Mapping and Tuning the Fluorescence of Perfluorinated Polyanilines Synthesized Through Liquid-Liquid Interfaces

Panagiotis Dallas, Ilija Rašović and Kyriakos Porfyrakis.*

Department of Materials, University of Oxford, OX1 3PH, UK

ABSTRACT A series of light-emitting perfluorinated polyanilines were synthesized by the oxidative polymerization of 3-perfluorooctyl aniline through a variety of aqueous/organic interfaces. According to the interfacial tension between the two solvents (the organic being chloroform, dichloromethane, perfluorinated ethers, toluene or o-dichlorobenzene, we obtain distinctive classes of materials based on the crystal packing, protonation and oxidation state of the polymeric chains. We distinguish between soluble fractions with a distinctive, strong and red-shifted photoluminescence pattern and an insoluble precipitate which can be subsequently solubilized in a mixture of acetone and toluene. The emission maximum for the insoluble fraction is located in the ultraviolet or blue region with a small Stokes shift; maxima for the soluble counterparts are in the green to yellow region. The soluble derivatives demonstrate a significantly smaller band gap compared to the monomer and large Stokes shifts up to 163 nm; the emission maximum for the most red-shifted emission was located at $\lambda_{\text{em}} = 548$ nm. Their redox activity towards silver nanoparticles, their sensor reactivity with organic acid and bases, and the subsequent

changes in the optical properties were demonstrated and the structure of the materials was evaluated with NMR, X-Ray Diffraction and FTIR/Raman spectroscopy.

Introduction

Liquid-liquid (L-L) interfaces play a fundamental role in biomedical engineering, biology, materials science and biomimetics. The interface between two immiscible liquids can be considered as a thin membrane, with a thickness close to 1 nm that enables selective and controlled charge and mass transfer through an imaginary boundary. Important physical and chemical processes such as electron transfer, catalysis and extraction may take place across this interface.¹⁻⁴ Due to their unique characteristics, L-L interfaces offer a versatile scaffold for the self-assembly of polymers, organic and inorganic nanomaterials, and they enable both the synthesis and the self-organization of matter that may possess hydrophilic or organophilic character through addition of numerous different surfactants.⁵

Interfaces have been utilized for the synthesis of conventional plastic materials like polyamides, polyesters and polyurethanes mostly through radical-mediated addition or condensation polymerization.⁶⁻⁷ The family of conductive polymers has revolutionized materials science, chemistry and physics since the discovery of an efficient method for the doping of polyacetylene, leading to unexpected conductivity values in 1977.⁸ This class of polymers exhibits unique features such as charged macromolecular chains, formation of polaron bands, high conductivity that can be tuned at will and redox and sensing properties according to changes in the resistance and the optical absorbance spectrum.

The most important examples of conductive polymers are polyaniline (PANI), polypyrrole (PPY), and poly-(3,4-ethylenedioxythiophene) (PEDOT).⁹⁻¹¹ All of them have been proven to significantly improve physical, energy storage and chemical sensing properties when they possess a nanofibrillar morphology instead of randomly arranged bulk structures.¹² In that sense, a number of advantages arise from L-L interface polymerization such as improved crystallinity, finely shaped fibrillar morphology and high

conductivity.¹³ On the other hand, perfluorinated organic materials feature the unique characteristics of the carbon-fluoride bond. These include a high polarity and electron-withdrawing ability, unique solubility in supercritical carbon dioxide and hydrophobicity, with the two latter properties placing them as excellent candidates for niche applications like enhanced oil recovery.¹⁴⁻¹⁷ According to Dalvia et al, who have undertaken atomistic molecular simulations, the hydrophobicity of the fluorocarbon arises from a less densely packed fluorocarbon chain thus leading to poorer van der Waals interactions with water¹⁶, as proven by contact-angle simulations of water on self-assembled monolayers of hydrocarbon and fluorocarbon thiols. Furthermore, recent studies indicated that the very high electronegativity of the fluorine group results in a much lower LUMO level which can be of interest in photovoltaic and optoelectronics applications due to an easier electron extraction from the electrode of the device.¹⁸⁻¹⁹ A series of perfluorinated polymers exhibited unusually high quantum yields of 68 %, expanding the gallery of light-emitting polymeric materials suitable for optoelectronic applications.²⁰ The materials were synthesized through a Suzuki cross-coupling reaction on fluorinated phenylene monomers.

To that end, we report for the first time the optical properties and their tuning through acid-base and redox reactions on a series of perfluorinated polyanilines synthesized via interfacial polymerization. We distinguish between different classes of light emitting macromolecules based on the interfacial tension and the oxidation and protonation states. The materials exhibit a bright emission with Stokes shifts up to 163 nm which is remarkably high and their sensor applications based on photoluminescence changes upon acid or base titration were demonstrated. Thus these perfluorinated fluorophores hold great promise for the development of sensor devices since they possess interesting photophysical properties from a simple, well established and high-yielding synthesis.

1. Experimental section

1.1. Interfacial polymerization through different aqueous/organic interfaces

The polymers were synthesized through a two phase, interfacial oxidative polymerization. 7 ml of two different aqueous solutions were prepared, where 0.4 ml of HCl and 0.24 g of $\text{Na}_2\text{S}_2\text{O}_8$ (1 mmol-Conc.A) were dissolved for the first concentration series, and 0.8 ml HCl and 0.48 mg of $\text{Na}_2\text{S}_2\text{O}_8$ (2 mmol-conc.B) for the second concentration series. The organic phase consisted of 12 ml of either chloroform, 3MTM Novec 7300TM, pentane, 1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-(trifluoromethyl) (HFE) or toluene and 0.4 g (0.78 mmol-conc.A) or 0.3 g (0.59 mmol-conc.B) of 3-perfluorooctyl aniline (denoted from now as 3FAN) monomer. The reaction proceeded for 48 hours, the organic phase was filtered and the precipitate and the supernatant were collected separately. The precipitate was isolated by filtration and repeatedly washed with toluene or dichloromethane to remove any impurities. It was subsequently dissolved in a mixture of 1:1 acetone: toluene for further characterization. The samples are consequently denoted as Sol.X for the soluble fraction or Prec.X. for the insoluble precipitate.

1.2. Silver nitrate reduction

30 mg of the insoluble polymer fraction derived from dichlorobenzene was dispersed in 10 ml of water under sonication until it formed a cloudy suspension. Into this solution 10 mg of silver nitrate were added and readily dissolved. Four different reaction vessels were prepared for recording the optical properties after 15 minutes, 1 hour, 3 hours and 48 hours of reaction. In order to recover the polymer suspension from the aqueous phase where ions were still dissolved, 20 ml of toluene were added to the mixture under vigorous stirring. After a few seconds of relaxation the two phases start separating. The toluene phase was isolated for further characterization. Samples are denoted as Ag/P3FN-X (X = 15, 60, 180 minutes or 14 days). The latter was left to stabilize for 14 days and used for the acid base titration.

1.3. Titration with organic acid and base

We prepared solutions of 4-benzoyl benzoic acid (7 mg in 3 ml of isopropanol) and ethylene diamine (0.62 μl in 1 ml in isopropanol). We subsequently added 0.1, 0.1, 0.2, 0.2, 0.3 and 0.3 ml of solution to a 2 mg/ml silver-polymer toluene solution and the photoluminescence excitation dependence maps were recorded without any time delays.

2. Characterization techniques

The UV-Visible absorbance spectra were recorded on a Jasco V-570 spectrometer and the excitation dependent photoluminescence maps on a Jasco 7200 model. The FTIR spectra were recorded on a Varian Excalibur FTS 3500 FT-IR, while the Raman spectra were recorded on a JY Horiba LabRAM ARAMIS imaging confocal Raman microscope (532 nm laser). DSC thermographs were recorded on a Perkin Elmer Diamond DSC with Hyper DSC through a heat-cool-heat cycle from -20 °C to 120 °C. The HOMO and LUMO bonding and antibonding orbitals were calculated with Chem3D-ChemOffice. Matrix-assisted laser-desorption ionization time-of-flight mass spectra (MALDI-TOF MS) were obtained from a Bruker MALDI-TOF spectrometer using trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) and dithranol as a matrix. XRD patterns were recorded on powder samples on a Bruker D500 diffractometer. NMR spectra were recorded in toluene-d₈ solutions on a Bruker 400 MHz. SEM images were recorded on a Carl Zeiss Merlin SEM.

3. Results and discussion

3.1. Synthesis and characterization

We employed the interfacial polymerization of the 3FAN monomer in five different solvents immiscible with water, with substantially different characteristics in terms of polarity, aromaticity and interfacial tension with water. Two different monomer to oxidant/acid molar ratios were employed in order to further study the polymerization process, in a similar manner with polypyrrole or polyaniline. In the case of interfacial polymerization of polypyrrole since the polymer is completely insoluble in any solvent, it readily forms a thin film on the interface that can be easily cast.²¹ On the other hand, polyaniline is proven to be slightly hydrophilic and thus migrates to the aqueous phase, but in the present work the hydrophobic perfluorinated materials were transferred exclusively to the organic phase as can be seen in Figures 1 and S1a. Interfacial polymerization of aniline is well known to lead to the formation of fibers, with the polymer

generated in the interface and subsequently migrating in the aqueous phase. In order to identify the morphology of our perfluorinated derivatives we recorded the SEM images of the insoluble fractions derived from two different solvents, dichloromethane and toluene (Figure 1b-c and S14). In both cases the materials demonstrate a flat, flake-like morphology since their growth is taking place exclusively in the interface with step-wise addition of the monomer from the organic phase.

The interfacial tension, a force arising from the imbalance of forces in the interface, depends on intermolecular- interactions and is a force parallel to the interface.²² For the solvents we chose the interfacial tension has the following values against water: perfluorinated carbon with water can be considered approximately 52 mN/m, chloroform 31.6 mN/m, dichloromethane 28.2 mN/m, toluene 36.1 mN/m, 1,2 dichlorobenzene 40 mN/m.²³ Since the interface can be considered a separate entity where a selective mass and charge diffusion can take place we expect to realize differences in the reaction products depending on the structure and the thickness of the liquid-liquid boundary. It is interesting to notice here, that this boundary is not a smooth and homogenous entity but can be a host for thermal and concentration fluctuations.²⁴ Therefore, the addition of the organic molecules is expected to further alter the interfacial tension of the system.

3M™ Novec™ 7300

Figure 1. a) The course of the polymerization between two immiscible liquids. Interfacial tension values for I) Water/perfluoroether: 52 mN/m II) Water/chloroform: 31 mN/m III) Water/toluene: 37 mN/m IV) Water/dichloromethane: 28 mN/m V) Water/o-dichlorobenzene: 40 mN/m. SEM images of the insoluble fraction derived from b) dichloromethane (conc.B) and c) toluene (conc.A).

The oxidative polymerization of anilines is a highly complex procedure that is initiated by a radical cation $[(\text{PhNH}_2)]^+$. This subsequently reacts with another aniline molecule through the para position to produce the linear polyaniline or rarely through the ortho or the meta positions when further oxidation may lead

to the formation of the phenazine units.²⁵ In the case of the meta-substituted perfluorinated aniline we have to take into account the effect of the strongly electron with-drawing CF₂- and CF₃ groups that make the aromatic ring even more electron deficient. Before discussing the properties of the polymeric products in detail we will present the pristine monomer characterization through molecular spectroscopy. The 3FN monomer exhibits an absorbance onset at 410 nm with an n-p* transition located at $\lambda_{\text{max}}=350$ nm. In contrast the polymers have a considerably smaller bandgap with a red shifted absorbance onset which appears to be similar for both the soluble and the insoluble fractions (Figure 2a). According to the fluorescence study of the monomer dissolved in toluene the emission maximum is located at 350 nm upon excitation at 326 nm, a significantly small Stokes shift of 24 nm. Large Stokes shifts accompanied from high quantum yields are necessary for real life applications of bio or gas sensors, light emitting organic or in-organic materials for optoelectronics. For example, the light emitting organoboron compounds which have promised applications in organic light-emitting diodes (OLEDs), nonlinear optics, fluorescent molecular probes, and intracellular fluorescence imaging, demonstrate crucial disadvantages due to their very small Stokes shifts, which are approximately 10 nm.²⁶ As a result, this extremely small Stokes shift, which could reduce the emission intensity via self-absorption, has hindered their applications. This has led to an enormous activity by many research groups in order to achieve a respectable red shift increase of the emission maximum through multi-step functionalization that requires tedious organic reactions. Substitution in organic fluorophores is influencing the HOMO/LUMO levels, the band gap and the optical properties²⁷⁻²⁸ and with respect to that we present the molecular orbitals representation for the monomer and the dimer in different oxidation states (Figure 2). While the HOMO frontier orbitals seem to be localized in the electron accepting C-F bonds in the monomer this picture appear to change in the dimer with the location of the orbitals to be further influenced by the oxidation and protonation state of the bridging nitrogen units.

Figure 2. a) UV-Visible spectrum of the monomer in toluene (black), the HFE soluble part after 24 and 48 hours of reaction and the precipitate from chloroform and dichloromethane b) Excitation dependent photoluminescence map of the 3FN monomer in toluene. c) Representation of the frontier HOMO (left) and LUMO (right) bonding and antibonding orbitals for I) Monomer II) Dimer with different oxidation states and protonation states.

In order to identify the structure of the reaction products we employed vibrational spectroscopy which is a powerful tool for characterizing polymeric materials. Initially, we recorded the Raman spectra since they provide information not only on the polarizable chemical bonds present on the molecules but also on its crystallinity and chain packing. The spectra for the monomer and the polymer derived from the different organic phases are shown in Figure 3 and demonstrate the presence of the fingerprint region sharp and strong bands of the C-F bond located at 300 cm^{-1} (torsional vibration), 384 cm^{-1} (deformation), 1002 cm^{-1} , 1382 (symmetric stretching of CF_3) cm^{-1} . In the case of the polymer precipitates it is noteworthy the appearance of a new peak centered at 1072 cm^{-1} . This splitting of the F-C-F vibration is assigned to the formation of a polymeric unit cell. Similar peak splitting in a crystalline polymer state compared to an amorphous state have been previously observed in polyethylene. In this case the H-C-H scissor vibration splits in two closely located peak with the frequency difference between them to correspond to the difference between the in and out of phase vibrations.²⁹ Due to the intense fluorescence of the soluble fractions their Raman spectra could not be recorded. Furthermore they appear to decompose and burn under the laser beam.

In a second step we employed FTIR spectroscopy which can provide information on the protonation and oxidation states of the materials. The FTIR spectra shown in Figure 3b and Figure S3 (S.I) demonstrated the nature of the chemical bond between the monomeric units. In the insoluble fractions, the symmetric and anti-symmetric $-\text{NH}_2$ bands of the monomer which can be seen at 3428 and 3354 cm^{-1} are shifting to a medium band centered at 2600 cm^{-1} which is typical of the ammonium cation $-\text{NH}_2^+$ while the presence of vibrations in the range 3140 and 3050 cm^{-1} have been attributed to the presence of benzene ring adjacent to amine groups and to protonated amines $-\text{NH}=\text{C}_6\text{H}_4=\text{NH}$ and $-\text{NH}_2^+-\text{C}_6\text{H}_4-\text{NH}_2^+$ in polyaniline chains. The sample cast from HFE, the solvent with the highest interfacial tension to water and the highest affinity for the hydrophobic part of the monomer reveals a spectrum where the $-\text{NH}=\text{C}_6\text{H}_4=\text{NH}$ and $-\text{NH}_2^+-\text{C}_6\text{H}_4-\text{NH}_2^+$ modes are shifting to lower energy by 76 and 34 cm^{-1} . This can be further correlated with the Raman data that demonstrate that the ratio between the 1072 and 1002 cm^{-1} peaks is the lowest

in this sample, with the latter to be considerably weaker compared to the DCM/water, o-DCB/water and toluene/water systems. This is a strong indication for a different crystal packing and conformation for the materials synthesized through a hydrofluoroether/water interface. Interestingly, the highest molecular weight fragments in the mass spec analysis are observed for the soluble fraction derived from the HFE and the smallest fractions for the corresponding precipitate alongside the Prec.o-DCB. According to the m/z values the largest fragment of the soluble fraction corresponds to 4 ($m/z=2044$) monomer units of a non-protonated or oxidized tetramer. In contrast, a more uniform picture is observed for the ortho-dichlorobenzene and chloroform derivatives with 2 and 3 monomer units to be the dominant mass spec features. All mass spectra with either positive or negative ionization or DCTB as matrix can be seen in the Figure S8-S9 (Supporting information section-S.I).

In contrast, the FTIR spectrum of the soluble fraction is still possessing the strong $-NH_2$ vibration bands at 3428 and 3354 cm^{-1} . For further characterization on the samples, we performed DSC analysis in the monomer, the soluble and the insoluble fractions (Figure S2). The graphs are given in the supporting information section (Figure S2-S.I). The monomer is showing a melting point at 35 °C accompanied by a reversible crystallization at the same temperature. In contrast, the soluble fractions cast from HFE exhibit a melting point at 30 °C and the fraction cast from chloroform a weak transition at 39 °C. None of these transition are observed in the insoluble precipitates under heating up to 120 °C.

Figure 3. a) Raman spectra of the insoluble fraction derived from different organic solvent and water interfaces. The organic solvent for each sample is indicated as an inset b) FTIR spectra

The presence of crystal orientations and a lamellar structure was proven by XRD analysis (Figure 4). The powder diffraction patterns demonstrate the presence of common diffraction patterns with relative intensity variations based on the organic solvent used. The samples derived from hydrocarbons, dichloromethane and chlorobenzene are showing the pronounced peaks at 10.6 Å and 5 Å which may be assigned to the distance between the fluorocarbon chains on oxidized rings. The pristine monomer has only two peaks at 31.5 Å and the strongest at 15.7 Å which is close the length of the fluorocarbon chain

and the sample from HFE appears to be a combination of both. Again, similarly with Raman observations the HFE derived sample is showing the closest similarity with the monomer crystal.

Figure 4. XRD patterns of the monomer and three different insoluble fractions and minimized energy structures of a monomer and a quinoid-benzenoid dimer depicting the different arrangement between the aromatic rings and the perfluorinated chains.

3.2. Soluble fraction: Separation of the reaction products, and analysis on their optical properties and molecular structures

The excitation dependent photoluminescence maps were recorded for excitation wavelengths 300-500 nm and emission range 320-900 nm in the reaction solvent for the soluble fractions and in an acetone: toluene 1:1 mixture for the insoluble fractions. We will initially focus on the optical properties of the soluble products of each reaction. The excitation dependence photoluminescence 3D maps can be seen in Figure 4 (we present the spectra from 320-650 nm for clarity since no emission is observed higher than 650 nm) for two different molar ratios between the acid/oxidant and the monomer. In all cases the emission maximum is significantly red shifted compared to the monomer and is located in the green region of the

spectrum. There is a substantial difference in terms of the excitation spectrum. As the interfacial tension decreases, for example dichloromethane compared to the aromatic solvents and the per-fluorinated ether, the emission maximum can be achieved through excitation at lower wavelength, i.e. $\lambda_{\text{exc}}=370\text{-}375\text{ nm}$ (Figure 5). This is particularly pronounced in the experiment with a monomer to oxidant molar ratio of 0.78. Again, the strongest emission at $\lambda_{\text{em}}=517\text{-}548\text{ nm}$ takes place through excitation at a smaller Stokes shift, namely at $\lambda_{\text{exc}}=470\text{-}480\text{ nm}$.

Figure 5. Excitation dependent photoluminescence maps of the soluble fractions as derived from the reaction mixture. The abbreviation for each sample is given above each spectrum.

Since the excitation-emission 3D maps in Figure 4 correspond to the reaction mixture where especially in the dichloromethane and chloroform derived samples, various oxidation states and molecular weight fractions may be present, we tried to purify the soluble fraction through column silica chromatography. We evaporated the low boiling point chloroform and solubilized the materials in toluene. During the

elution of the mixture through the silica column we distinguished fractions with different colors. In Figure 6 we present the excitation dependent photoluminescence maps for four different fractions, with fraction 1 to be isolated at lower elution time than fraction 2, 3 and 4. The UV-Visible spectra are presented in Figure 5c and demonstrate apparent similarities between fraction 1&2 and 3&4, with the latter to feature a pronounced peak centered at 440 nm (2.82 eV).

Figure 6. The separation of the different soluble fractions of the sample derived from water-dichloromethane with column chromatography (a) and their corresponding 3D PL maps (b-I-IV), UV-Vis (c) spectra. Chloroform was evaporated and the material was re-dissolved in toluene prior to injection to

the silica column. We present the analysis of four fractions: 1 with $\lambda_{\text{exc}}=330; 370; 480$ and $\lambda_{\text{em}}=368; 487; 529$ nm - 2 with $\lambda_{\text{exc}}=335; 364; 480$ and $\lambda_{\text{em}}=378; 410; 532$ nm- 3 with $\lambda_{\text{exc}}=335; 364; 480$ and $\lambda_{\text{em}}=378; 452; 532$ nm - 4 with $\lambda_{\text{exc}}=373; 475$ nm and $\lambda_{\text{em}}=536$ nm.

The mass spec analysis further revealed the similarity between the structures of 1&2 and 3&4 oligomers. These pairs demonstrate a similar fragmentation as can be seen in Figure 7c. ^1H NMR spectroscopy also reveals a similarity in the structures of Fractions 1 and 2. The peak position and the splitting in the region of 6.75 and 8.10 ppm (see Figure 6c) are common to both fractions, suggesting similar sites of attachment on most phenyl rings. We detected one singlet at a chemical shift of 8.1 ppm, two doublets at 7.6 ppm and 7.15 ppm and three singlets between 6.78-6.9 ppm. The aromatic singlets arise from protons adjacent to two carbons, one with a C-F group and one with a N=C bond and the doublets from the protons next to non-perfluorinated aromatic carbons with one hydrogen atom.³⁰ On the other hand, we detected two more doublets and one more singlet peaks in the Fraction 2 in up field region, something that indicates a more complicated environment. Thus we assign to the Fraction 2 the structure depicted in Figure 7. All fractions except Fraction 1 have a peak at between 2.5 and 3.5 ppm, which we believe corresponds to non-aromatic protons in quinoid-benzenoid rings as seen in the structure in Figure S12.³¹ Fraction 2 also exhibits a singlet at 7.07 ppm which can be assigned to N-H among oxidized heterojunctions. Thus, we suggest that Fraction 1 is in the fully oxidized form. These NMR data are in agreement with the characteristic strong absorbance peak at 440 nm in the UV-vis spectrum since pronounced blue shifted peaks are typical for polyanilines in other than the emeraldine salt states. I/V curves on drop casted films indicated a low conductivity and Ohmic behavior for Fraction 2 (Fig.S15). The ^1H NMR spectra of 3 and 4 (see Fig.S12) are markedly different compared to both each other and to 1 and 2, with 3 also exhibiting two new ^{19}F environments (Fig.6 and S13.). Fraction 3 exhibits a very complicated spectrum while Fraction 4 has peaks mostly at the vinyl region, 6 ppm; 6.3 ppm; 6.7 ppm. The downfield NMR peaks seem to correspond to the more red shifted PL emissions. Finally, the optical images under violet (400

nm) and green (532 nm) laser excitation were recorded and can be seen in Figure 6. The materials provide a range of emitting colors ranging from deep blue to yellow under 400 nm excitation, while a deep orange-yellow fluorescence was clearly visible under a green laser 532 nm excitation.

Figure 7. a) The illumination of the reaction mixture (a) and the fractions 1-4 with 400 nm and 532 nm laser (b) c-I) MALDI-TOF MS analysis (negative ionization, DCTB matrix). Fractions 1&2 and 3&4 give

apparent similarities in accordance with the PL and UV-Vis spectra. C-II) ^1H NMR/ ^{19}F NMR for fractions 1;2;4 and the proposed structure for the basic unit of Fraction 2. The ^1H NMR of fraction 3 and the full ^{19}F and ^1H NMR are shown in S.I.

3.3. Light emitting properties of the insoluble fractions

We then turn our attention to the precipitates of the reaction. Besides the well-known aniline there are other types of aromatic amines that have been polymerized through oxidative polymerization, either chemically or electrochemically, with a recent example to be the porphyrin dye 5, 10, 15, 20-tetrakis (4-aminophenyl) porphyrin (TAPP).³² In that case the polymerization occurs in a manner analogous to that of aniline, except that the ortho rather than the para attack is favored. This leads to the redox-active phenazine/dihydrophenazine units that can be strong candidates for sensing applications. In our case, due to the presence of the electron withdrawing and thus strongly deactivating perfluorinated chain the substitution may be directed to a meta position. From the FTIR spectra we confirm that the backbone consists from the emeraldine salt form of polyaniline.

In Figure 8 we present the excitation dependent photoluminescence maps for the precipitates when dissolved in a toluene: acetone 1:1 mixture. We observe two distinctive features of the spectra. In the case of HFE, that has the highest interfacial tension and thus is not enabling the effective diffusion of the oxidant and the monomer in the interface and the organic phase, what is observed a highly localized emission which appears to be independent on the concentration of the monomer and the oxidative persulfate ion. In contrast, both chloroform and dichloromethane exhibit a second red shifted peak, which appear at $\lambda_{\text{em}}=410$ nm with a bright blue visible fluorescence. The Stokes shifts are significantly lower compared to the soluble counterparts, at 30 nm for all samples signaling the formation of similar vibronic structures and non-radiative pathways among all the polymers.

Figure 8. Excitation dependent photoluminescence maps of the precipitate fractions solubilized in an acetone:toluene 1:1 mixture. The abbreviations for each sample is given above the corresponding spectrum. a-b) HFE c-d) Chloroform e-f) dichloromethane. The presence of a similar oxidation and protonation state is proven for all samples with the exception of the powder derived from dichloromethane. f) Illumination of the Prec.DCM.Conc.B sample with violet (400 nm) laser light.

3.4. Photoluminescence mechanism and band gap

Previous works on the fluorescence of polyaniline nanomaterials indicated a weak emission located in the ultraviolet region ³³ that can be further red shifted and tuned upon doping with aromatic molecules like perylene tetracarboxylic acid (PTCA) that acts as doping counter ion and results in a green emission. This fluorescence is easily distinguished with the naked eye compared to reddish emission of the pristine dopant PTCA. ³⁴ There is a number of factors that are influencing the electronic transport and optical properties of conjugated polymers. The crystallinity and pi-pi stacking between adjacent macromolecular chains leads to higher electron delocalization and thus it is expected to facilitate the charge transport and close the band gap. The conjugation further stabilizes the π electrons and drops the energy levels and the energy band gap. A further lowering of the LUMO molecular orbital levels is due to electron accepting fluorine atoms. Still these materials essentially resemble the inorganic semiconductors where the conductivity increases by introducing an oxidizing or reducing agent, a dopant, that either creates holes which are positive charge carriers or adds electrons near the LUMO levels.

The acid doping in the polyaniline backbone takes place on the formerly unprotonated —N= site and this process results to the formation of not fully occupied polaron bands thus allowing intra band transitions with either in low or high energy. These optical transitions are observed in the both the blue part and the red and NIR regions resulting in the characteristic three band UV-Visible spectrum for the conductive emeraldine salt form of polyaniline. ³⁵⁻³⁶ Furthermore the solvent from which the polyaniline macromolecular chains are cast towards the formation of films or powders results to different chains conformation and to different electronic transport properties. This is crucial since the band gap and the intra-chain and inter-chain charge transfer depends on the elongation and crystal packing of the polymer chains. To further prove the solvent effects on the polymer properties, D'Arcy et al realized a versatile method for depositing polyaniline or PEDOT polymeric nanostructures with respect to an interfacial gradient between a series of immiscible solvents. ³⁷ Their simple and thermodynamically driven solution-based process lead to the growth of thin films of adsorbed polymer nanofibers by employing chlorocarbon solvents like carbon tetrachloride, chloroform and methylene chloride as the water immiscible phase.

With respect to the above we constructed a mapping of the optical properties for each derivative with the interfacial tension since it will dictate the structure of the interface, the arrangement of the monomer and the diffusion of the oxidant and the acid dopant. In Figure 9 we present the optical band gaps as derived and calculated by the photoluminescence excitation dependence maps for the monomer, a typical soluble and an insoluble derivative. The smallest Stokes shifts due to vibrational relaxations are observed for the HFE/water system and are significantly close to the values of the pristine monomer. In contrast the soluble fraction derived from hydrocarbon/water systems has a smaller band gap and remarkably large Stokes shifts. It is well established that conventional non-perfluorinated polyaniline exhibits photoluminescence only its fully reduced form of leucoemeraldine ($S_1 \rightarrow S_0$, $\lambda_{em}=460$ nm at $\lambda_{exc}=365$ nm), which is something that correlates well with our FTIR and PL studies.³⁸ Regarding the effect of different acid doping, initial efforts to polymerize the 3FN through organic acids, like citric acid were not successful. No visible progress of the reaction took place after one week reaction time and the insoluble fraction could not be subsequently dissolve in a sodium citrate solution. By adding chloroform and toluene it migrated to the organic phase (Figure S1e).

Figure 9. a) The optical band gap of the monomer compared with the radiative and non-radiative pathways for the soluble and non-soluble polymer derivatives as derived from the λ_{em} . Diagrams mapping the λ_{em} (b) and the Stokes shift (c) as detected in the soluble and insoluble fractions compared to the interfacial tension of the interface.

3.5. Reduction of noble metal ions and acid/base reactions

Amine based polymers, including polyaniline salts, have been repeatedly reported to be able to reduce noble metal cations like silver or gold for example the decoration on triazine based 3-D networks with reduced silver nanoparticles.³⁹⁻⁴⁰ After the reduction of silver nitrate, the resulting silver nanomaterials are entrapped on the surface of the polymers through the nitrogen units and are decorating their surface, thus inheriting them both with a strong surface plasmon resonance absorption and an antibacterial activity. In these works, phosphotriazine based polymers with aromatic diamines as bridging units were synthesized through nucleophilic attack on the chlorine atoms of phosphonitrilic chloride and was proven that they could reduce silver ions. This reduction led to the formation of nanocomposites that served as very efficient antibacterial agents towards a range of fungi and bacteria.

Figure 10. a) Schematic representation of the reduction of silver nitrate b) Raman spectrum of the monomer, polymer and silver-polymer composite. c) The UV-Vis spectra for different reaction times demonstrating the emergence of the silver surface plasmon resonance band at 420 nm. d) XRD pattern

Since the reaction results in a deprotonation or further oxidation of the nitrogen containing aromatic units of the polymeric backbone we tested the effect of this reaction on the light emitting optical properties of the polymers. We dispersed 30 mg of the insoluble fraction of the polymer in water and added 10 mg of silver nitrate. After vigorous mixing in room temperature we added 20 ml of toluene that solubilized the polymer and carried it in the aqueous phase. Since the parent polymer is insoluble in toluene we achieve an efficient and quick separation. The formation of silver nanoparticles can be monitored and demonstrated through the evolution of the characteristic surface plasmon resonance band in the region of 400-450 nm. In Figure 10 we present the proposed reaction scheme and the evolution of the UV-Visible spectra in different reaction times. The powder diffraction XRD pattern (Figure 10d) indicated the presence of silver nanoparticles.⁴¹ The Raman spectrum (Figure 10b) showed pronounced peaks at the

C-N region (1420; 1492; 1592 cm^{-1}) and the C-F peak shifts at 997 cm^{-1} without the crystallinity induced splitting that we observed in the neat polymers. These results are similar with those previously observed in SERS studies of amidine functionalized silver indicating different crystal packing due to the deprotonation and attachment on the silver nanoparticles and an enhancement of these particular signals due to absorption on the plasmon resonance surface.⁴²

We performed kinetic analysis by testing the effect of the silver nitrate reduction through 15 min, 60 min, 180 min and 48 hours of reaction time intervals and the excitation dependence photoluminescence maps are shown in Figure 10a-d. An expansion of the light emitting region is readily observed which significant red shifts of the optimum λ_{exc} and the λ_{em} to be observed even after 15 min of reaction time. The products stabilize in a specific oxidation state. The mass spec (S.I) analysis is demonstrating that the polymer after the reaction with silver nitrate is less prone to fragmentation, with clusters of $m/z=5624$ (11 monomer sub units) to be the largest that could be observed (Figure S9, S.I). In general MALDI-TOF analysis of polyaniline is leading to a pronounced fragmentation of the polymer chain and a detailed mass spec analysis of our materials by employing a series of matrices instead of DCTB is out of the scope of the present work.⁴³⁻⁴⁴

Figure 11. The insoluble powder derived from o-dichlorobenzene, Prec.o-DCB, was dispersed in water with sonication and after addition of AgNO_3 it was extracted with toluene. The excitation dependent photoluminescence maps were recorded for 4 samples in different time intervals for each of them. a) Initial spectrum in toluene: acetone 1:1 before addition of AgNO_3 b) After 15 min reaction c) After 60 min reaction d) After 180 min e) After 48 hours and 14 days (f) g) The Stokes shifts distribution with respect to the reaction time i) The toluene phase under 400 nm laser illumination.

We further investigate the effectiveness of these materials as acid and base sensors based on their acidic or basic behavior inherited by the amine sites of the polymer backbone. We employed 4-

benzoyl benzoic acid and ethylene diamine as an organic acid and base respectively, both dissolved in isopropanol. We present all the spectra recorded during the different titration steps in Figure 12 and S7, S.I. Indeed interesting push-pull patterns and activated-deactivated pathways similar with other switchable fluorophores were observed.⁴⁵ The pattern during the acid doping a gradual decrease of the emission intensity that can be perfectly fitted with a biexponential decay model (Figure 12a). This is indicating a dual mechanism on the fluorescence quenching originating from protonation of both the quinoid and benzenoid rings.

In contrast, during a titration with an organic base like ethylene diamine a more complicated and interesting picture is taking shape (Figure 12b). The fluorescence mapping of the Ag-P3FN sample is indicating an initial splitting and quenching of the low energy transition ($\lambda_{em.529}$ nm) and an increase on the intensity of the high energy transition ($\lambda_{em.475}$ nm) with the same Stokes shift of 50 nm. The quenching of the low energy ($\lambda_{em.529}$ nm) fluorescence is again following a bi-exponential decay mechanism. The increase of the $\lambda_{em.475}$ nm emission according to volume of amine solution is following a sigmoidal function, similar with an acid-base titration curve. Upon excitation with green laser the solution appears to be brightly red something that merits further investigation towards biomedical applications. When the insoluble fraction of the polymer (P3FN) was titrated with the same base, the emission maximum linearly shifted to the same $\lambda_{em.475}$ nm peak but this time from an initial state with higher energy transition ($\lambda_{em.360}$ nm) and following a linear increase of the relative intensity.

Figure 12. Normalized fluorescence intensity during titration with a) 4-benzoyl benzoic acid for Ag-P3FN b) Ethylene diamine. Blue sphere: λ_{em} .529 nm (2.34 eV) for Ag-P3FN, Red sphere: λ_{em} .475 nm (2.61 eV) for Ag-P3FN, Black sphere: λ_{em} .475 nm (2.61 eV) for P3FN. The spectra during the acid (c) and base (d) titration for the Ag-P3FN and the illumination of the basic solution with violet (400 nm) and green (532 nm) laser light. The residual fitting data for the biexponential decay and the sigmoidal Boltzmann curve and the corresponding UV-Vis spectra are shown in S.I (Fig.S10-S11).

4. Conclusions

In this work we report a series of light emitting per-fluorinated polyanilines synthesized by the versatile interfacial polymerization route. We employed five different organic solvents with

variable polarity and interfacial tensions against water and two different monomer to oxidant molar ratios in order to clarify their effect on the optical properties of these materials. Based on the optical studies of our materials we can demonstrate a tuning of the λ_{em} of our products resulting in multi-emitting perfluorinated polymers with high crystallinity that can be further used as sensor materials. In a similar manner with previous polymers based on aromatic amines, the materials can reduce noble metal ions, for example silver, and react with organic acids and bases something that results in a change in the optical properties. A biexponential decay was observed for the low energy transition upon addition of acid and base and a substantial increase of the organic nanomaterials fingerprint $S_0 \rightarrow S_1$ at 475 nm took place simultaneously. It is noteworthy that ethylene diamine addition lead to a significant increase in a high energy transition which can be fitted with a sigmoidal function.

Supporting Information. DSC curves, FTIR spectra, full range ^1H and ^{19}F NMR, mass spec, fluorescence maps, I/V curve and residual fitting data regarding the titration related optical properties are available free of charge via the internet.

AUTHOR INFORMATION

Corresponding Author

* panagiotis.dallas@materials.ox.ac.uk; (Tel: +44(0)1865273724; Fax: +44(0)1865273789

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

The Authors would like to acknowledge EPSRC for grant support (EP/K030108/1).

ACKNOWLEDGMENT

The Authors would like to acknowledge Susan Warren and Phil Holdway (OMCS) for recording the DSC and the XRD patterns respectively and Dr.Pascal Gehring for his assistance on the I/V measurement. Also, Mr.Alexej Dens from 3M Company, UK, for providing perfluorinated solvents and for useful discussion regarding their applications, health and safety data.

REFERENCES

1. Michael, D.; I. Benjamin. Electronic spectra of dipolar solutes at liquid/liquid interfaces: Effect of interface structure and polarity. *J. Chem. Phys.* **1997**, *107*, 5684-5693
2. Volkov, A.G.; Deamer. D.W. *Liquid interface theory and methods*. CRC Press, Inc, New York, 1996
3. Fermín, D.J.; Duong, H.D.; Ding, Z.; Brevet, P.F.; Girault, H.H. Photoinduced Electron Transfer at Liquid/Liquid Interfaces. Part III. Photoelectrochemical Responses Involving Porphyrin Ion Pairs. *J. Am. Chem. Soc.* **1999**, *121*, 10203-10210
4. Kong, Y.T.; Imabayashi, S.; Kakiuchi, T. Two-Phase Azo-Coupling Reactions Driven by Phase-Boundary Potential Across the Liquid|Liquid Interface *J. Am. Chem. Soc.* **2000**, *122*, 8215-8219
5. Uchiyama, Y.; Kitamori, T.; Sawada, T. Role of the Liquid/Liquid Interface in a Phase-Transfer Catalytic Reaction As Investigated by in Situ Measurements Using the Quasi-Elastic Laser Scattering Method. *Langmuir* **2000**, *16*, 6597-6600
6. Wittbecker, E.L.; Morgan, P.W. Interfacial polycondensation.I. *J Polym Sci Part A: Polym Chem.* **1996**, *34*, 521-529.

7. Dhumal, S.; Suresh, A.K. A comprehensive model for kinetics and development of film structure in interfacial polycondensation *Polymer* **2009**, *50*, 5851-5864
8. Tsukamoto, J. Recent advances in highly conductive polyacetylene. *Adv.Phys.* **1992**, *41*, 509-546
9. Huang, J.; Virji, S.; Kaner, R.B.; Weiller, B.H. Nanostructured Polyaniline Sensors. *Chem.Eur.J.* **2004**, *10*, 1314-1319
10. Zhou, X.; Ma, P.; Wang, A.; Yu, C.; Qian, T.; Wu, W.; Shen, J. Dopamine fluorescent sensors based on polypyrrole/graphene quantum dots core/shell hybrids *Biosensors and Bioelectronics* **2015**, *64*, 404-410
11. Nuraje, N.; Su, K.; Yang, N.L.; Matsui, H. Liquid/Liquid Interfacial Polymerization To Grow Single Crystalline Nanoneedles of Various Conducting Polymers *ACS Nano* **2008**, *2*(3), 502-506.
12. Dallas, P.; Georgakilas, V. Interfacial polymerization of conductive polymers: generation of polymeric nanostructures in a 2-D space. *Adv.Coll.Int.Sci.* **2015**, *224*, 64-61
13. Miller, T.M. Atomic and molecular polarizabilities. CRC Handbook of Chemistry and Physics, ed DR Lide (CRC, Boca Raton, FL), Internet Version **2010**, 10193–10202.
14. Buhler, E.; Dobrynin, A.V.; DeSimone, J.M.; Rubinstein, M. Light-Scattering Study of Diblock Copolymers in Supercritical Carbon Dioxide: CO₂ Density-Induced Micellization Transition. *Macromolecules.* **1998**, *31*, 7347–7355.
15. Galindo, C.M.C.; Blas, F.J.; Gubbins, K.E. Phase behavior of carbon dioxide mixtures with n-alkanes and n-perfluoroalkanes *Fluid Phase Equilibria* **2004**, *222–223*, 77–85
16. Dalvia, V.H.; Rossky, P.J. Molecular origins of fluorocarbon hydrophobicity. *Proc.Nat.Acad.Sciences.* **2010**, *107*, 13603-13607
17. Xu, J.; Wlaschin, A.; Enick, R. Thickening Carbon Dioxide With the Fluoroacrylate-Styrene Copolymer *SPE Journal* **2003**, *8*(2)

18. Lu, W.; Kuwabara, J.; Iijima, T.; Higashimura, H.; Hayashi, H.; Kanbara, T. Synthesis of π -Conjugated Polymers Containing Fluorinated Arylene Units via Direct Arylation: Efficient Synthetic Method of Materials for OLEDs *Macromolecules* **2012**, *45*, 4128-4133
19. Giovanella, U.; Botta, C.; Galeotti, F.; Vercelli, B.; Battiato, S.; Pasini, M. Perfluorinated polymer with unexpectedly efficient deep blue electroluminescence for full-colour OLED displays and light therapy applications *J.Mater.Chem.C*. **2013**, *1*(34), 5322-5329
20. Morales-Vidal, M.; Boj, P.G.; Villalvilla, J.M.; Quintana, J.A.; Yan, Q.; Lin, N.T.; Zhu, X.; Ruangsapapichat, N.; Casado, J.; Tsuji, H. et al. Carbon-bridged oligo(*p*-phenylenevinylene)s for photostable and broadly tunable, solution-processable thin film organic lasers *Nat.Comm.* **2015**, *6*, 8458-8465
21. Dallas, P.; Niarchos, D.; Vrbancic, D.; Boukos, N.; Pejovnik, S.; Trapalis, C.; Petridis, D. Interfacial polymerization of pyrrole and in situ synthesis of polypyrrole/silver nanocomposites. *Polymer* **2007**, *48*, 2007-2013
22. Marchand, A.; Weijs, J.H.; Scoeijer, J.H.; Andreotti, B. Why is surface tension a force parallel to the interface? *Am.J.Phys.* **2011**, *79*, 999-1008
23. Bahramian, A.; Danesh, A. Prediction of liquid–liquid interfacial tension in multi-component systems *Fluid Phase Equilibria* **2004**, *221*, 197-205
24. Aarts, D.G.A.L.; Schmidt, M.; Lekkerkerker, J.N.W. Direct Visual Observation of Thermal Capillary Waves *Science* **2004**, *304*, 847-850
25. Tran, H.D.; D`Arcy, J.M.D.; Wang, Y.; Beltramo, P.J.; Strong, V.A.; Kaner, R.B. The oxidation of aniline to produce “polyaniline”: a process yielding many different nanoscale structures *J.Mater.Chem.* **2010**, *21*, 3534-3550
26. Horvath, P.S.; Sebej, P.; Šolomek, T.; Klan, P.; Small-Molecule Fluorophores with Large Stokes Shifts: 9-Iminopyronin Analogues as Clickable Tags *J. Org. Chem.* **2015**, *80*, 1299–1311

27. Jin, J.L.; Li, H.B.; Geng, Y.; Wu, Y.; Duan, Y.A.; Su, Z.M. Theoretical Insight into the Origin of Large Stokes Shift and Photophysical Properties of Anilido-Pyridine Boron Difluoride Dyes *Chem.Phys.Chem.* **2012**, *13*, 3714 – 3722
28. Koepnick, B.D.; Lipscomb, J.S.; Taylor, D.K. Effect of Substitution on the Optical Properties and HOMO–LUMO Gap of Oligomeric Paraphenylenes *J.Phys.Chem.A.* **2010**, *114*, 13228-13332
29. Strobl, G. The physics of polymers: concepts for understanding their structure and behavior. Springer-Verlag Berlin Heidelberg, 2007
30. Wang, X.; Sun, T.; Wang, C.; Wang, C.; Zhang, W.; Wei, Y. ¹H NMR Determination of the Doping Level of Doped Polyaniline *Macrom.Chem.Phys.* **2010**, *211*, 1814-1819
31. Ravat,P.; Baumgarten, M. “Tschitschibabin type biradicals”: benzenoid or quinoid? *Phys.Chem.Chem.Phys.* **2015**, *17*, 983-991
32. Day, N.U.; Walter, M.G.; Wamser, C. Preparations and Electrochemical Characterizations of Conductive Porphyrin Polymers *J. Phys. Chem. C.* **2015**, *119*, 17378-17388
33. Dispenzaa, C.; Sabatino, M.A.; Chmielewska, D.; LoPresti, C.; Battagli, B. *React.Funct.Pol.* Inherently fluorescent polyaniline nanoparticles in a dynamic landscape **2012**, *72*, 185–197
34. Rana, U.; Chakrabarti, K.; Malik, S. *In situ* preparation of fluorescent polyaniline nanotubes doped with perylene tetracarboxylic acids *J. Mater. Chem.* **2011**, *21*, 11098-11100
35. Stafstrom, S.; Bredas, J.L.; Epstein, A.J.; Woo, H.S.; Tanner, D.B.; Huang, W.S.; MacDiarmid, A.G. Polaron lattice in highly conducting polyaniline: Theoretical and optical studies *Phys.Rev.Lett.* **1987**, *59*, 1464-1467
36. Stejskal; J. Kratochvil, P. Polyaniline dispersions 2. UV—Vis absorption spectra *Synth.Met* **1993**, *61*, 225-231

37. D'Arcy, J.M.D.; Tran, H.D.; Tung, V.C.; Tucker-Schwartz, A.K.; Wong, R.P.; Yang, Y.; Kaner, R.B. Versatile solution for growing thin films of conducting polymers
Proc.Nat.Acad.Sciences. **2010**, *107*(46), 19673–19678
38. Ram, M.K.; Mascetti, J.; Paddeu, S.; Maccioni, S.; Nicolini, K. Optical, structural and fluorescence microscopic studies on reduced form of polyaniline: The leucoemeraldine base. *Synth.Met.* **1997**, *89*, 63-69
39. Stejskal, J.; Trchova, M.; Kovarova, J.; Brozova, L.; Prokes, J. The reduction of silver nitrate with various polyaniline salts to polyaniline-silver composites. *React.Funct.Pol.* **2009**, *69*, 86-90
40. Dallas, P.; Tucek, J.; Jancik, D.; Kolar, M.; Panacek, A.; Zboril, R. Magnetically Controllable Silver Nanocomposite with Multifunctional Phosphotriazine Matrix and High Antimicrobial Activity *Adv.Funct.Mater.* **2010**, *20*(14), 2347-2354.
41. Campi, G.; Mari, A.; Amenitsch, H.; Pifferi, A.; Cannas, C.; Suber, L. Monitoring early stages of silver particle formation in a polymer solution by *in situ* and time resolved small angle X-ray scattering *Nanoscale* **2010**, *2*, 2447-2455
42. Cure, J.; Coppel, Y.; Dammak, T.; Fazzini, P.F.; Mlayah, A.; Chaudret, B.; Fau, P. Monitoring the Coordination of Amine Ligands on Silver Nanoparticles Using NMR and SERS *Langmuir* **2015**, *31*, 1362–1367
43. Dolan, A.R.; Wood, T.D Analysis of polyaniline oligomers by laser desorption ionization and solventless MALDI *J.Am.Soc.Mass.Spec.* **2004**, *15*(6), 893-899
44. Laska, J.; Widlarz, J. Spectroscopic and structural characterization of low molecular weight fractions of polyaniline *Polymer* **2005**, *46*, 1485-1495
45. Yapici, I.; Lee, K.S.S.; Berbasova, T.; Nosrati, M.; Jia, X.; Vasileiou, C.; Wang, W.; Santos, E.M.; Geiger, J.H.; Borhan, B. *J.Am.Chem.Soc.* “Turn-On” Protein Fluorescence: In Situ Formation of Cyanine Dyes **2015**, *137*, 1073-1080

Table of contents