39** was obtained as a bright yellow solid in a 42% yield after purification ready for polymerisation.

4.3.1.4 Methoxy-nitrofluorenylvinyl monomer synthesis via the radical method

Although work on the 2-ethylhexyloxy derivative showed that the use of the protected aldehyde **4.18b** could be used to give the desired monomer with the advanced

intermediate, that is, (*E*)-nitroTHP-alkene **4.35**, since for the synthesis of methoxy monomer **4.41**, methoxy-dimethylvinylnitrofluorene **4.25b** is in hand, so it was decided to activate the benzylic groups using the standard radical procedure.

The synthesis of methoxy-nitrofluorenylvinyl monomer **4.41** is shown in Scheme **4-28**.



4.25b **4.40** **4.41**

Scheme 4- 28. *Reactions and conditions:* (i) a. NBS, AIBN, CCl_4, Δ; b. NaOAc, AcOH, Δ; (ii). HCl, Dioxane, Δ

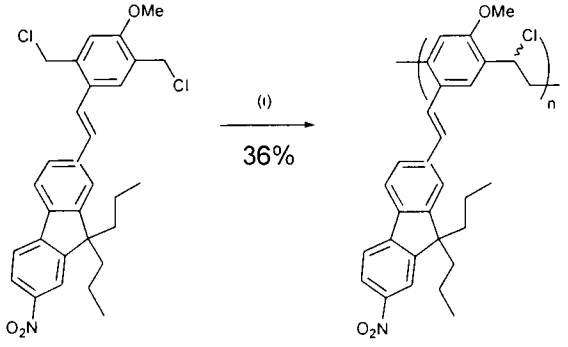
Wohl-Ziegler bromination of methoxy-dimethylvinylnitrofluorene **4.25b** under free-radical conditions yielded an inseparable mixture of brominated compounds. Acetylation of the mixture of brominated compounds with sodium acetate in glacial acetic acid heated at reflux resulted in the usual mixture of *mono*- and *bis*-acetates, and *mono*- and *bis*-aldehydes. The desired nitro*bis*-acetate **4.40** was isolated in a 21% yield over the two steps. Chlorination of nitro*bis*-acetate **4.40** was achieved by treatment with concentrated hydrochloric acid in 1,4-dioxane heated at reflux to yield the monomer **4.41** in an 89% yield.

With both the alkoxy-nitrofluorenyl monomers **4.39** and **4.41** prepared it was now possible to study their polymerisation.

4.3.2 Polymerisation of the Alkoxy-nitrofluorenylvinyl monomers

4.3.2.1 Synthesis and properties of the Methoxy-nitrofluorenylvinyl-PPV precursor polymer and the conjugated polymer

The synthesis of precursor polymer **4.42** (Σ-M-NO_2FVPPV) from methoxy-nitrofluorenylvinyl monomer **4.41** is shown in Scheme **4-29**.



4.41 **4.42**

Scheme 4- 29. *Reactions and conditions:* (i) $KOBu^t$, THF

The polymerisation of monomer **4.41** was carried out by adding 0.9 equivalents of potassium *t*-butoxide as a 0.2 M solution in tetrahydrofuran to a 0.2 M monomer solution in tetrahydrofuran at room temperature under argon. Purification of the crude polymer **4.42** from unreacted monomer and oligomers was carried out first by the precipitation into ice-cold methanol. The polymer residue was recovered by centrifugation and

decanting of the supernatant. The polymer was dissolved in tetrahydrofuran and this precipitation procedure was repeated twice to give a light yellow solid that was dried under vacuum for minimal time (to prevent any dehydrochlorination reaction in the precursor polymer affecting its solubility) to give Σ-M-NO_2FVPPV **4.42** in an ~36% yield.

Σ-M-NO_2FVPPV **4.42** was characterised by g.p.c., TGA, DSC, ^{1}H n.m.r., infrared and U.V.-visible spectroscopy. G.p.c. studies showed precursor polymer **4.42** had a molecular weight, $\overline{M}_w$ of 2.5 × 10^5 g/mol and PD of 2.0. The ^{1}H n.m.r. spectrum of **4.42** is shown in Figure **4-10**.

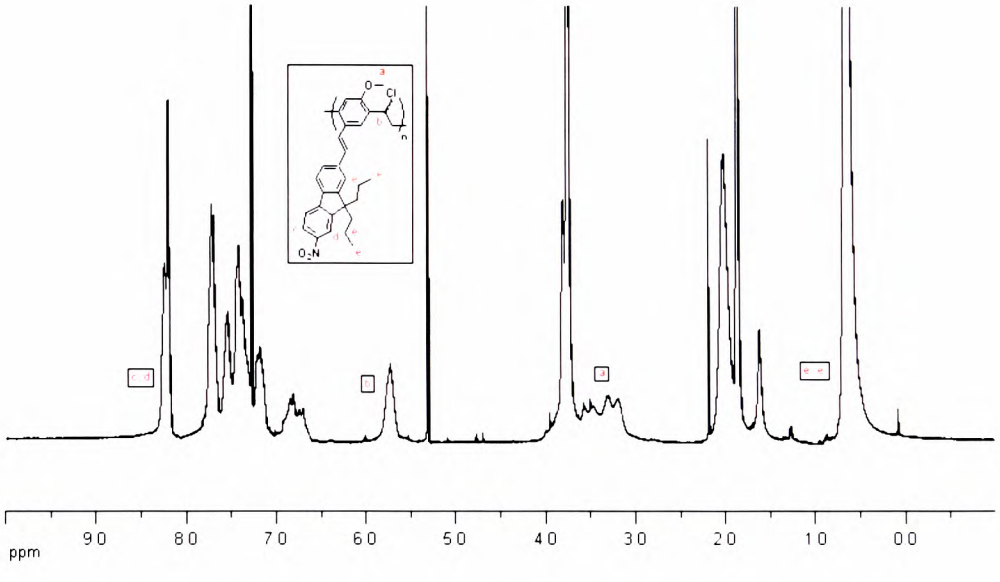


Figure 4 - 10: ^{1}H-n.m.r. spectrum of Σ-M-NO_2FVPPV **4.42** in $CDCl_3$

The formation of precursor polymer is indicated by the presence of methine proton at ~5.8 p.p.m. The ratio of the integrals for aromatic protons (6-H and 8-H of the fluorenyl ring) at 8.2-8.4 p.p.m. was consistent to the CHCl proton indicating no elimination of

hydrogen chloride in the polymer. The absence of signals due to benzylic protons at ~2.8 p.p.m. in the ^{1}H n.m.r. of **4.42** indicated the absence head-to-head defects in the polymer.

Thermogravimetric analysis of Σ-M-NO_2FVPPV **4.42**, Figure **4-11**, showed the precursor polymer **4.42** undergoes dehydrochlorination to form the conjugated polymer, I-M-NO_2FVPPV **4.43** at 208 °C with a mass loss of ~8% (theoretical mass loss, 8%). The similarity in experimental and theoretical weight loss percentages for dehydrohalogenation step is in agreement with the ^{1}H n.m.r. spectrum of **4.42** (Figure **4-10**). The I-M-NO_2FVPPV **4.43** was found to be thermally stable up to 290 °C and decomposed thereafter in two steps.

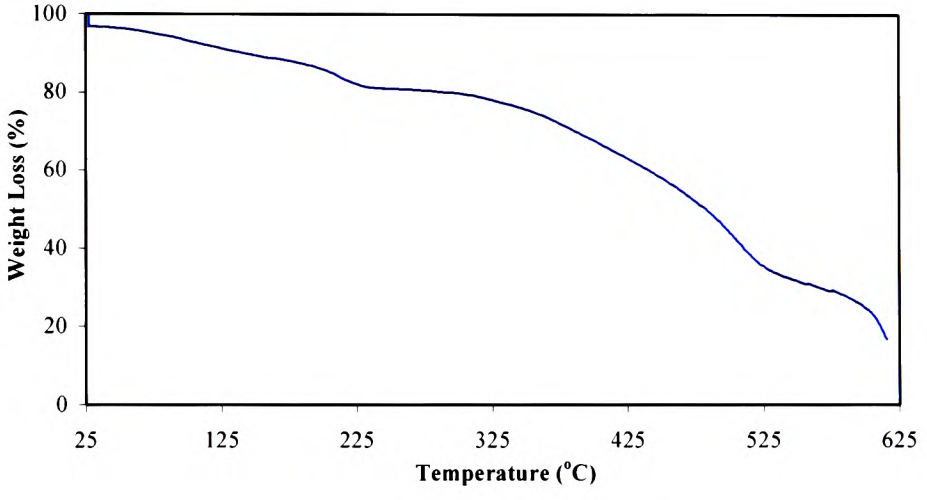
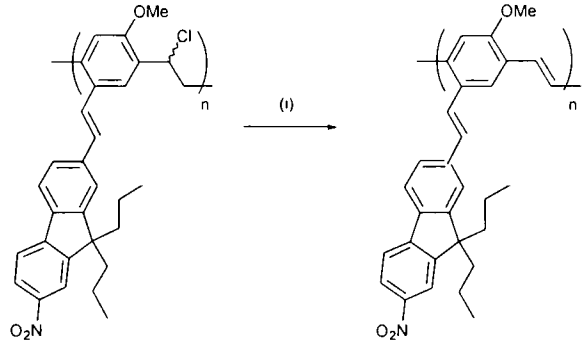


Figure 4 - 11: TGA of Σ-M-NO_2FVPPV **4.42**

The conversion of Σ-M-NO_2FVPPV **4.42** to I-M-NO_2FVPPV **4.43** was followed by U.V.-visible and infrared spectroscopy. Σ-M-NO_2FVPPV **4.42** was drop cast onto a KBr disc for the infrared study, and was spin-coated on to quartz substrate for the

U.V.-visible absorption study. The residual solvent was allowed to evaporate under ambient conditions before recording the infrared and U.V.-visible spectra. Both the spectra were recorded again after thermal conversion of the precursor polymer **4.42**. Thin films of **4.42** were heated at 210 °C for 17 hours to form the conjugated polymer I-M-NO_2FVPPV **4.43**, Scheme **4-30**.



4.42 **4.43**

Scheme 4- 30. *Reactions and conditions:* (i) 210 °C, Vacuum

The infrared spectra of thin films of Σ-M-NO_2FVPPV **4.42** and I-M-NO_2FVPPV **4.43** were recorded, Figure **4-12**. In the infrared spectrum of Σ-NO_2M-FVPPV **4.42**, there as weak absorption at 959 cm^{-1} due to the C=C-H *trans*-vinylene C-H out-of-plane-bend of the vinyl linkage. After thermal conversion of Σ-M-NO_2FVPPV **4.42** to conjugated polymer I-M-NO_2FVPPV **4.43** the absorption due to the C=C-H *trans*-vinylene C-H out-of-plane-bend at 961 cm^{-1}, was observed. Since vinyl linkages were initially present in **4.42** therefore the formation of additional vinyl linkages upon thermal conversion to **4.43** was not clearly noticed. The presence of vinyl linkages in **4.42** makes the conversion difficult to follow by infrared study.

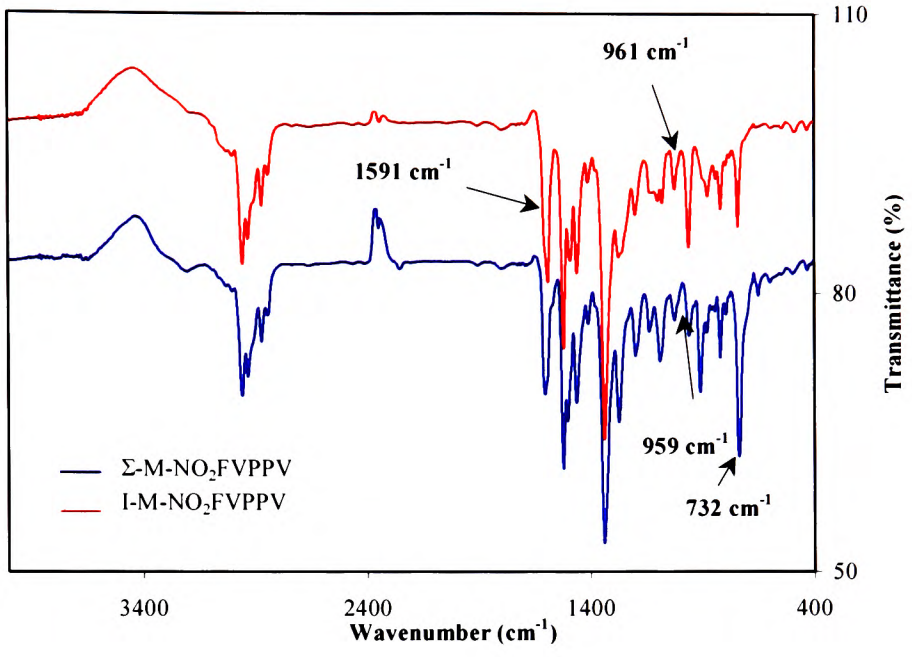


Figure 4 - 12: Infrared spectra of Σ-M-NO_2FVPPV **4.42** and I-M-NO_2FVPPV **4.43**

The absorptions at 1518 cm^{-1} and 1331 cm^{-1} corresponding to the antisymmetric and symmetric stretch of the nitro group respectively in the Σ-M-NO_2FVPPV **4.42** were found to be unaffected in the spectrum of the I-M-NO_2FVPPV **4.43**. This indicated that the nitro group is not eliminated during thermal conversion at 210 °C of **4.42**.

Films of Σ-M-NO_2FVPPV **4.42** were obtained by spin-coating the polymer from tetrahydrofuran or chloroform solution onto quartz substrates for U.V.-visible analysis. The U.V.-visible spectra of methoxy-dimethylphenylvinylnitrofluorene **4.25b** in dichloromethane and methoxy-dimethylphenylnitrofluorene **2.23b** in *n*-hexane, and films of Σ-M-NO_2FVPPV **4.42**, I-M-NO_2FVPPV **4.43** and, I-M-NO_2FPPV **2.28** (biphenyl linkage between the fluorenyl side-chain and polymer backbone) are shown in Figure **4-13**. The films obtained were of good quality before and after thermal conversion.

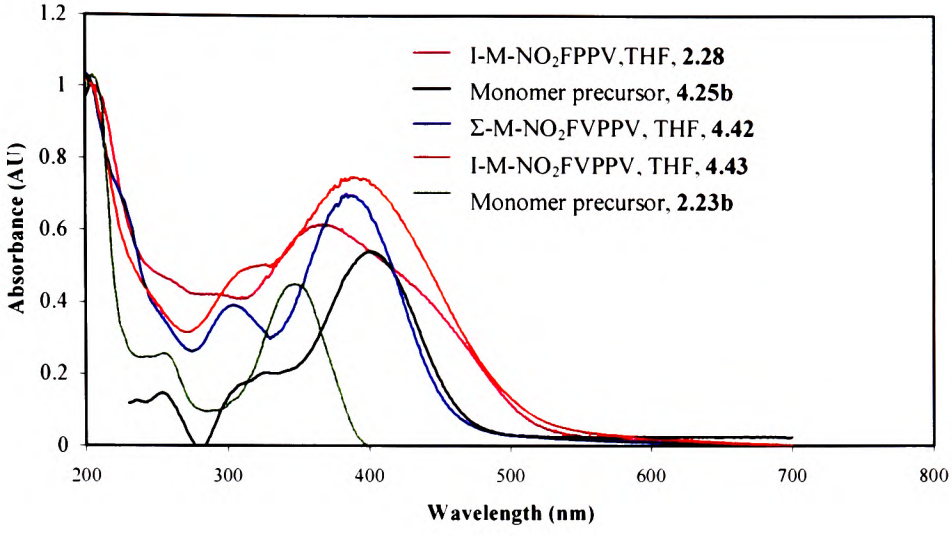


Figure 4 - 13: U.V.-visible spectra of monomer precursors **4.25b** and **2.23b** (dichloromethane), Σ-M-NO_2FVPPV **4.42**, I-M-NO_2FVPPV **4.43**, and I-M-NO_2FPPV **2.28**

For polymer **4.42** three maxima were observed in the spectra. The two longer wavelength absorptions centered at ~384 and ~305 nm correspond to the "nitrofluorenylvinylphenyl" chromophore as indicated by the presence of similar absorptions in the spectra for **4.25b**. The spectra of polymer films coated from chloroform and tetrahydrofuran were the same before and after thermal conversion. Thermal conversion to conjugated polymer film **4.43** resulted in an onset of absorption at longer wavelength indicating an increase in conjugation length along the polymer backbone. The localised π-π* transitions were observed at ~200 nm for both **4.42** and **4.43** polymers. The degree of conjugation obtained for the conjugated polymer can be normally understood by comparison of the ratios of the localised to the delocalised π-π* transitions, the smaller the ratio the better

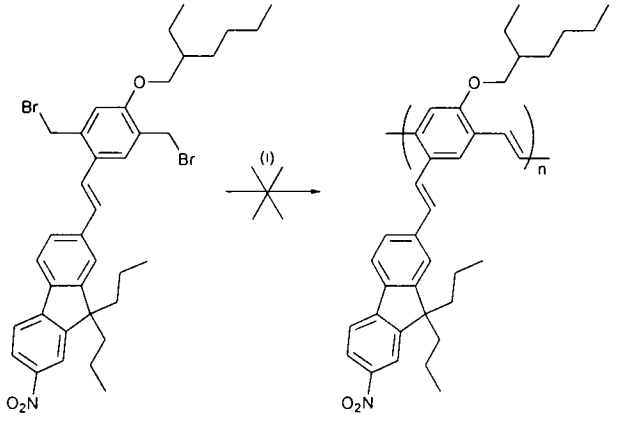
the delocalisation. However, such an interpretation on degree of delocalisation cannot be done for the conjugated polymer **4.43** as there was an overlap between delocalised π-π* transitions and monomer chromophore. In comparison with biphenyl linked dimethyl compound **2.32b** and I-M-NO_2FPPV **2.28** analogue, vinyl linked dimethyl compound **4.25b** I-M-NO_2FVPPV **4.43** showed an apparent bathochromic shift in both the monomer chromophore and weighting of the delocalised π-π* transitions due to the presence of additional vinyl unit in latter. However, again a direct comparison of the delocalisation of two polymers backbone is difficult due to the overlap of the chromophores with the delocalised π-π* transitions. The fact that the longer wavelength absorption onset is similar suggests that the longest delocalised polymer segments are similar.

4.3.2.1.1 Summary

In summary, methoxy-nitrofluorenylvinyl monomer **4.41** has been synthesised. Base mediated polymerisation of monomer **4.41** to form the precursor polymer Σ-M-NO_2FVPPV **4.42** has been studied. Good quality films of methoxy-nitrofluorenylvinyl-PPV **4.43** polymer were obtained. Polymer **4.43** has a broader and stronger absorbance in its U.V.-visible spectrum. The yield of the precursor monomer, methoxy-dimethylvinylnitrofluorene **4.25b** has been improved by introduction of vinyl and halo functionality in an alternative synthetic methodology in the Heck reaction.

4.3.2.2 Attempted synthesis of the Ethylhexyloxy-nitrofluorenylvinyl-PPV

Polymerisation of nitrofluorenylvinyl-*bis*-bromide **4.39** to form ethylhexyloxy-nitrofluorenylvinyl-PPV **4.44** (S-EH-NO_2FVPPV), Scheme **4-31** was attempted using two different bases namely potassium *t*-butoxide and lithium di-*iso*-propylamide.



4.39 **4.44**

Scheme 4- 31. *Reactions and conditions:* (i) cf. Table **4-5**

The conditions used to polymerise monomer **4.39** are summarised in Table **4-5**. In the attempts of polymerisation of nitrofluorenylvinyl-*bis*-bromide **4.39** using potassium *t*-butoxide, a 0.2 M solution of monomer in tetrahydrofuran was treated with 5.0 equivalents of 0.2 M solution of base. Potassium *t*-butoxide solution in tetrahydrofuran was added to the solution of monomer at room temperature (Entry 1).

Table 4-5: Reaction conditions used for polymerisation of nitrofluorenylvinyl-*bis*-bromide **4.39**

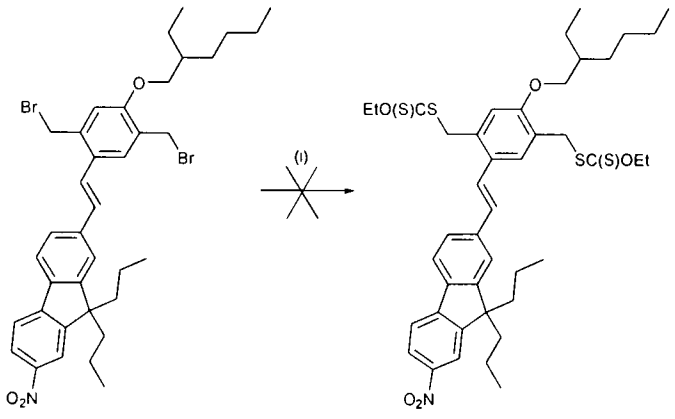
Entry	[4.39] (M)	[Base] (M)	Temp. (°C)	Time (h)	Polymerisation
1	0.2	0.2	r.t.	3.5	No
2	0.2	0.2	r.t. → 67	3 → 24	No
3	0.2	2.0	0	2	pentamer
4	0.2	2.0	0 → 40	16	octamer

The reaction colour changed from yellow to orange on addition of base solution. After 3.5 hours, no polymer was detected by g.p.c. analysis. In another attempt (Entry 2) conditions similar to polymerise fluorenylvinyl monomer were used (Scheme **4-16**), after addition a solution of potassium *t*-butoxide (0.2 M) to the solution of monomer **4.39** (0.2 M) the reaction mixture was stirred at room temperature for 3 hours and then heated at reflux for 24 hours. The polymerisation reaction was monitored by g.p.c. analysis. No polymerisation was observed in the g.p.c. trace. A different base, lithium di-*iso*-propylamide, was utilised to promote polymerisation of **4.39**. The choice for lithium di-*iso*-propylamide was based on the fact that it proved successful over potassium *t*-butoxide for the coupling reaction of THP-aldehyde **4.18b** with nitrofluorenylphosphonate ester **4.34** to introduce a double bond in THP-protected monomer precursor **4.35** (Scheme **4-25**) in good yields earlier. The concentration of monomer solution was increased from 0.2 M to 0.3 M to facilitate polymerisation of **4.39**.

A 0.3 M solution of monomer **4.39** was reacted with 5.0 equivalents of 2.0 M solution of lithium di-*iso*-propylamide in THF/*n*-heptane at 0 °C under nitrogen (Entry 3). After 2 hours, only oligomers were detected by the g.p.c. analysis. In final attempt (Entry 4), the polymerisation reaction was thermally assisted after addition of 10 equivalents of lithium di-*iso*-propylamide solution (under similar conditions as for Entry 3) at 0 °C and then heated at 40 °C for 16 hours. Only oligomers were detected by g.p.c. and ^{1}H n.m.r. analysis. The lack of polymerisation of monomer **4.39** is similar to that observed for its non-nitrated analogue, that is, fluorenylvinyl monomer **4.20**.

4.3.3 Attempted synthesis of the Nitrofluorenyl-*bis*-xanthate monomer

Since the nitrofluorenyl-*bis*-bromide monomer **4.39** failed to polymerise it was decided to synthesise nitrofluorenyl-*bis*-xanthate monomer **4.45**. The conversion of nitrofluorenyl-*bis*-bromide **4.39** to nitrofluorenyl-*bis*-xanthate monomer **4.45** was attempted (Scheme **4-32**) by treatment with potassium *O*-ethylxanthate and tetra-*n*-butylammonium bromide in dichloromethane at room temperature. No significant change was observed on t.l.c. analysis and hence the reaction mixture was heated at reflux for 18 hours. After work-up and purification impure nitrofluorenyl-*bis*-xanthate **4.45** in a poor yield (~20%) was isolated with no nitrofluorenyl-*bis*-bromide **4.39** being recovered.



4.39 **4.45**

Scheme 4- 32. *Reactions and conditions*: (i) KS(CS)OEt, TBAB, DCM, r.t. → 40 °C

4.3.3.1.1 Summary

In summary, the synthesis of ethylhexyloxy substituted nitrofluorenylvinyl monomer with bromide, as a leaving group was synthesised using protection method. The nitrofluorenyl-*bis*-bromide monomer **4.39** was failed to polymerise under the polymerisation conditions studied. The synthesis of nitrofluorenylvinyl monomer with a different leaving group, nitrofluorenyl-*bis*-xanthate **4.45** was attempted. The failure of polymerisation of **4.39** and its transformation to **4.45** is due to the instability of **4.39** under the reaction conditions. No further study on the formation of ethylhexyloxy-nitrofluorenylvinyl-PPV **4.44** (S-EH-NO_2FVPPV) was carried out.

4.4 Conclusions

In conclusion, a new class of conjugated polymers with and without electron withdrawing nitro group namely, fluorenylvinyl PPV and nitrofluorenylvinyl PPVs was

investigated. The polymers were synthesised as soluble conjugated when ethylhexyloxy was the electron donating group (EDG) and as insoluble conjugated polymer *via* soluble precursor route when methoxy was the EDG.

The soluble conjugated fluorenylvinyl PPV was synthesised from the *bis*-bromide monomer and characterised successfully in spite of instability of both the polymer and monomer towards light, temperature, and solvent. Although the polymer was found to be susceptible to oxidation, a strong effect of vinyl linkage between fluorenyl side chain and PPV backbone was observed. This effect was explained in terms of extended conjugation between the polymer backbone and the co-planar fluorenyl side groups. The *bis*-bromide monomer was synthesised successfully *via* the protection route over the free-radical route.

Amongst nitrofluorenylvinyl PPVs, the methoxy analogue was successfully synthesised and characterised as insoluble conjugated polymer *via* soluble precursor route. The methoxy-nitrofluorenylvinyl PPV precursor polymer was stable in both solvents and at high temperature as used for its conversion to the conjugated polymer. However the polymer with longer ED ethylhexyloxy group failed to polymerise under similar conditions as utilised for the methoxy analogue, which could be attributed to the poor stability of either the monomer or the intermediates under the polymerisation conditions studied. The synthesis of alternative *bis*-xanthate monomer by substitution reaction of bromo groups of the *bis*-bromide monomer with xanthate groups was not successful. This could be again explained on the basis of instability of the monomer under the reaction conditions. The introduction of vinyl-linkage between electron donating and withdrawing half was studied under Heck conditions, the yield and

purification of the coupled product was found to be dependent on the nature of alkoxy group as indicated by the better yields of methoxy over ethylhexyloxy analogue. The free-radical method was used for the methoxy-nitrofluorenylvinyl monomer involving activation of the methyl groups after introduction of vinyl linkage but protection method was used for the ethylhexyloxy-nitrofluorenylvinyl monomer to activate the methyl groups before the introduction of vinyl linkage.

SUMMARY & OUTLOOK

Chapter 5

5 SUMMARY AND OULOOK

In last decade, the light harvesting efficiency of polymer-based photovoltaic cells has reached a value of 3-5%[7,48,60]. However, still the efficiencies are far below their inorganic competitors. The key processes that dictate the efficiency are light absorption, charge separation of the exciton, charge transport of the separated charges and their collection at the respective electrodes. The optimisation of a solar cell depends upon both the geometry of the device and the nature of light absorbing material. Light absorption is reliant on the optical density of the polymer and the intermolecular charge separation has been generally achieved by blending an electron acceptor with the polymer film. This thesis describes the preparation of poly(1,4-phenylenevinylene) derivatives containing dipoles in which the process of charge separation can be achieved intramolecularly in an effort to improve the efficiency of polymer based solar cells. The dipole was created by attaching electron donating alkoxy groups to the polymer backbone, and electron withdrawing nitro group via different length fluorenyl side chains. These groups are believed to facilitate the dissociation of the photogenerated exciton, and potentially stabilise the holes and electrons that are formed when the exciton is separated.

A family of PPV polymers with pendant fluorenyl (Chapter 2) and *bis*-fluorenyl (Chapter 3) groups attached directly to the polymer backbone with or without the electron withdrawing nitro group were synthesised. The U.V.-visible spectra of the polymers with the electron withdrawing group was found to be red shifted as compared to the polymers without dipole but all showed a weak absorption at the longer wavelengths associated with the delocalised π–π^* transitions. The lower absorbance of delocalised π–π^* transitions to the localised π–π^* transitions in the biphenyl-linked PPV polymers was due

to the twisting of polymer backbone caused by the "biphenyl linkage" formed in joining the fluorene unit to the polymer backbone thereby shortening the effective conjugation length of the polymer. The twisting of the polymer structure would give rise to a more disordered film with poorer charge mobility leading to lower device efficiencies. The photophysical properties of the polymers were studied. For poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] it was found that the photoluminescence quantum yield dropped by a factor of eight relative to the polymer without the nitro group. Light induced electron spin resonance studies showed that on excitation there was an increase free electron spins indicating that the exciton had been at least in part charge separated. Simple solar cells comprised of the polymers with the dipole showed modest performance. To avoid the effect of twisting of polymer backbone at biphenyl link, a vinyl linkage was introduced between the fluorene moiety and the backbone of the polymer (Chapter 4). The monomer with a methoxy electron donating group and a nitro as electron withdrawing group was polymerised successfully while monomer with the longer 2-ethylhexyloxy group was found to be unstable. The presence of vinyl link between the fluorene unit and the polymer backbone was found to improve the planarity and delocalization in the polymer backbone as indicated by an improvement in the ratio of delocalised to localised π–π^* transitions observed in the U.V.-visible spectrum.

Since dipole strength and charge trapping is a function of the electron donating and withdrawing capability of the various functional groups and the dipole is affected by the conjugation length between the chromophores therefore the future work will involve studying these aspects. For example, the conjugation length of the side-chain could be

increased from two fluorenyl units to four or the electron acceptor chromophore could be linked to the polymer backbone via a non-conjugated link. The latter approach is similar to blending an electron acceptor into a polymer matrix although this has the advantage that it is covalently linked to the polymer backbone potentially giving some control over the aggregation of the different components. It is clear from the photophysical and device studies, that the while charge is separated, it is getting trapped on the polymer chain. In particular it has been shown that electron transport is a key problem as devices with an electron transporting material blended with the polymer layer had improved device performance. To understand this a series of polymers with different electron donating (e.g., dialkylamines, alkyl, or thioethers) and/or withdrawing groups (e.g., CN, aldehyde, sulfoxide, or sulfone) could be prepared. The initial figure of merit of the effect of these structural changes would be whether the luminescence was quenched. This would be followed by light-induced ESR measurements to determine whether there was an increase in electron spins, and finally solar cells would be produced to determine whether there was an improvement in performance or whether there were further charge transport issues that need to be addressed.

EXPERIMENTAL

Chapter 6

6 EXPERIMENTAL

6.1 General procedures

^{1}H n.m.r. spectra were recorded on Bruker DPX-200 (200 MHz), Bruker DPX-400 (400 MHz), Bruker DQX-400 (400 MHz) and Bruker AMX-500 (500 MHz) spectrometers. ^{13}C n.m.r. spectra were recorded on Bruker DQX-400 (400 MHz) and Bruker AMX 500 (500 MHz) spectrometers. Chemical shifts are reported in parts per million (p.p.m.) and are referenced to the residual solvent peak. Muliplicities are reported as broad (br), singlet (s), doublet (d), dd (doublet of doublet), triplet (t), quartet (q), and multiplet (m). Coupling constants (*J*) are rounded off and are reported in Hz.

Infrared spectra were recorded as a KBr disc or as a thin film on a KBr disc on a Spectrum 1000 Infrared spectrometer. Values of the absorption maxima are recorded as wavenumbers (cm^{-1}). U.V.-visible spectra were recorded on a Perkin-Elmer UV lambda 15 spectrometer and analysed as either a thin film on quartz or as a solution in spectroscopic grade hexane, methanol and dichloromethane. Spin coated samples were prepared by covering a substrate with a filtered polymer solution and spinning was carried out at 4500 r.p.m. for 60 seconds on a Dynapert PRS 14E spinner for photoresists; the solvent was allowed to evaporate under ambient conditions.

Chemical Ionisation mass spectra (*m/z*) were recorded either on a Hewlett Packard 1050 Atmospheric Pressure Chemical Ionisation mass spectrometer (APCI) or VG platform spectrometer. Electronic ionisation mass spectra (*m/z*) were recorded

on a VG Bio-Q spectrometer. Major peaks are listed with intensities quoted as percentages of the base peak.

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Microanalysis was carried out by Mrs. A. Douglas, Inorganic Chemistry Research Laboratory, University of Oxford, Oxford and Mr. Stephen Boyer, London Metropolitan University, London.

Gel permeation chromatography (g.p.c.) was carried out with a Polymer Laboratories PL gel 20 μm Mixed A column (600 mm length and 7 mm diameter) calibrated with polystyrene standards (580-11.2 × 10^6) in tetrahydrofuran with toluene as a flow marker. The U.V. detector was set at 245 nm and solvent was pumped at a flow rate of 1 ml/min. The tetrahydrofuran was degassed with nitrogen and pumped at a rate of 1 mL/min. at 30.0 ± 0.1 °C.

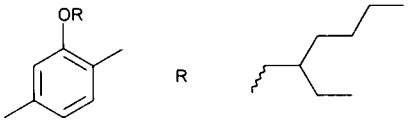
Thermal gravimetric analysis (TGA) was carried out on a Perkin Elmer Thermogravimetric Analyser, TGA 7, at a heating rate 10 and 2 °C/min under an atmosphere of nitrogen. Differential Scanning Calorimetry (DSC) analysis was carried out on a Perkin Elmer Differential Scanning Calorimeter, Pyris 1 at a heating rate of 10 °C/min. under an atmosphere of nitrogen.

Tetrahydrofuran was dried over sodium/benzophenone or lithium aluminium hydride and freshly distilled before use. *N,N*-Dimethylformamide was dried over activated 4 Å molecular sieves. Light petroleum refers to the fraction of boiling point 40-60 °C. Thin layer chromatography was performed on Merck aluminium plates coated with silica gel F_{254}. Column chromatography was performed using either gravity feed chromatography or the flash chromatography technique, with silica gel (flash) C60, 40-60. Where solvent mixtures are used their proportions are given by volume.

6.2 Experimental for Chapter 2

6.2.1 Synthesis of poly[2-(9,9-dipropylfluorenyl)-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene]

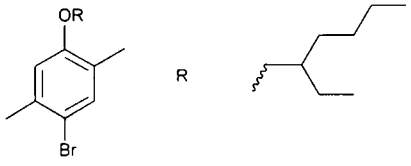
2-(2′-Ethylhexyloxy)-1,4-dimethylbenzene (2.2):



2.2

Potassium *t*-butoxide (220.0 g, 2.0 mol) was added portion-wise to a stirred solution of 2,5-dimethylphenol **2.1** (184.0 g, 1.6 mol) in acetonitrile (1.2 L) at 0 °C, over a period of 30 minutes. The mixture was stirred for 1 hour before drop-wise addition of 2-ethylhexyl bromide (350 mL, 2.0 mol). The reaction mixture was stirred at room temperature for 18 hours and then concentrated to give a yellow oil. The crude product was purified by filtering through a silica plug using light petroleum as eluent followed by vacuum distillation to remove unreacted 2-ethylhexyl bromide to give 2-(2′-ethylhexyloxy)-1,4-dimethylbenzene **2.2** (234.5 g, 100 %) as a colourless oil, bp 118 °C, 0.5 mmHg (lit.[113] 118 °C, 0.5 mmHg). A sample had an identical ^{1}H n.m.r. spectrum to that reported in the literature[113].

1-Bromo-4-(2′-ethylhexyloxy)-2,5-dimethylbenzene (2.3a):

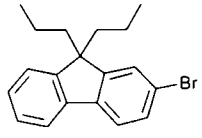


2.3a

Bromine (10.9 mL, 0.2 mol) was added to a solution of 2-(2′-ethylhexyloxy)-1,4-dimethylbenzene **2.2** (50.0 g, 0.2 mol) in a mixture of methanol (350 mL) and glacial

acetic acid (140 mL) under argon. The reaction mixture was stirred for 24 hours at room temperature. A saturated solution of sodium metabisulphite (100 mL) was added and the reaction mixture was allowed to stir for 30 minutes. The aqueous layer was extracted with ether (3 × 100 mL). The combined organic layers were washed with aqueous sodium hydroxide (5% w/v, 100 mL), a saturated solution of sodium bicarbonate (2 × 50 mL), and water (3 × 100 mL). The organic extract was dried over magnesium sulphate, filtered, and the solvent was removed to give a brown oil. Purification of the residue by filtering through a silica plug using light petroleum as eluent gave 1-bromo-4-(2'-ethylhexyloxy)-2,5-dimethylbenzene **2.3a** (56.0 g, 84%) as a colourless clear oil. The compound had an identical ^{1}H and ^{13}C n.m.r. spectrum to that reported in the literature[157].

9,9-Di(*n*-propyl)-2-bromofluorene (2.5):

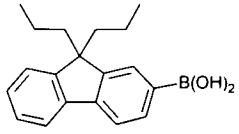


2.5

A suspension of 2-bromofluorene **2.4** (25.0 g, 0.1 mol), aqueous sodium hydroxide solution (50% w/w, 200 mL) and tetra-*n*-butylammonium bromide (1.6 g, 5.0 mmol) in toluene (150 mL) was stirred under argon at room temperature for 15 minutes. 1-Bromopropane (27.5 mL, 0.3 mol) was added and the stirred reaction mixture was heated at 60 °C for 20 hours. After allowing the reaction mixture to cool, the aqueous layer was extracted with ether (3 × 100 mL). The combined organic extracts were washed with brine (100 mL), dried over magnesium sulphate, filtered and the solvent was removed to give a green oil. Purification of the residue by filtering through a silica plug using light petroleum as eluent followed by recrystallisation from a

dichloromethane/ethanol mixture gave 9,9-di-*n*-propyl-2-bromofluorene **2.5** (30.2 g, 91%) as cream crystals, mp 74-75 °C (lit.[158] 74.5-75 °C). The compound had an identical ^{1}H n.m.r. to that reported in the literature[158].

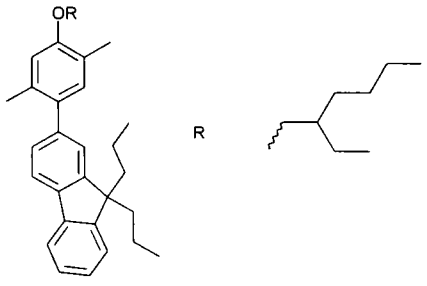
9,9-Di-*n*-propylfluorenyl-2-boronic acid (2.6):



2.6

n-Butyllithium (1.6 M in heptane, 100 mL, 160.0 mmol) was added drop-wise to a solution of 9,9-di-*n*-propyl-2-bromofluorene **2.5** (29.3 g, 89.1 mmol) in anhydrous tetrahydrofuran (200 mL) at -78 °C under nitrogen. After 1 hour trimethyl borate (40.0 mL, 356.8 mmol) was added and the reaction mixture was stirred at -78 °C for 30 minutes, and then at room temperature for 2 hours. Aqueous hydrochloric acid (100 mL) was added and the aqueous layer was extracted with ether (3 × 100 mL). The combined organic extracts were washed with water (3 × 150 mL), brine (150 mL), dried over magnesium sulphate, and filtered. The solvent was removed under vacuum. Purification of the crude by filtering through a silica plug using light petroleum as eluent then by dichloromethane gave 9,9-di-*n*-propylfluorenyl-2-boronic acid **2.6** (19.2 g, 74%). The compound had an identical ^{1}H and ^{13}C n.m.r. spectrum to that reported in the literature[159].

2-[4-(2'-Ethylhexyloxy)-2,5-dimethyl-phenyl]-9,9-dipropyl-9*H*-fluorene (2.7):

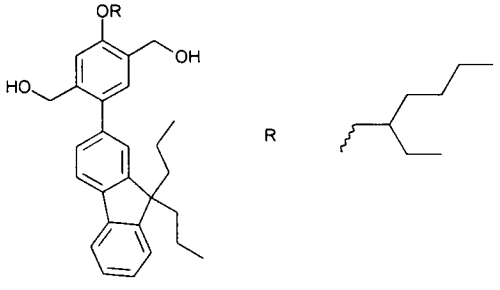


2.7

Nitrogen was bubbled through a mixture of 1-bromo-4-(2'-ethylhexyloxy)-2,5-dimethylbenzene **2.3** (2.6 g, 8.3 mmol), 9,9-di-*n*-propylfluorenyl-2-boronic acid **2.6** (2.0 g, 6.8 mmol), aqueous sodium bicarbonate (2 M, 25 mL) in toluene (25 mL) for 15 minutes. *Tetrakis*(triphenylphosphine)palladium (0) (0.2 g, 0.2 mmol) was added, and the reaction mixture was heated at reflux under nitrogen for 15 hours. After cooling, the aqueous phase was separated and the organic layer was washed with water (2 × 50 mL), aqueous hydrochloric acid (3 M, 2 × 30 mL), brine (50 mL), and dried over magnesium sulphate. The mixture was filtered and the solvent removed to give a brown oil. Purification of the residue by flash chromatography over silica gel using a light petroleum:dichloromethane mixture (6:1) as eluent gave 2-[4-(2'-ethylhexyloxy)-2,5-dimethyl-phenyl]-9,9-dipropyl-9*H*-fluorene **2.7** (1.8 g, 54%) as a colourless oil, bp 220 °C, 0.1 mmHg. (Found: C, 87.08; H, 9.60. $C_{35}H_{46}O$ requires C, 87.08; H, 9.60%); ν_{max} (KBr disc)/cm^{-1} 3018 (aromatic C–H), and 2924 (aliphatic C–H); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon/dm^3mol^{-1}cm^{-1}$) 312 (3.82), 288 (3.84), and 230 (3.75); δ_H ($CDCl_3$, 400 MHz) 0.65-0.78 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 0.95-1.04 (6 H, m, 2 × CH_3), 1.38-1.64 (8 H, m, 4 × CH_2), 1.78-1.86 (1 H, m, CH), 1.98-2.06 (4 H, m, 2 × $ArCH_2$), 2.28 (3 H, s, $ArCH_3$), 2.32 (3 H, s, $ArCH_3$), 3.91 (2 H, d, *J* 6, $ArOCH_2$), 6.79 (1 H, s, ArH), 7.14 (1 H, s, ArH), 7.34 (5 H, m, 5 × ArH), and 7.74 (2 H, d, *J* 8, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 11.3, 14.1, 14.5, 15.8, 17.3, 20.6, 23.1, 24.1, 29.1, 30.8,

39.6, 42.8, 55.2, 70.2, 112.7, 119.2, 119.6, 122.8, 124.1, 126.7, 128.0, 132.0, 133.2, 133.6, 134.0, 139.3, 140.7, 141.0, 150.4, 150.9, and 156.5; *m/z* (EI^+) 482 (M^+, 50%), 370 ($[M-112]^+$, 64%), and 327 (M-155, 100%); Exact mass 482.3563. $C_{35}H_{46}O_3$ requires 482.3549.

[5-(9,9-Dipropyl-9*H*-fluoren-2-yl)-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol (2.8):

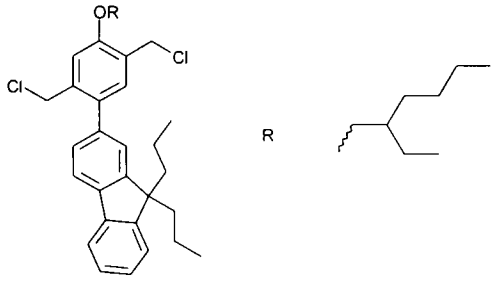


2.8

Nitrogen was bubbled through a mixture of 2-[4-(2′-ethylhexyloxy)-2,5-dimethyl-phenyl]-9,9-dipropyl-9*H*-fluorene **2.7** (5.7 g, 11.8 mmol), *N*-bromosuccinimide (3.1 g, 26.0 mmol) in carbon tetrachloride (50 mL) for 10 minutes. 2,2′-Azo-*bis*(isobutyronitrile) (0.7 g, 4.1 mmol) was added and the reaction mixture was heated at reflux for 2 hours. On cooling, the reaction mixture was filtered through a silica plug using dichloromethane as eluent. Solvent was removed to give a pale yellow oil. The mixture of yellow oil, and sodium acetate (9.7 g, 118.2 mmol) in glacial acetic acid (100 mL) was heated at reflux for 5 hours. After cooling, water (100 mL) was added. The aqueous phase was extracted with ether (3 × 100 mL). The combined ethereal extracts were washed with sodium hydroxide solution (5% w/v, 100 mL), saturated solution of sodium bicarbonate (2 × 25 mL), and water (100 mL). The organic phase was dried over magnesium sulphate, and filtered. Solvent removal gave a brown oil. The oil was dissolved in anhydrous tetrahydrofuran (125 mL), stirred at 0

°C under nitrogen before portion-wise addition of lithium aluminium hydride (0.9 g, 24 mmol). After 15 minutes, the reaction was further stirred at room temperature for 2 hours. The reaction mixture was carefully quenched with aqueous hydrochloric acid (3 M, 10 mL) and water (100 mL) was added. The aqueous phase was extracted with ether (3 × 75 mL). The combined organic extracts were washed with water (2 × 100 mL), brine (100 mL), and dried over magnesium sulphate. The mixture was filtered and solvent removal gave pale yellow oil. Purification of the residue by column chromatography over silica gel using a gradient elution with dichloromethane:methanol mixture (50:0 to 49:1) as eluent gave [5-(9,9-dipropyl-9*H*-fluoren-2-yl)-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **2.8** (2.0 g, 32%) as a pale white solid, mp 97-98 °C. (Found: C, 81.45; H, 9.01. $C_{35}H_{46}O_3$ requires C, 81.67; H, 9.01%); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/$dm^3mol^{-1}cm^{-1}$) 311 (4.88), 285 (4.91), and 228 (4.87); ν_{max} (KBr disc)/cm^{-1} 3360 (O–H); δ_H ($CDCl_3$, 400 MHz) 0.68-0.81 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 0.96-1.04 (6 H, m, 2 × CH_3), 1.48-1.63 (8 H, m, 4 × CH_2), 1.84-1.92 (1 H, m, CH), 1.98-2.03 (4 H, m, 2 × $ArCH_2$), 4.08 (2 H, d, *J* 6, $ArOCH_2$), 4.72 (2 H, s, CH_2O), 4.81 (2 H, s, CH_2O), 7.24 (1 H, s, ArH), 7.32 (6 H, m, 6 × ArH), and 7.76 (2 H, dd, *J* 8, *J* 2, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 11.3, 14.1, 14.6, 17.3, 23.1, 24.2, 29.1, 30.8, 39.5, 42.8, 55.3, 62.0, 63.1, 70.5, 119.4, 119.7, 122.9, 123.9, 126.9, 127.1, 127.9, 128.3, 130.3, 133.7, 138.9, 139.0, 140.0, 140.8, 150.8, 150.9, 151.0, and 156.6; *m/z* (EI^+) 514 (M^+, 100%); Exact mass 514.3439. $C_{35}H_{46}O_3$ requires 514.3447.

2-[2,5-*Bis*-chloromethyl-4-(2′-ethylhexyloxy)-phenyl]-9,9-dipropyl-9*H*-fluorene (2.9):

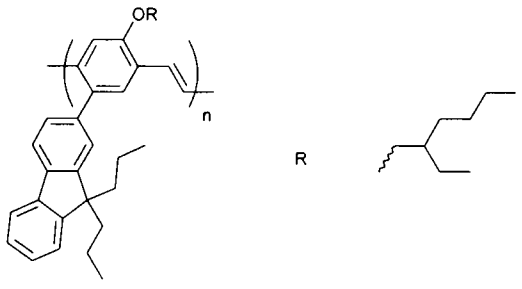


2.9

Thionyl chloride (4.4 mL, 59.4 mmol) was added to a solution of 2-[4-(2′-ethylhexyloxy)-2,5-dimethyl-phenyl]-9,9-dipropyl-9*H*-fluorene **2.8** (1.7 g, 3.3 mmol) in anhydrous dichloromethane at 0 °C under nitrogen. After addition, the reaction mixture was allowed to warm up to room temperature and stirred for 3 hours. The reaction mixture was concentrated under vacuum. Water (20 mL) was added and aqueous phase was extracted with dichloromethane (2 × 30 mL). The organic extracts were combined, dried over magnesium sulphate, and filtered. The solvent was removed under vacuum. Purification of the crude mixture by flash chromatography over silica gel using a light petroleum:dichloromethane mixture (1:1) as eluent gave 2-[2,5-*bis*-chloromethyl-4-(2′-ethylhexyloxy)-phenyl]-9,9-dipropyl-9*H*-fluorene **2.9** (1.8 g, 96%) as a pale oil, which solidifies on standing as a creamy solid, mp 58-59 °C. (Found: C, 76.18; H, 8.14. $C_{35}H_{46}Cl_2O$ requires C, 76.21; H, 8.04%); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 311 (4.27), 283 (4.30), and 229 (4.42); ν_{max} (KBr disc)/cm^{-1} 739 (C–Cl); δ_H ($CDCl_3$, 400 MHz) 0.75-0.88 (10 H, m, 2 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 0.98-1.10 (6 H, m, 2 × CH_3), 1.46-1.78 (8 H, m, 4 × CH_2), 1.92-1.99 (1 H, m, CH), 2.04-2.14 (4 H, m, 2 × $ArCH_2$), 4.12 (2 H, d, *J* 5, $ArOCH_2$), 4.63 (2 H, s, CH_2Cl), 4.81 (2 H, s, CH_2Cl), 7.02 (1 H, s, ArH), 7.45 (5 H, m, 5 × ArH), 7.62 (1 H, s, ArH), and 7.84 (2 H, dd, *J* 8, *J* 2, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 11.3, 14.2,

14.6, 17.4, 22.8, 23.2, 29.2, 30.7, 39.6, 41.5, 42.8, 44.8, 55.4, 70.6, 113.2, 119.6, 119.9, 123.0, 124.0, 126.6, 126.9, 127.3, 128.0, 132.3, 134.9, 136.6, 138.3, 140.4, 140.8, 150.9, 151.0, and 156.6; *m/z* (EI^+) 554, 552, and 550 (M^+, 22%, 75%, and 100%); Exact mass 550.2769. $C_{35}H_{44}Cl_2O$ requires 550.2769.

Poly[2-(9,9-dipropylfluorenyl)-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (2.11):



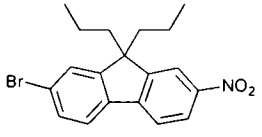
2.11

Potassium *t*-butoxide (570 mg, 5.1 mmol) in dry tetrahydrofuran (25.5 mL) was added to a stirred solution of 2-[2,5-*bis*-chloromethyl-4-(2′-ethylhexyloxy)-phenyl]-9,9-dipropyl-9*H*-fluorene **2.9** (560 mg, 1.0 mmol) in anhydrous tetrahydrofuran (5.1 mL) at room temperature under nitrogen in dark. The reaction mixture was stirred for 3 hours. The colourless solution turned to viscous yellow green solution. The solution was filtered through a cotton-wool plug and precipitated in ice-cold methanol (100 mL). The mixture was centrifuged (4500 r.p.m., 5 minutes) and the supernatant was decanted. The yellow residue obtained was dissolved in tetrahydrofuran (65 mL) and precipitated in ice-cold methanol (120 mL). The precipitate obtained was separated by centrifugation (4500 r.p.m., 5 minutes) and decantation of the supernatant. The residue was dried under vacuum for 18 hours to give poly[2-(9,9-dipropylfluorenyl)-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] **2.11** (180 mg, 37%) as a yellow solid. ν_{max} (film, KBr disc)/cm^{-1} 951 (C=C–H trans); λ_{max} (film)/nm 441 sh, 311, 281, and

212; δ_H ($CDCl_3$, 400 MHz) 0.34-0.93 (16 H, br m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$, 2 × CH_3) , 1.18-2.18 (13 H, br m, 4 × CH_2, CH, 2 × $ArCH_2$), 3.68-4.04 (2 H, br d, $ArOCH_2$), and 7.01-7.64 (10 H, br m, vinylH, 9 × ArH); $\overline{M}_w = 4.3 \times 10^6$, $\overline{M}_n = 1.9 \times 10^6$, and PD = 2.3; Thermogravimetric analysis: 380 °C (Temperature of degradation)

6.3.1 Synthesis of poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-methoxy-1,4-phenylenevinylene]

2-Bromo-9,9-di(*n*-propyl)-7-nitrofluorene (2.16):

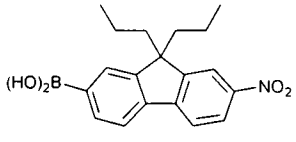


2.16

Method 1: Silica gel (100 g) was soaked in aqueous sulphuric acid (70% v/v, 140 mL) for 5 minutes. The silica gel was filtered, dried at room temperature using an aspirator for 5 hours and oven-dried at 130 °C for 24 hours to give activated silica and was used as the heterogeneous catalyst. A heterogeneous mixture of 2-bromo-9,9-di-*n*-propylfluorene **2.5** (15.6 g, 47.4 mmol) and silica catalyst (75 g) in dichloromethane (470 mL) was stirred for 10 minutes. Concentrated nitric acid (0.7 mL, 45.6 mmol) was added and the slurry was stirred at room temperature for 24 hours. Filtration and solvent removal gave an orange oil. Purification of the crude by column chromatography using a light petroleum:dichloromethane mixture (7:3) as eluent followed by recrystallisation from dichloromethane/methanol mixture gave 2-bromo-7-nitro-9,9-di-*n*-propylfluorene **2.16** (11.6 g, 66%) as yellow crystals, mp 105-106 °C (lit.[118] 104-106 °C), which had an identical ^1H n.m.r. spectrum to an authentic sample prepared according to the method described[118].

Method 2: Concentrated nitric acid (68%, 28.0 mL, 0.6 mol) was added to a stirred suspension of 2-bromo-9,9-di-*n*-propylfluorene **2.5** (40.0 g, 0.1 mol) in glacial acetic acid (300 mL) at 50 °C under nitrogen. After addition, the reaction mixture was heated at reflux for 1.5 hours. After cooling, water (200 mL) was added and the aqueous layer was extracted with ether (3 × 100 mL). The organic layers were combined, washed with water (3 × 150 mL), aqueous sodium hydroxide (5% w/v, 100 mL), saturated sodium bicarbonate solution (3 × 150 mL), and brine (150 mL). The organic layer was dried over magnesium sulphate, filtered and solvent was removed to give an orange solid. Purification of the crude by column chromatography using a gradient elution with light petroleum:dichloromethane mixture (1:0 to 1:1) followed by recrystallisation from a dichloromethane/methanol mixture gave 2-bromo-7-nitro-9,9-di-*n*-propylfluorene **2.16** (32.9 g, 72%) as a yellow solid.

Attempted synthesis of 9,9-di-*n*-propyl-7-nitrofluorenyl-2-boronic acid (2.17):

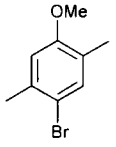


2.17

n-Butyllithium (2.5 M in heptane, 0.7 mL, 1.7 mmol) was added drop-wise to a solution of 9,9-di-*n*-propyl-2-bromofluorene **2.16** (0.5 g, 1.3 mmol) in anhydrous tetrahydrofuran (10 mL) stirred at -78 °C under nitrogen. After 1 hour, trimethyl borate (0.3 mL, 2.6 mmol) was added to the reaction mixture and the reaction was stirred at -78 °C for 30 minutes then at room temperature for 25 hours. Aqueous hydrochloric acid (3 M, 10 mL) was added and the aqueous was extracted with ether (3 × 20 mL). The organic layers were combined, washed with water (3 × 20 mL) and brine (10 mL), dried over magnesium sulphate, and filtered. The solvent was removed

to give a red solid (0.5 g). Purification of the residue by flash chromatography over silica gel using dichloromethane as eluent followed by ethyl acetate gave a mixture of unknown compounds. ^{1}H n.m.r. of the collected fractions showed no formation of 9,9-di-*n*-propyl-7-nitrofluorenyl-2-boronic acid **2.17**.

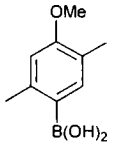
1-Bromo-4-methoxy-2,5-dimethylbenzene (2.3b):



2.3b

Bromine (37.7 mL, 0.7 mol) was added to a stirred solution of 2,5-dimethylanisole **2.18** (100.0 g, 0.7 mol) in methanol (300 mL) and glacial acetic acid (120 mL) at 0 °C. After 3 hours of stirring the reaction mixture was quenched with aqueous sodium metabisulphite (5% w/v, 100 mL). Water (1.5 L) was added and the aqueous layer was extracted with ether (3 × 200 mL). The organic extracts were combined, washed with aqueous sodium hydroxide (5% w/v, 200 mL), a saturated solution of sodium bicarbonate (3 × 400 mL) and water (3 × 300 mL). The organic extract was dried over magnesium sulphate, filtered and the solvent was removed to give yellow oil. Purification of the residue by filtering through a silica plug using a light petroleum:dichloromethane mixture (2:1) as eluent gave 1-bromo-4-methoxy-2,5-dimethylbenzene **2.3b** (152.5 g, 97%) as a pale oil which solidified on standing to a white solid, mp 32-37 °C (lit.[160] 34-38 °C),. The compound had an identical ^{1}H n.m.r. spectrum[109] to that reported in the literature.

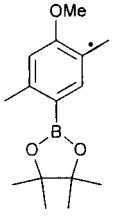
Attempted synthesis of 4-methoxy-2,5-dimethylphenyl-2-boronic acid (2.20b):



2.20b

n-Butyllithium (2.5 M in heptane, 1.2 mL, 3.0 mmol) was added to a solution of 1-bromo-4-methoxy-2,5-dimethylbenzene **2.3b** (0.5 g, 2.3 mmol) in anhydrous tetrahydrofuran (10 mL) stirred at -78 °C under nitrogen. After 1 hour trimethyl borate (0.5 mL, 4.5 mmol) was added. The reaction mixture was stirred at -78 °C for 30 minutes then at room temperature for 20 hours. Aqueous hydrochloric acid (3 M, 10 mL) was added and aqueous phase was extracted with ether (3 × 20 mL). The organic layers were combined, washed with water (3 × 20 mL) and brine (10 mL), dried over magnesium sulphate, and filtered. The removal of solvent gave a white solid (0.4 g). The crude was purified by flash chromatography over silica gel using dichloromethane as eluent followed by ethyl acetate. Two fractions were collected, namely fraction 1 (80 mg) and fraction 2 (25 mg). The fractions showed complicated t.l.c. and ^{1}H n.m.r. spectra.

2-[4-Methoxy-2,5-dimethyl-phenyl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (2.21b):

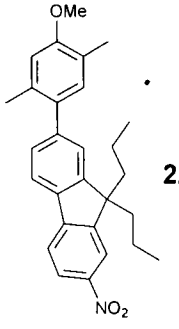


2.21b

t-Butyllithium (1.7 M in pentane, 100.0 mL, 170 mmol) was added drop-wise to a stirred solution of 1-bromo-4-methoxy-2,5-dimethylbenzene **2.3b** (20.3 g, 94 mmol) in dry tetrahydrofuran (250 mL) at -78 °C under argon. The reaction mixture was

stirred for 1 hour at -78 °C before the drop-wise addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (25.0 mL, 119.4 mmol). The reaction mixture was stirred at -78 °C for 15 minutes and thereafter at room temperature for 2 hours. Water (100 mL) and ether (100 mL) was added. The aqueous layer was extracted with ether (3 × 100 mL). The organic extracts were combined, washed with brine (100 mL), and dried over magnesium sulphate. The solution was filtered and solvent was removed. Purification of the residue by column chromatography over silica gel using a gradient elution with light petroleum:dichloromethane mixture (1:0 to 0:1) gave 2-[4-methoxy-2,5-dimethyl-phenyl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **2.21b** (23.0 g, 93%) as a white solid, mp 77-78 °C. (Found: C, 68.67; H, 8.83; $C_{15}H_{23}BO_3$ requires C, 68.72; H, 8.84%); ν_{max} (KBr disc)/cm^{-1} 1337 (B–O), and 1243 (O–C–O); λ_{max} (*n*-pentane)/nm ($\log_{10}\varepsilon$/$dm^3mol^{-1}cm^{-1}$) 245 (4.24), and 210 (4.79); δ_H ($CDCl_3$, 400 MHz) 1.35 (12 H, s, 4 × CH_3), 2.18 (3 H, s, $ArCH_3$) 2.55 (3 H, s, $ArCH_3$), 3.85 (3 H, s, $ArOCH_3$), 6.68 (1 H, s, ArH), and 7.56 (1 H, s, ArH); δ_C ($CDCl_3$, 100 MHz) 15.5, 22.3, 24.9, 55.1, 83.1, 111.6, 122.6, 138.3, 144.8, and 159.8; *m/z* (CI^+) 263 (MH^+, 100%).

2-(4-Methoxy-2,5-dimethylphenyl)-7-nitro-9,9-dipropyl-9*H*-fluorene (2.23b):

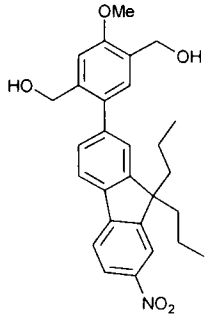


2.23b

A mixture of 2-[4-methoxy-2,5-dimethyl-phenyl]-4,4,5,5-tetramethyl-1,3,2]dioxaborolane **2.21b**

(7.0 g, 26.7 mmol), 2-bromo-7-nitro-9,9-di-*n*-propyl-9*H*-fluorene **2.16** (6.7 g, 17.2 mmol) and aqueous sodium carbonate (2 M, 160 mL) in toluene (240 mL) was deoxygenated with argon for 10 minutes. *Tetrakis*(triphenylphosphine)palladium (0) (0.5 g, 0.4 mmol) was added and the reaction mixture was heated at reflux for 24 hours. After cooling, aqueous hydrochloric acid (3 M, 100 mL) was added carefully. The aqueous layer was extracted with ether (3 × 100 mL). The combined organic extracts were washed with water (3 × 100 mL), brine (100 mL), dried over magnesium sulphate, filtered, and solvent was removed to give a yellow oil. Purification of the residue by column chromatography over silica using light petroleum:dichloromethane mixture (3:1) as eluent and recrystallisation from dichloromethane/methanol mixture gave 2-(4-methoxy-2,5-dimethylphenyl)-7-nitro-9,9-dipropyl-9*H*-fluorene **2.23b** (6.5 g, 76%) as light yellow crystals, mp 142-143 °C. (Found: C, 78.07; H, 7.25; N, 3.28. $C_{28}H_{31}NO_3$ requires C, 78.29; H, 7.27; N, 3.26%); ν_{max} (KBr disc)/cm^{-1} 2926 (C–H), 1511 (NO_2 anti), and 1331 (NO_2 sym); λ_{max} (*n*-pentane)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 349 (4.73), 256 (4.51), and 204 (4.26); δ_H ($CDCl_3$, 400 MHz) 0.60-0.71 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 1.95-2.15 (4 H, m, 2 × $ArCH_2$), 2.29 (3 H, s, $ArCH_3$), 2.32 (3 H, s, $ArCH_3$), 3.90 (3 H, s, $ArOCH_3$), 6.78 (1 H, s, ArH), 7.10 (1 H, s, ArH), 7.35 (2 H, m, 2 × ArH), 7.80 (2 H, d, *J* 8, 2 × ArH), 8.24 (1 H, d, *J* 2, ArH), and 8.27 (1 H, dd, *J* 2, *J* 8, ArH); δ_C ($CDCl_3$, 100 MHz) 14.4, 15.7, 17.2, 20.6, 42.4, 55.5, 55.8, 112.1, 118.3, 119.6, 120.8, 123.4, 124.1, 124.4, 128.8, 132.0, 133.6, 133.6, 136.9, 143.0, 146.9, 147.60, 152.1, 152.2, and 157.1; *m/z* (CI^+) 430 (MH^+, 100%).

4-Hydroxymethyl-2-methoxy-5-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)phenylmethanol (2.24b):

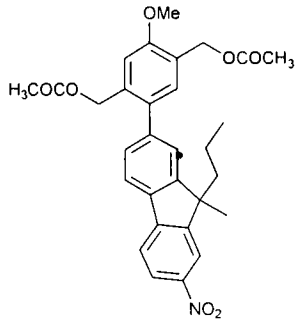


2.24b

Argon was bubbled through a mixture of 2-(4-methoxy-2,5-dimethylphenyl)-7-nitro-9,9-dipropyl-9*H*-fluorene **2.23b** (3.5 g, 8.1 mmol) and *N*-bromosuccinimide (5.6 g, 31.6 mmol) in carbon tetrachloride (30 mL) for 10 minutes. 2,2'-Azo-*bis*(isobutyronitrile) (0.5 g, 2.9 mmol) was added and the reaction mixture was heated at reflux for 4 hours. The reaction mixture was allowed to cool, diluted with dichloromethane (10 mL) and filtered through a silica plug using dichloromethane as eluent. Removal of solvent gave a yellow solid. Sodium acetate (6.6 g, 80.4 mmol) and glacial acetic acid (50 mL) was added to the yellow solid and the reaction mixture was heated at reflux for 5 hours. After allowing the reaction mixture to cool, water (50 mL) was added, and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic extracts were washed with water (3 × 150 mL), and saturated aqueous solution of sodium bicarbonate (3 × 50 mL). The solution was dried over magnesium sulphate, filtered, and solvent was removed to give a brown solid. The residue was dissolved in tetrahydrofuran (40 mL) and stirred at -15 °C for 5 minutes. Lithium aluminium hydride (0.6 g, 15.8 mmol) was added portion-wise and the reaction mixture stirred at -15 °C for 2 hours. Aqueous hydrochloric acid (3 M, 10 mL) was added carefully. The aqueous layer was extracted with ether (3 × 100 mL), washed with brine (100 mL), and dried over magnesium sulphate. The solution was

filtered, and the solvent was removed to give a yellow solid. Column chromatography of the crude over silica gel using a dichloromethane:methanol mixture (49:1) as eluent followed by recrystallisation from a dichloromethane/light petroleum mixture gave 4-hydroxymethyl-2-methoxy-5-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)phenylmethanol **2.24b** (0.9 g, 23%) as a light yellow crystals, mp 172-173 °C; ν_{max} (KBr disc)/cm^{-1} 3321 (O–H); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 360 (5.38), 261 (5.21), and 228 (5.28); δ_H ($CDCl_3$, 400 MHz) 0.60-0.80 (10 H, m, 2 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 1.95-2.10 (4 H, m, 2 × $ArC\underline{H_2}$), 3.98 (3 H, s, $ArOCH_3$), 4.48 (2 H, s, $C\underline{H_2}OH$), 4.68 (2 H, s, $C\underline{H_2}OH$), 7.18 (1 H, s, ArH), 7.30 (1 H, s, ArH), 7.40 (2 H, m, 2 × ArH), 7.84 (2 H, d, *J* 7.2, 2 × ArH), 8.21 (1 H, d, *J* 2, ArH), and 8.30 (1 H, dd, *J* 2, *J* 7.2, ArH); δ_C ($CDCl_3$, 100 MHz) 14.4, 17.3, 42.3, 55.6, 55.9, 61.7, 63.1, 110.1, 118.3, 119.75, 120.9, 123.4, 124.2, 128.4, 128.6, 130.4, 133.2, 137.6, 138.8, 141.3, 147.1, 147.3, 152.0, 152.4, and 157.2; *m/z* (EI^+) 461 (M^+, 33%); Exact mass 461.2209. $C_{28}H_{31}NO_5$ requires 461.2202.

2-Methoxy-4-methylcarbonyloxymethyl-5-[2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)]benzyl acetate (2.25b):



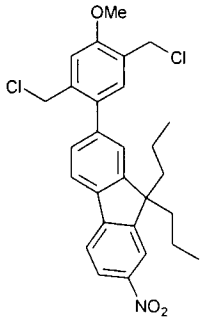
2.25b

A mixture of 2-(4-methoxy-2,5-dimethylphenyl)-7-nitro-9,9-dipropyl-9*H*-fluorene **2.23b** (25.0 g, 58.3 mmol), *N*-bromosuccinimide (20.7 g, 116.3 mmol) in carbon

tetrachloride (100 mL) was deoxygenated with argon for 10 minutes. 2,2'-Azo-*bis*(isobutyronitrile) (3.8 g, 23.1 mmol) was added and the reaction mixture was heated at reflux for 4 hours. The reaction mixture was allowed to cool to room temperature, diluted with dichloromethane (50 mL) and passed through a silica plug using dichloromethane as eluent. The solvent was removed and the residue obtained was taken up in glacial acetic acid (100 mL). Sodium acetate (47.8 g, 0.6 mol) was added and the reaction mixture was heated at reflux for 5 hours. After cooling, water (50 mL) was added and the aqueous layer was extracted with ether (3 × 200 mL). The combined organic extracts were washed with aqueous sodium hydroxide (5% w/v, 150 mL), water (3 × 200 mL), and a saturated solution of sodium bicarbonate (3 × 100 mL). The solution was dried over magnesium sulphate, filtered, and solvent was removed to give a brown solid. Purification of the residue by column chromatography over silica gel using a gradient elution with light petroleum:dichloromethane:ethyl acetate mixture (1:2:0 to 0:1:0 then 0:0:1) followed by recrystallisation from a dichloromethane/methanol mixture gave 2-methoxy-4-methylcarbonyloxymethyl-5-[2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)]benzyl acetate **2.25b** (16.9 g, 53%) as yellow crystals, mp 144-145 °C. (Found: C, 70.35; H, 6.43; N, 2.47. $C_{32}H_{35}NO_7$ requires C, 70.44; H, 6.47; N, 2.57%); ν_{max} (KBr disc)/cm^{-1} 1736 (C=O); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/$dm^3mol^{-1}cm^{-1}$) 358 (4.34), 260 (4.28), and 229 (4.34); δ_H ($CDCl_3$, 400 MHz) 0.64-0.76 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 1.94-2.08 (4 H, m, 2 × $ArCH_2$), 2.16 (3 H, s, $OCOCH_3$), 2.17 (3 H, s, $OCOCH_3$), 3.95 (2 H, s, $ArOCH_3$), 5.04 (2 H, s, CH_2O), 5.23 (2 H, s, CH_2O), 7.08 (1 H, s, ArH), 7.37 (3 H, m, 3 × ArH), 7.83 (2 H, m, 2 × ArH), and 8.27 (2 H, dd, *J* 2, *J* 8, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 14.3, 17.2, 21.0, 42.4, 55.8, 55.9, 61.4, 64.5, 112.2, 118.3, 119.8, 121.0, 123.4, 124.3, 124.7, 128.7, 131.3, 134.3, 134.6, 137.7, 140.9, 147.1, 147.2, 152.1, 152.3, 157.0, 170.5, and

170.9; *m/z* (EI^+) 545 (M^+, 100%); Exact mass 545.2421. $C_{32}H_{35}NO_7$ requires 545.2414.

2-[2,5-*Bis*(chloromethyl)-4-methoxyphenyl]-7-nitro-9,9-dipropyl-9*H*-fluorene (2.26b):



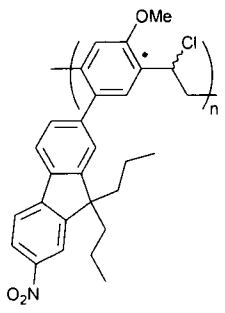
2.26b

Method 1: Thionyl chloride (2.2 mL, 30.2 mmol) was added to a stirred solution of 4-hydroxymethyl-2-methoxy-5-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)phenylmethanol **2.24b** (0.8 g, 1.7 mmol) in dichloromethane (15 mL) at 0 °C for 5 minutes. The reaction temperature was raised to room temperature and the reaction mixture was stirred for 2 hours. Water (5 mL) was added carefully and the aqueous layer was extracted with ether (3 × 30 mL). The combined organic extracts were washed with water (2 × 50 mL) and dried over magnesium sulphate. The solution was filtered and the solvent was removed to give a green oil. Purification of the residue by column chromatography using a light petroleum:dichloromethane mixture (1:1) as eluent followed by recrystallisation from a dichloromethane/methanol mixture gave 2-[2,5-*bis*(chloromethyl)-4-methoxyphenyl]-7-nitro-9,9-dipropyl-9*H*-fluorene **2.26b** (0.4 g, 44%) as a bright yellow solid, mp 271-272 °C. (Found: C, 67.50; H, 5.86; N, 2.81. $C_{28}H_{29}Cl_2NO_2$ requires C, 67.47; H, 5.86; N, 2.81%); ν_{max} (KBr disc)/cm^{-1} 742 (C–Cl); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon/dm^3mol^{-1}cm^{-1}$) 391 (4.33), 263 (4.19), and 228 (4.43); δ_H ($CDCl_3$, 400 MHz) 0.60-0.85 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 2.01-2.18 (4 H, m, 2 × $ArCH_2$), 3.98 (3 H, s, $ArOCH_3$), 4.50 (2 H, s, CH_2Cl), 4.73 (2 H, s, CH_2Cl), 7.10 (1 H, s, ArH), 7.40 (2 H, m, 2 × ArH), 7.43 (2 H, m, 2 × ArH), 7.55 (1 H, s, ArH), 7.85

(2 H, m, 2 × ArH), 8.27 (1 H, d, *J* 2, ArH), and 8.30 (1 H, dd, *J* 2, *J* 8, ArH); δ_C ($CDCl_3$, 100 MHz) 14.3, 17.3, 41.0, 42.3, 44.5, 55.9, 56.0, 112.7, 118.3, 119.9, 121.1, 123.4, 124.3, 126.5, 128.6, 132.2, 134.5, 136.6, 137.9, 140.5, 147.1, 147.2, 152.2, 152.5, and 157.1; *m/z* (CI^+) 502, 500, 498, (MH^+, 3%, 11%, and 16%), and 400 (M-97, 100%).

Method 2: Concentrated hydrochloric acid (35%, 50 mL) was added to a solution of 2-methoxy-4-methylcarbonyloxymethyl-5-[2-(7-nitro-9,9-dipropyl-9H-fluoren-2-yl)]benzyl acetate **2.25b** (8.0 g, 14.7 mmol) in 1,4-dioxane (50 mL) under nitrogen. The reaction mixture was heated at reflux for 15 hours. After allowing the reaction mixture to cool, the organic layer was separated, washed with water (3 × 50 mL) and a saturated solution of sodium bicarbonate (3×50 mL), and dried over magnesium sulphate. The solution was filtered and solvent removal gave a yellow solid. The crude was purified by column chromatography using light petroleum:dichloromethane mixture (1:1) as eluent followed by recrystallisation from a dichloromethane/methanol mixture gave 2-[2,5-*bis*(chloromethyl)-4-methoxyphenyl]-7-nitro-9,9-dipropyl-9H-fluorene **2.26b** (5.8 g, 80%) as a yellow solid.

Poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-methoxy-1,4-phenylene-(1-chloroethylene)] (2.27):

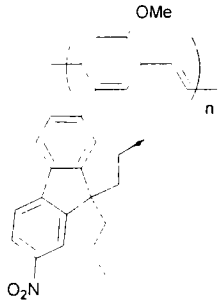


2.27

Potassium *t*-butoxide (41 mg, 0.37 mmol) in dry tetrahydrofuran (1.8 mL) was added to a stirred solution of 2-[2,5-*bis*(chloromethyl)-4-methoxyphenyl]-7-nitro-9,9-

dipropyl-9*H*-fluorene **2.26b** (200 mg, 0.40 mmol) in dry tetrahydrofuran (2 mL) at room temperature under argon. The yellow solution became viscous soon after the addition of potassium *t*-butoxide solution and formed a gel. Tetrahydrofuran (2 mL) was added and the reaction mixture was kept in a sonicator for 2 hours under argon. The solution was filtered through a plug of cotton-wool and precipitated in ice-cold methanol (5 mL). The mixture was centrifuged (4500 r.p.m., 5 minutes), the supernatant was decanted and a yellow residue of poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-methoxy-1,4-phenylene-(1-chloroethylene)] **2.27** (~62 mg, ~33%) was dissolved in tetrahydrofuran (5 mL). ν_{max} (film, KBr disc)/cm^{-1} 742 (C–Cl); λ_{max} (film)/nm 357 and 202; δ_H ($CDCl_3$, 400 MHz) 0.33-1.12 (10 H, br s, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 1.75-2.02 (4 H, br m, 2 × $ArCH_2$), 3.02-3.95 (3 H, br m, $ArOCH_3$), 5.02-5.53 (1 H, br s, CHCl), 6.82-7.94 (6 H, br m, 6 × ArH), 8.11-8.44 (2 H, br m, 2 × ArH); $\overline{M}_w = 6.5 \times 10^5$, $\overline{M}_n = 1.1 \times 10^5$, and PD = 6.2; Thermogravimetric analysis: 210 °C (theoretical weight loss: 7.2%, expected weight loss: 7.8%); Differential scanning calorimetry: T_g = 68 °C.

Poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-methoxy-1,4-phenylenevinylene] (2.28):



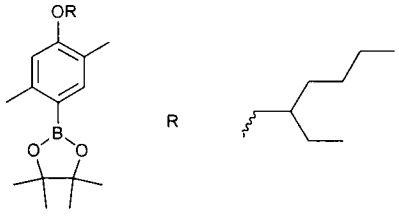
2.28

Thin films of poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-methoxy-1,4-phenylene-(1-chloroethylene)] **2.27** were heated at 215 °C for 17 hours under a dynamic vacuum to

give poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-methoxy-1,4-phenylenevinylene] **2.28**. ν_{max} (film, KBr disc)/cm^{-1} 970 (C=C–H trans); λ_{max} (film)/nm 463 sh, 367, and 202.

6.4.1 Synthesis of poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene]

2-[4-(2′-Ethylhexyloxy)-2,5-dimethyl-phenyl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (2.21a):

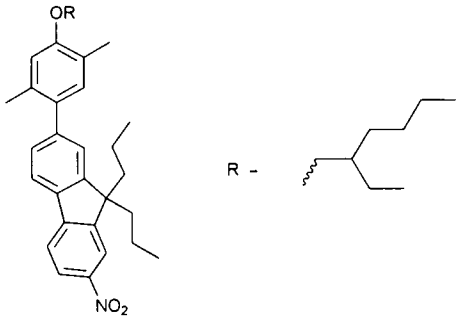


2.21a

t-Butyllithium (1.7 M in pentane, 100.0 mL, 170.0 mmol) was added to a solution of 1-bromo-4-(2′-ethylhexyloxy)-2,5-dimethylbenzene **2.3** (29.6 g, 94.5 mmol) in anhydrous tetrahydrofuran (250 mL) at -78 °C under argon,. The reaction mixture showed a colour change from colourless to yellow. The reaction mixture was stirred for 1 hour at -78 °C before the addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (25.0 mL, 120 mmol). The reaction mixture was further stirred at -78 °C for 15 minutes then at room temperature for 20 hours. The reaction mixture was quenched with water (200 mL) and the aqueous layer was extracted with ether (3 × 200 mL). The organic extracts were combined, washed with water (2 × 200 mL) and brine (250 mL), and dried over magnesium sulphate. The solution was filtered and solvent was removed. Purification of the crude by column chromatography over silica gel using light petroleum:dichloromethane mixture (3:1) as the eluent gave 2-[4-(2′-ethylhexyloxy)-2,5-dimethyl-phenyl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **2.21a**

(20.4 g, 34%) as a yellow oil. The compound had an identical ^{1}H n.m.r. and ^{13}C n.m.r. spectrum to that reported in the literature[161].

2-[4-(2′-Ethylhexyloxy)-2,5-dimethyl-phenyl]-7-nitro-9,9-dipropyl-9*H*-fluorene (2.23a):

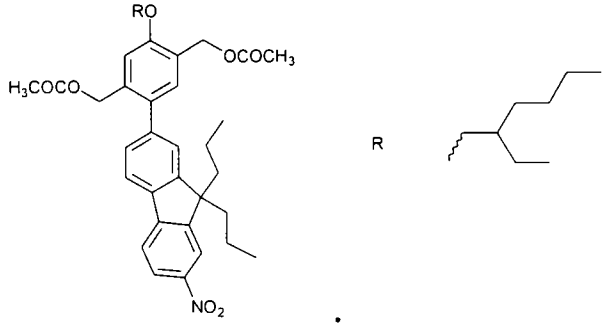


2.23a

Nitrogen was bubbled through a mixture of 2-[4-(2′-ethylhexyloxy)-2,5-dimethyl-phenyl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **2.21a** (18.3 g, 50.7 mmol), 2-bromo-7-nitro-9,9-di-*n*-propyl-9*H*-fluorene **2.16** (15.8 g, 42.3 mmol), and aqueous sodium carbonate (2 M, 100 mL) in toluene (100 mL) for 15 minutes before the addition of *tetrakis*(triphenylphosphine)palladium (0) (1.9 g, 1.7 mmol). The reaction mixture was heated at reflux for 48 hours. After allowing the reaction mixture to cool, aqueous hydrochloric acid (3 M, 100 mL) was added carefully. The aqueous layer was extracted with ether (3 × 100 mL) and organic extracts were combined. The organic layer was washed with water (3 × 100 mL) and brine (100 mL), dried over magnesium sulphate, filtered, and solvent was removed to give a yellow oil. Purification of the oil by column chromatography over silica gel using a gradient elution with light petroleum:dichloromethane mixture (1:0 to 4:1) as the eluent followed by recrystallisation from a dichloromethane/methanol mixture gave 2-[4-(2′-ethylhexyloxy)-2,5-dimethyl-phenyl]-7-nitro-9,9-dipropyl-9*H*-fluorene **2.23a** (16.2 g,

74%) as light yellow crystals, mp 115-117 °C. (Found: C, 79.71; H, 8.60; N, 2.66. $C_{35}H_{45}NO_3$ requires C, 79.66; H, 8.59; N, 2.65%); ν_{max} (KBr disc)/cm^{-1} 2924 (C–H), 1513 (NO_2 anti), and 1330 (NO_2 sym); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 366 (4.48), 266 (4.34), and 230 (4.29); δ_H ($CDCl_3$, 400 MHz) 0.64-0.78 (10 H, m, 2 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 0.92-1.05 (6 H, m, 2 × CH_3), 1.35-1.67 (8 H, m, 4 × CH_2), 1.78-1.86 (1 H, m, CH), 1.98-2.13 (4 H, m, 2 × $ArCH_2$), 2.29 (3 H, s, $ArCH_3$), 2.31 (3 H, s, $ArCH_3$), 3.94 (2 H, d, *J* 5, $ArOCH_2$), 6.80 (1 H, s, ArH), 7.12 (1 H, s, ArH), 7.37 (2 H, m, 2 × ArH), 7.82 (2 H, d, *J* 8, 2 × ArH), and 8.28 (2 H, dd, *J* 2, *J* 8, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 11.3, 14.1, 14.4, 15.8, 17.3, 20.6, 23.1, 24.1, 29.1, 30.7, 39.6, 42.4, 55.8, 70.2, 112.8, 118.3, 119.6, 120.8, 123.4, 124.3, 124.4, 128.8, 131.9, 133.2, 133.5, 136.9, 143.2, 146.9, 147.6, 152.0, 152.1, and 156.9; *m/z* (CI^+) 545 ($[MNH_4]^+$, 100%); Exact mass 527.3396. $C_{35}H_{45}NO_3$ requires 527.3399.

2-(2′-Ethylhexyloxy)-4-methylcarbonyloxymethyl-5-[2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)]benzyl acetate (2.25a):

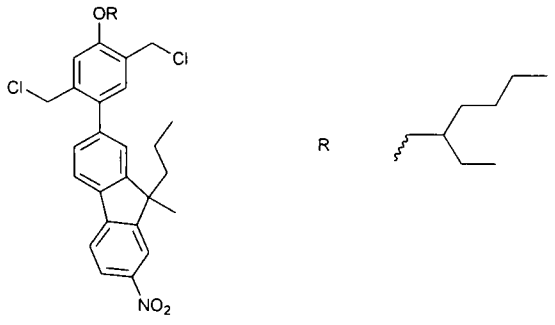


2.25a

A solution of 2-[4-(2′-ethylhexyloxy)-2,5-dimethyl-phenyl]-7-nitro-9,9-dipropyl-9*H*-fluorene **2.23a** (16.1 g, 30.5 mmol), *N*-bromosuccinimide (11.2 g, 62.9 mmol) in carbon tetrachloride (70 mL) was deoxygenated with argon for 10 minutes. 2,2′-Azo-*bis*(isobutyronitrile) (2.1 g, 12.6 mmol) was added and the reaction mixture was heated at reflux for 4 hours. The reaction mixture was allowed to cool to room

temperature, diluted with dichloromethane (30 mL) and passed through a silica plug using dichloromethane as eluent. The solvent was removed and the residue was taken up in glacial acetic acid (70 mL). Sodium acetate (27.8 g, 0.32 mol) was added and the reaction mixture was heated at reflux for 5 hours. After cooling, water (50 mL) was added to the reaction mixture and the aqueous layer was extracted with ether (3 × 75 mL). The combined organic extracts were washed with aqueous sodium hydroxide (5% w/v, 50 mL, water (3 × 150 mL), and a saturated solution of sodium bicarbonate (3 × 50 mL). The solution was dried over magnesium sulphate, filtered and solvent was removed to give a brown solid. Purification of the crude by flash chromatography using a gradient elution with light petroleum:dichloromethane mixture (1:1 to 0:1) followed by recrystallisation from a dichloromethane/methanol mixture gave 2-(2′-ethylhexyloxy)-4-methylcarbonyloxymethyl-5-[2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)]benzyl acetate **2.25a** (8.6 g, 42%) as yellow crystals, mp 103.5-104.5 °C. (Found: C, 72.88; H, 7.68; N, 2.18. $C_{39}H_{49}NO_7$ requires C, 72.76; H, 7.67; N, 2.18%); ν_{max} (KBr disc)/cm^{-1} 1730 (C=O); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/$dm^3mol^{-1}cm^{-1}$) 359 (4.40), 262 (4.22) and 228 (4.28); δ_H ($CDCl_3$, 400 MHz) 0.68-0.75 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 0.94-1.01 (6 H, m, 2 × CH_3), 1.34-1.58 (8 H, m, 4 × CH_2), 1.75-1.84 (1 H, m, CH), 1.98-2.08 (4 H, m, 2 × $ArCH_2$), 2.27 (3 H, s, $OCOCH_3$), 2.28 (3 H, s, $OCOCH_3$), 3.98 (2 H, d, *J* 5, $ArOCH_2$), 5.04 (2 H, s, CH_2O), 5.22 (2 H, s, CH_2O), 7.07 (1 H, s, ArH), 7.38 (3 H, m, 3 × ArH), 7.83 (2 H, d, *J* 8, 2 × ArH), and 8.28 (2 H, dd, *J* 2, *J* 8, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 11.3, 14.1, 14.3, 17.2, 21.0, 21.1, 23.1, 24.0, 29.1, 30.6, 39.4, 42.4, 55.8, 61.7, 64.6, 70.4,112.8, 118.3, 119.8, 121.0, 123.4, 124.3, 124.8, 128.7, 131.4, 134.2, 134.3, 137.7, 141.0, 147.1, 147.2, 152.1, 152.3, 156.8, 170.5, and 170.9; *m/z* (CI^+) 661 ($[MNH_4]^+$, 41%) and 584 ($[M\text{-}OCOCH_3]^+$, 100%); Exact mass 643.1361. $C_{39}H_{49}NO_7$ requires 643.3509.

2-[2,5-*Bis*-chloromethyl-4-(2′-ethylhexyloxy)-phenyl]-7-nitro-9,9-dipropyl-9*H*-fluorene (2.26a):

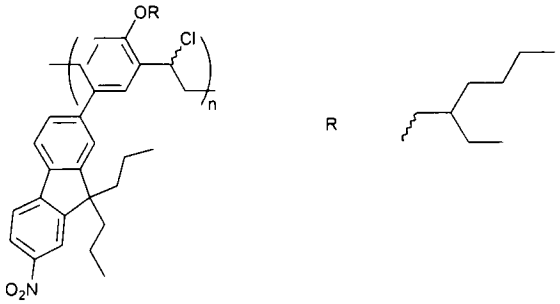


2.26a

A mixture of 2-(2′-ethylhexyloxy)-4-methylcarbonyloxymethyl-5-[2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)]benzyl acetate **2.25a** (7.4 g, 11.5 mmol) and concentrated hydrochloric acid (35%, 160 mL) in 1,4-dioxane (160 mL) was heated at reflux under nitrogen for 18 hours. On cooling, the aqueous layer was separated and extracted with ether (3 × 50 mL). The organic extracts were combined and washed with aqueous sodium hydroxide solution (5% w/v, 50 mL), water (3 × 100 mL), saturated solution of sodium bicarbonate (2 × 50 mL) and brine (50 mL). The organic layer was dried over magnesium sulphate, filtered and concentrated under vacuum. Column chromatography of the crude over silica gel using a light petroleum:dichloromethane mixture (1:1) as the eluent gave a yellow solid (6.0 g). Further purification by recrystallisation from a dichloromethane/methanol mixture gave 2-[2,5-*bis*-chloromethyl-4-(2′-ethylhexyloxy)-phenyl]-7-nitro-9,9-dipropyl-9*H*-fluorene **2.26a** (5.6 g, 83%) as yellow crystals, mp 84-85 °C. λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/$dm^3mol^{-1}cm^{-1}$) 356 (4.52), 258 sh (4.34), 239 sh (4.47), and 227 (4.51); ν_{max} (KBr disc)/cm^{-1} 741 (C–Cl); δ_H ($CDCl_3$, 400 MHz) 0.67-0.79 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 0.95-1.06 (6 H, m, 2 × CH_3), 1.36-1.77 (8 H, m, 4 × CH_2), 1.83-1.89 (1 H, m, CH), 2.06-2.14 (4 H, m, 2 × $ArCH_2$), 4.04 (2 H, d, *J* 5, $ArOCH_2$), 4.53 (2 H, s, CH_2Cl), 4.72 (2 H, s, CH_2Cl),

7.12 (1 H, s, ArH), 7.44 (2 H, dd, *J* 8, *J* 2, 2 × ArH), 7.57 (1 H, s, ArH), 7.87 (2 H, m, *J* 8, 2 × ArH), and 8.30 (2 H, dd, *J* 8, *J* 2, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 11.3, 14.1, 14.3, 17.3, 23.1, 24.1, 29.1, 30.6, 39.5, 41.2, 42.4, 44.6, 56.0, 70.6,113.2, 118.3, 119.9, 121.1, 123.4, 124.3, 126.7, 128.6, 132.1, 134.1, 136.5, 137.9, 140.6, 147.2, 152.2, 152.5, and 156.8; *m/z* (CI^+) 615, 613 ($[MNH_4]^+$, 9%, 11%), 600, 598, 596 (MH^+, 8%, 47%, 61%), and 560 ($[M-Cl]^+$, 100%); Exact mass 595.2602. $C_{35}H_{43}Cl_2NO_3$ requires 595.2620.

Poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-(2′-ethylhexyloxy)-1,4-phenylene(1-chloroethylene)] (2.29):

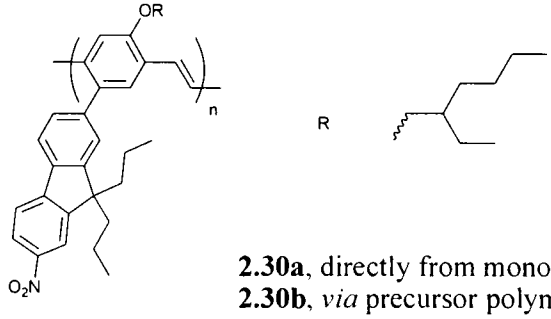


2.29

Potassium *t*-butoxide (0.1 M, 0.45 mL, 0.045 mmol) in dry tetrahydrofuran was added to a stirred solution of 2-[2,5-*bis*-chloromethyl-4-(2′-ethylhexyloxy)-phenyl]-7-nitro-9,9-dipropyl-9*H*-fluorene **2.26a** (30 mg, 0.050 mmol) in dry tetrahydrofuran (0.5 mL) at room temperature under nitrogen. After 3.5 hours, the reaction mixture was filtered through a cotton-wool plug in ice-cold methanol (2 mL). The mixture was centrifuged (4500 r.p.m., 5 minutes), the supernatant was decanted and the residue obtained was dissolved in tetrahydrofuran (0.5 mL). The solution was precipitated in ice-cold methanol (1 mL) and the mixture centrifuged and a light yellow solid of poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-(2′-ethylhexyloxy)-1,4-phenylene(1-chloroethylene)] **2.29** (~ 28 mg, ~ 31%) was dissolved in tetrahydrofuran (3 mL). ν_{max} (film, KBr

disc)/cm^{-1} 1523 (NO_2 anti),1336 (NO_2 sym), and 742 (C–Cl); λ_{max} (film)/nm 352, 236 sh, and 207; δ_H ($CDCl_3$, 400 MHz) 0.29-2.07 (29 H, br, m, 2 × $ArCH_2C\underline{H_2}C\underline{H_3}$, 2 × CH_3, 4 × CH_2 , CH, 2 × $ArCH_2$), 3.01-4.02 (br m, $ArOCH_2$), 4.78-5.53 (1 H, br m, CHCl), 6.7-8.0 (6 H, br m, 6 × ArH), and 8.12-8.56 (2 H, br m, 2 × ArH); $\overline{M}_w = 6.0 \times 10^5$, $\overline{M}_n = 7.4 \times 10^4$, and PD = 8.1; Thermogravimetric analysis: 143 °C (theoretical weight loss: 6%, expected weight loss: 7%) .

Poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (2.30a/b):



2.30a, directly from monomer **2.26a**
2.30b, *via* precursor polymer **2.29**

2.30a / b

Method 1. Potassium *t*-butoxide (660 mg, 5.9 mmol) solution in dry tetrahydrofuran (58.6 mL) was added to a stirred solution of 2-[2,5-*bis*-chloromethyl-4-(2′-ethylhexyloxy)-phenyl]-7-nitro-9,9-dipropyl-9*H*-fluorene **2.26a** (0.7 g, 1.2 mmol) in dry tetrahydrofuran (23.4 mL) at room temperature under nitrogen. The reaction mixture was stirred in dark for 3.5 hours. The solution was precipitated in ice-cold methanol (100 mL), centrifuged (4500 r.p.m., 5 minutes) and the supernatant was decanted. The residue was taken up in tetrahydrofuran (50 mL), dissolved and filtered through cotton-wool plug before precipitating again in ice-cold methanol (40 mL). The process of redissolution, and precipitation was repeated once more. The final residue obtained was dried under vacuum for 16 hours to give poly[2-(7-nitro-9,9-

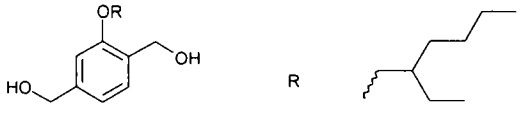
dipropylfluorenyl)-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] **2.30a** (284 mg, 46%) as yellow solid. ν_{max} (film, KBr disc)/cm^{-1} 965 (C=C–H trans), 1523 (NO_2 anti), and 1338 (NO_2 sym); λ_{max} (film)/nm 422 sh, 352, 236 sh, and 204; δ_H ($CDCl_3$, 400 MHz) 0.28-2.08 (29 H, br m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$, 2 × CH_3, 4 × CH_2, CH, 2 × $ArCH_2$), 3.68-4.12 (2 H, br d, $ArOCH_2$), 6.78-7.92 (7 H, br m, vinylH, 7 × ArH), and 8.08-8.52 (2 H, br m, 2 × ArH); $\overline{M}_w$ = 3.2 × 10^5, $\overline{M}_n$ = 0.5 × 10^5, and PD = 7.0; Thermogravimetric analysis: 310 °C (Temperature of degradation)

Method 2: Thin films of poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-(2'-ethylhexyloxy)-1,4-phenylene(1-chloroethylene)] **2.29** were heated at 160 °C for 17 hours under a dynamic vacuum to give poly[2-(7-nitro-9,9-dipropylfluorenyl)-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] **2.30b**. ν_{max} (film, KBr disc)/cm^{-1}) 1523 (NO_2 anti), 1338 (NO_2 sym), and 969 (C=C–H trans); λ_{max} (film)/nm 460, 350, 236 sh, and 201.

6.3 Experimental for Chapter 3

6.5.1 Synthesis of poly{2-[7-(9,9-dipropylfluorenyl)-9,9-dipropylfluorenyl]-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene}

1,4-*Bis*(hydroxymethyl)-2-(2′-ethylhexyloxy)benzene 3.1:

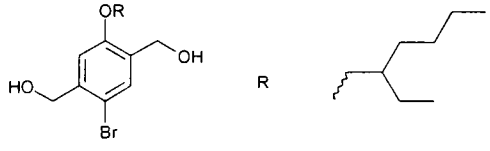


3.1

Argon was bubbled through a mixture of 2-(2′-ethylhexyloxy)-1,4-dimethylbenzene **2.2** (50.0 g, 0.2 mol), and *N*-bromosuccinimide (76.0 g, 0.4 mol) in carbon tetrachloride (1 L) for 30 minutes before the addition of 2,2′-azo-*bis*(isobutyronitrile) (14.0 g, 85.0 mmol). The reaction mixture was heated at reflux for 4 hours. After allowing the reaction to cool, the reaction mixture was passed through a silica plug using dichloromethane as the eluent. The filtrate was concentrated to give crude 1,4-*bis*(bromomethyl)-2-(2′-ethylhexyloxy)benzene (65.0 g) as a yellow oil. The mixture of yellow residue (65.0 g) and sodium acetate (104.8 g, 1.2 mol) in glacial acetic acid (500 mL) was heated at reflux for 5 hours under argon. After allowing the reaction mixture to cool, solvent was removed.and the residue obtained was dissolved in ether (200 mL). The organic layer was washed with water (2 × 250 mL), aqueous sodium hydroxide (5% w/v, 2 × 100 mL), saturated solution of sodium bicarbonate (100 mL), and brine (250 mL). The ethereal extract was dried over magnesium sulphate, filtered, and the solvent was removed. A preliminary purification of the crude was carried out by column chromatography over silica gel using a gradient

elution with light petroleum:ethyl acetate (40:1 to 10:1) to give 1,4-*bis*(acetoxymethyl)-2-(2′-ethylhexyloxy)benzene (65.0 g) as a yellow oil. A suspension of the crude *bis*-acetate in aqueous potassium hydroxide solution (10 M, 85 mL), methanol (170 mL), and dichloromethane (85 mL) was stirred at room temperature for 19 hours. The solvent was removed and residue was dissolved in ether (200 mL). The organic layer was washed with water (2 × 200 mL), aqueous hydrochloric acid (3 M, 2 × 100 mL), and brine (100 mL). The ethereal extract was dried over magnesium sulphate, filtered, and the solvent was removed. Purification of the crude by column chromatography over silica gel using a light petroleum:dichloromethane:ethyl acetate mixture (1:0:50 then 0:10:1), followed by a methanol:dichloromethane mixture (1:25) as eluent gave 1,4-*bis*(hydroxymethyl)-2-(2′-ethylhexyloxy)benzene **3.1** (19.5 g, 35%) as a light yellow oil. The compound had an identical ^{1}H n.m.r. and ^{13}C n.m.r. spectrum to an authentic sample[129].

[5-Bromo-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol 3.2:



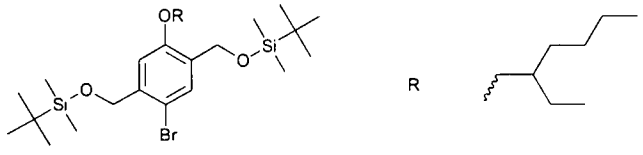
3.2

Method 1: A mixture of 1,4-*bis*(hydroxymethyl)-2-(2′-ethylhexyloxy)benzene **3.1** (13.3 g, 50.0 mmol) and *N*-bromosuccinimide (9.8 g, 55.0 mmol) in anhydrous *N,N*-dimethylformamide (50 mL) was stirred at room temperature for 20 hours under nitrogen in dark. The reaction mixture was poured in water (500 mL) and the precipitate obtained was collected by filtration and washed with water (2 × 200 mL). Purification of the precipitate by recrystallisation from methanol/water mixture gave [5-bromo-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **3.2** (11.5 g, 66%)

as a white solid, mp 115-116 °C. ν_{max} (KBr disc)/cm^{-1} 3307 (O–H), and 762 (C–Br); λ_{max} (CH_3OH)/nm ($\log_{10}\varepsilon/dm^3mol^{-1}cm^{-1}$) 285 (4.32), and 229 (4.34); δ_H ($(CD_3)_2SO$, 400 MHz) 0.85-0.90 (6 H, m, 2 × CH_3), 1.22-1.49 (8 H, m, 4 × CH_2), 1.65-1.70 (1 H, m, CH), 3.17 (2 H, d, *J* 5, $ArOCH_2$), 4.16 (4 H, t, *J* 6, 2 × $C\underline{H}_2OH$), 5.18 (1 H, t, *J* 6, $CH_2O\underline{H}$), 5.45 (1 H, t, *J* 6, $CH_2O\underline{H}$), 7.10 (1 H, s, ArH), and 7.46 (1 H, s, ArH); δ_C ($(CD_3)_2SO$, 100 MHz) 11.8, 14.8, 23.3, 24.3, 29.3, 30.9, 39.5, 49.4, 58.0, 63.4, 70.8, 111.6, 130.3, 132.1, 140.7, and 155.6. *m/z* (Cl^+) 362 ($[MNH_4]^+$, 4%), and 347, 345 (MH^+, 98%, 100%); Exact mass 344.0983. $C_{16}H_{25}O_3Br$ requires 344.0987.

Method 2: Bromine (5.6 mL, 0.11 mmol) was added to a mixture of 1,4-*bis*(hydroxymethyl)-2-2′-ethylhexyloxy)benzene **3.1** (28.8 g, 0.11 mmol) in methanol (450 mL) and glacial acetic acid (150 mL), and stirred at room temperature for 20 hours under nitrogen in dark. The reaction mixture was quenched with a saturated solution of sodium metabisulphite (50 mL). The precipitate obtained was filtered and washed with water (2 L). The precipitate was triturated with light petroleum (300 mL), filtered and washed with light petroleum (150 mL). The solid was dried under vacuum for 24 hours to give [5-bromo-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **3.2** (33.5, 90%) as a white solid, mp 115-116 °C. δ_H ($(CD_3)_2SO$, 400 MHz) 0.85-0.90 (6 H, m, 2 × CH_3), 1.22-1.49 (8 H, m, 4 × CH_2), 1.65-1.70 (1 H, m, CH), 3.17 (2 H, d, *J* 5, $ArOCH_2$), 4.16 (4 H, t, *J* 6, 2 × $C\underline{H}_2OH$), 5.18 (1 H, t, *J* 6, $CH_2O\underline{H}$), 5.45 (1 H, t, *J* 6, $CH_2O\underline{H}$), 7.10 (1 H, s, ArH), and 7.46 (1 H, s, ArH).

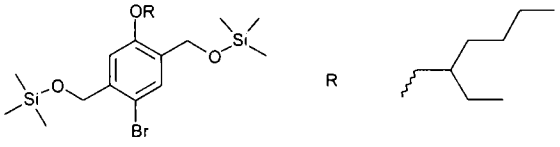
1-Bromo-2,5-*bis*-(*t*-butyl-dimethyl-silanyloxymethyl)-4-(2'-ethylhexyloxy)-benzene 3.3:



3.3

Imidazole (78 mg, 6.8 mmol) and *t*-butyldimethylsilyl trifluoromethanesulphonate (0.1 mL, 0.4 mmol) were added to a solution of [5-bromo-2-(2'-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **3.2** (60 mg, 0.2 mmol) in anhydrous *N,N*-dimethylformamide (5 mL) under nitrogen. The reaction mixture was stirred at room temperature for 16 hours. Water (5 mL) was added and the aqueous layer was extracted with ether (3 × 5 mL). The organic layers were combined, washed with water (2 × 5 mL) and brine (5 mL), and dried over magnesium sulphate. Filtration and solvent removal gave brown oil. Purification of the residue by flash chromatography over silica gel using a light petroleum:dichloromethane mixture (6:3) as eluent gave 1-bromo-2,5-*bis*-(*t*-butyl-dimethyl-silanyloxymethyl)-4-(2'-ethylhexyloxy)-benzene **3.3** (0.9 g, 89%) as a colourless oil. ν_{max} (KBr disc)/cm^{-1} 1254 (Si–CH_3), and 1091 (O–Si); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 285 (3.39), and 231 (4.11); δ_H ($CDCl_3$, 500 MHz) 0.19 (6 H, s, 2 × $SiCH_3$), 0.20 (6 H, s, 2 × $SiCH_3$), 0.92-1.08 (24 H, m, 2 × $SiC(CH_3)_3$, 2 × CH_3), 1.32-1.57 (8 H, m, 4 × CH_2), 1.78-1.83 (1 H, m, CH), 3.93 (2 H, d, *J* 6, $ArOCH_2$), 4.83 (4 H, s, 2 × $ArCH_2OSi$), 7.12 (1 H, s, ArH), and 7.62 (1 H, s, ArH); δ_C ($CDCl_3$, 125 MHz) -5.6, -5.4, -5.3, -5.2, -5.1, 11.1, 14.1, 18.1, 18.7, 22.7, 23.2, 24.1, 24.5, 25.6, 29.7, 31.9, 39.2, 59.5, 64.7, 70.4, 110.2, 111.0, 130.1, 130.3, 139.1, and 154.9. *m/z* (FI^+) 574, and 572 (M^+, 100%, 88%).

1-Bromo-4-(2′-ethylhexyloxy)-2,5-*bis*-trimethylsilanyloxymethyl-benzene 3.5:



3.5

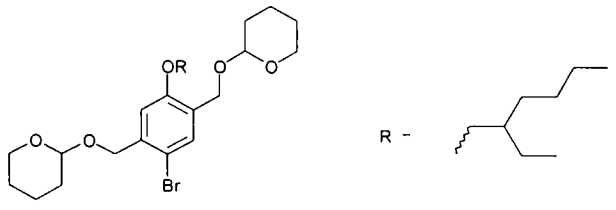
Method 1: A mixture of [5-bromo-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **3.2** (0.2 g, 0.6 mmol), imidazole (0.3 g, 4.2 mmol), and 4-*N,N*-dimethylaminopyridine (ca. 3 mg, 4 mol%) in anhydrous dichloromethane (15 mL) and tetrahydrofuran (10 mL) was stirred for 15 minutes at room temperature under nitrogen. A solution of chlorotrimethylsilane (0.3 mL, 2.3 mmol) in anhydrous dichloromethane (5 mL) was added drop-wise. The reaction mixture was heated at reflux for 15 hours. On cooling, water (10 mL) was added and the organic layer was separated. The organic layer was washed with water (2 × 5 mL) and brine, dried over magnesium sulphate and filtered. The solvent was removed to give a yellow oil. ^{1}H n.m.r. analysis revealed product (40 mg, 2%) present where the rest was un-reacted reactant (0.18 g, 89%) along with other by-products.

Method 2: Sodium hydride (60% dispersion in oil, 60 mg, 2.3 mmol) was added in portion-wise to a solution of [5-bromo-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **3.2** (0.2 g, 0.6 mmol) in tetrahydrofuran (10 mL). The reaction mixture was stirred at room temperature for 15 minutes before the addition of chlorotrimethylsilane (0.2 mL, 1.5 mmol). After 2 hours, only starting material was observed by t.l.c. analysis of the crude. An extra amount of sodium hydride (60% dispersion in oil, 60 mg, 2.3 mmol) was added to the reaction mixture, followed by the further addition of chlorotrimethylsilane (0.2 mL, 1.5 mmol). The reaction mixture was further stirred at room temperature for 17 hours. The reaction mixture was

concentrated and passed through a celite plug using ethyl acetate as eluent. ^{1}H n.m.r. analysis showed the presence of starting material (0.19 g, 97%).

Method 3: A solution of 1,1,1,3,3,3-hexamethyldisilazane (3.5 mL, 16.5 mmol) in anhydrous dichloromethane (10 mL) was added drop-wise to a solution of [5-bromo-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **3.2** (1.9 g, 5.5 mmol) and iodine (30 mg, 0.1 mmol) in anhydrous dichloromethane (15 mL) and tetrahydrofuran (5 mL). The reaction mixture was heated at reflux for 24 hours under nitrogen. After allowing the reaction mixture to cool, a saturated solution of sodium metabisulphite (10 mL) was added. The aqueous layer was separated and extracted with ether (2 × 20 mL). The organic layers were combined, washed with water (2 × 20 mL) and brine (10 mL), dried over magnesium sulphate, and filtered. The solvent removal gave a yellow oil. Purification of the residue by column chromatography over silica gel using a light petroleum:ethyl acetate mixture (7:1) as eluent gave 1-bromo-4-(2′-ethylhexyloxy)-2,5-*bis*-trimethylsilanyloxymethyl-benzene **3.5** (2.5 g, 92%) as a yellow oil. ν_{max} (KBr disc)/cm^{-1} 1256 (Si–CH_3) and 1019 (O–Si); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 286 (3.26), and 234 (4.01); δ_H ($CDCl_3$, 400 MHz) 0.18 (9 H, s, 3 × $SiCH_3$), 0.21 (9 H, s, 3 × $SiCH_3$), 0.92-0.97 (6 H, m, 2 × CH_3), 1.32-1.54 (8 H, m, 4 × CH_2), 1.72-1.81 (1 H, m, CH), 3.82 (2 H, d, *J* 6, $ArOCH_2$), 4.69 (4 H, s, 2 × $ArCH_2OSi$), 7.03 (1 H, s, ArH), and 7.53 (1 H, s, ArH); δ_C ($CDCl_3$, 100 MHz) -0.8, -0.7, -0.5, -0.4, -0.2, -0.1, 11.2, 14.1, 23.1, 24.1, 29.1, 30.7, 39.3, 58.9, 64.3, 70.4, 110.3, 111.2, 130.2, 130.4, 139.0, and 155.1; *m/z* (EI^+) 490, and 488 (M^+, 100%, 90%); Exact mass 488.1786. $C_{24}H_{41}BrO_3Si_2$ requires 488.1772.

2-[5-Bromo-2-(2′-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxy]tetrahydro-2*H*-pyran 3.9:



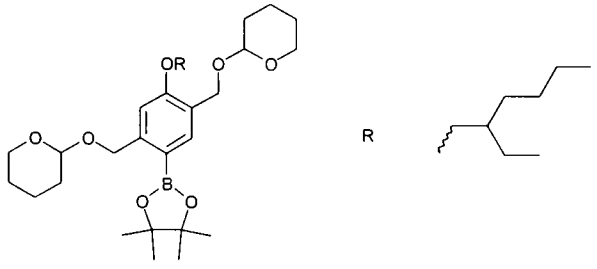
3.9

Method 1: 3,4-Dihydropyran (0.7 mL, 7.2 mmol) and *p*-toluenesulphonic acid monohydrate (55 mg, 4 mol%) was added to a solution of [5-bromo-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **3.2** (1.0 g, 2.9 mmol) in anhydrous tetrahydrofuran (20 mL) at room temperature. The reaction mixture was stirred at room temperature for 16 hours under nitrogen. Water (30 mL) was added and the aqueous phase was extracted with ether (2 × 40 mL). The combined organic layers were washed with aqueous sodium hydroxide (5% w/v, 10 mL), water (2 × 20 mL), and brine (20 mL). The organic extract was dried over magnesium sulphate, filtered and the solvent was removed. Preliminary purification of the crude product by column chromatography over silica gel using dichloromethane as eluent gave crude 2-[5-bromo-2-(2′-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxy]tetrahydro-2*H*-pyran **3.9** as a yellow oil. Further purification was carried out by column chromatography using a light petroleum:ether mixture (9:1) as eluent to give 2-[5-bromo-2-(2′-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxy]tetrahydro-2*H*-pyran **3.9** (1.5 g, 82%) as a clear colourless oil.

Method 2: 3,4-Dihydropyran (0.35 mL, 3.6 mmol) was added to a solution of [5-bromo-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **3.2** (0.5 g, 1.5

mmol) and pyridinium-*p*-toluene sulphonate (15 mg, 4 mol%) in anhydrous tetrahydrofuran (20 mL). The reaction mixture was stirred at room temperature for 18 hours under nitrogen. Water (30 mL) was added and the aqueous phase was extracted with ether (2 × 40 mL). The combined ethereal extracts were washed with water (2 × 20 mL) and brine (20 mL), dried over magnesium sulphate, filtered and the solvent was removed. Preliminary purification by column chromatography over silica gel using dichloromethane as eluent gave crude 2-[5-bromo-2-(2′-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxy]tetrahydro-2*H*-pyran as a yellow oil. The yellow oil was further purified by column chromatography using a light petroleum:ether mixture (9:1) as eluent to give 2-[5-bromo-2-(2′-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxy]tetrahydro-2*H*-pyran **3.9** (0.7 g, 92%) as a clear oil. (Found: C, 60.86; H, 8.05. $C_{26}H_{41}O_5Br$ requires C, 60.81; H, 8.05%); ν_{max} (KBr disc)/cm^{-1} 1160 (O–C–O); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 286 (4.02), and 232 (5.28); δ_H ($CDCl_3$, 400 MHz) 0.86-0.98 (6 H, m, 2 × CH_3), 1.26-1.98 (21 H, m, 10 × CH_2, CH), 3.52-3.61 (2 H, m, -OCH_2(THP)), 3.64-3.78 (2 H, m, *J* 5.5, ArOCH_2), 3.84-4.00 (2 H, m, -OCH_2(THP)), 4.52-4.60 (2 H, q, Ar$C\underline{H}_2O$), 4.72-4.84 (4 H, m, Ar$C\underline{H}_2O$, 2 × -OCH (THP)), 7.00 (1 H, s, ArH), and 7.55 (1 H, s, ArH); δ_C ($CDCl_3$, 100 MHz) 11.2, 14.1, 19.3, 19.5, 23.0, 23.9, 25.4, 25.5, 29.1, 30.5, 30.6, 39.3, 61.9, 62.4, 63.4, 68.7, 70.4, 98.3, 98.4, 111.7, 112.6, 128.2, 131.8, 137.3, and 155.9; *m/z* (CI^+) 532, and 530 ($[MNH_4]^+$, 100%, 98%); Exact mass 530.2479. $C_{26}H_{45}NO_5Br$ $[MNH_4]^+$ requires 530.2481.

2-[2-(2′-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyloxy]tetrahydro-2*H*-pyran 3.10:

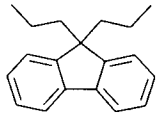


3.10

t-Butyllithium (4.3 mL, 7.4 mmol) was added to a stirred solution of 2-[5-bromo-2-(2′-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxy]tetrahydro-2*H*-pyran **3.9** (3.0 g, 5.7 mmol) in dry ether (100 mL) at -78 °C under nitrogen. The reaction mixture colour changed from colourless to yellow. After 30 minutes 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.5 mL, 7.4 mmol) was added to the mixture and the reaction was stirred at -78 °C for 15 minutes, and then at room temperature for 2 hours. Water (100 mL) was added and the aqueous layer was extracted with ether (3 × 75 mL). The combined organic extracts were washed with water (2 × 50 mL) and brine (50 mL), dried over magnesium sulphate and filtered. Solvent removal gave a yellow oil. The crude product was purified by column chromatography over silica gel using a gradient elution with a light petroleum:ethyl acetate mixture (5:0.75 to 5:1) to give 2-[2-(2′-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyloxy]tetrahydro-2*H*-pyran **3.10** (3.0 g, 91%) as a colourless oil. ν_{max} (KBr disc)/cm^{-1} 1340 (B–O); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 273sh (3.94), and 248 (4.22); δ_H ($CDCl_3$, 400 MHz) 0.86-0.98 (6 H, m, 2 × CH_3), 1.34 (12 H, s, 4 × $C(CH_3)$), 1.42-1.98 (21 H, m, 10 × CH_2, CH), 3.52-3.61 (2 H, m, -OCH_2(THP)), 3.92-4.00 (4 H, m, $ArOCH_2$, OCH_2(THP)), 4.48-4.58 and 4.72-4.90 (6 H, m, 2 × $ArC\underline{H}_2O$,

2 × -OCH (THP)), 7.05 (1 H, s, ArH), and 7.81 (1 H, s, ArH); δ_C ($CDCl_3$, 100 MHz) 11.2, 14.1, 19.3, 19.7, 23.1, 23.9, 24.8, 25.6, 29.1, 30.5, 30.8, 39.4, 61.8, 62.3, 64.4, 68.7, 70.0, 83.2, 98.4, 110.8, 124.7, 137.9, 146.8, and 159.6. *m/z* (EI^+) 560 (M^+, 5%) and 514 ($[M-46]^+$, 100%); Exact mass 560.3884. $C_{32}H_{53}BO_7$ requires 560.3884.

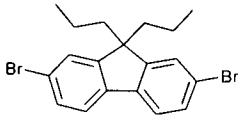
9,9-Dipropyl-9H-fluorene 3.12:



3.12

Potassium *t*-butoxide (61.0 g, 0.5 mol) was added portion-wise to a stirred solution of fluorene **3.11** (30.0 g, 150.0 mmol) in dimethyl sulphoxide (180 mL) at room temperature under argon. The colour of the reaction mixture changed from colourless to purple. The reaction mixture was heated to 45 °C for 1 hour before the drop-wise addition of *n*-propyl bromide (40 mL, 0.4 mol) and was then further stirred at 45 °C for 19 hours. After allowing the reaction mixture to cool, the reaction mixture was acidified using aqueous hydrochloric acid (3 M, 100 mL) to pH 1 and the aqueous layer was extracted with ether (3 × 120 mL). The combined organic layers were washed with water (3 × 200 mL) and brine (100 mL), dried over magnesium sulphate and filtered. The solvent was removed to give a yellow oil. Purification of the residue by filtering through a silica plug using light petroleum as eluent followed by recrystallisation from methanol (r.t. → -18 °C) gave 9,9-dipropyl-9*H*-fluorene **3.12** (27.6 g, 61%) as a white solid, mp 36-37 °C (lit.,[162] 37-38 °C). The compound had an identical ^1H n.m.r. to that reported in the literature[163].

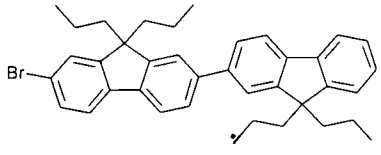
2,7-Dibromo-9,9-dipropyl-9H-fluorene 3.13.



3.13

Bromine (10.8 mL, 0.2 mol) was added to a solution of 9,9-dipropyl-9H-fluorene **3.12** (21.8 g, 87.7 mmol) in chloroform (200 mL) and the reaction mixture was stirred at room temperature for 4 hours. A saturated aqueous solution of sodium metabisulphite (100 mL) was added and the aqueous layer was extracted with chloroform (3 × 50 mL). The organic layers were combined, washed with water (2 × 100 mL) and brine (100 mL), and dried over magnesium sulphate. The solution was filtered and the solvent was removed to give a yellow solid (40.8 g). Purification of the residue by recrystallisation from ethanol/dichloromethane mixture gave 2,7-dibromo-9,9-dipropyl-9H-fluorene **3.13** (31.1 g, 87%) as a white solid, mp 136-138 °C (lit.,[163] 137-137.5 °C). The compound had an identical ^{1}H n.m.r. to that reported in the literature[163].

7-Bromo-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl 3.14:

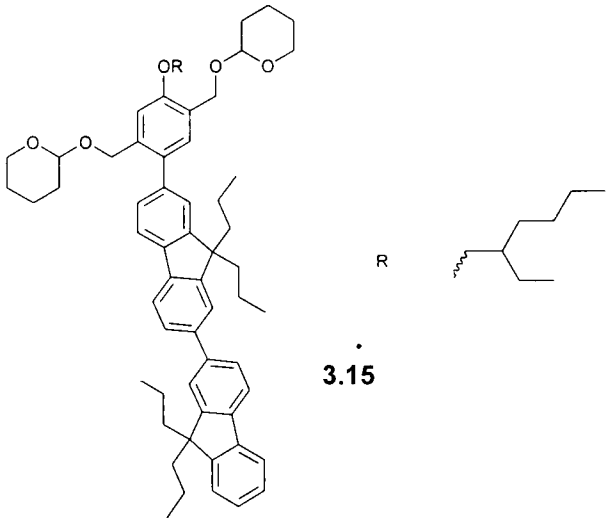


3.14

Tetrakis(triphenylphosphine)palladium (0) (1.2 g, 1.0 mmol) was added to a nitrogen purged suspension of 2,7-dibromo-9,9-dipropyl-9*H*-fluorene **3.13** (11.2, 27.3 mmol), 9,9-di-*n*-propylfluorenyl-2-boronic acid **2.6** (6.0 g, 16.1 mmol) and aqueous sodium carbonate (2 M, 100 mL) in toluene (150 mL). The reaction mixture was heated at reflux for 48 hours. After allowing the reaction mixture to cool, the organic layer was

separated, washed with aqueous hydrochloric acid (3 M, 50 mL), water (2 × 100 mL) and brine (100 mL), and dried over magnesium sulphate. The solution was filtered and concentrated to give a brown solid. The crude product was purified by filtering through a silica plug using light petroleum as eluent to recover unreacted 2,7-dibromo-9,9-dipropyl-9*H*-fluorene **3.13** (4.9 g, 44%), followed by elution with a light petroleum:dichloromethane mixture (49:1) gave crude 7-bromo-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl as a white solid (6.9 g). Further purification by recrystallisation from dichloromethane/methanol mixture gave 7-bromo-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl **3.14** (6.5 g, 69%) as white crystals. The compound had an identical ^{1}H n.m.r. to that reported in the literature[164].

2-[2-[7-(9,9-dipropyl-9*H*-2-fluorenyl)-9,9-dipropyl-9*H*-2-fluorenyl]-5-(2'-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxy]tetrahydro-2*H*-pyran 3.15:

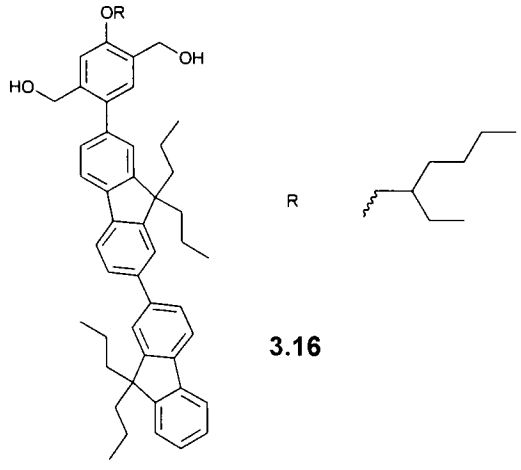


3.15

Tetrakis(triphenylphosphine)palladium (0) (0.4 g, 0.4 mmol) was added to a nitrogen purged suspension of 7-bromo-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl (4.2 g, 7.3 mmol) **3.14**, 2-[2-(2'-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethyl-5-

(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyloxy]tetrahydro-2*H*-pyran **3.10** (3.5 g, 6.1 mmol) and sodium carbonate solution (2 M, 150 mL) in toluene (150 mL) under nitrogen. The reaction mixture was heated at reflux for 20 hours. After allowing the reaction mixture to cool to room temperature the organic layer was separated, and washed with aqueous hydrochloric acid (3 M, 50 mL) and water (3 × 75 mL), and dried over magnesium sulphate. The solution was filtered and solvent removal gave black oil. Purification of the residue by flash chromatography over silica gel using dichloromethane as eluent gave 2-[2-[7-(9,9-dipropyl-9*H*-2-fluorenyl)-9,9-dipropyl-9*H*-2-fluorenyl]-5-(2'-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxy]tetrahydro-2*H*-pyran **3.15** (3.2 g, 46%) as a white solid, mp 59-60 °C. (Found: C, 82.47; H, 8.80. $C_{64}H_{82}O_5$ requires C, 82.54; H, 8.87%); ν_{max} (KBr disc)/cm^{-1} 1121 (O–C–O); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon/dm^3mol^{-1}cm^{-1}$) 338 (5.05) and 313 sh (4.68); δ_H ($CDCl_3$, 400 MHz) 0.58-0.89 (20 H, m, 4 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 0.92-1.03 (6 H, m, 2 × CH_3), 1.34-1.55 (20 H, m, 10 × CH_2), 1.88-1.95 (1 H, m, CH), 1.96-2.16 (8 H, m, 4 × $ArCH_2$), 3.48-3.65 (2 H, m, -OCH_2(THP)), 3.82-4.08 (4 H, m, $ArOCH_2$, -OCH_2(THP)), 4.47-4.52, 4.64-4.72 and 4.78-4.93 (6 H, m, 2 × $ArC\underline{H_2}O$, 2 × -OCH (THP)), 6.21 (1 H, s, ArH), 7.34 (6 H, m, 6 × ArH), 7.46 (1 H, s, ArH), and 7.67 (4 H, m, 4 × ArH); δ_C ($CDCl_3$, 100 MHz) 11.2, 14.2, 14.6, 17.3, 17.4, 19.5, 19.7, 23.1, 24.0, 25.5, 25.6, 29.2, 30.7, 30.9, 39.5, 42.8, 55.4, 62.1, 62.4, 64.2, 67.5, 70.3, 98.4, 98.6, 112.0, 119.3, 119.7, 119.9, 121.3, 122.9, 124.2, 126.0, 126.1, 126.5, 126.8, 127.0, 128.3, 130.6, 134.3, 135.5, 139.3, 139.6, 140.2, 140.3, 140.8, 150.7, 151.0, 151.4, 151.7, and 156.1. *m/z* (EI^+) 930 (M^+, 20%), and 629 ([M-301]$^+$, 100%); Exact mass 948.6542. $C_{64}H_{86}NO_5$ (MNH_4^+) requires 948.6506.

[2-(2'-Ethylhexyloxy)-4-hydroxymethyl-5-(9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl-7-yl)-phenyl]-methanol 3.16:

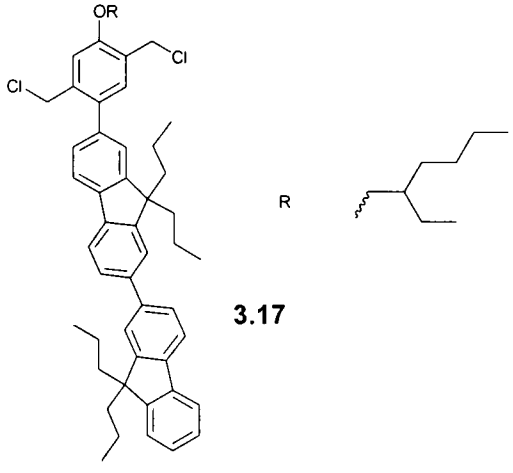


3.16

p-Toluenesulphonic acid monohydrate (12 mg, 20 mol%) was added to a solution of 2-[2-[7-(9,9-dipropyl-9*H*-2-fluorenyl)-9,9-dipropyl-9*H*-2-fluorenyl]-5-(2'-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxy]tetrahydro-2*H*-pyran **3.15** (0.3 g, 0.3 mmol) in ether (25 mL) and methanol (30 mL). The reaction mixture was stirred at room temperature for 16 hours under nitrogen and then concentrated to give a white solid. Purification of the crude by column chromatography over silica gel using a dichloromethane:methanol mixture (97:3) as eluent followed by recrystallisation from dichloromethane:hexane mixture gave [2-(2'-ethylhexyloxy)-4-hydroxymethyl-5-(9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl-7-yl)-phenyl]-methanol **3.16** (0.2 g, 85%) as a white solid, mp 175-177 °C. ν_{max} (KBr disc)/cm^{-1} 3415 (O–H); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 338 (5.36) and 312 sh (5.04); δ_H ($CDCl_3$, 500 MHz) 0.72-0.98 (20 H, m, 4 × $ArCH_2C\underline{H}_2C\underline{H}_3$)), 0.99-1.12 (6 H, m, 2 × CH_3), 1.38-1.71 (8 H, m, 4 × CH_2), 1.85-1.94 (1 H, m, CH), 2.05-2.21 (4 H, m, 2 × $ArCH_2$), 4.12 (2 H, d, *J* 6, OCH_2), 4.76 (2 H, s, $C\underline{H}_2OH$), 4.86 (2 H, s, $C\underline{H}_2OH$), 7.25 (1 H, s, ArH), 7.38 (6 H, m, 6 × ArH), 7.73 (4 H, m, 4 × ArH), and 7.85 (4 H, m, 4 × ArH); δ_C ($CDCl_3$, 125 MHz) 11.2, 14.1, 14.6, 17.3, 17.4, 22.9, 24.2, 29.1, 30.8, 39.5,

42.8, 55.4, 62.1, 63.2, 70.5, 110.6, 119.5, 119.7, 119.9, 120.0, 121.4, 122.9, 123.9, 126.2, 126.8, 127.0, 127.9, 128.4, 130.4, 133.7, 138.8, 138.9, 139.7, 139.9, 140.3, 140.4, 140.6, 140.8, 151.0, 151.1, 151.5, 151.6, and 156.6. *m/z* (EI^+) 762 (M^+, 100%); Exact mass 762.4996. $C_{54}H_{66}O_3$ requires 762.5006.

7-[2,5-*Bis*-chloromethyl-4-(2-ethylhexyloxy)-phenyl]-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl 3.17:

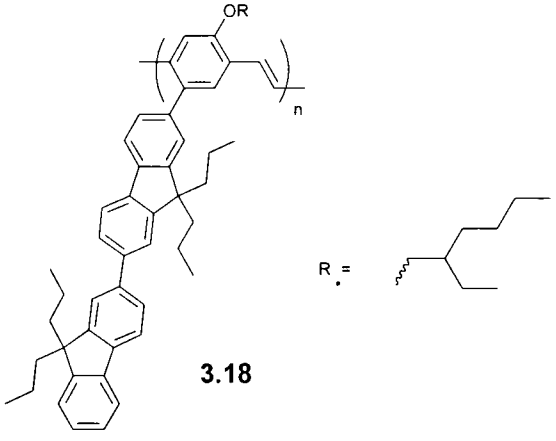


3.17

Thionyl chloride (0.3 mL, 3.6 mmol) was added to a solution of [2-(2'-ethylhexyloxy)-4-hydroxymethyl-5-(9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl-7-yl)-phenyl]-methanol **3.16** (150 mg, 0.2 mmol) in dry dichloromethane (20 mL) at 0 °C under nitrogen and the reaction mixture was stirred for 3 hours. The excess thionyl chloride was removed under vacuum and water (5 mL) was added carefully. The aqueous layer was extracted with ether (2 × 5 mL). The organic layers were combined, washed with water (2 × 5 mL), dried over magnesium sulphate, filtered and the solvent was removed. The residue was purified by column chromatography over silica gel using a light petroleum:dichloromethane mixture (4:1) as eluent to give 7-[2,5-*bis*-chloromethyl-4-(2-ethylhexyloxy)-phenyl]-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl **3.17** (100 mg, 64%) as a white solid, mp 71-72 °C. (Found: C, 81.14;

H, 7.90. $C_{54}H_{64}Cl_2O$ requires C, 81.07; H, 8.06%); ν_{max} (KBr disc)/cm^{-1} 740 (C–Cl); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon/dm^3mol^{-1}cm^{-1}$) 338 (5.24), and 313 sh (4.97); δ_H ($CDCl_3$, 400 MHz) 0.68-0.90 (20 H, m, 4 × $ArCH_2C\underline{H}_2C\underline{H}_3$)), 0.91-1.14 (6 H, m, 2 × CH_3), 1.38-1.69 (8 H, m, 4 × CH_2), 1.82-1.91 (1 H, m, CH), 1.95-2.16 (4 H, m, 2 × $ArCH_2$), 4.01 (2 H, d, *J* 6, OCH_2), 4.55 (2 H, s, CH_2Cl), 4.72 (2 H, s, CH_2Cl), 7.08 (1 H, s, ArH), 7.36 (5 H, m, 5 × ArH), 7.48 (1 H, s, ArH), 7.66 (4 H, m, 4 × ArH), and 7.78 (4 H, m, 4 × ArH); δ_C ($CDCl_3$, 100 MHz) 11.3, 14.1, 14.5, 17.3, 17.4, 23.1, 24.1, 29.1, 30.7, 39.5, 41.3, 42.8, 44.8, 55.4, 55.5, 70.6, 113.1, 119.6, 119.7, 119.9, 120.0, 121.3, 121.4, 122.9, 124.0, 126.1, 126.2, 126.5, 126.8, 127.0, 128.0, 132.2, 134.8, 136.5, 138.1, 139.9, 140.0, 140.3, 140.4, 140.7, 140.8, 151.0, 151.2, 151.5, 151.7, and 156.5. *m/z* (EI^+) 802, 800, and 798 (M^+, 30%, 60%, 100%); Exact mass 798.4355. $C_{54}H_{64}Cl_2O$ requires 798.4329.

Poly{2-[7-(9,9-dipropylfluorenyl)-9,9-dipropylfluorenyl]-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene} 3.18:



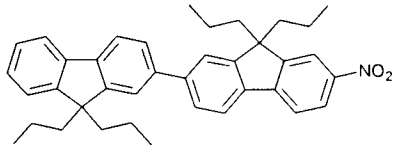
3.18

A solution of potassium *t*-butoxide (50 mg, 0.44 mmol) in anhydrous tetrahydrofuran (2.2 mL) was added to a stirred solution of 7-[2,5-*bis*-chloromethyl-4-(2-ethylhexyloxy)-phenyl]-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl **3.17** (70 mg,

0.09 mmol) solution in anhydrous tetrahydrofuran (0.45 mL) at room temperature under nitrogen. The reaction mixture changed colour from colourless to yellow. The reaction was allowed to stir for 3 hours under nitrogen in dark before quenching in ice-cold methanol (10 mL). The mixture was centrifuged (4500 r.p.m., 5 minutes) and the supernatant was decanted. The yellow residue obtained was dissolved in tetrahydrofuran (6 mL) and precipitated in ice-cold methanol (10 mL). The procedure of dissolution, precipitation and centrifugation was repeated one more time. The orange residue obtained was dried under vacuum for 48 hours in dark to give poly{2-[7-(9,9-dipropylfluorenyl)-9,9-dipropylfluorenyl]-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene} **3.18** (24 mg, 38%) as a yellow solid. ν_{max} (film, KBr disc)/cm^{-1} 969 (C=C–H trans); λ_{max} (film)/nm 475, 363, and 212; δ_H ($CDCl_3$, 400 MHz) 0.38-0.95 (26 H, br m, 4 × $ArCH_2C\underline{H}_2C\underline{H}_3$, 2 × CH_3), 1.19-1.63 (9 H, br m, 4 × CH_2, CH), 1.79-2.46 (8 H, br m, 4 × $ArCH_2$), 3.74-4.20 (2 H, br d, $ArOCH_2$), 6.82-7.95 (16 H, br m, vinylH, 15 × ArH); $\overline{M}_w$ = 1.9 × 10^6, $\overline{M}_n$ = 1.6 × 10^5, and PD = 12.2; Thermogravimetric analysis: 401 °C (temperature of degradation)

6.6.1 Synthesis of poly{2-[7-(7-nitro-9,9-dipropylfluorenyl)-9,9-dipropylfluorenyl]-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene}

7-Nitro-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl 3.19:

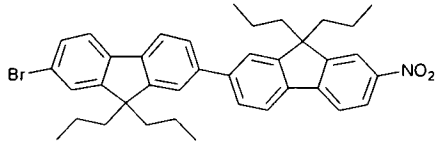


3.19

Tetrakis(triphenylphosphine)palladium (0) (1.0 g, 0.9 mmol) was added to a nitrogen bubbled suspension of 2-bromo-9,9-di(*n*-propyl)-7-nitrofluorene **2.16** (8.3 g, 22.3

mmol), 9,9-di-*n*-propylfluorenyl-2-boronic acid **2.6** (7.9 g, 26.8 mmol), and sodium carbonate (2 M, 200 mL) in toluene (100 mL). The reaction mixture was heated at reflux for 66 hours. After allowing the reaction mixture to cool, the aqueous phase was separated and extracted with ether (2 × 100 mL). The combined organic layers were washed with aqueous hydrochloric acid (3 M, 50 mL), water (2 × 50 mL) and brine (50 mL), dried over magnesium sulphate, and filtered through a celite plug using dichloromethane as eluent. The solvent was removed to give a brown residue. Column chromatography over silica gel using a light petroleum:dichloromethane mixture (2:1) as eluent gave a yellow solid. Purification by recrystallisation from dichloromethane/methanol mixture gave 7-nitro-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl **3.19** (5.8 g, 48%) as a yellow solid, mp 154-155 °C. (Found: C, 83.96; H, 7.56; N, 2.53. $C_{38}H_{41}NO_2$ requires C, 83.94; H, 7.60; N, 2.58%); ν_{max} (KBr disc)/cm^{-1} 1519 (NO_2 anti) and 1338 (NO_2 sym); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 377 (4.66) and 310 sh (4.33); δ_H ($CDCl_3$, 400 MHz) 0.69-0.98 (20 H, m, 4 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 2.00-2.19 (8 H, m, 4 × $ArCH_2$), 7.38 (3 H, m, 3 × ArH), 7.78 (8 H, m, 8 × ArH), and 8.31 (2 H, dd, *J* 8, *J* 2, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 14.4, 14.5, 17.3, 42.4, 42.8, 55.5, 56.0, 118.3, 119.7, 119.9, 120.0, 121.4, 121.5, 121.6, 123.0, 123.4, 126.3, 126.8, 126.9, 127.3, 137.8, 139.7, 140.5, 140.9, 142.9, 147.0, 147.4, 151.0, 151.6, 152.2, and 153.1; *m/z* (EI^+) 543 (M^+, 100%).

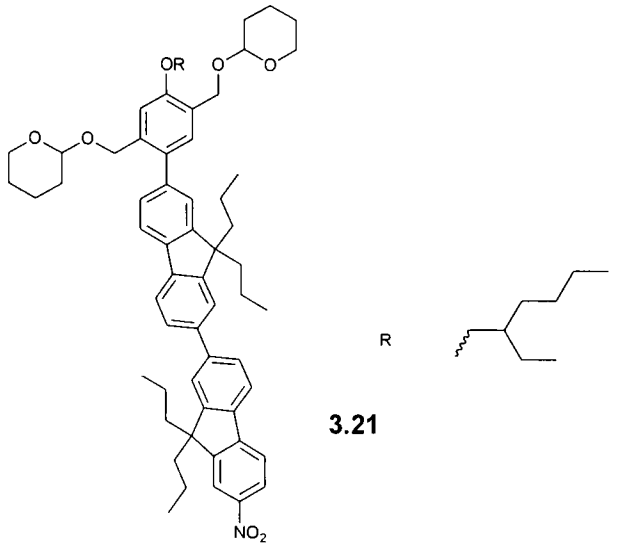
7-Bromo-7'-nitro-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl 3.20:



3.20

Bromine (0.6 mL, 11.5 mmol) was added to a solution of 7-nitro-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl **3.19** (5.7 g, 10.4 mmol) in dry dichloromethane (50 mL). The reaction mixture was stirred at room temperature for 2.5 hours in the dark. The excess bromine was quenched with a saturated solution of sodium metabisulphite (20 mL). The organic layer was separated, washed with water (2 × 75 mL) and dried over magnesium sulphate. The solution was filtered and concentrated to give a yellow residue. Purification by of the crude by filtering through a silica plug using dichloromethane as eluent followed by recrystallisation from dichloromethane:methanol mixture gave 7-bromo-7'-nitro-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl **3.20** (5.8 g, 90%) as yellow crystals, mp 259-261 °C. (Found: C, 73.25; H, 6.46; N, 2.21. $C_{38}H_{40}BrNO_2$ requires C, 73.30; H, 6.48; N, 2.25%); ν_{max} (KBr disc)/cm^{-1} 742 (C–Br); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 375 (4.74), and 321 (4.47); δ_H ($CDCl_3$, 400 MHz) 0.68-0.89 (20 H, m, 4 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 1.98-2.14 (8 H, m, 4 × $ArC\underline{H}_2$), 7.52 (2 H, dd, *J* 8, *J* 1, 2 × ArH), 7.68 (4 H, m, 4 × ArH), 7.73 (1 H, d, *J* 8, ArH), 7.79 (1 H, d, *J* 8, ArH), 7.87 (2 H, m, 2 × ArH), and 8.30 (2 H, dd, *J* 8, *J* 2, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 14.4, 14.5, 17.2, 42.4, 42.7, 55.8, 56.0, 118.3, 119.8, 120.2, 121.2, 121.3, 121.4, 121.5, 121.6, 123.4, 126.3, 126.5, 126.8, 130.1, 137.9, 139.6, 139.8, 140.2, 142.6, 147.0, 147.3, 151.3, 152.2, 153.2, and 153.3. *m/z* (EI$^+$) 623, and 621 (M^+, 94%, 100%).

5-(2′-Ethylhexyloxy)-2-[7-(7-nitro-9,9-dipropyl-9*H*-2-fluorenyl)-9,9-dipropyl-9*H*-2-fluorenyl]-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxytetrahydro-2*H*-pyran 3.21:

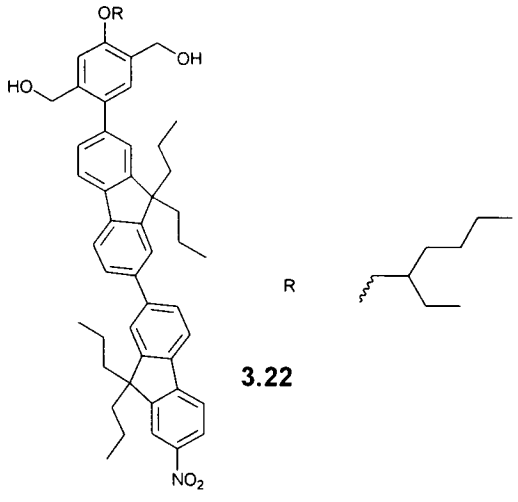


3.21

Tetrakis(triphenylphosphine)palladium (0) (0.2 g, 0.2 mmol) was added to a nitrogen purged suspension of 7-bromo-7'-nitro-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl **3.20** (2.0 g, 3.2 mmol), 2-[2-(2'-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyloxy]tetrahydro-2*H*-pyran **3.10** (2.2 g, 3.9 mmol), and aqueous sodium carbonate (2 M, 50 mL) in toluene (150 mL) and heated at reflux for 48 hours. The reaction mixture was allowed to cool to room temperature and water (50 mL) was added followed by careful addition of aqueous hydrochloric acid (3M, 50 mL). The aqueous layer was extracted with ether (2 × 75 mL) and the organic layers were combined, washed with brine (150 mL), dried over magnesium sulphate, filtered and solvent was removed to give a yellow oil. Purification of the residue by flash chromatography over silica gel using dichloromethane as eluent gave 5-(2'-ethylhexyloxy)-2-[7-(7-nitro-9,9-dipropyl-9*H*-2-fluorenyl)-9,9-dipropyl-9*H*-2-fluorenyl]-4-tetrahydro-2*H*-2-

pyranyloxymethylbenzyloxytetrahydro-2*H*-pyran **3.21** (2.5 g, 80%) as a yellow oil. ν_{max} (KBr disc)/cm^{-1} 1520 (NO_2 anti) and 1337 (NO_2 sym), and 1121 (O–C–O); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 380 (4.65), 324 (4.47), and 301 (4.50); δ_H ($CDCl_3$, 400 MHz) 0.84-0.92 (20 H, m, 4 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 0.95-1.04 (6 H, m, 2 × CH_3), 1.38-1.92 (20 H, m, 5 × CH_2), 1.92-2.01 (1 H, m, CH), 2.05-2.19 (8 H, m, 4 × $ArCH_2$), 3.48-3.66 (2 H, m, -OCH_2 (THP)), 3.91-4.07 (4 H, m, -OCH_2, -OCH_2 (THP)), 4.48-4.54, 4.68-4.74 and 4.83-4.88 (6 H, m, 2 × $ArCH_2O$, 2 × -OCH (THP)), 7.14 (1 H, s, ArH), 7.49 (3 H, m, 3 × ArH), 7.80 (8 H, m, 8 × ArH), and 8.32 (2 H, dd, *J* 8, *J* 2, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 11.3, 14.2, 14.4, 14.6, 14.8, 17.3, 17.4, 19.5, 19.7, 23.1, 24.1, 25.6, 29.2, 30.7, 30.9, 39.6, 42.5, 42.9, 56.0, 55.5, 62.1, 62.4, 64.3, 67.5, 70.3, 98.3, 98.3, 112.1, 118.3, 119.5, 119.8, 120.1, 121.5, 121.6, 123.4, 124.3, 126.4, 126.6, 126.8, 128.4, 130.6, 134.3, 135.5, 137.8, 139.1, 140.0, 140.8, 142.9, 147.0, 147.4, 150.8, 151.9, 152.2, and 153.2. *m/z* (ES^+) 1034 (MNH_4^+ + CH_3CN, 54%), and 993 ($[MNH_4]^+$, 54%); Exact mass 993.6368. $C_{64}H_{85}N_2O_7$ ($[MNH_4]^+$ requires 993.6357.

[2-(2'-Ethylhexyloxy)-4-hydroxymethyl-5-(7'-nitro-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl-7-yl)-phenyl]-methanol 3.22:

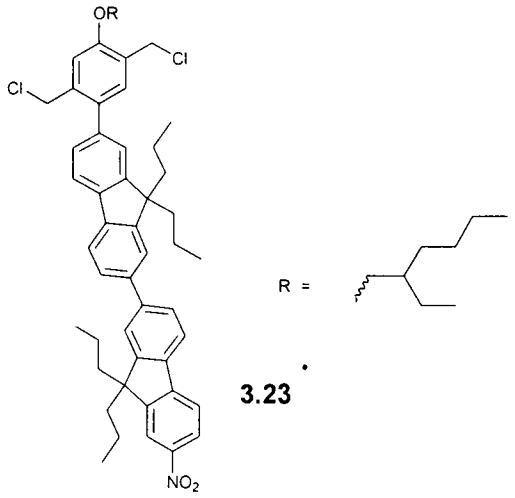


3.22

A mixture of 5-(2'-ethylhexyloxy)-2-[7-(7-nitro-9,9-dipropyl-9*H*-2-fluorenyl)-9,9-dipropyl-9*H*-2-fluorenyl]-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxytetrahydro-2*H*-pyran **3.21** (0.3 g, 0.3 mmol), *p*-toluenesulphonic acid monohydrate (11 mg, 20 mol%), ether (20 mL) and methanol (10 mL) stirred at room temperature for 18 hours under nitrogen. Water (10 mL) was added and the organic layer was separated. The aqueous layer was extracted with ether (2 × 25 mL). The combined organic phases were washed with brine (20 mL), dried over magnesium sulphate, filtered and the solvent was removed to give yellow oil. Purification of the crude product by column chromatography over silica gel using a gradient elution with a dichloromethane:methanol mixture (99:1 to 98:2) followed by recrystallisation from dichloromethane:hexane mixture gave [2-(2'-ethylhexyloxy)-4-hydroxymethyl-5-(7'-nitro-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl-7-yl)-phenyl]-methanol **3.22** (0.2 g, 72%) as a yellow solid, mp 175-177 °C. (Found: C, 79.48; H, 7.61, N 1.55. $C_{54}H_{65}NO_5$ requires C, 80.26; H, 8.11; N 1.73%); ν_{max} (KBr disc)/cm^{-1} 3402 (O–H), 1523 (NO_2), and 1346 (NO_2); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 380 (4.90), 323

(4.70), and 300 (4.69); δ_H ($CDCl_3$, 400 MHz) 0.69-0.88 (20 H, m, 4 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 0.92-1.00 (6 H, m, 2 × CH_3), 1.32-1.64 (8 H, m, 4 × CH_2), 1.80-1.88 (1 H, m, CH), 2.01-2.18 (8 H, m, 4 × $ArCH_2$),), 4.05 (2 H, d, *J* 5, OCH_2), 4.71 (2 H, s, $C\underline{H}_2OH$), 4.79 (2 H, s, $C\underline{H}_2OH$), 7.20 (1 H, s, ArH), 7.34 (3 H, m, 3 × ArH), 7.70 (3 H, m, 3 × ArH), 7.73 (1 H, d, *J* 9, ArH), 7.78 (1 H, d, *J* 8, ArH), 7.85 (3 H, m, 3 × ArH), and 8.30 (2 H, dd, *J* 8, *J* 2, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 11.2, 14.1, 14.4, 14.6, 17.3, 17.4, 23.1, 24.2, 29.1, 30.8, 39.5, 42.4, 42.8, 55.5, 56.0, 62.1, 63.2, 70.5, 110.7, 118.3, 119.6, 119.8, 120.1, 121.5, 121.6, 123.4, 124.0, 126.4, 126.8, 128.1, 128.4, 130.4, 133.6, 137.8, 138.8, 139.2, 139.5, 139.8, 140.6, 142.8, 147.0, 147.4, 151.1, 151.8, 152.2, 153.2, and 156.7. *m/z* (EI^+) 807 (M^+, 100%); Exact mass 807.4852. $C_{54}H_{65}NO_5$ requires 807.4857.

7-[2,5-*Bis*-chloromethyl-4-(2'-ethylhexyloxy)-phenyl]-7'-nitro-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl 3.23:

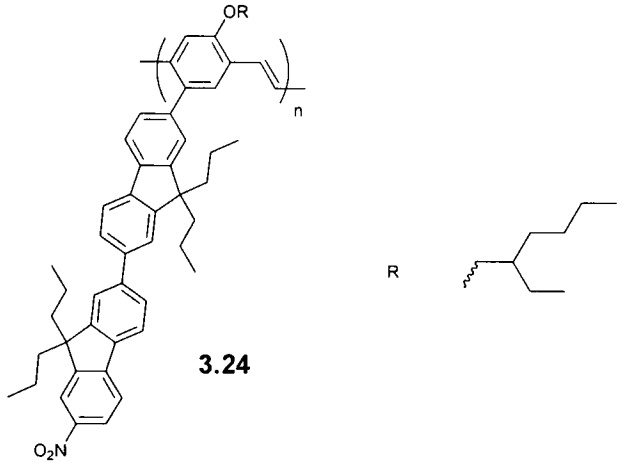


3.23

Thionyl chloride (0.2 mL, 2.8 mmol) was added to a stirred solution of [2-(2'-ethylhexyloxy)-4-hydroxymethyl-5-(7'-nitro-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl-7-yl)-phenyl]-methanol **3.22** (120 mg, 0.2 mmol) in dry dichloromethane (5 mL) at 0 °C under nitrogen. The reaction mixture was stirred at

room temperature for 3 hours. Water was carefully added (5 mL). The organic layer was separated, washed with brine (5 mL) and dried over magnesium sulphate. Filtration and solvent removal gave a yellow solid. Purification of the crude by flash chromatography over silica gel using a light petroleum:dichloromethane mixture (1:1) gave 7-[2,5-*bis*-chloromethyl-4-(2'-ethylhexyloxy)-phenyl]-7'-nitro-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl **3.23** (66 mg, 53%) as a yellow solid, mp 88-91 °C. (Found: C, 76.85; H, 7.41; N, 1.56. $C_{54}H_{64}Cl_2NO_3$ requires C, 76.76; H, 7.51; N, 1.66%); ν_{max} (KBr disc)/cm^{-1} 735 (C–Cl); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/$dm^3mol^{-1}cm^{-1}$) 378 (4.83), 323sh (4.65), and 300 (4.69); δ_H ($CDCl_3$, 400 MHz) 0.68-0.87 (20 H, m, 4 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 0.93-1.08 (6 H, m, 2 × CH_3), 1.38-1.72 (8 H, m, 4 × CH_2), 1.84-1.92 (1 H, m, CH), 2.09-2.12 (8 H, m, 4 × $ArCH_2$), 4.06 (2 H, d, *J* 5, OCH_2), 4.58 (2 H, s, CH_2Cl), 4.75 (2 H, s, CH_2Cl), 7.12 (1 H, s, ArH), 7.44 (2 H, dd, *J* 5, *J* 2, 2 × ArH), 7.54 (1 H, s, ArH), 7.70 (1 H, s, ArH), 7.75 (2 H, dd, *J* 5, *J* 2, 2 × ArH), 7.85 (2 H, m, 2 × ArH), 7.88 (2 H, dd, *J* 7, *J* 2, 2 × ArH), 7.90 (1 H, d, *J* 2, ArH), 8.31 (1 H, d, *J* 2, ArH), and 8.33 (1 H, dd, *J* 8, *J* 2, ArH); δ_C ($CDCl_3$, 100 MHz) 11.3, 14.2, 14.4, 14.6, 17.3, 17.5, 23.1, 24.1, 29.1, 30.7, 39.5, 41.3, 42.5, 42.8, 44.8, 55.6, 56.1, 70.6, 113.2, 118.3, 119.8, 120.2, 121.5, 121.6, 123.4, 124.1, 126.4, 126.5, 126.8, 128.1, 132.2, 134.8, 136.6, 137.8, 138.5, 139.8, 139.9, 140.6, 142.8, 147.1, 147.4, 151.2, 151.9, 152.5, 153.2, and 156.6. *m/z* (EI^+) 847, 845, and 843 (M^+, 25%, 80%, 100%). Exact mass 843.4204. $C_{54}H_{64}Cl_2NO_3$ requires 843.4179.

Poly{2-[7-(7-nitro-9,9-dipropylfluorenyl)-9,9-dipropylfluorenyl]-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene} 3.24:



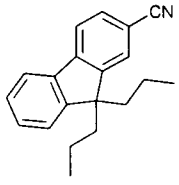
3.24

Potassium *t*-butoxide (44 mg, 0.40 mmol) solution in anhydrous tetrahydrofuran (1.9 mL) was added to a stirred solution of 7-[2,5-*bis*-chloromethyl-4-(2'-ethylhexyloxy)-phenyl]-7'-nitro-9,9,9',9'-tetrapropyl-9*H*,9'*H*-[2,2']bifluorenyl **3.23** (65 mg, 0.08 mmol) was dissolved in tetrahydrofuran (0.4 mL) at room temperature under nitrogen. The reaction mixture was stirred for 3.5 hours in dark and then poured in ice-cold methanol (6 mL). The mixture was centrifuged (4500 r.p.m., 5 minutes) and supernatant was removed by decantation. The residue was dissolved in tetrahydrofuran (2 mL) and precipitated in ice-cold methanol (6 mL). The process was repeated one more time. The final residue obtained was dried under vacuum for 24 hours to give poly{2-[7-(7-nitro-9,9-dipropylfluorenyl)-9,9-dipropylfluorenyl]-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene} **3.24** (35 mg, 58%) as a yellow solid. ν_{max} (film, KBr disc)/cm^{-1} 970 (C=C–H trans); λ_{max} (film)/nm 450 sh, 380, 302, and 212; δ_H ($CDCl_3$, 400 MHz) 0.25-1.07 (26 H, br m, 4 × $ArCH_2C\underline{H_2}C\underline{H_3}$, 2 × CH_3), 1.15-1.68 (9 H, br m, 4 × CH_2, CH), 1.74-2.36 (8 H, br m, 4 × $ArCH_2$), 3.76-4.23 (2 H, br d, $ArOCH_2$), 6.82-7.87 (13 H, br m, vinylH, 12 × ArH) and 8.18-8.34 (2 H, br m, 2 × ArH); $\overline{M}_w$ = 3.2 × 10^5, $\overline{M}_n$ = 4.5 × 10^4, and PD = 7.2; Thermogravimetric analysis: 345 °C (Temperature of degradation)

6.4 Experimental for Chapter 4

6.7.1 Synthesis of poly{2-[(*E*)-2-(9,9-dipropylfluorenyl)vinyl]-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene}

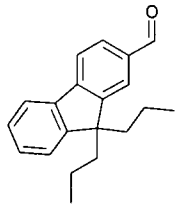
9,9-Dipropyl-9*H*-fluorene-2-carbonitrile 4.2:



4.2

Copper (I) cyanide (71.2 g, 0.8 mol) was added to a nitrogen purged solution of 9,9-dipropyl-2-bromofluorene **2.5** (65.4 g, 0.2 mol) in *N,N*-dimethylformamide (150 mL) and the reaction was heated at reflux for 16 hours under nitrogen. After allowing the reaction to cool to room temperature, a solution of iron (III) chloride (20.0 g) in aqueous hydrochloric acid (3 M, 200 mL) was carefully added and the aqueous phase was extracted with ether (3 × 200 mL). The ethereal extracts were combined, washed with water (3 × 200 mL) and brine (200 mL), dried over magnesium sulphate and filtered. The solvent was removed to give a yellow solid (52.0 g). Purification of the residue by flash chromatography over silica gel using a light petroleum:dichloromethane mixture (2:1) as eluent followed by recrystallisation from dichloromethane/methanol gave 9,9-dipropyl-9*H*-fluorene-2-carbonitrile **4.2** (46.1 g, 84%) as white crystals, mp 137-139 °C (lit.[158] 139-140 °C). The compound had an identical ^{1}H n.m.r. spectrum to that reported in the literature[158]

9,9-Dipropyl-9*H*-fluorene-2-carbaldehyde 4.1:



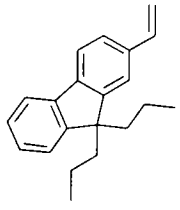
4.1

Method 1: *n*-Butyllithium (1.6 M in heptane, 10.0 mL, 16.0 mmol) was added drop-wise to a stirred solution of 9,9-di-*n*-propyl-2-bromofluorene **2.5** (3.0 g, 9.1 mmol) in dry tetrahydrofuran (50 mL) at -78 °C under nitrogen. After 1.5 hour *N,N*-dimethylformamide (30.0 mL, 0.4 mol) was added to the reaction mixture and the reaction was stirred at -78 °C for 30 minutes, then at room temperature for 1 hour. Water (50 mL) was added and the aqueous layer was extracted with ether (3 × 75 mL). The organic extracts were combined, washed with water (3 × 100 mL) and brine (100 mL), dried over magnesium sulphate and filtered. The solvent was removed to give a colourless oil. Purification of the crude product by flash chromatography over silica gel using a gradient elution with a light petroleum:dichloromethane mixture (1:0 to 4:1) gave an impure 9,9-dipropyl-9*H*-fluorene-2-carbaldehyde **4.1** (0.8 g) and several unidentifiable compounds.

Method 2: DIBAL-H (1.5 M in toluene, 98.2 mL, 147.3 mmol) was added drop-wise to a stirred solution of 9,9-dipropyl-9*H*-fluorene-2-carbonitrile **4.2** (26.9 g, 97.7 mmol) in anhydrous dichloromethane (500 mL) and toluene (500 mL) at -78 °C under argon. After the addition, the reaction mixture was stirred at -78 °C for an hour and then at room temperature for 3 hours. Aqueous hydrochloric acid (3 M, 300 mL) was added drop-wise carefully. The organic phase was separated, washed with water (3 × 350 mL) and brine (300 mL), and dried over magnesium sulphate. The solution was filtered and concentrated to give yellow oil. Purification of the residue by column

chromatography over silica gel using a light petroleum:dichloromethane mixture (2:1) as eluent gave 9,9-dipropyl-9*H*-fluorene-2-carbaldehyde **4.1** (27.1 g, 99%) as a white solid, mp 67-68 °C. (Found: C, 86.37; H, 7.90. $C_{20}H_{22}O$ requires C, 86.29; H, 7.97%); ν_{max} (KBr disc)/cm^{-1} 1697 (C=O); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 326 (4.64), 306 sh (4.41), and 247 sh (3.95); δ_H ($CDCl_3$, 400 MHz) 0.56-0.68 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 1.90-2.08 (4 H, m, 2 × $ArC\underline{H}_2$), 7.39 (3 H, m, 3 × ArH), 7.79 (1 H, d, *J* 8, ArH), 7.87 (3 H, m, 3 × ArH), and 10.09 (1 H, s, CHO); δ_C ($CDCl_3$, 100 MHz) 14.3, 17.1, 42.5, 55.4, 119.9, 120.9, 123.0, 123.1, 127.2, 128.8, 130.5, 135.3, 139.5, 147.5, 151.5, 152.2 and 192.4; *m/z* (CI^+) 296 ($[MNH_4]^+$, 12%) and 279 (MH^+, 100%); Exact mass 279.1748. $C_{20}H_{23}O$ requires 279.1749.

9,9-Di(*n*-propyl)-2-vinylfluorene 4.3:

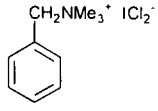


4.3

A mixture of methyltriphenylphosphonium iodide (8.4 g, 20.7 mmol) and potassium *t*-butoxide (2.3 g, 20.4 mmol) was stirred in anhydrous tetrahydrofuran (20 mL) at room temperature for 30 minutes under argon before the addition of a solution of 9,9-dipropyl-9*H*-fluorene-2-carbaldehyde **4.1** (4.4 g, 16.0 mmol) in tetrahydrofuran (20 mL). The reaction mixture was stirred for 17 hours. Water (100 mL) was added and the aqueous layer was extracted with ether (3 × 50 mL). The ethereal extracts were combined, washed with water (3 × 50 mL) and brine (20 mL), dried over magnesium sulphate and filtered. The solvent was removed to give brown oil. Purification of the oily residue by column chromatography over silica gel using light petroleum as eluent gave 9,9-di(*n*-propyl)-2-vinylfluorene **4.3** (3.9 g, 88%) as a clear colourless oil.

(Found: C, 91.24; H, 8.74. $C_{21}H_{24}$ requires C, 91.25; H, 8.75%); ν_{max} (KBr disc)/cm^{-1} 1620 (C=C); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/$dm^3mol^{-1}cm^{-1}$) 283 (3.45), and 273 (4.54); δ_H ($CDCl_3$, 400 MHz) 0.62-0.75 (10 H, m, 2 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 1.95-2.03 (4 H, m, 2 × $ArCH_2$), 5.28 (1 H, dd, *J* 11, *J* 1, vinylH), 5.83 (1 H, dd, *J* 17, *J* 1, vinylH), 6.83 (1 H, dd, *J* 17, *J* 11, Ar-vinylH), 7.35 (4 H, m, ArH), 7.43 (2 H, dd, *J* 2, *J* 8, ArH), and 7.69 (2 H, m, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 14.5, 17.2, 42.8, 55.2, 113.0, 119.7, 120.5, 122.9, 125.3, 126.8, 127.0, 136.5, 137.4, 140.8, 141.0, 151.0, and 151.1. *m/z* (EI^+) 277, and 276 (M^+, 25%, 100%); Exact mass 276.1878. $C_{21}H_{24}$ requires 276.1873.

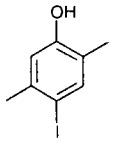
Benzyltrimethylammonium dichloroiodate 4.6:



4.6

A solution of benzyltrimethyammmonium chloride (6.3 g, 49.8 mmol) in water (30 mL) was added drop-wise to a stirred solution of iodine monochloride (5.5 g, 33.9 mmol) in dichloromethane (60 mL) and the resultant mixture was stirred at room temperature for 30 minutes. The dichloromethane layer was separated, washed with water (2 × 100 mL), dried over magnesium sulphate and filtered. The solvent was removed to give orange residue. Purification of the crude by recrystallisation from dichloromethane/ether mixture gave benzyltrimethylammonium dichloroiodate **4.6** (7.5 g, 64%) as yellow needles, mp 123-125 °C (lit.[160] 124-126 °C; lit.[165] 125-126 °C).

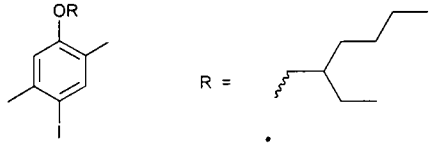
4-Iodo-2,5-dimethyl-phenol 4.5:



4.5

Benzyltrimethylammonium dichloroiodate **4.6** (7.0 g, 20.1 mmol) and calcium carbonate (5.0 g, 50.0 mmol) was added to a solution of 2,5-dimethyl-phenol **2.1** (2.2 g, 18.2 mmol) in dichloromethane (50 mL) and methanol (20 mL). The reaction mixture was stirred at room temperature for 3 hours. Water (20 mL) was added and the aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic extracts were washed with aqueous hydrochloric acid (3 M, 2 × 10 mL) and brine (10 mL), dried over magnesium sulphate, and filtered. The solvent was removed to give a yellow solid (3.8 g). Purification by recrystallisation from dichloromethane/light petroleum mixture gave 4-iodo-2,5-dimethyl-phenol **4.5** (3.1 g, 65%) as white crystals, mp 94-96 °C (lit.[166] 95-96 °C). The compound had an identical ^{1}H n.m.r. spectrum to that reported in the literature[166].

1-Iodo-4-(2′-ethylhexyloxy)-2,5-dimethylbenzene 4.4:



4.4

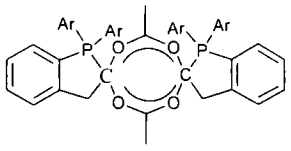
Method 1: A solution of 2-(2′-ethylhexyloxy)-1,4-dimethylbenzene **2.2** (20.0 g, 85.3 mmol) in chloroform (30 mL) was added to a mixture of silver acetate (11.5 g, 68.4 mmol) and iodine (17.4 g, 68.4 mmol) in chloroform (160 mL) that had been pre-stirred at room temperature under nitrogen in dark for an hour. The reaction mixture was stirred for 19 hours and then filtered through a plug of silica using

dichloromethane as eluent. The filtrate was washed with a saturated solution of sodium metabisulphite (3 × 100 mL), dried over magnesium sulphate, filtered and solvent was removed. The crude was purified by column chromatography over silica gel using light petroleum as eluent gave 1-iodo-4-(2′-ethylhexyloxy)-2,5-dimethylbenzene **4.4** (2.4 g, 8%) as a clear colourless oil. Unreacted 2-(2′-ethylhexyloxy)-1,4-dimethylbenzene **2.2** (17.5 g, 88%) was recovered.

Method 2: 4 Potassium *t*-butoxide (0.8 g, 6.8 mmol) was added portion-wise to a solution of 4-iodo-2,5-dimethyl-phenol **4.5** (1.5 g, 6.0 mmol) in acetonitrile (20 mL) at 0 °C under argon and stirred for 30 minutes. 2-Ethylhexyl bromide (2.2 mL, 12.0 mmol) was added and the reaction mixture was stirred at 0 °C for 30 minutes and then at room temperature for a further 16 hours. The reaction mixture was filtered through a plug of silica using dichloromethane as eluent. The solvent was removed to give brown oil. Purification by column chromatography over silica gel using a light petroleum:dichloromethane mixture (2:1) as eluent followed by vacuum distillation (125 °C, 0.12 mm Hg) gave 1-iodo-4-(2′-ethylhexyloxy)-2,5-dimethylbenzene **4.4** (1.4 g, 66%) as a clear colourless oil. (Found: C, 53.45; H, 6.87. $C_{16}H_{25}IO$ requires C, 53.34; H, 6.99%); ν_{max} (KBr disc)/cm^{-1} 1247 (C–O); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/$dm^3mol^{-1}cm^{-1}$) 283 (3.45), and 273 (4.54); δ_H ($CDCl_3$, 400 MHz) 0.90-1.20 (6 H, m, 2 × CH_3), 1.32-1.60 (8 H, m, 4 × CH_2), 1.72-1.86 (1 H, m, CH), 2.20 (3 H, s, $ArCH_3$), 2.44 (3 H, s, $ArCH_3$), 3.87 (2 H, d, *J* 6,·$ArOCH_2$), 6.77 (1 H, s, ArH), and 7.57 (1 H, s, ArH); δ_C ($CDCl_3$, 100 MHz) 11.3, 14.2, 15.4, 23.1, 24.1, 28.1, 29.2, 30.7, 39.5, 70.2, 88.8, 112.6, 126.6, 139.3, 139.9, and 157.7. *m/z* (EI^+) 360 (M^+, 19%), and 248 (M-112, 100%); Exact mass 360.0940. $C_{16}H_{25}OI$ requires 360.0950.

trans-Di-μ-acetato*bis*[2-(di-*o*-tolylphosphino)benzyl]dipalladium(II)

***(Herrmann's catalyst)* 4.8:**

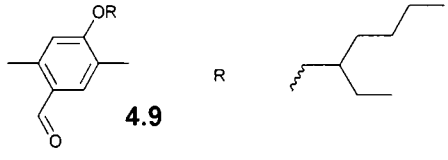


Ar = *o*-tolyl

4.8

A mixture of palladium (II) acetate (2.8 g, 2.6 mmol) and *tri*(o-tolylphosphine) (5.0 g, 16.3 mmol) in toluene (320 mL) was stirred at 60 °C for an hour under argon. On cooling, the solution was filtered through a celite plug using toluene as eluent. The filtrate was concentrated followed by trituration with hexane (300 mL). The yellow solid obtained was filtered and dried under vacuum to give *trans*-di-μ-acetato*bis*[2-(di-*o*-tolylphosphino)benzyl]dipalladium (II) (Herrmann's catalyst[136]) **4.8** (4.8 g, 82%) as a yellow solid. The compound had an identical infrared spectrum to that reported in the literature[138].

4-(2'-Ethylhexyloxy)-2,5-dimethylbenzaldehyde 4.9:

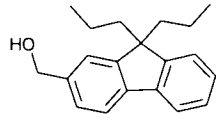


4.9

n-Butyllithium (1.6 M in heptane, 3.2 mL, 5.1 mmol) was added drop-wise to stirred solution of 1-bromo-4-(2'-ethylhexyloxy)-2,5-dimethylbenzene **2.3a** (1.5 g, 4.8 mmol) in anhydrous tetrahydrofuran (50 mL) at -78 °C under nitrogen. The reaction mixture was stirred at -78 °C for 30 minutes before the addition of anhydrous *N,N*-dimethylformamide (3 mL). After 30 minutes, the mixture was allowed to warm to room temperature and stirred for 16 hours. Water (20 mL) was added and the aqueous phase was extracted with ether (2 × 20 mL). The combined ethereal extracts were washed with water (3 × 20 mL) and brine (20 mL), dried over magnesium

sulphate, filtered and solvent was removed. The crude was purified by flash chromatography over silica gel using a light petroleum:dichloromethane mixture as eluent to give 4-(2'-ethylhexyloxy)-2,5-dimethylbenzaldehyde **4.9** (0.9 g, 71%) as a yellow oil. The compound had an identical ^{1}H n.m.r. and ^{13}C n.m.r. spectrum to that reported in the literature[113].

(9,9-Dipropyl-9*H*-fluoren-2-yl)-methanol 4.10:

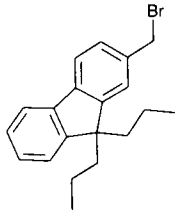


4.10

Sodium borohydride (14.7 g, 0.4 mol) was added portion-wise to a solution of 9,9-dipropyl-9*H*-fluorene-2-carbaldehyde **4.1** (27.1 g, 93.3 mmol) in *i*-propanol (200 mL) and ethanol (200 mL) at room temperature and the reaction mixture was stirred for 3 hours. The reaction was carefully quenched with aqueous hydrochloric acid (3 M, 500 mL). The aqueous phase was extracted with ether (3 × 150 mL). The combined organic extracts were washed with brine (200 mL), dried over magnesium sulphate and filtered. The solvent was removed to give yellow oil. Purification of the crude by column chromatography over silica gel using dichloromethane followed by dichloromethane:methanol mixture (98:2) as eluent gave (9,9-dipropyl-9*H*-fluoren-2-yl)-methanol **4.10** (26.0 g, 100%) as a clear colourless oil which solidifies to a white solid on standing, mp 54-55 °C. (Found: C, 85.77; H, 8.73. $C_{20}H_{24}O$ requires C, 85.67; H, 8.63%); ν_{max} (KBr disc)/cm^{-1} 3268 (O–H); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 307 (4.22), 295 (4.06), 274 (4.39), 269 sh (4.38), and 247 (4.12); δ_H ($CDCl_3$, 400 MHz) 0.59-0.76 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 2.05-2.07 (4 H, m, 2 × $ArCH_2$), 4.78 (2 H, s, $ArCH_2O$), 7.41 (5 H, m, 5 × ArH), and 7.77 (2 H, dd, *J* 8, *J* 2, 2 × ArH); δ_C

($CDCl_3$, 100 MHz) 14.6, 17.3, 42.9, 55.3, 65.5, 119.8, 121.6, 122.9, 125.9, 126.9, 127.1, 139.9, 140.7, 140.9, 150.9, and 151.2; *m/z* (EI^+) 280 (M^+, 67%), and 237 ([M-C_3H_7]$^+$, 100%); Exact mass 280.1819. $C_{20}H_{24}O$ requires 280.1827.

2-Bromomethyl-9,9-dipropyl-9*H*-fluorene 4.11:

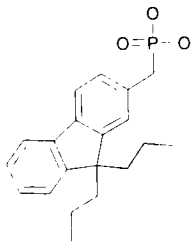


4.11

Phosphorous tribromide (1.4 mL, 14.8 mmol) was added to (9,9-dipropyl-9*H*-fluoren-2-yl)-methanol **4.10** (0.2 g, 0.7 mmol) at -10 °C under nitrogen. The reaction mixture was heated at 100 °C for 15 hours with a guard tube on the water condenser. After allowing the reaction mixture to cool, the reaction mixture was carefully poured in an ice-bath followed by the addition of ether (10 mL). The aqueous layer was separated and extracted with ether (3 × 10 mL). The organic layers were combined, washed with water (3 × 20 mL), saturated solution of sodium bicarbonate (10 mL) and brine (50 mL), dried over magnesium sulphate and filtered. The solvent was removed to give yellow oil. Purification of the residue by column chromatography over silica gel using light petroleum as eluent gave 2-bromomethyl-9,9-dipropyl-9*H*-fluorene **4.11** (0.2 g, 77%) as a clear colourless oil. ν_{max} (KBr disc)/cm^{-1} 741 (C–Br); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 347 (4.36), 311 sh (4.01), and 259 (4.01); δ_H ($CDCl_3$, 400 MHz) 0.63-0.75 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 1.95-2.01 (4 H, m, 2 × $ArCH_2$), 4.64 (2 H, s, $ArCH_2Br$), 7.36 (5 H, m, 5 × ArH), and 7.71 (2 H, dd, *J* 7, *J* 2, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 14.5, 17.2, 34.6, 42.6, 55.3, 119.9, 122.9, 123.6, 126.9, 127.4,

128.0, 136.5, 139.9, 140.4, 141.5, 151.0, and 151.3; *m/z* (EI^+) 344, 342 (M^+, 13%, 14%), and 263 ($[M-Br]^+$, 100%); Exact mass 342.0973. $C_{20}H_{23}Br$ requires 342.0983.

(9,9-Dipropyl-9H-fluoren-2-ylmethyl)-phosphonic acid dimethyl ester 4.12:

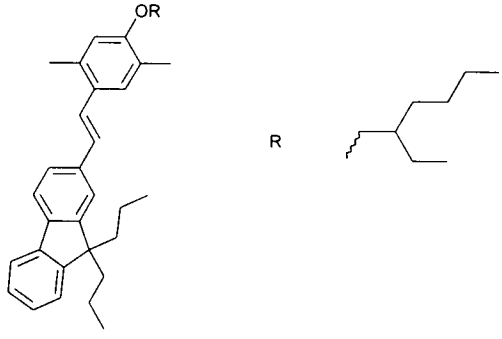


4.12

Tri-methylphosphite (19.4 mL, 0.2 mol) was added to 2-bromomethyl-9,9-dipropyl-9*H*-fluorene **4.11** (10.8 g, 31.5 mmol) and the mixture was heated at 80 °C for 4 hours under argon. After allowing the reaction mixture to cool, ether (50 mL) and water (50 mL) was added. The ether layer was separated and dried over magnesium sulphate. The solution was filtered and solvent was removed to give a pale white solid. Purification of the crude by filtering through a plug of silica using light petroleum:ethyl acetate mixture (1:2) as eluent gave (9,9-dipropyl-9H-fluoren-2-ylmethyl)-phosphonic acid dimethyl ester **4.12** (10.1 g, 82%) as a white solid, mp 69-70 °C. (Found: C, 70.91; H, 7.98. $C_{22}H_{29}O_3P$ requires C, 70.95; H, 7.85%); ν_{max} (KBr disc)/cm^{-1} 1247 (P=O), 1055 (P–O) and 1018 (P–O); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon/dm^3mol^{-1}cm^{-1}$) 308 (4.25), 296 (4.08), and 275 (4.42); δ_H ($CDCl_3$, 400 MHz) 0.58-0.70 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 1.91-1.97 (4 H, m, 2 × $ArCH_2$), 3.26 (2 H, d, *J* 22, CH_2P), 3.66 (6 H, d, *J* 9, 2 × $POCH_3$), 7.31 (5 H, m, 5 × ArH), and 7.71 (2 H, dd, *J* 8, *J* 1, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 14.4, 17.2, 33.8 ($^1J_{PC}$ 138), 42.7, 52.9 ($^2J_{POC}$ 7), 55.15, 119.6, 119.8, 122.8, 124.3, 126.8, 127.0, 128.3, 129.8, 140.0, 140.7, 150.6, and 151.1; *m/z* (EI^+) 372 (M^+, 53%), 329 ($[M-C_3H_7]^+$, 100%), and 219

($[M\text{-}C_3H_7\text{-}HP(O)(OCH_3)_2]^+$, 96%); Exact mass 372.1856. $C_{22}H_{29}O_3P$ requires 372.1854.

2-{(*E*)-2-[4-(2′-Ethylhexyloxy)-2,5-dimethyl-phenyl]-vinyl}-9,9-dipropyl-9H-fluorene 4.7:



4.7

Method 1: A mixture of 1-iodo-4-(2′-ethylhexyloxy)-2,5-dimethylbenzene **4.4** (150 mg, 0.4 mmol), 9,9-di(*n*-propyl)-2-vinylfluorene **4.3** (140 mg, 0.5 mmol) and potassium phosphate (120 mg, 0.6 mmol) in *N,N*-dimethylacetamide (3 mL) was de-oxygenated on a Schlenk line by applying high vacuum first and then purging with nitrogen. The process was repeated at 3 minutes interval twice. Palladium (II) acetate (ca. 5 mg, 4 mol%) was added and mixture was heated at 144 °C for four days. After allowing the reaction mixture to cool, the mixture was poured in water (10 mL) and the aqueous phase was extracted with ether (3 × 10 mL). The ethereal extracts were combined, washed with brine (5 mL), dried over magnesium sulphate, filtered and concentrated. Purification of the residue by column chromatography over silica using a gradient elution with light petroleum:dichloromethane mixture (25:0 to 24:1) gave 2-{(*E*)-2-[4-(2′-ethylhexyloxy)-2,5-dimethyl-phenyl]-vinyl}-9,9-dipropyl-9*H*-fluorene **4.7** (77 mg, 34%) as a white solid.

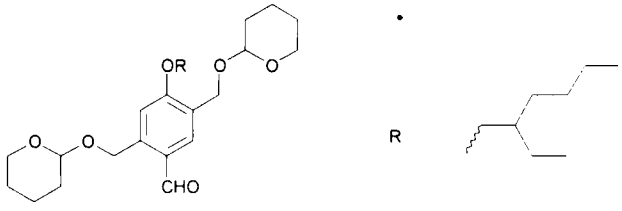
Method 2: A mixture of 1-iodo-4-(2′-ethylhexyloxy)-2,5-dimethylbenzene **4.4** (300 mg, 0.8 mmol), 9,9-di(*n*-propyl)-2-vinylfluorene **4.3** (270 mg, 1.0 mmol), anhydrous sodium carbonate (130 mg, 1.3 mmol), and 2,6-di-*t*-butyl-*p*-cresol (40 mg, 0.2 mmol) in *N,N*-dimethylacetamide (3 mL) were deoxygenated thoroughly over 15 minutes by alternate exposure to high vacuum and flushing with argon whilst being stirred vigorously. Herrmann's catalyst **4.8** (8 mg, 4 mol%) was added and the reaction mixture was heated at reflux in dark for 4 days. After allowing the reaction mixture to cool, aqueous hydrochloric acid (3 M, 5 mL) was added slowly. The aqueous layer was extracted with ether (3 × 10 mL), washed with water (2 × 5 mL) and brine (5 mL), dried over magnesium sulphate, filtered and solvent was removed to give a brown solid. Purification of the crude by column chromatography over silica gel using a light petroleum:dichloromethane mixture (25:0 to 24:1) as eluent followed by recrystallisation from dichloromethane/methanol mixture gave 2-{(*E*)-2-[4-(2′-ethylhexyloxy)-2,5-dimethyl-phenyl]-vinyl}-9,9-dipropyl-9*H*-fluorene **4.7** (131 mg, 30%) as a white solid.

Method 3: A mixture of (9,9-dipropyl-9*H*-fluoren-2-ylmethyl)-phosphonic acid dimethyl ester **4.12** (2.0 g, 5.4 mmol), 4-(2′-ethylhexyloxy)-2,5-dimethyl-benzaldehyde **4.9** (1.2 g, 4.5 mmol) and potassium *t*-butoxide (0.6 g, 5.4 mmol) in dry tetrahydrofuran (30 mL) was stirred at room temperature for 18 hours under nitrogen. Water (50 mL) was added and the aqueous was extracted with ether (3 × 50 mL). The organic layers were combined, washed with water (2 × 50 mL) and brine (50 mL), dried over magnesium sulphate and filtered. The solvent was removed to give a white solid (3.1 g). Iodine (ca. 10 mg, 0.02 mmol) and toluene (20 mL) was added to the white solid (3.1 g) and the mixture was heated at reflux for 3 hours under nitrogen. On cooling, a saturated solution of sodium metabisulphite was added; the organic layer

was separated and washed with brine (30 mL), dried over magnesium sulphate, filtered and solvent was removed. Purification of the crude by column chromatography over silica gel using a gradient elution with light petroleum:dichloromethane mixture (10:0 to 10:1) followed by recrystallisation from dichloromethane/methanol mixture gave 2-{(*E*)-2-[4-(2′-ethylhexyloxy)-2,5-dimethyl-phenyl]-vinyl}-9,9-dipropyl-9*H*-fluorene **4.7** (2.4 g, 88%) as a white solid, mp 115-117 °C; ν_{max} (KBr disc)/cm^{-1} 1603 (C=C); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 356 (4.66), and 232 (4.66); δ_H ($CDCl_3$, 400 MHz) 0.68-0.84 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 0.97-1.11 (6 H, m, 2 × CH_3), 1.38-1.70 (8 H, m, 4 × CH_2), 1.78-1.90 (1 H, m, CH), 2.00-2.12 (4 H, m, 2 × $ArCH_2$), 2.32 (3 H, s, $ArCH_3$), 2.53 (3 H, s, $ArCH_3$), 3.95 (2 H, d, *J* 6, $ArOCH_2$), 6.73 (1 H, s, ArH), 7.08 (1 H, d, *J* 16, vinylH), 7.41 (4 H, m, 4 × ArH), 7.53 (2 H, s, 2 × ArH), 7.60 (I H, d, *J* 8, ArH), and 7.75 (2 H, m, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 11.3, 14.1, 14.5, 15.9, 17.2, 20.0, 23.1, 24.1, 29.1, 30.7, 39.6, 42.8, 55.2, 70.2, 112.7, 119.5, 119.8, 120.9, 122.8, 124.6, 124.9, 125.6, 126.7, 126.8, 127.5, 128.0, 128.1, 134.4, 137.1, 140.4, 140.9, 150.9, 151.2, and 157.0; *m/z* (EI$^+$) 508 (M$^+$, 100%); Exact mass 508.3718. $C_{37}H_{48}O$ requires 508.3705.

4-(2′-Ethylhexyloxy)-2,5-*bis*(tetrahydro-2*H*-2-pyranyloxymethyl)benzaldehyde

4.18b:

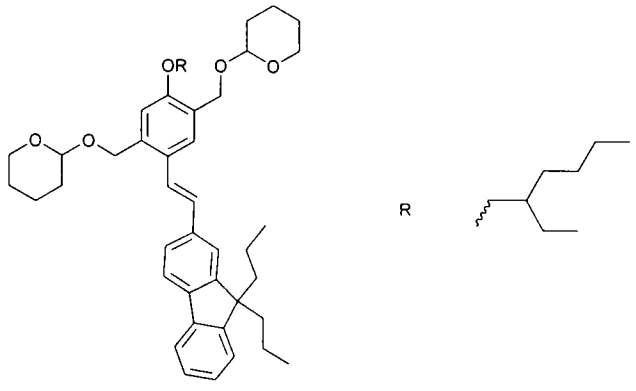


4.18b

t-Butyllithium (1.7 M in pentane, 2.3 mL, 3.8 mmol) was added drop-wise to a stirred solution of 2-[5-bromo-2-(2′-ethylhexyloxy)-4-tetrahydro-2*H*-2-

pyranyloxymethylbenzyloxy]tetrahydro-2*H*-pyran **3.9** (1.5 g, 2.9 mmol) in dry tetrahydrofuran (10 mL) at -78 °C under nitrogen and stirred for 45 minutes. *N,N*-dimethylformamide (1.2 mL, 14.6 mmol) was added and the mixture was stirred further at -78 °C for 15 minutes and then at room temperature for 2 hours. Water (15 mL) was added and aqueous phase was extracted with ether (2 × 50 mL. The organic extracts were combined, washed with aqueous hydrochloric acid (3 M, 10 mL), water (2 × 50 mL) and brine (50 mL). The solution was dried over magnesium sulphate, filtered and concentrated to give yellow oil. The crude was purified by column chromatography over silica gel using a light petroleum:ethyl acetate mixture (4:1) as eluent to give 4-(2'-ethylhexyloxy)-2,5-*bis*(tetrahydro-2*H*-2-pyranyloxymethyl)benzaldehyde (1.1 g, 81%) **4.18b** as a clear colourless oil; ν_{max} (KBr disc)/cm^{-1} 1687 (CHO); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/$dm^3mol^{-1}cm^{-1}$) 284 (4.46), and 232 (4.56); δ_H ($CDCl_3$, 400 MHz) 0.78-0.95 (6 H, m, 2 × CH_3), 1.26-1.98 (21 H, m, 10 × CH_2, CH), 3.50-3.60 (2 H, m, -OCH_2(THP)), 3.86-4.02 (2 H, d, *J* 5.5, ArOCH_2), 4.57 (1 H, d, *J* 14), 4.97 (1 H, d, *J* 14), 4.72-4.81 (3 H, m), 5.17 (1 H, d, *J* 14), 7.20 (1 H, s, ArH), 7.91 (1 H, s, ArH), and 10.11 (1 H, s, CHO); δ_C ($CDCl_3$, 100 MHz) 11.0, 13.9, 19.3, 19.6, 22.6, 22.9, 23.8, 25.3, 25.4, 27.6, 29.0, 30.5, 39.2, 41.2, 61.8, 62.5, 63.4, 66.4, 70.5, 98.3, 98.5, 110.0, 126.0, 126.1, 133.5, 142.9, 160.9, and 191.2; *m/z* (ES^+) 485 ($[MNa]^+$, 100%), 480 ($[MNH_4]^+$, 16%) and 463 (M^+, 32%); Exact mass 463.3058. $C_{27}H_{43}O_6$ requires 463.3060.

2-[2-[(*E*)-2-(9,9-dipropyl-9*H*-2-fluorenyl)-1-ethenyl]-5-(2′-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxy]tetrahydro-2*H*-pyran 4.19:

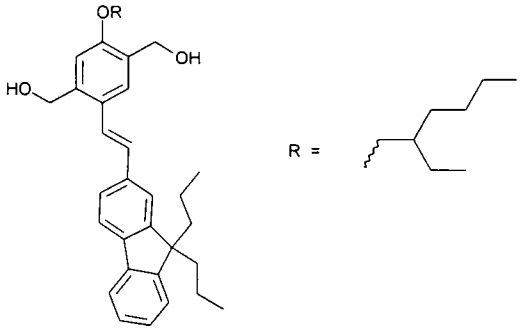


4.19

Lithium diisopropylamide (2.0 M in heptane, 2.5 mL, 4.9 mmol) was added to a solution of (9,9-dipropyl-9*H*-fluoren-2-ylmethyl)-phosphonic acid dimethyl ester **4.12** (1.6 g, 4.2 mmol) and 4-(2′-ethylhexyloxy)-2,5-*bis*(tetrahydro-2*H*-2-pyranyloxymethyl)benzaldehyde **4.18b** (1.7 g, 3.7 mmol) in dry tetrahydrofuran (50 mL) at 0 °C under nitrogen. After addition, the mixture was stirred at room temperature for 45 minutes and then quenched with a saturated solution of ammonium chloride (30 mL). The aqueous layer was extracted with ether (2 × 50 mL) and ethereal extracts were combined, washed with water (2 × 50 mL) and brine (50 mL), dried over magnesium sulphate, and filtered. Removal of solvent gave a yellow oil. The oil was purified by column chromatography over silica gel using dichloromethane as eluent. The main fraction was eluted and concentrated. The compound was further purified by flash chromatography over silica gel using a light petroleum:ethyl acetate mixture (12:1) as eluent to give 2-[2-[(*E*)-2-(9,9-dipropyl-9*H*-2-fluorenyl)-1-ethenyl]-5-(2′-ethylhexyloxy)-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxy]tetrahydro-2*H*-pyran **4.19** (2.2 g, 87%) as a yellow oil. (Found: C, 79.63; H, 9.06. $C_{47}H_{64}O_5$ requires C, 79.62; H, 9.10%); ν_{max} (KBr disc)/cm^{-1} 1606 (C=C), and 1120 (C–O–C); λ_{max}

(CH_2Cl_2)/nm ($\log_{10}\varepsilon/dm^3mol^{-1}cm^{-1}$) 368 sh (3.52), 352 (3.73), and 234 (3.44); δ_H ($CDCl_3$, 400 MHz) 0.68-0.82 (10 H, m, 2 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 0.92-1.04 (6 H, m, 2 × CH_3), 1.35-1.90 (20 H, m, 10 × CH_2), 1.92-2.09 (5 H, m, CH, 2 × $ArCH_2$), 3.61-3.68 (2 H, m, -OCH_2(THP)), 3.96-4.00 (2 H, m, *J* 5.5, $ArOCH_2$), 4.02-4.11 (2 H, m, OCH_2(THP)), 4.62-4.75, 4.84-4.89 and 4.99-5.02 (6 H, m, 2 × $ArCH_2O$, 2 × -OCH (THP)), 6.99 (1 H, s, ArH), 7.09 (1 H, d, *J* 16, vinylH), 7.45 (3 H, s, 3 × ArH), 7.53 (3 H, s, 3 × ArH), 7.72 (2 H, m, 2 × ArH), and 7.78 (1 H, s, ArH); δ_C ($CDCl_3$, 100 MHz) 11.2, 14.3, 14.5, 17.2, 19.6, 23.1, 23.9, 25.2, 25.6, 29.1, 30.6, 30.7, 39.5, 42.6, 55.2, 62.1, 62.5, 64.2, 67.3, 70.3, 98.0, 98.4, 112..0, 119.6, 119.8, 120.6, 122.8, 123.0, 123.1, 124.8, 125.5, 126.5, 126.8, 127.0, 127.1, 128.8, 129.1, 135.7, 137.0, 140.5, 140.9, 150.9, 151.2, and 156.4; *m/z* (EI^+) 708 (M^+, 100%).

[5-[(*E*)-2-(9,9-Dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2'-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol 4.13:



4.13

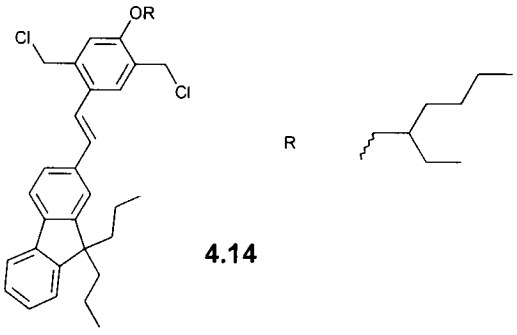
Method 1: A mixture of 2-{(*E*)-2-[4-(2'-ethylhexyloxy)-2,5-dimethyl-phenyl]-vinyl}-9,9-dipropyl-9*H*-fluorene **4.7** (9.9 g, 19.4 mmol), *N*-bromosuccinimide (6.9 g, 38.7 mmol) and 2,2'-azo-*bis*(isobutyronitrile) (1.3 g, 7.7 mmol) in carbon tetrachloride (45 mL) was heated at reflux for 4 hours. After cooling, the reaction mixture was diluted with dichloromethane (50 mL) and filtered through a plug of silica using

dichloromethane as eluent. The solvent was removed to give crude *bis*-bromide as a brown oil. Glacial acetic acid (50 mL) and sodium acetate (15.9 g, 0.19 mol) was added to the brown oil and the reaction mixture was heated at reflux for 5 hours. After cooling, water (250 mL) was added and the aqueous phase was extracted with ether (3 × 100 mL). The combined organic fractions were washed with water (3 × 100 mL) and saturated sodium bicarbonate (2 × 200 mL), dried over magnesium sulphate, filtered and solvent was removed to give crude *bis*-acetate as a brown solid. The residue was dissolved in anhydrous ether (100 mL) and stirred at -18 °C before the portion-wise addition of lithium aluminium hydride (1.3 g, 34 mmol). The reaction was stirred at room temperature for 2 hours. Aqueous hydrochloric acid (3 M, 50 mL) was carefully added and the ether layer was separated. The aqueous phase was extracted with ether (3 × 50 mL). The organic extracts were combined, washed with brine (50 mL), dried over magnesium sulphate and filtered. Solvent removal gave a dark brown oil. Purification of the crude by column chromatography over silica gel using a gradient elution with dichloromethane:methanol mixture (50:0 to 48:2) as eluent followed by recrystallisation from dichloromethane/light petroleum mixture at 0 °C gave [5-[(*E*)-2-(9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **4.13** (0.3 g, 3%) as white crystals, mp 125-127 °C. (Found: C, 82.26; H, 8.85. $C_{37}H_{48}O_3$ requires C, 82.18; H, 8.95%); ν_{max} (KBr disc)/cm $^{-1}$ 3312 (O–H), 1606 (C=C); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 351 (4.84), and 231 (4.46); δ_H ($CDCl_3$, 400 MHz) 0. 54-0.78 (10 H, m, 2 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 0.88-1.24 (6 H, m, 2 × CH_3), 1.36-1.58 (8 H, m, 4 × CH_2), 1.76-1.87 (1 H, m, CH), 1.97-2.30 (4 H, m, 2 × $ArCH_2$), 3.98 (2 H, d, *J* 5, $ArOCH_2$), 4.77 (2 H, s, $ArCH_2O$), 4.89 (2 H, s, $ArCH_2O$), 7.01 (1 H, s, ArH), 7.08 (1 H, d, *J* 16, vinylH), 7.33 (4 H, m, 4 × ArH), 7.48 (1 H, s, ArH), 7.52 (1 H, d, *J* 8, ArH), 7.65 (1 H, s, ArH), and 7.69 (2 H, m, *J* 8, *J*

1, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 11.2, 14.1, 14.5, 17.2, 23.0, 24.1, 29.1, 30.7, 39.5, 42.8, 55.2, 62.0, 63.2, 70.5, 110.7, 119.7, 119.9, 121.0, 122.9, 123.7, 125.3, 126.2, 126.8, 127.0, 128.3, 128.9, 130.2, 136.5, 138.6, 140.7, 140.8, 151.0, 151.3, and 156.7; *m/z* (EI^+) 540 (M^+, 100%); Exact mass 540.3618. $C_{37}H_{48}O_3$ requires 540.3603.

Method 2: A mixture of *p*-toluenesulphonic acid monohydrate *p*-toluenesulphonic acid monohydrate (30 mg, 10 mol%), 2-5-(2′-ethylhexyloxy)-2-[(*E*)-2-(9,9-dipropyl-9*H*-2-fluorenyl)-1-ethenyl]-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxytetrahydro-2*H*-pyran **4.19** (1.1 g, 1.6 mmol), methanol (55 mL) and dichloromethane (55 mL) was stirred at room temperature for 15 hours under nitrogen. Water (50 mL) was added and the aqueous phase was extracted with dichloromethane (2 × 50 mL). The organic layers were combined, washed with water (2 × 50 mL), dried over magnesium sulphate, and filtered. The solvent was removed to give yellow oil (0.8 g). Preliminary purification of the crude product was carried out by flash chromatography over silica gel using a light petroleum:ethyl acetate mixture (6:1) followed by recrystallisation from dichloromethane/hexane mixture at 0 °C gave [5-[(*E*)-2-(9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **4.13** (0.6 g, 73%) as a white solid.

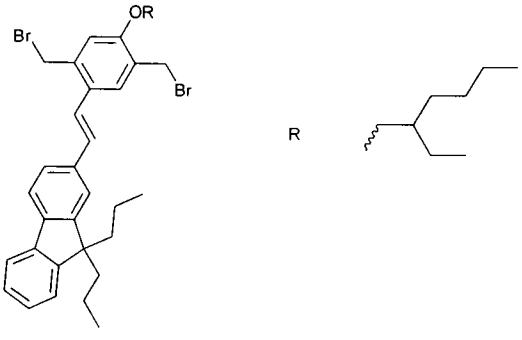
Attempted synthesis of 2-{(*E*)-2-[2,5-*bis*-chloromethyl-4-(2-ethylhexyloxy)-phenyl]-vinyl}-9,9-dipropyl-9*H*-fluorene 4.14:



4.14

Thionyl chloride (0.18 mL, 2.5 mmol) was added to a stirred solution of [5-[(*E*)-2-(9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2'-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **4.13** (80 mg, 0.14 mmol) in anhydrous dichloromethane (5 mL) at 0 °C for 1 hour. The reaction temperature was raised to room temperature and stirred for 16 hours. Water (5 mL) was carefully added and the aqueous layer was extracted with ether (3 × 5 mL). The combined organic extracts were washed with water (2 × 5 mL), dried over magnesium sulphate, filtered and the solvent was removed to give a brown oil. Column chromatography of the crude over silica gel using a light petroleum:dichloromethane mixture (1:1) as eluent followed by purification by recrystallisation from dichloromethane/methanol mixture gave an impure 2-{(*E*)-2-[2,5-*bis*-chloromethyl-4-(2-ethylhexyloxy)-phenyl]-vinyl}-9,9-dipropyl-9*H*-fluorene **4.14**.

2-{(*E*)-2-[2,5-*Bis*-bromomethyl-4-(2-ethylhexyloxy)-phenyl]-vinyl}-9,9-dipropyl-9*H*-fluorene 4.20:



4.20

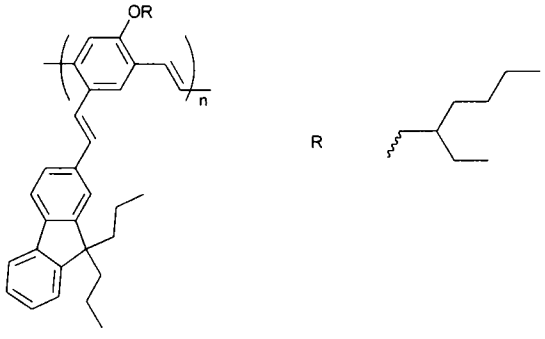
Method 1: Hydrobromic acid (33% w/w acetic acid, 0.2 mL, 1.1 mmol) was added to a solution of [5-[(*E*)-2-(9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2'-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **4.13** (30 mg, 0.06 mmol) in glacial acetic acid (2 mL) at 60 °C under nitrogen. The mixture was stirred at 60 °C for 40 minutes under nitrogen. The reaction mixture was allowed to cool, water (5 mL) was carefully added and the precipitate obtained was filtered, and washed with water (2 × 10 mL). Column chromatography of the crude over silica gel using a light petroleum:dichloromethane mixture (1:1) as eluent gave impure 2-{(*E*)-2-[2,5-*bis*-bromomethyl-4-(2-ethylhexyloxy)-phenyl]-vinyl}-9,9-dipropyl-9*H*-fluorene **4.20**.

Method 2: Hydrobromic acid (33% w/w acetic acid, 0.4 mL, 1.8 mmol) was added to a solution of [5-[(*E*)-2-(9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2'-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **4.13** (50 mg, 0.09 mmol) in glacial acetic acid (2mL), and the reaction mixture was stirred at room temperature under nitrogen for 1.5 hours. Water (5 mL) was carefully added and the aqueous phase was extracted with dichloromethane (3 × 5 mL), washed with a saturated solution of sodium bicarbonate (5 mL). The dichloromethane layers were combined, dried over magnesium sulphate, filtered and solvent was removed to give brown oil. Column

chromatography of the oil over silica gel using a light petroleum:dichloromethane mixture (1:1) as eluent gave impure 2-{(*E*)-2-[2,5-*bis*-bromomethyl-4-(2-ethylhexyloxy)-phenyl]-vinyl}-9,9-dipropyl-9*H*-fluorene **4.20**.

Method 3: Phosphorous tribromide (130 μL, 1.4 mmol) was added to a solution of [5-[(*E*)-2-(9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2'-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **4.13** (300 mg, 0.6 mmol) in anhydrous dichloromethane (20 mL) and the reaction was heated at reflux for 1.5 hour under nitrogen and a change in colour from colourless to pink was observed. After allowing the reaction mixture to cool, water (5 mL) was carefully added and the aqueous was extracted with dichloromethane (2 × 10 mL). The organic layers were combined, washed with water (2 × 10 mL) and dried over magnesium sulphate. Filtration and solvent removal gave a pink oil residue. Column chromatography of the crude over silica gel using a light petroleum:dichloromethane mixture (1:1) gave 2-{(*E*)-2-[2,5-*bis*-bromomethyl-4-(2'-ethylhexyloxy)-phenyl]-vinyl}-9,9-dipropyl-9*H*-fluorene **4.20** (140 mg, 37%) as a clear oil which solidifies on standing to a white solid, mp 34-35 °C. ν_{max} (KBr disc)/cm^{-1} 1607 (C=C), and 737 (C–Br); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon/dm^3mol^{-1}cm^{-1}$) 351 (4.82), 264 sh (4.49), and 245 sh (4.60); δ_H ($CDCl_3$, 500 MHz) 0.68-0.84 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 0.98-1.09 (6 H, m, 2 × CH_3), 1.48-1.70 (8 H, m, 4 × CH_2), 1.80-1.88 (1 H, m, CH), 2.04-2.13 (4 H, m, 2 × $ArCH_2$), 4.04 (2 H, d, *J* 6, $ArOCH_2$), 4.62 (2 H, s, $ArCH_2Br$), 4.72 (2 H, s, $ArCH_2Br$), 6.93 (1 H, s, ArH), 7.18 (1 H, d, *J* 16, vinylH), 7.38 (4 H, m, 4 × ArH), 7.54 (1 H, s, ArH), 7.66 (1 H, d, *J* 16, vinylH), 7.74 (1 H, s, ArH), and 7.79 (2 H, d, *J* 8, 2 × ArH); δ_C ($CDCl_3$, 125 MHz) 11.3, 14.4, 16.9, 23.1, 23.8, 28.6, 28.8, 30.6, 32.5, 39.4, 43.1, 55.6, 71.3, 112.5, 119.4, 119.9, 121.3, 122.5, 123.2, 125.1, 126.3, 126.8, 126.9, 128.1, 128.8, 130.1, 135.6, 135.8, 140.2, 140.5, 150.6, 151.1, and 155.6; *m/z* (EI^+) 668, 666, and 664 (M^+, 25%, 100%, 28%).

Poly{2-[(*E*)-2-(9,9-dipropylfluorenyl)vinyl]-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene} 4.21:



4.21

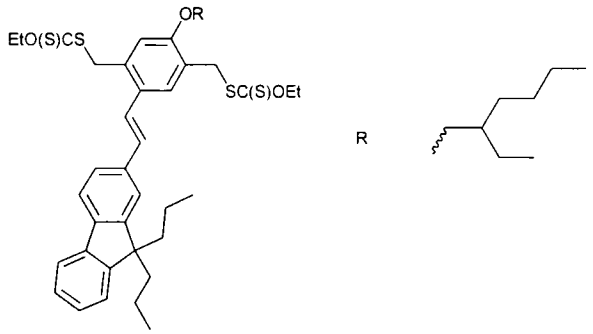
Method 1: A solution of potassium *t*-butoxide (85 mg, 0.75 mmol) in anhydrous tetrahydrofuran (3.3 mL) was added to a stirred solution of 2-{(*E*)-2-[2,5-*bis*-bromomethyl-4-(2′-ethylhexyloxy)-phenyl]-vinyl}-9,9-dipropyl-9*H*-fluorene **4.20** (100 mg, 0.15 mmol) in tetrahydrofuran (1.5 mL) under nitrogen. The reaction was allowed to stir at room temperature for 24 hours in dark. No polymerisation was detected by g.p.c. analysis.

Method 2: A solution of potassium *t*-butoxide (85 mg, 0.75 mmol) in anhydrous tetrahydrofuran (3.3 mL) was added to a solution of 2-{(*E*)-2-[2,5-*bis*-bromomethyl-4-(2′-ethylhexyloxy)-phenyl]-vinyl}-9,9-dipropyl-9*H*-fluorene **4.20** (100 mg, 0.15 mmol) in tetrahydrofuran (1.5 mL) under nitrogen. The reaction mixture was heated at reflux for 24 hours. G.p.c. analysis showed the presence of oligomers and the monomer.

Method 3: A solution of potassium *t*-butoxide (85 mg, 0.75 mmol) in anhydrous tetrahydrofuran (3.3 mL) was added to a solution of 2-{(*E*)-2-[2,5-*bis*-bromomethyl-4-(2′-ethylhexyloxy)-phenyl]-vinyl}-9,9-dipropyl-9*H*-fluorene **4.20** (100 mg, 0.15 mmol) in tetrahydrofuran (1.5 mL) under nitrogen. The reaction mixture was stirred at

room temperature for 3 hours then heated at reflux for 24 hours in dark. G.p.c. analysis and ^{1}H n.m.r. spectrum showed the formation of polymer. A small batch of crude polymer was purified using preparatory gel permeation chromatography. Poly{2-[(*E*)-2-(9,9-dipropylfluorenyl)vinyl]-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene} **4.21** was obtained as a yellow solid. ν_{max} (film, KBr disc)/cm^{-1} 1726 (C=O), 1600 cm^{-1} (C=C), and 962 (C=C–H trans); λ_{max} (film)/nm 409 sh, and 340; $\overline{M}_w = 3.1 \times 10^4$ g/mol, $\overline{M}_n = 0.9 \times 10^4$, and PD = 3.54.

Attempted synthesis of dithiocarbonic acid *S*-{4-ethoxythiocarbonylsulfanylmethyl-2-(2′-ethylhexyloxy)-5-[(*E*)-2-(9,9-dipropyl-9H-fluorenyl) vinyl]benzyl} ester *O*-ethyl ester 4.22:



4.22

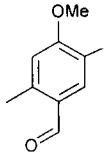
Method 1: Potassium *O*-ethylxanthate (30 mg, 0.18 mmol) was added to a solution of 2-{(*E*)-2-[2,5-*bis*-bromomethyl-4-(2′-ethylhexyloxy)-phenyl]-vinyl}-9,9-dipropyl-9H-fluorene **4.20** (20 mg, 0.03 mmol) and tetra-*n*-butylammonium bromide (ca. 5 mg, 20 mol%) in dichloromethane (5 mL) and the reaction mixture was stirred at 0 °C for 2 hours and then at room temperature for 16 hours under argon. Water (5 mL) was added and the aqueous layer was extracted with ether (3 × 10 mL). The organic layers were combined, washed with water (3 × 5 mL), dried over magnesium sulphate, and filtered. The removal of solvent gave brown oil. Column

chromatography of the crude over silica gel using a gradient elution with light petroleum:dichloromethane mixture (1:0 to 8:5) gave impure 2-{(*E*)-2-[-[2,5-*bis*-bromomethyl-4-(2′-ethylhexyloxy)-phenyl]-vinyl}-9,9-dipropyl-9H-fluorene **4.20** (20 mg) and no dithiocarbonic acid *S*-{4-ethoxythiocarbonylsulfanylmethyl-2-(2′-ethylhexyloxy)-5-[(*E*)-2-(9,9-dipropyl-9H-fluorenyl)vinyl]benzyl}ester *O*-ethyl ester **4.22** was obtained.

Method 2: Potassium *O*-ethylxanthate (30 mg, 0.18 mmol), 2-{(*E*)-2-[2,5-*bis*-bromomethyl-4-(2′-ethylhexyloxy)-phenyl]-vinyl}-9,9-dipropyl-9H-fluorene **4.20** (20 mg, 0.03 mmol) and tetra-*n*-butylammonium bromide (5 mg, 20 mol%) in dichloromethane (5 mL) was heated at reflux for 5 hours. The reaction mixture was concentrated and column chromatography over silica gel using a light petroleum:dichloromethane (8:3) as eluent gave impure dithiocarbonic acid *S*-{4-ethoxythiocarbonylsulfanylmethyl-2-(2′-ethylhexyloxy)-5-[(*E*)-2-(9,9-dipropyl-9H-fluorenyl) vinyl]benzyl} ester *O*-ethyl ester **4.22** as a brown oil. T.l.c. plate of the brown oil showed the presence of several unidentifiable spots.

6.8.1 Synthesis of poly{2-[(*E*)-2-(7-nitro-9,9-dipropylfluorenyl)vinyl]-5-methoxy-1,4-phenylenevinylene}

4-Methoxy-2,5-dimethylbenzaldehyde 4.23:



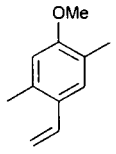
4.23

Method 1: Phosphorous oxychloride (76.0 mL, 0.8 mol) was added slowly to a stirred anhydrous *N,N*-dimethylformamide (150 mL) followed by the drop-wise addition of

2,5-dimethylanisole **2.18** (10.0 g, 69.9 mmol) in anhydrous *N,N*-dimethylformamide (50 mL) at 0 °C. The reaction mixture was heated slowly, temperature being carefully raised to 124 °C, at which the reaction initiation occurred. The reaction flask was removed from the hot plate and after 15 minutes the reaction mixture was stirred at 100 °C for 3 hours. After allowing the reaction mixture to cool, water (100 mL) was added carefully. The aqueous layer was extracted with ether (3 × 100 mL). The combined organic extracts were washed with water (3 × 100 mL) and brine (100 mL), dried over magnesium sulphate, and filtered. The removal of solvent gave a black oil. The crude was purified by column chromatography over silica gel using a light petroleum:dichloromethane mixture (3:2) as eluent to give 4-methoxy-2,5-dimethylbenzaldehyde **4.23** (7.6 g, 62%) as a creamy solid, mp 33-34 °C (lit.[167] 34 °C). The compound had an identical ^{1}H n.m.r spectrum to that reported in the literature[167].

Method 2: *t*-Butylithium (1.7 M in pentane, 100 mL, 0.17 mol) was added drop-wise to a solution of 1-bromo-4-methoxy-2,5-dimethylbenzene **2.3b** (23.6 g, 0.1 mol) in anhydrous tetrahydrofuran (150 mL) at -78 °C under nitrogen and stirred for 1 hour. *N,N*-dimethylformamide (27 mL, 0.3 mol) was added and reaction mixture stirred at -78 °C for 30 minutes and thereafter at room temperature for 18 hours. Water (100 mL) was added and aqueous phase was extracted with dichloromethane (3 × 150 mL). The organic layers were combined, washed with water (3 × 150 mL) and brine (100 mL), dried over magnesium sulphate, and filtered. The solvent was removed to give a yellow oil. Purification of the residue by column chromatography over silica gel using a light petroleum:dichloromethane mixture (1:1) as eluent gave 4-methoxy-2,5-dimethylbenzaldehyde **4.23** (14.8 g, 82%) as a creamy solid.

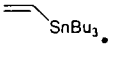
1-Methoxy-2,5-dimethyl-4-vinylbenzene 4.24:



4.24

A mixture of methytriphenylphosphonium iodide (32.0 g, 79.0 mmol) and potassium *t*-butoxide (8.8 g, 79.0 mmol) was stirred in anhydrous tetrahydrofuran (100 mL) at room temperature for 30 minutes under argon to give a bright yellow solution. A solution of 4-methoxy-2,5-dimethylbenzaldehyde **4.23** (10.0 g, 60.9 mmol) in anhydrous tetrahydrofuran (20 mL) was added and the reaction was stirred for 17 hours. Water (100 mL) was added and the aqueous layer was extracted with ether (3 × 100 mL), washed with water (3 × 100 mL) and brine (100 mL), dried over magnesium sulphate, and filtered. The solvent was removed to give brown oil. Purification of the crude by filtering through a silica plug using a light petroleum:dichloromethane mixture (1:1) as eluent followed by recrystallisation from methanol gave 1-methoxy-2,5-dimethyl-4-vinylbenzene **4.24** (6.4 g, 65%) as white crystals, mp 44-46 °C (lit.[168] 45-46 °C). The compound had an identical ^{1}H n.m.r. spectrum to that reported in the literature[168].

Tri-*n*-butylvinyl stannane 4.27:

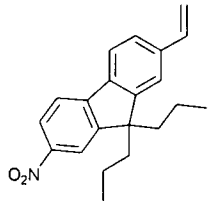


4.27

Tri-*n*-butyltin chloride (30.4 mL, 0.11 mol) was added drop-wise to a stirred solution of vinylmagnesium chloride **4.26** (1.6 M in tetrahydrofuran, 70 mL, 0.11 mol) in a flame-dried cool flask at room temperature under argon. The reaction mixture was heated at reflux for 2.5 hours. The solvent was removed to give light yellow oil.

Dichloromethane (50 mL) was added and the solution was filtered through a plug of silica using dichloromethane as eluent. The solvent was removed followed by vacuum distillation, 110 °C, 1 mmHg (lit.[169] 114 °C, 3 mmHg) gave tri-*n*-butylvinyl stannane **4.27** (32.6 g, 92%) as a clear colourless oil.

9,9-Di(*n*-propyl)-2-nitro-7-vinylfluorene 4.28:



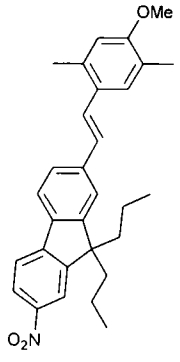
4.28

Tetrakis(triphenylphosphine)palladium (0) (0.3 g, 0.3 mmol) was added to an argon purged solution of 2-bromo-9,9-di(*n*-propyl)-7-nitrofluorene **2.16** (5.0 g, 13.3 mmol), tri-*n*-butylvinyl stannane **4.27** (6.4 g, 20.2 mmol), and 2,6-di-*t*-butylcresol (0.6 g, 2.7 mmol) in toluene (100 mL). The reaction mixture was heated at reflux for 16 hours in dark. After cooling, aqueous hydrochloric acid (3 M, 10 mL) was added carefully. The aqueous layer was extracted with ether (3 × 50 mL). The organic extracts were combined, washed with water (3 × 50 mL) and brine (50 mL), dried over magnesium sulphate, filtered and solvent was removed to give a light yellow oil. Purification of the oil by column chromatography over silica gel using a light petroleum:dichloromethane mixture (4:1) followed by recrystallisation from light petroleum gave 9,9-di(*n*-propyl)-2-nitro-7-vinylfluorene **4.28** (2.7 g, 63%) as yellow crystals, mp 95-97 °C. (Found: C, 78.65; H, 7.23; N, 4.33. $C_{29}H_{40}BrNO_2$ requires C, 78.47; H, 7.21; N, 4.36%); ν_{max} (KBr disc)/cm^{-1} 1610 (C=C); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 363 (4.60), 270 (4.18), and 228 (4.09); δ_H ($CDCl_3$, 400 MHz) 0.53 – 0.70 (10 H, m, 2 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 1.98-2.09 (4 H, m, 2 × $ArCH_2$), 5.36 (1 H,

d, *J* 11, vinylH), 5.36 (1 H, d, *J* 18, vinylH), 6.83 (1 H, dd, *J* 18, *J* 11, Ar-vinyl-H), 7.45 (1 H, d, *J* 1, ArH), 7.47 (1 H, dd, *J* 1, *J* 8, ArH), 7.76 (2 H, m, 2 × ArH), 8.23 (1 H, d, *J* 2, ArH), and 8.27 (1 H, dd, *J* 2, *J* 8, ArH); δ_C ($CDCl_3$, 100 MHz) 14.3, 17.1, 42.4, 55.8, 114.8, 118.2, 119.7, 120.8, 121.3, 123.3, 125.8, 136.8, 138.5, 138.7, 147.0, 147.3, 152.2, and 152.8 ; *m/z* (CI^+) 322 (MH^+, 10%), and 292 ($[M-C_2H_5]^+$, 100%).

2-[(*E*)-2-(4-Methoxy-2,5-dimethylphenyl)vinyl]-7-nitro-9,9-dipropyl-9*H*-fluorene

4.25b:



4.25b

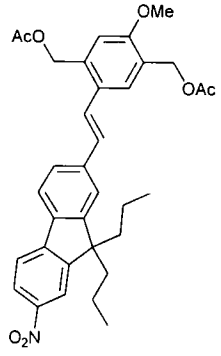
Method 1: A mixture of 2-bromo-7-nitro-9,9-di-*n*-propyl-9*H*-fluorene **2.16** (12.9 g, 34.4 mmol), 1-methoxy-2,5-dimethyl-4-vinylbenzene **4.24** (6.7 g, 41.3 mmol), anhydrous sodium carbonate (5.5 g, 51.9 mmol), 2,6-di-*t*-butyl-*p*-cresol (1.5 g, 6.9 mmol), Hermann's catalyst (0.3 g, 0.3 mmol) in *N,N*-dimethylacetamide (100 mL) was deoxygenated thoroughly over 30 minutes by alternate exposure to high vacuum and flushing with argon whilst being stirred vigorously. The yellow mixture was heated at reflux for 4 days in dark. After cooling, aqueous hydrochloric acid (3 M, 50 mL) was added slowly. The aqueous layer was extracted with chloroform (3 × 100 mL). The organic layers were combined, washed with water (3 × 100 mL) and brine (100 mL), dried over magnesium sulphate, filtered and solvent was removed to give a brown solid. Purification of the residue by column chromatography over silica gel using a light petroleum:dichloromethane mixture (4:1) as eluent followed by

recrystallisation from dichloromethane/methanol mixture gave 2-[(*E*)-2-(4-methoxy-2,5-dimethylphenyl)vinyl]-7-nitro-9,9-dipropyl-9*H*-fluorene **4.25b** (1.9 g, 12%) as orange crystals.

Method 2: A mixture of 1-bromo-4-methoxy-2,5-dimethylbenzene **2.3b** (0.8 g, 3.7 mmol), 9,9-di(*n*-propyl)-2-nitro-7-vinylfluorene **4.28** (1.0 g, 3.1 mmol), anhydrous sodium carbonate (0.4 g, 3.8 mmol), 2,6-di-*t*-butyl-p-cresol (0.1 g, 0.5 mmol), Hermann's catalyst (4.3 mg, 0.03 mmol) in *N,N*-dimethylacetamide (20 mL) was purged with argon for 30 minutes. The reaction was heated at reflux for 4 days in the dark under argon. After cooling, aqueous hydrochloric acid (3 M, 10 mL) was added slowly and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic extracts were washed with water (3 × 50 mL) and brine (50 mL), dried over magnesium sulphate and filtered. The solvent was removed to give a brown solid. Purification of the crude by column chromatography over silica gel using a light petroleum:dichloromethane mixture (4:1) as eluent followed by recrystallisation from dichloromethane/methanol mixture gave 2-[(*E*)-2-(4-methoxy-2,5-dimethylphenyl)vinyl]-7-nitro-9,9-dipropyl-9*H*-fluorene **4.25b** (0.6 g, 52%) as orange crystals, mp 216-217 °C; ν_{max} (KBr disc)/cm^{-1} 1600 (C=C); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 400 (4.30), 307 (3.98), and 231 (3.98); δ_H ($CDCl_3$, 400 MHz) 0.55-0.74 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 1.96-2.10 (4 H, m, 2 × $ArCH_2$), 2.25 (3 H, s, $ArCH_3$), 2.48 (3 H, s, $ArCH_3$), 3.87 (3 H, s, $ArOCH_3$), 6.68 (1 H, s, ArH), 7.05 (1 H, d, *J* 16, vinylH), 7.41 (1 H, d, *J* 16, vinylH), 7.47-7.49 (2 H, d, *J* 7.5, 2 × ArH), 7.60 (1 H, d, *J* 8, ArH), 7.65 (2 H, m, 2 × ArH), 8.22 (1 H, d, *J* 2, ArH), and 8.26 (1 H, dd, *J* 2, *J* 8, ArH); δ_C ($CDCl_3$, 100 MHz) 14.3, 15.9, 17.2, 20.0, 42.4, 55.3, 55.8, 112.0, 118.2, 119.5, 121.1, 121.4, 123.4, 124.4, 125.5, 127.0, 127.4, 127.7, 127.9,

134.8, 137.8, 139.4, 146.8, 147.5, 152.1, 153.0, and 157.56; *m/z* (CI^+) 456 (MH^+, 100%); Exact mass 455.2539. $C_{30}H_{33}NO_3$ requires 455.2525.

2-Methoxy-4-methylcarbonyloxymethyl-5-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)vinyl]benzyl acetate 4.40:

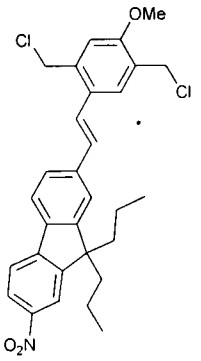


4.40

2,2'-Azo-*bis*(isobutyronitrile) (0.8 g, 5.1 mmol) was added to an argon purged solution of 2-[(*E*)-2-(4-methoxy-2,5-dimethylphenyl)vinyl]-7-nitro-9,9-dipropyl-9*H*-fluorene **4.25b** (5.8 g, 12.7 mmol), and *N*-bromosuccinimide (5.0 g, 28.1 mmol) in carbon tetrachloride (150 mL) and heated at reflux for 4 hours. The reaction mixture was allowed to cool to room temperature, diluted with dichloromethane (20 mL) and filtered through a plug of silica using dichloromethane as eluent. The solvent was removed to give a brown residue of crude *bis*-bromides. Glacial acetic acid (180 mL), and sodium acetate (10.4 g, 126.8 mmol) was added and the reaction mixture was heated at reflux for 5 hours. After cooling, water (50 mL) was added and the aqueous layer was extracted with ether (3 × 50 mL). The organic extracts were combined, washed with aqueous sodium hydroxide (5% w/v, 50 mL), water (3 × 100 mL) and a saturated solution of sodium bicarbonate (2 × 50 mL). The solution was dried over magnesium sulphate, filtered and solvent was removed to give a brown solid. Purification of the crude by flash chromatography over silica gel using a gradient

elution with light petroleum:dichloromethane mixture (1:0 to 0:1) followed by recrystallisation from dichloromethane/methanol mixture gave 2-methoxy-4-methylcarbonyloxymethyl-5-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)vinyl]benzyl acetate **4.40** (1.5 g, 21%) as bright yellow crystals, mp 139-140 °C; ν_{max} (KBr disc)/cm^{-1} 1726 (C=O), and 1595 (C=C); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 391 (4.68), and 308 (4.36); δ_H ($CDCl_3$, 400 MHz) 0.62-0.74 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 1.96-2.10 (4 H, m, 2 × $ArCH_2$), 2.10 (3 H, s, $OCOCH_3$), 2.15 (3 H, s, $OCOCH_3$), 3.91 (3 H, s, $ArOCH_3$), 5.21 (2 H, s, CH_2O), 5.32 (2 H, s, CH_2O), 6.95 (1 H, s, ArH), 7.08 (1 H, d, *J* 16, vinylH), 7.36 (1 H, d, *J* 16, vinylH), 7.50 (1 H, d, *J* 1, ArH), 7.55 (1 H, dd, , *J* 1, *J* 8, ArH), 7.70 (1 H, s, ArH), 7.77 (1 H, d, *J* 8, ArH), 7.79 (1 H, d, *J* 8, ArH), 8.20 (1 H, d, *J* 2, ArH), and 8.21 (1 H, dd, *J* 2, *J* 8, ArH); δ_C ($CDCl_3$, 100 MHz) 14.3, 17.2, 20.9, 21.1, 42.4, 55.7, 55.8, 61.4, 64.1, 112.0, 118.2, 119.6, 121.4, 121.5, 123.4, 125.0, 125.2, 125.7, 127.9, 128.9, 129.8, 134.7, 138.3, 138.6, 147.0, 147.2, 152.2, 153.0, 157.3, 170.7, and 171.0; *m/z* (CI^+) 572 (MH^+, 65%); Exact mass 571.2648. $C_{34}H_{37}NO_7$ requires 571.2570.

2-(*E*)-2-[2,5-*Bis*(chloromethyl)-4-methoxyphenyl]vinyl-7-nitro-9,9-dipropyl-9*H*-fluorene 4.41:

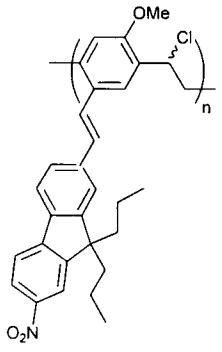


4.41

A mixture of 2-methoxy-4-methylcarbonyloxymethyl-5-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)vinyl]benzyl acetate **4.40** (0.9 g, 1.7 mmol), and concentrated

hydrochloric acid (40 mL) in 1,4-dioxane (100 mL) was heated at reflux for 16 hours. After allowing the reaction mixture to cool, water (50 mL) was added and the aqueous layer was extracted with ether (3 × 50 mL). The organic layers were combined, washed with water (3 × 50 mL) and brine (25 mL), dried over magnesium sulphate and filtered. Removal of solvent gave a yellow residue. The residue was purified by column chromatography over silica gel using light petroleum:dichloromethane mixture (1:1) as eluent followed by recrystallisation from dichloromethane/methanol mixture and gave 2-(*E*)-2-[2,5-*bis*(chloromethyl)-4-methoxyphenyl]vinyl-7-nitro-9,9-dipropyl-9*H*-fluorene **4.41** (0.8 g, 89%) as bright yellow crystals, mp 187-188 °C. (Found: C, 68.54; H, 5.98; N, 2.51. $C_{30}H_{31}Cl_2NO_3$ requires C, 68.70; H, 5.96; N, 2.67%); ν_{max} (KBr disc)/cm^{-1} 1518 (C=C), and 729 (C–Cl); $\lambda_{max}(CH_2Cl_2)$/nm ($\log_{10}\varepsilon/dm^3mol^{-1}cm^{-1}$) 391 (4.68), and 308 (4.36); δ_H ($CDCl_3$, 400 MHz) 0.62-0.74 (10 H, m, 2 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 2.02-2.12 (4 H, m, 2 × $ArCH_2$), 3.95 (3 H, s, $ArOCH_3$), 4.69 (2 H, s, CH_2Cl), 4.77 (2 H, s, CH_2Cl), 6.92 (1 H, s, ArH), 7.13 (1 H, d, *J* 16, vinylH), 7.47 (1 H, d, *J* 16, vinylH), 7.50 (1 H, s, ArH), 7.65 (1 H, dd, *J* 1, *J* 8, ArH), 7.73 (1 H, s, ArH), 7.77 (2 H, d, *J* 8, 2 × ArH), 8.22 (1 H, d, *J* 2, ArH), and 8.27 (1 H, dd, *J* 2, *J* 8, ArH); δ_C ($CDCl_3$, 100 MHz) 14.3, 17.2, 41.0, 42.4, 44.3, 55.8, 112.4, 118.3, 119.7, 121.5, 121.7, 123.4, 124.7, 125.7, 126.9, 128.6, 129.2, 130.4, 136.3, 138.4, 139.5, 152.2, 153.0, and 156.9; *m/z* (CI^+) 528, 526, and 524 (MH^+, 12%, 74%, 100%).

Poly{2-[(*E*)-2-(7-nitro-9,9-dipropylfluorenyl)vinyl]-5-methoxy-phenyl]-1-chloroethylene} 4.42:

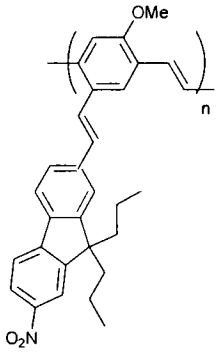


4.42

A solution of potassium *t*-butoxide (38 mg, 0.34 mmol) in anhydrous tetrahydrofuran (1.7 mL) was added to a stirred solution of 2-(*E*)-2-[2,5-*bis*(chloromethyl)-4-methoxyphenyl]vinyl-7-nitro-9,9-dipropyl-9*H*-fluorene **4.41** (200 mg, 0.38 mmol) in anhydrous tetrahydrofuran (1.9 mL) under argon. The reaction mixture was stirred at room temperature for 4 hours. The solution was filtered through a cotton-wool plug and precipitated in ice-cold methanol (2 mL). The mixture was centrifuged (4500 r.p.m., 5 minutes), the supernatant was decanted and the residue was dissolved in tetrahydrofuran (1 mL). The solution was poured in ice-cold methanol (2 mL) and the mixture again centrifuged (4500 r.p.m., 5 minutes). The supernatant was decanted and the bright yellow residue of poly{2-[(*E*)-2-(7-nitro-9,9-dipropylfluorenyl)vinyl]-5-methoxy-phenyl]-1-chloroethylene} **4.42** (~67 mg, ~36%) was dissolved in tetrahydrofuran (3 mL). ν_{max} (film, KBr disc)/cm^{-1} 1603 (C=C), 959 (C=CH), and 733 (C–Cl); λ_{max} (film)/nm 384, 305, and 220 sh; δ_H ($CDCl_3$, 400 MHz) 0.40-0.90 (10 H, br, 2 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 1.90-2.15 (4 H, br, 2 × $ArC\underline{H_2}$), 3.10-4.00 (3 H, br m, $ArOCH_3$), 5.60-5.80 (1 H, br, CHCl), 6.60-6.80 (2 H, br m, CHCH), 7.10-7.85 (6 H, br m, 6 × ArH) and 8.10-8.30 (2 H, br m, 2 × ArH); $\overline{M}_w = 2.5 \times 10^5$, $\overline{M}_n = 1.3 \times 10^5$,

and PD = 1.96; Thermogravimetric analysis: 208 °C (observed weight loss: 7.6%, expected weight loss: 7.6%); Differential scanning calorimetry: T_g = 98 °C.

Poly{2-[(*E*)-2-(7-nitro-9,9-dipropylfluorenyl)vinyl]-5-methoxy-1,4-phenylenevinylene} 4.43:

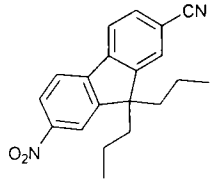


4.43

Thin films of poly{2-[(*E*)-2-(7-nitro-9,9-dipropylfluorenyl)vinyl]-5-methoxy-phenyl]-1-chloroethylene} **4.42** were heated at 210 °C for 17 hours under a dynamic vacuum to give poly{2-[(*E*)-2-(7-nitro-9,9-dipropylfluorenyl)vinyl]-5-methoxy-1,4-phenylenevinylene} **4.43**. ν_{max} (film, KBr)/cm^{-1} 1591 (C=C), and 961 (C=CH); λ_{max} (film)/nm 388, 318 sh, and 202.

6.9.1 Synthesis of poly{2-[(*E*)-2-(7-nitro-9,9-dipropylfluorenyl)vinyl]-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene}

7-Nitro-9,9-dipropyl-9*H*-fluorene-2-carbonitrile 4.30:

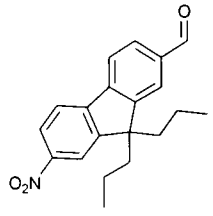


4.30

Copper (I) cyanide (28.3, 0.32 mol) was added to a nitrogen bubbled solution of 2-bromo-7-nitro-9,9-di-*n*-propyl-9*H*-fluorene **2.16** (59.3 g, 0.16 mol) in anhydrous

N,N-dimethylformamide (350 mL) and the reaction was heated at reflux for 48 hours under nitrogen. The reaction mixture was allowed to cool to room temperature and a solution iron (III) chloride (20 g) in aqueous hydrochloric acid (3 M, 200 mL) was added. The aqueous solution was extracted with ether (2 × 250 mL). The organic extracts were combined, washed with water (3 × 200 mL) and brine (200 mL), dried over magnesium sulphate and filtered. The solvent was removed to give a green solid. The crude was purified by filtering through a plug of silica using dichloromethane as eluent to give a yellow solid (45.3 g). Recrystallisation of the solid using a dichloromethane/hexane mixture gave 7-nitro-9,9-dipropyl-9*H*-fluorene-2-carbonitrile **4.30** (41.5 g, 82%) as a yellow solid, mp 160-162 °C (lit.[170] 161-161.5 °C). The compound had an identical ^{1}H n.m.r. and infrared spectrum to that reported in the literature[170].

7-Nitro-9,9-dipropyl-9*H*-fluorene-2-carbaldehyde 4.31:

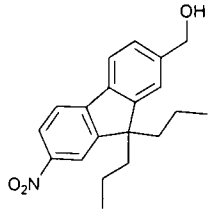


4.31

In a three-neck flask, DIBAL-H (10 mL, 1.5 mmol) was added drop-wise to a stirred solution of 7-nitro-9,9-dipropyl-9*H*-fluorene-2-carbonitrile **4.30** (4.0 g, 1.3 mmol) in dry dichloromethane (50 mL) and toluene (50 mL) at -78 °C over a period of 1 hour using a syringe pump, maintaining the reaction temperature ≤ -78 °C under nitrogen. After addition, reaction stirred at -78 °C for 30 minutes and then at room temperature for 4 hours. Aqueous hydrochloric acid (3 M, 50 mL) was carefully added. The organic phase was separated, washed with water (2 × 50 mL) and brine (50 mL), dried

over magnesium sulphate and filtered. The removal of solvent gave a yellow solid. Column chromatography of the crude over silica gel using a light petroleum:ether mixture (5:1) as eluent gave 7-nitro-9,9-dipropyl-9*H*-fluorene-2-carbaldehyde **4.31** (3.7 g, 93%) as a yellow solid, mp 124.5-126.5 °C. (Found: C, 74.13; H, 6.71; N, 4.29. $C_{20}H_{21}NO_3$ requires C, 74.28; H, 6.55; N, 4.33%); ν_{max} (KBr disc)/cm^{-1} 1696 (C=O), 1520 (NO_2 anti), and 1339 (NO_2 sym); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon/dm^3mol^{-1}cm^{-1}$) 342 (4.54), 321 sh (4.38), 288 sh (4.07), and 236 (3.90); δ_H ($CDCl_3$, 400 MHz) 0.51-0.69 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 2.02-2.13 (4 H, m, 2 × $ArCH_2$), 7.93 (4 H, m, 4 × ArH), 8.27 (2 H, *J* 8, *J* 2, 2 × ArH), and 10.11 (1 H, s, CHO); δ_C ($CDCl_3$, 100 MHz) 14.2, 17.1, 42.1, 56.2, 118.4, 121.2, 121.6, 123.3, 123.4, 130.4, 136.7, 144.5, 145.7, 148.1, 153.0, 153.3, and 192.0; *m/z* (EI^+) 323 (M^+, 42%), 280 ($[M-C_3H_7]^+$, 78%), and ($[M-85]^+$, 100%); Exact mass 323.1517. $C_{20}H_{21}NO_3$ requires 323.1521.

(7-Nitro-9,9-dipropyl-9*H*-fluoren-2-yl)-methanol 4.32:

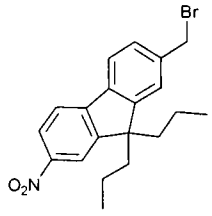


4.32

$NaBH_4$ (4.7 g, 124.2 mmol) was added portion-wise to a stirred solution of 7-nitro-9,9-dipropyl-9*H*-fluorene-2-carbaldehyde **4.31** (10 g, 30.9 mmol) in *i*-propanol (200 mL) and ethanol (200 mL) over a period of 30 minutes. After addition, the reaction mixture was stirred for 2 hours and then carefully quenched with aqueous hydrochloric acid (3 M, 100 mL). The aqueous solution was extracted with ether (2 × 250 mL). The organic layers were combined, washed with water (2 × 100 mL) and

brine (500 mL), dried over magnesium sulphate, filtered and solvent was removed to give a yellow oil. Purification of the residue by filtering through a silica plug using dichloromethane as eluent gave (7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)-methanol **4.32** (9.5 g, 99%) as a yellow solid, mp 98-100 °C. (Found: C, 73.91; H, 7.12; N, 4.25. $C_{20}H_{23}NO_3$ requires C, 73.82; H, 7.12; N, 4.30%); ν_{max} (KBr disc)/cm^{-1} 3411 (O–H); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 348 (5.26), 310 sh (4.90), and 241 (4.88); δ_H ($CDCl_3$, 400 MHz) 0.52-0.69 (10 H, m, 2 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 1.98-2.11 (4 H, m, 2 × $ArCH_2$), 4.84 (2 H, s, $ArCH_2O$), 7.40 (2 H, dd, *J* 7, *J* 4, 2 × ArH), 7.79 (2 H, m, 2 × ArH), and 8.24 (2 H, dd, *J* 8, *J* 2, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 14.3, 17.1, 42.3, 55.8, 65.4, 118.3, 119.7, 121.2, 121.5, 123.3, 126.1, 138.2, 142.3, 147.0, 147.3, 152.0, and 152.8; *m/z* (EI$^+$) 325 (M$^+$, 53%) and 282 ([M-C_3H_7])$^+$, 100%); Exact mass 325.1678. $C_{20}H_{23}NO_3$ requires 325.1678.

2-Bromomethyl-7-nitro-9,9-dipropyl-9*H*-fluorene 4.33:

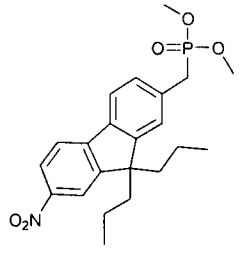


4.33

(7-Nitro-9,9-dipropyl-9*H*-fluoren-2-yl)-methanol **4.32** (8.2 g, 25.3 mmol) stirred at -10 °C (ice and $CaCl_2$) for 10 minutes under nitrogen before the addition of phosphorous tribromide (47 mL, 0.5 mol). The reaction was heated at 100 °C for 15 hours with a guard tube on top of the condenser. After allowing the reaction mixture to cool, the reaction mixture was carefully poured in ice-cold water (200 mL). The aqueous was extracted with ether (2 × 100 mL). The organic fractions were combined, washed with a saturated solution of sodium bicarbonate (2 × 100 mL), dried over

magnesium sulphate and filtered. The solvent was removed to give a brown oil. Purification of the crude by filtering through a plug of silica using light petroleum as eluent gave 2-bromomethyl-7-nitro-9,9-dipropyl-9*H*-fluorene (9.8 g, 81%) **4.33** as a pale yellow solid, mp 108-111 °C. (Found: C, 61.71; H, 5.64; N, 3.51%. $C_{20}H_{22}BrNO_2$ requires C, 61.86; H, 5.71; N, 3.61%); ν_{max} (KBr disc)/cm^{-1} 739 (C–Br); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 347 (5.02), 313 sh (4.72), and 259 (4.67); δ_H ($CDCl_3$, 400 MHz) 0.53-0.71 (10 H, m, 2 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 1.98-2.08 (4 H, m, 2 × $ArCH_2$), 4.62 (2 H, s, CH_2Br), 7.44 (2 H, m, 2 × ArH), 7.78 (2 H, m, 2 × ArH), 8.21 (1 H, d, *J* 2, ArH), and 8.27 (1 H, dd, *J* 2, *J* 8, ArH); δ_C ($CDCl_3$, 100 MHz) 14.3, 17.2,33.7, 42.2, 55.9, 118.3, 120.0, 121.5, 123.4, 123.9, 128.5, 138.9, 139.0, 146.8, 147.3, 152.3, and 152.9; *m/z* (EI$^+$) 389, 387 (M^+, 7%, 8%), and 308 ($[M-Br]^+$, 100%); Exact mass 387.08454. $C_{20}H_{23}BrNO_2$ requires 387.0834.

(7-Nitro-9,9-dipropyl-9*H*-fluoren-2-ylmethyl)-phosphonic acid dimethyl ester 4.34:

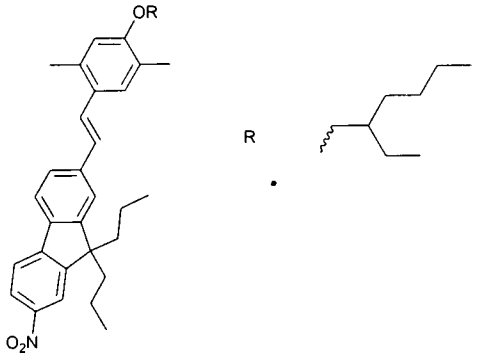


4.34

A mixture of 2-bromomethyl-7-nitro-9,9-dipropyl-9*H*-fluorene **4.33** (8.9 g, 22.9 mmol) in trimethyl phosphite (13.5 mL, 114.4 mmol) was heated at 80 °C for 5 hours under nitrogen. The reaction mixture was allowed to cool to room temperature and water (50 mL) was added and the aqueous layer was extracted with ethylacetate (2 × 100 mL), dried over magnesium sulphate and filtered. The filtrate was concentrated to dryness to give yellow oil. Purification of the crude by filtering through a plug of

silica using a light petroleum:ethylacetate mixture (1:0 then 1:2) as eluent followed by recrystallisation from dichloromethane/hexane gave (7-nitro-9,9-dipropyl-9*H*-fluoren-2-ylmethyl)-phosphonic acid dimethyl ester **4.34** (8.8 g, 99%) as a yellow solid, mp 108-110 °C. (Found: C, 63.23; H, 6.74; N, 3.27. $C_{22}H_{28}NO_5P$ requires C, 63.30; H, 6.76; N, 3.36%); ν_{max} (KBr disc)/cm^{-1} 1249 (P=O), 1058 (P–O), and 1027 (P–O); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 348 (4.36), and 241 (4.09); δ_H ($CDCl_3$, 400 MHz) 0.58-0.68 (10 H, m, 2 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 1.95-2.07 (4 H, m, 2 × $ArCH_2$), 3.28 (2 H, d, *J* 22, CH_2P), 3.68 (6 H, d, *J* 12, 2 × $POCH_3$), 7.34 (2 H, m, 2 × ArH), 7.75 (2 H, dd, *J* 8, *J* 1, ArH), 8.23 (1 H, d, *J* 2, ArH), and 8.27 (1 H, dd, *J* 2, *J* 8, ArH); δ_C ($CDCl_3$, 100 MHz) 14.3, 17.1, 33.4 ($^1J_{PC}$ 138), 42.3, 52.3 ($^2J_{POC}$ 7), 55.8, 118.2, 119.7, 121.3, 123.3, 124.7, 129.0, 132.6, 137.6, 147.1, 147.2, 151.9, and 152.8; *m/z* (EI^+) 417 (M^+, 54%), 374 ($[M-C_3H_7]^+$, 100%) and 219 ($[M-C_3H_7-HP(O)(OCH_3)_2]^+$, 96%); Exact mass 417.1703. $C_{22}H_{28}NO_5P$ requires 417.1705.

2-{(*E*)-2-[4-(2′-Ethylhexyloxy)-2,5-dimethyl-phenyl]-vinyl}-7-nitro-9,9-dipropyl-9*H*-fluorene 4.25a:

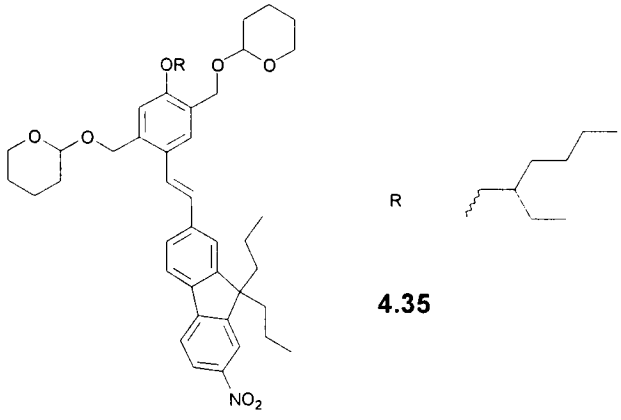


4.25a

A reaction mixture of 9,9-di(*n*-propyl)-2-nitro-7-vinylfluorene **4.28** (1.4 g, 3.9 mmol), 1-bromo-4-(2′-ethylhexyloxy)-2,5-dimethylbenzene **2.3a** (1.8 g, 5.8 mmol)

sodium carbonate (0.6 g, 5.8 mmol), and 2,6-di-*t*-butyl-*p*-cresol (0.2 g, 0.8 mmol) in anhydrous *N,N*-dimethylacetamide (20 mL) was bubbled with argon for 20 minutes before the addition of Herrmann's catalyst **4.8** (ca. 37 mg, 0.04 mmol). The reaction was heated at reflux for 4 days. On cooling, aqueous hydrochloric acid (3 M, 10 mL) was carefully added and the aqueous layer was extracted with ether (3 × 20 mL). The ethereal extracts were combined, washed with water (3 × 10 mL) and brine (10 mL), dried over magnesium sulphate, and filtered. The solvent was removed to give a brown oil. Purification of the crude by column chromatography over silica gel using a light petroleum:dichloromethane mixture (4:1) as eluent followed by recrystallisation from a dichloromethane/methanol mixture gave 2-{(*E*)-2-[4-(2'-ethylhexyloxy)-2,5-dimethyl-phenyl]-vinyl}-7-nitro-9,9-dipropyl-9*H*-fluorene **4.25a** (0.6 g, 28%) as a yellow oil; ν_{max} (KBr disc)/cm^{-1} 1599 (C=C); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 400 (4.61), and 308 (4.41); δ_H ($CDCl_3$, 400 MHz) 0.54-0.79 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 0.88-0.98 (6 H, m, 2 × CH_3), 1.28-1.67 (8 H, m, 4 × CH_2), 1.72-1.84 (1 H, m, CH), 1.98-2.15 (4 H, m, 2 × $ArCH_2$), 2.24 (3 H, s, $ArCH_3$), 2.48 (3 H, s, $ArCH_3$), 3.88 (2 H, d, *J* 6, $ArOCH_2$), 6.67 (1 H, s, ArH), 7.02 (1 H, d, *J* 16, vinylH), 7.40 (1 H, d, *J* 16, vinylH), 7.48 (2 H, m, 2 × ArH), 7.57 (1 H, m, ArH), 7.79 (2 H, m, 2 × ArH), and 8.24 (2 H, m, *J* 8, *J* 2, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 11.2, 14.1, 14.3, 15.9, 17.1, 19.9, 23.1, 24.1, 29.1, 30.7, 39.5, 42.4, 55.8, 70.2, 112.7, 118.2, 119.5, 121.1, 121.4, 123.4, 124.7, 125.4, 127.1, 127.2, 127.5, 127.6, 134.7, 137.7, 139.5, 146.8, 147.5, 152.1, 153.0, and 157.3; *m/z* (EI^+) 553 (M^+, 100%); Exact mass 553.3532. $C_{37}H_{47}NO_3$ requires 553.3556.

5-(2′-Ethylhexyloxy)-2-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-2-fluorenyl)-1-ethenyl]-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxytetrahydro-2*H*-pyran 4.35:

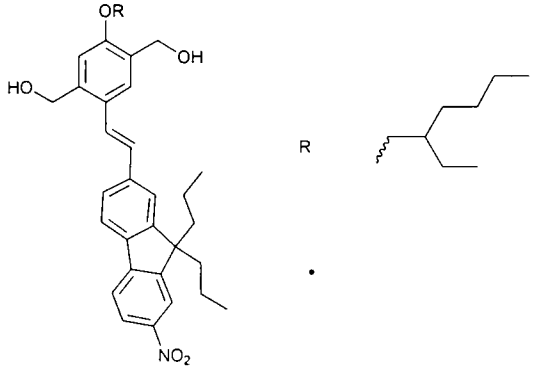


4.35

Lithium diisopropylamide (2.0 M in THF/*n*-heptane, 3.3 mL, 6.5 mmol) was added to a solution of (7-nitro-9,9-dipropyl-9*H*-fluoren-2-ylmethyl)-phosphonic acid dimethyl ester **4.34** (2.5 g, 6.2 mmol) and 4-(2′-ethylhexyloxy)-2,5-*bis*(tetrahydro-2*H*-2-pyranyloxymethyl)benzaldehyde **4.18b** (2.5 g, 5.4 mmol) in anhydrous tetrahydrofuran (100 mL) at 0 °C under nitrogen. The reaction mixture changed colour from yellow to green, which finally turned yellow. After addition, the reaction mixture was stirred at room temperature for an hour and was then quenched with a saturated solution of ammonium chloride (20 mL). The aqueous layer was extracted with ether (2 × 50 mL). The ethereal extracts were combined, washed with water (2 × 50 mL) and brine (50 mL), dried over magnesium sulphate, and filtered. Solvent removal gave a yellow oil. The oil was preliminary purified by column chromatography over silica gel using dichloromethane as eluent. The main band was eluted, concentrated and purified further by flash chromatography over silica gel using a light petroleum:ethyl acetate mixture (6:1) as eluent gave 5-(2′-ethylhexyloxy)-2-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-2-fluorenyl)-1-ethenyl]-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxytetrahydro-2*H*-pyran **4.35** (4.0 g, 97%) as a yellow oil, solidifies on standing, mp 60-61 °C. (Found: C, 74.78; H, 8.51; N,

1.72. $C_{47}H_{63}NO_7$ requires C, 74.87; H, 8.42; N, 1.86%); ν_{max} (KBr disc)/cm^{-1} 1598 (C=C), and 1123 (C–O–C); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon/dm^3mol^{-1}cm^{-1}$) 398 (4.64), 308 (4.36), and 245 sh (4.23); δ_H ($CDCl_3$, 400 MHz) 0.58-0.76 (10 H, m, 2 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 0.88-0.98 (6 H, m, 2 × CH_3), 1.29-1.98 (21 H, m, 10 × CH_2, CH), 1.98-2.12 (4 H, m, 2 × $ArCH_2$), 3.55-3.64 (2 H, m, -OCH_2(THP)), 3.92-3.98 (2 H, m, *J* 5.5, $ArOCH_2$), 3.84-4.09 (2 H, m, -OCH_2(THP)), 4.59-4.72 (2 H, q, $ArCH_2O$), 4.78-4.86 and 4.98-5.01 (4 H, m, $ArCH_2O$, 2 × -OCH_2(THP)), 6.96 (1 H, s, ArH), 7.08 (1 H, d, *J* 16, vinylH), 7.55 (3 H, s, 10 × ArH), 7.72 (1 H, d, *J* 16, vinylH), 7.80 (2 H, dd, *J* 8, *J* 2, 2 × ArH), and 8.25 (2 H, dd, *J* 8, *J* 2, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 11.2, 14.1, 14.3, 17.2, 19.5, 19.6, 23.1, 24.0, 25.5, 25.6, 29.1, 30.6, 30.7, 30.8, 39.5, 42.4, 55.8, 62.2, 62.5, 64.2, 67.2, 70.3, 98.0, 98.5, 112.3, 136.1, 137.9, 139.4, 146.9, 147.5, 152.1, 152.9, and 156.7; *m/z* (EI^+) 753 (M^+, 100%).

[5-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol 4.36:

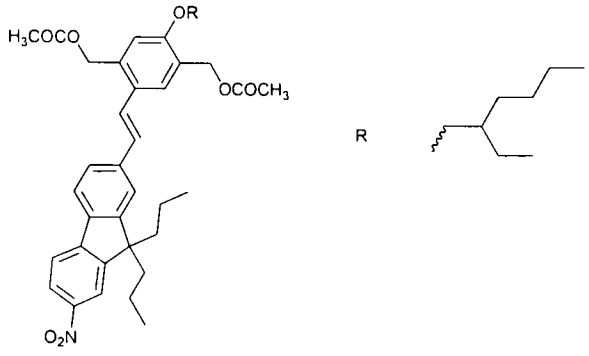


4.36

p-Toluenesulphonic acid monohydrate (75 mg, 10 mol%) was added to a solution of 5-(2′-ethylhexyloxy)-2-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-2-fluorenyl)-1-ethenyl]-4-tetrahydro-2*H*-2-pyranyloxymethylbenzyloxytetrahydro-2*H*-pyran **4.35** (2.8 g, 3.6 mmol) in methanol (50 mL) and dichloromethane (50 mL) under nitrogen. The

reaction mixture was stirred at room temperature for 15 hours. Water (50 mL) was added and the aqueous layer was extracted with dichloromethane (2 × 75 mL). The organic layers were combined, washed with water (2 × 50 mL), dried over magnesium sulphate, filtered and reduced to dryness to give yellow oil (2.1 g). Preliminary purification was carried out by flash chromatography over silica gel using a gradient elution with a dichloromethane:methanol mixture (100:0 to 99:1) followed by recrystallisation from dichloromethane:hexane mixture gave [5-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2'-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **4.36** (1.8 g, 83%) as a yellow crystals, mp 102-104 °C; ν_{max} (KBr disc)/cm^{-1} 3336 (O–H), 1597 (C=C); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon/dm^3mol^{-1}cm^{-1}$) 395 (4.71), 308 (4.39) and 244 sh (4.24); δ_H ($CDCl_3$, 400 MHz) 0.54-0.76 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 0.89-0.98 (6 H, m, 2 × CH_3), 1.28-1.57 (8 H, m, 4 × CH_2), 1.74-1.82 (1 H, m, CH), 1.98-2.12 (4 H, m, 2 × $ArCH_2$), 3.97 (2 H, d, *J* 5, $ArOCH_2$), 4.76 (2 H, s, $ArCH_2O$), 4.90 (2 H, s, $ArCH_2O$), 7.01 (1 H, s, ArH), 7.19 (1 H, d, *J* 16, vinylH), 7.45 (1 H, s, ArH), 7.49 (2 H, m, ArH), 7.58 (1 H, d, *J* 8, ArH), 7.66 (1 H, s, ArH), 7.75 (2 H, m, ArH), and 8.25 (2 H, m, *J* 8, *J* 1, 2 × ArH); δ_C ($CDCl_3$, 100 MHz) 11.2, 14.1, 14.3, 17.2, 23.0, 24.1, 29.1, 30.7, 39.4, 42.4, 55.8, 61.8, 63.2, 70.5, 110.8, 118.2, 119.6, 121.3, 121.5, 123.4, 125.4, 125.7, 126.1, 127.8, 128.9, 129.2, 138.1, 138.8, 138.9, 146.9, 147.4, 152.1, 153.0, and 156.9; *m/z* (EI^+) 585 (M^+, 100%); Exact mass 585.3468. $C_{37}H_{47}NO_5$ requires 540.3454.

2- (2′-Ethylhexyloxy) -4-methylcarbonyloxymethyl-5-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)vinyl]benzyl acetate 4.38:

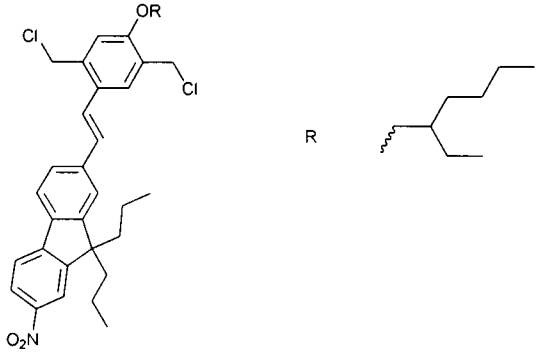


4.38

Acetic anhydride (0.15 mL, 1.5 mmol) was added to a mixture of [5-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **4.36** (200 mg, 0.3 mmol), 4-*N*,*N*-dimethylaminopyridine (21 mg, 0.2 mmol), and triethylamine (0.20 mL, 1.4 mmol) in anhydrous dichloromethane under nitrogen and the mixture was stirred at room temperature for 48 hours. Water (10 mL) was added and the organic layer was separated. The organic layer was washed with a saturated solution of sodium bicarbonate (2 × 5 mL) and brine (5 mL), dried over magnesium sulphate, and filtered. Removal of solvent gave a yellow oil. Column chromatography of the crude over silica gel using dichloromethane as eluent gave 2-(2′-ethylhexyloxy)-4-methylcarbonyloxymethyl-5-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)vinyl]benzyl acetate **4.38** (170 mg, 98%) as a yellow oil; ν_{max} (KBr disc)/cm^{-1} 1737 (C=O), and 1601 (C=C); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon$/dm^{3}mol^{-1}cm^{-1}) 392 (4.70), 309 (4.35), and 244 sh (4.23); δ_H ($CDCl_3$, 500 MHz) 0.67-0.81 (10 H, m, 2 × $ArCH_2C\underline{H_2}C\underline{H_3}$), 0.98-1.05 (6 H, m, 2 × CH_3), 1.38-1.64 (8 H, m, 4 × CH_2), 1.82-1.86 (1 H, m, CH), 2.08-2.14 (4 H, m, 2 × $ArCH_2$), 2.19 (6 H, s, 2 × $OCOCH_3$), 4.12 (2 H, d, *J* 6, $ArOCH_2$), 5.25 (2 H, s, CH_2O), 5.36 (2 H, s, CH_2O), 6.98 (1 H, s, ArH), 7.12 (1 H, d, *J* 16, vinyl H), 7.44 (1 H, d, *J* 16, vinyl H), 7.56 (1 H, s, ArH), 7.64 (1 H, m,

ArH), 7.75 (1 H, s, ArH), 7.83 (12 H, m, ArH), and 8.24 (2 H, m, *J* 8, *J* 2, 2 × ArH); δ_C ($CDCl_3$, 125 MHz) 11.2, 13.9, 14.1, 17.3, 21.0, 21.2, 23.7, 28.8, 30.6, 39.4, 41.9, 55.6, 61.9, 63.8, 70.1, 112.6, 118.1, 119.4, 120.1, 121.3, 123.1, 124.4, 124.6, 125.2, 127.5, 128.1, 129.1, 134.3, 136.9, 137.2, 146.3, 146.5, 151.9, 152.5, 156.3, 170.1, and 170.3; *m/z* (EI^+) 669 (M^+, 100%); Exact mass 669.3480. $C_{41}H_{51}NO_7$ requires 669.3666.

Attempted synthesis of 2-{(*E*)-2-[2,5-*bis*-chloromethyl-4-(2′-ethylhexyloxy)-phenyl]-vinyl}-7-nitro-9,9-dipropyl-9*H*-fluorene 4.37:



4.37

Method 1: Thionyl chloride (0.16 mL, 2.2 mmol) was added to a stirred solution of [5-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **4.36** (60 mg, 0.1 mmol) in anhydrous dichloromethane (2 mL) at 0 °C. After addition, the reaction mixture was stirred at r.t. for 2 hour. Water (5 mL) was carefully added and the aqueous layer was extracted with ether (3 × 5 mL). The organic extracts were combined, washed with water (2 × 5 mL), dried over magnesium sulphate and filtered. The solvent was removed to give a yellow oil. Purification of the crude by column chromatography over silica gel using a light petroleum:dichloromethane mixture (1:1) as eluent followed by recrystallisation

from dichloromethane/methanol mixture gave impure 2-{(*E*)-2-[2,5-*bis*-chloromethyl-4-(2'-ethylhexyloxy)-phenyl]-vinyl}-7-nitro-9,9-dipropyl-9*H*-fluorene **4.37**.

Method 2: Thionyl chloride (0.3 mL, 0.04 mmol) was added to a solution of [5-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2'-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **4.36** (50 mg, 0.09 mmol), and freshly distilled pyridine (0.15 mL) in anhydrous dichloromethane (5 mL) under nitrogen and the mixture stirred at room temperature for 1.5 hours. The reaction mixture was concentrated and water (5 mL) was carefully added. The aqueous layer was extracted with ether (3 × 5 mL) and the organic extracts were combined, washed with water (3 × 5 mL), and dried over magnesium sulphate. Filtration and removal of solvent gave a yellow oil. Purification of the crude by column chromatography over silica gel using a light petroleum:dichloromethane mixture (1:1) as eluent gave impure 2-{(*E*)-2-[2,5-*bis*-chloromethyl-4-(2'-ethylhexyloxy)-phenyl]-vinyl}-7-nitro-9,9-dipropyl-9H-fluorene **4.37**.

Method 3: 4-*N,N*-Dimethylaminopyridine (ca. 5 mg, 5 mol%), *p*-toluenesulphonyl chloride (36 mg, 0.19 mmol) and pyridine (catalytic amount) was added to a solution of [5-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2'-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **4.36** (50 mg, 0.09 mmol) in anhydrous tetrahydrofuran (5 mL) at 0 °C under nitrogen. After addition, the reaction mixture was allowed to warm to room temperature and stirred for further 19 hours. T.l.c. analysis of the reaction mixture showed the presence of starting material. The reaction mixture was heated at reflux for 22 hours. On cooling, water (5 mL) was added and the aqueous layer was extracted with ether (2 × 10 mL). The organic layers were

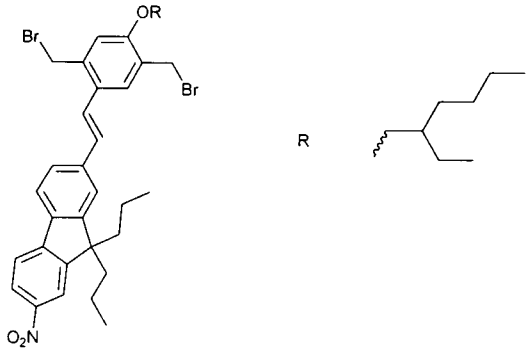
combined, washed with water (2 × 10 mL), dried over magnesium sulphate, and filtered. The solvent was removed to give a yellow oil. Purification of the crude by column chromatography over silica gel using a light petroleum:dichloromethane mixture (7:3) as eluent gave impure 2-{(*E*)-2-[2,5-*bis*-chloromethyl-4-(2'-ethylhexyloxy)-phenyl]-vinyl}-7-nitro-9,9-dipropyl-9*H*-fluorene **4.37**.

Method 4: A solution [5-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2'-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **4.36** (50 mg, 0.09 mmol) in anhydrous toluene (5 mL) was added to a 14 hour pre-stirred suspension of triphenyl phosphine (120 mg, 0.43 mmol) in carbon tetrachloride (0.05 mL, 0.53 mmol) under nitrogen. The reaction mixture was heated at reflux for 15 hours. After cooling, water (5 mL) was added and the organic layer was separated, washed with water (2 × 10 mL), dried over magnesium sulphate, filtered and solvent was removed. ^{1}H n.m.r. of the crude indicated no 2-{(*E*)-2-[2,5-*bis*-chloromethyl-4-(2'-ethylhexyloxy)-phenyl]-vinyl}-7-nitro-9,9-dipropyl-9*H*-fluorene **4.37** was formed. [(*E*)-2-(7-Nitro-9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2'-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **4.36** (0.04 g, 80%) was recovered by trituration of the crude in light petroleum followed by filtration.

Method 5: A mixture of 2-(2'-ethylhexyloxy)-4-methylcarbonyloxymethyl-5-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)vinyl]benzyl acetate **4.38** (100 mg, 0.15 mmol), concentrated hydrochloric acid (2 mL) in 1,4-dioxane (5 mL) was heated at reflux for 2.5 hours. After allowing the reaction mixture to cool, water (5 mL) was added and the aqueous layer was extracted with ether (3 × 5 mL). The organic extracts were combined, washed with water (3 × 5 mL) and brine (5 mL), dried over magnesium

sulphate, filtered and removal of solvent gave a yellow residue. Purification of the crude by column chromatography using a light petroleum:dichloromethane mixture (1:1) as eluent gave impure 2-{(*E*)-2-[2,5-*bis*-chloromethyl-4-(2′-ethylhexyloxy)-phenyl]-vinyl}-7-nitro-9,9-dipropyl-9*H*-fluorene **4.37**.

2-{(*E*)-2-[2,5-*bis*-bromomethyl-4-(2′-ethylhexyloxy)-phenyl]-vinyl}-7-nitro-9,9-dipropyl-9*H*-fluorene 4.39:

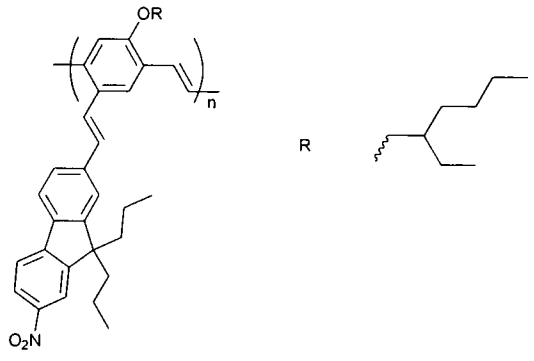


4.39

Method 1: Hydrobromic acid (33 w/w% in acetic acid, 0.4 mL, 1.8 mmol) was added to a solution of [5-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2′-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **4.36** (50 mg, 0.09 mmol) in glacial acetic acid (2 mL) under nitrogen and the reaction mixture was stirred at room temperature for 1.5 hours. Water was added and the aqueous layer was extracted with dichloromethane (2 × 5 mL). The organic extracts were combined, washed with water (2 × 5mL), dried over magnesium sulphate, filtered and solvent was removed to give a yellow oil. Column chromatography over silica gel using a light petroleum:dichloromethane mixture (1:1) gave impure 2-{(*E*)-2-[2,5-*bis*-bromomethyl-4-(2′-ethylhexyloxy)-phenyl]-vinyl}-7-nitro-9,9-dipropyl-9*H*-fluorene **4.39**.

Method 2: Phosphorous tribromide (0.08 mL, 0.75 mmol) was added to a solution of [5-[(*E*)-2-(7-nitro-9,9-dipropyl-9*H*-fluoren-2-yl)-vinyl]-2-(2'-ethylhexyloxy)-4-hydroxymethyl-phenyl]-methanol **4.36** (200 mg, 0.34 mmol) in anhydrous ether (10 mL) at 0 °C. The reaction mixture was stirred at 0 °C for an hour and then room temperature for another hour under nitrogen in dark. The reaction mixture was concentrated to give a brown residue. The residue was purified by flash chromatography over silica gel using a light petroleum:dichloromethane mixture (1:1) gave 2-{(*E*)-2-[2,5-*bis*-bromomethyl-4-(2'-ethylhexyloxy)-phenyl]-vinyl}-7-nitro-9,9-dipropyl-9*H*-fluorene **4.39** (100 mg, 42%) as a yellow solid, mp 54-55 °C; ν_{max} (KBr disc)/cm^{-1} 1600 (C=C), and 740 (C–Br); λ_{max} (CH_2Cl_2)/nm ($\log_{10}\varepsilon/dm^3mol^{-1}cm^{-1}$) 393 (5.05), 332 (4.64), 257 sh (4.68), and 231 (4.87); δ_H ($CDCl_3$, 500 MHz) 0.67-0.76 (10 H, m, 2 × $ArCH_2C\underline{H}_2C\underline{H}_3$), 0.96-1.02 (6 H, m, 2 × CH_3), 1.39-1.63 (8 H, m, 4 × CH_2), 1.78-1.85 (1 H, m, CH), 2.07-2.17 (4 H, m, 2 × $ArCH_2$), 3.99 (2 H, d, *J* 6, $ArOCH_2$), 4.60 (2 H, s, $ArCH_2Br$), 4.67 (2 H, s, $ArCH_2Br$), 6.90 (1 H, s, ArH), 7.16 (1 H, d, *J* 16, vinylH), 7.52 (2 H, m, ArH), 7.75 (2 H, m, ArH), 7.80 (2 H, m, ArH), and 8.26 (2 H, m, *J* 8, *J* 1, 2 × ArH); δ_C ($CDCl_3$, 125 MHz) 10.3, 13.1, 13.3, 16.2, 22.0, 23.0, 27.2, 28.1, 29.6, 30.7, 32.8, 38.5, 41.4, 54.8, 112.1, 117.3, 118.7, 120.5, 120.7, 122.4, 123.8, 124.6, 126.4, 127.9, 129.0, 135.6, 137.4, 137.6, 146.0, 146.2, 151.2, 152.1,. and 155.7; *m/z* (EI^+) 713, 711, and 709 (M^+, 35%, 100%, 32%); Exact mass 709.1735. $C_{37}H_{45}Br_2NO_3$ requires 709.1766.

Attempted synthesis of poly{2-[(*E*)-2-(7-nitro-9,9-dipropylfluorenyl)vinyl]-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene} 4.44:



4.44

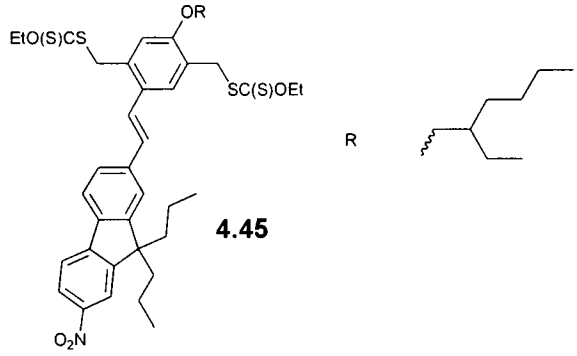
Method 1: A solution of potassium *t*-butoxide (50 mg, 0.44 mmol) in anhydrous tetrahydrofuran (2.2 mL) was added to a stirred solution of 2-{(*E*)-2-[2,5-*bis*-bromomethyl-4-(2'-ethylhexyloxy)-phenyl]-vinyl}-7-nitro-9,9-dipropyl-9*H*-fluorene **4.39** (50 mg, 0.07 mmol) in anhydrous tetrahydrofuran (0.45 mL) under nitrogen. The reaction mixture was stirred at room temperature for 3.5 hours in dark. No polymerisation was detected by g.p.c. analysis. The reaction mixture was heated at reflux for 2 hours. No change in g.p.c. trace was observed.

Method 2: Lithium di-*iso*-propylamide (2.0 M in THF/*n*-heptane, 40 μL, 0.08 mmol) was added to a solution of 2-{(*E*)-2-[2,5-*bis*-bromomethyl-4-(2'-ethylhexyloxy)-phenyl]-vinyl}-7-nitro-9,9-dipropyl-9*H*-fluorene **4.39** (ca. 11 mg, 0.02 mmol) in anhydrous tetrahydrofuran (77 μL) at 0 °C under nitrogen. The reaction mixture was stirred at 0 °C for an hour. G.p.c. analysis indicated the presence of low molecular weight material.

Method 3: Lithium di-*iso*-propylamide (2.0 M in THF/*n*-heptane, 0.1 mL, 0.2 mmol) was added to a solution of 2-{(*E*)-2-[2,5-*bis*-bromomethyl-4-(2'-ethylhexyloxy)-phenyl]-vinyl}-7-nitro-9,9-dipropyl-9*H*-fluorene **4.39** (ca. 11 mg, 0.02 mmol) in anhydrous tetrahydrofuran (0.1 mL) at 0 °C under nitrogen. After addition, the

reaction mixture was heated at 40 °C for 16 hours. Only oligomers were detected by g.p.c. analysis.

Attempted synthesis of dithiocarbonic acid *S*-{4-ethoxythiocarbonylsulfanylmethyl-2-(2'-ethylhexyloxy)-5-[(*E*)-2-(7-nitro-9,9-dipropyl-9H-fluorenyl) vinyl]benzyl} ester *O*-ethyl ester 4.45:



4.45

Potassium *O*-ethylxanthate (70 mg, 0.43 mmol) was added to a solution of 2-{(*E*)-2-[2,5-*bis*-bromomethyl-4-(2'-ethylhexyloxy)-phenyl]-vinyl}-7-nitro-9,9-dipropyl-9H-fluorene **4.39** (45 mg, 0.07 mmol) and tetra-*n*-butylammonium bromide (5 mg, 20 mol%) in dichloromethane (4 mL) and the reaction mixture was stirred at room temperature for 5.5 hours and then heated at reflux for 16 hours under argon. The reaction mixture was allowed to cool to room temperature, water (5 mL) was added and the aqueous layer was extracted with ether (3 × 10 mL). The ethereal extracts were combined, washed with water (3 × 5 mL), dried over magnesium sulphate and filtered. Solvent removal gave a yellow solid. The residue was purified by column chromatography over silica gel using a gradient elution with a light petroleum:dichloromethane mixture (1:0 to 8:5) to give an impure dithiocarbonic acid *S*-{4-ethoxythiocarbonylsulfanylmethyl-2-(2'-ethylhexyloxy)-5-[(*E*)-2-(7-nitro-9,9-dipropyl-9H-fluorenyl) vinyl]benzyl} ester *O*-ethyl ester **4.45**.

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