

Excitation Delocalization in Porphyrin Nanorings



Juliane Q. Gong
St John's College
University of Oxford

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Publications

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Structure-Directed Exciton Dynamics in Templated Molecular Nanorings. **J. Q. Gong**, P. Parkinson, D. V. Kondratuk, G. Gil-Ramírez, H. L. Anderson, and L. M. Herz. *Journal of Physical Chemistry C* 119, 11 (2015): 6414-6420.

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Abstract

This thesis is concerned with the photophysical properties of porphyrin nanorings. In particular, the impact of symmetry, conformation and structure on electronic delocalization, radiative rate and emission polarization memory loss are investigated and exciton migration is probed on a number of porphyrin nanorings. Ultrafast time-resolved spectroscopy techniques are used to study the fluorescence dynamics of these newly synthesized compounds.

First, photophysical implications of lifting the rotational symmetry are investigated using a number of small porphyrin rings specially modified for this purpose. For more severe symmetry distortions, increased optical transitions to the lowest excited state have been observed, which is dipole-forbidden due to symmetry reason. Also, the degeneracy in the allowed first excited state is lifted for broken symmetry, leading to a polarization switching effect.

The effect of conformation on emission depolarization memory loss is studied using a series of similarly sized porphyrin rings with rigid structures exhibiting various degrees of out-of-plane distortion. Excitations can access any segment on the nanoring and this is not affected by the conformation. However, severe out-of-plane distortions lead to lowered emission anisotropy; this conclusion is further supported by molecular dynamics simulation.

Finally, exciton migration within porphyrin ring complex is investigated. Russian doll complex which consists of two concentric porphyrin rings acts as a single emitter, even though spectral features of both ring components are found in the absorption spectrum. Lifetimes and radiative rates of the complex and the individual rings components further confirmed that excitons migrate from the outer 12-ring to the inner 6-ring within 40 ps. A nanotube consisting of two conjugated 6 porphyrin rings linked by dimers acting as staves also exhibits energy migration. Emission anisotropy measurements suggest that excitation is transferred from the staves of the nanotube to the ring plane effectively within 280 fs.

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Chapter 1

Introduction

Starting in the 1970s research into optical, electronic and magnetic properties of conjugated polymers has seen a steady rise in number and can boast with some great achievements. Discovery and development of conductive polymers [6] in 1977 established the field of synthetic metals, for which Heeger, MacDiarmid and Shirakawa were jointly awarded with the Nobel prize for chemistry in 2000. In 1990 electroluminescence under low voltages was demonstrated in phenyl-based polymers [4], opening up the new field of polymer optoelectronics. Combining their optical and electronic properties with flexibility and intrinsic processing advantage, conjugated polymers offer great potential for a diverse range of applications [9] such as organic light-emitting diodes [4, 8], field-effect transistors [3, 5] and polymer solar cells [1, 2]. Today, optoelectronic applications based on conjugated polymers have permeated our everyday life, ranging from mobile phone displays to large OLED lighting panels.

In the past decades, many synthetic polymer structures have been created with the ultimate goal of realizing artificial light harvesting systems [12]. The highly symmetric cyclic architecture of light-harvesting antenna complex in purple bacteria was first revealed in 1995, exhibiting extremely high energy transfer efficiency ($\sim 90\%$) due to exciton delocalization [7]. A synthetic system with

these properties would be desirable in many applications, such as photon detectors and biomimetic solar cells.

A promising candidate is nano-sized fully π -conjugated macrocycles based on porphyrin units, which have been realized using template-directed self-assembly [10, 11]. A promising approach to synthesis of nano-sized fully π -conjugated macrocycles based on porphyrin units has been developed using template-directed self-assembly [10, 11]. A great number of porphyrin nanoring structures of diverse size and shape have been synthesized and some of their photophysical properties are investigated in this thesis.

Chapter 2 provides a review of the electronic and optical properties of conjugated polymers and the exciton transfer dynamics are discussed. In particular, delocalization, radiative rate and polarization anisotropy are covered, which hold key positions during the experimental investigations in this thesis. In the last part of this chapter, a brief introduction to organic ring-like systems is presented, with the main focus on the porphyrin nanorings.

Chapter 3 gives a detailed description of the time-resolved spectroscopy methods used in this thesis to investigate the photophysical properties of the porphyrin nanorings. The fundamental principle and experimental set-up of the photoluminescence up-conversion (PLUC) and time-resolved single photon counting (TCSPC) technique are discussed, which can measure the fluorescence dynamics of the sample with a time resolution of 270 fs and 40 ps respectively. Furthermore, the instruments used for steady state photoluminescence spectroscopy are given.

Chapter 4 addresses the impact of lowering the rotational symmetry on the photophysical properties of the porphyrin nanorings. To this end, a series of six-porphyrin nanorings are deliberately modified to exhibit a gradual increase

of geometrical distortion from rotational symmetry. Their absorption, emission spectra, quantum yield and excitation dependent anisotropy data were analysed and compared with each other. Furthermore, a model for the energy level splitting was employed to explain the symmetry breaking effect and to account for the findings in these data.

In **Chapter 5** the impact of different conformations on exciton delocalization and emission depolarization in a range of different porphyrin nanoring topologies with comparable spatial extent is investigated. Recent advances in Vernier templating now allow large shape-persistent fully conjugated porphyrin nanorings to be synthesized, exhibiting unique electronic properties. Anisotropy dynamics were examined using the PLUC technique to investigate exciton delocalization and polarization memory loss. In the second part of the chapter, molecular dynamics and PL depolarization simulations were carried out at room temperature to link the experimental findings in emission depolarization with conformational changes of the porphyrin rings.

Chapter 6 explores energy migration within nanoring complexes. In this study, two rigid molecular complexes with fascinating structures are examined, each consisting of two conjugated porphyrin nanorings. Using time-resolved spectroscopy methods, supported by data in radiative rates, absorption and emission spectra, possible energy migration from a higher-energy absorbing component to a lower-energy emission component within the complex was probed on an ultrafast time scale.

Finally, **Chapter 7** provides a summary of the main findings in this thesis and an outlook of possible investigations in the future.

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Chapter 2

Electronic Processes in π -Conjugated Polymers

2.1 Excitations in π -conjugated polymers

2.1.1 π -bonds

Conjugated polymers are organic macromolecules based on a carbon backbone chain in sp^2 hybridization, which is formed by mixing the 2s orbital with the p_x and p_y orbitals (see Figure 2.1(a)). The bonds formed from the three sp^2 hybrid orbitals lying in one plane at 120° to each other are called σ -bonds, while the orthogonal p_z orbitals overlap to form π -bonds, as shown in Figure 2.1. The term *conjugated* refers to the alternating series of single (σ) and double (π) bonds. The σ -bonds give rise to highly localized electron density and define the chain structure, whereas the π -bonds generate delocalized electron density along the carbon backbone, just above and below the axis of the σ -bond [54]. Hence the π -electrons are responsible for the electronic conductivity in the conjugated polymer. Given a half-filled π -band, for example polyacetylene $(CH)_n$, one might naively expect metallic conductivity from a solid-state physics perspective. However, formation of such equidistant linear chain structure is un-

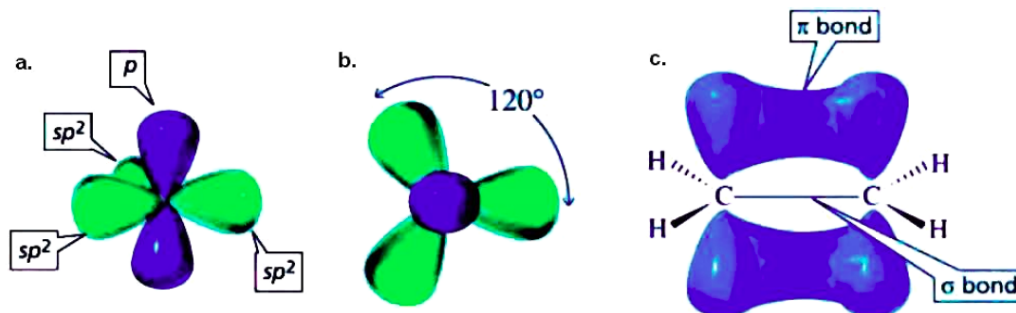


Figure 2.1: a) Schematic of a hybridized carbon atom with three sp^2 orbitals (green) and two orthogonal p_z orbitals (blue). b) The three sp^2 orbitals are lying in one plane and form 120° to each other. c) σ -bond (black) and π -bond (blue) in the double bonding of ethene. Taken from Ref. [8].

stable with respect to dimerization; the result is alternating shorter double and longer single bonds. Due to this additional periodic modulation an energy gap, termed the Peierls band gap, is formed in the centre of the Brillouin zone [50], as shown in Figure 2.2. The electronic energy is reduced by the gap, which in turn makes the distorted chain energetically favourable. Therefore, conjugated polymers are of semiconducting or insulating nature depending on the size of the energy gap.

To a first approximation, the electronic structure of π -conjugated molecules is described using *Hückel molecular orbital theory* (tight binding model), where the overall molecular orbital wavefunctions are linear combination of the atomic orbitals [64].

2.1.2 Excitons

Conjugated polymers can be studied using the exciton model. The absorption of a photon by a π -electron excites it into a higher lying unoccupied orbital leaving

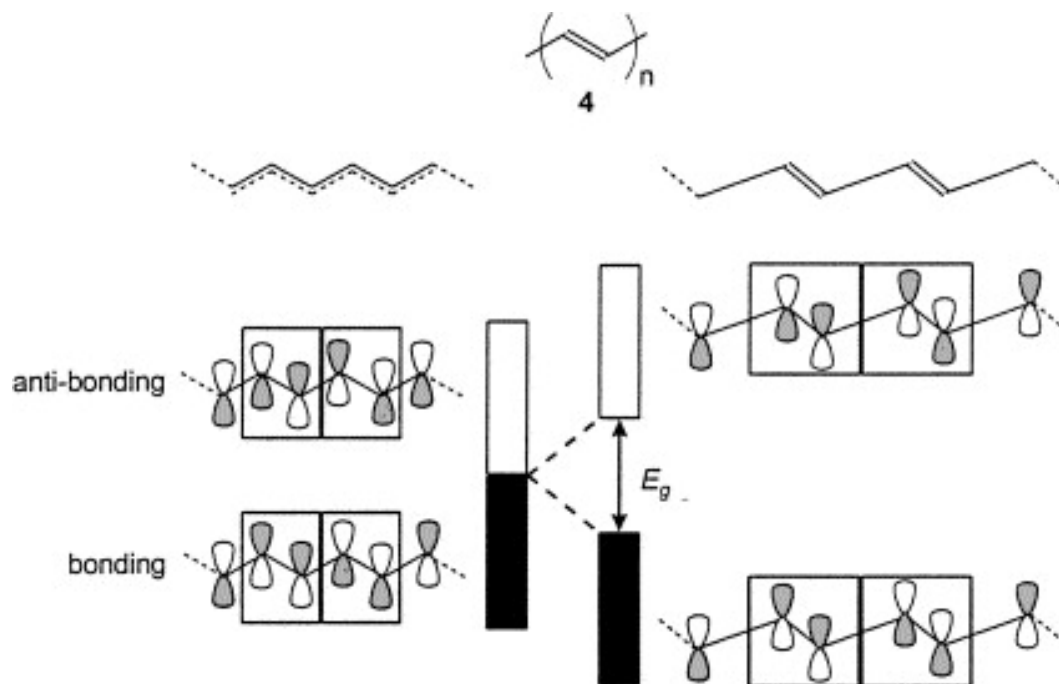


Figure 2.2: Schematic of band gap formation due to bond-length alternation in *trans*-polyacetylene.

a hole behind, forming an electron-hole system. Due to the lack of intrinsic free carriers and low dielectric screening, Coulomb interaction results in a bound state between these two with an energy level lying between the bandgap of the semiconductor. This bound state is a bosonic quasiparticle and called an *exciton*. To describe the excitons in the systems, both the strength of electron-electron interaction and the inter-molecular coupling need to be considered. There are two species of exciton: Wannier-Mott excitons are often found in inorganic materials, they are weakly bound and have large radii, because the large dielectric constants in the inorganic materials achieves effective screening of electron-hole interaction; Frenkel excitons are strongly bound and hence have smaller radii. The excitons created in conjugated polymers are local to the molecule, we expect strongly bound Frenkel-type excitons [6]. Studies from Raucher *et al.* supported the exciton concept and indicated the failure of free

electron model for treating the excitations in conjugated polymers like poly(p-phenylenevinylene) (PPV) [56], this is further confirmed by Chandross *et al.* [9, 10].

2.1.3 Absorption and emission spectra

The highest occupied molecular orbital (HOMO) is the bonding π -state and the lowest unoccupied molecular orbital (LUMO) is the anti-bonding π^* -state, thus excitations of an electron in the p_z -orbital are referred to as $\pi - \pi^*$ transitions. Each electronic energy level is split into a singlet and three degenerate triplet states due to the spin configuration. Simplified wavefunctions can be used to account for the form of absorption and emission spectra. One major simplification is provided by the Born-Oppenheimer approximation. Due to the large difference in the nuclear and electron masses, motions of electrons are more rapid than those of the nuclei. Electron excitation in p_z -orbital occurs on a time scale of 10^{-15} s, whereas the characteristic time for molecular vibrations is 10^{-10} – 10^{-12} s. Under this approximation, positions and momenta of the nuclei can be considered as static during an electron transition. Figure 2.3 shows energy surfaces of the ground (S_0) and the first excited (S_1) state plotted against the generalized configuration coordinate Q . The electronic configuration is changed in the excited state, resulting in a configuration shift ΔQ between the energy surfaces. Transitions between S_0 and S_1 can be considered as ‘vertical’, assuming that no change in internuclear separation occurs. This is known as the *Franck-Condon principle* [65].

Upon excitation of an electron, the nuclei is slightly brought out of its equilibrium position and will respond with vibrations. Thus for each electronic state,

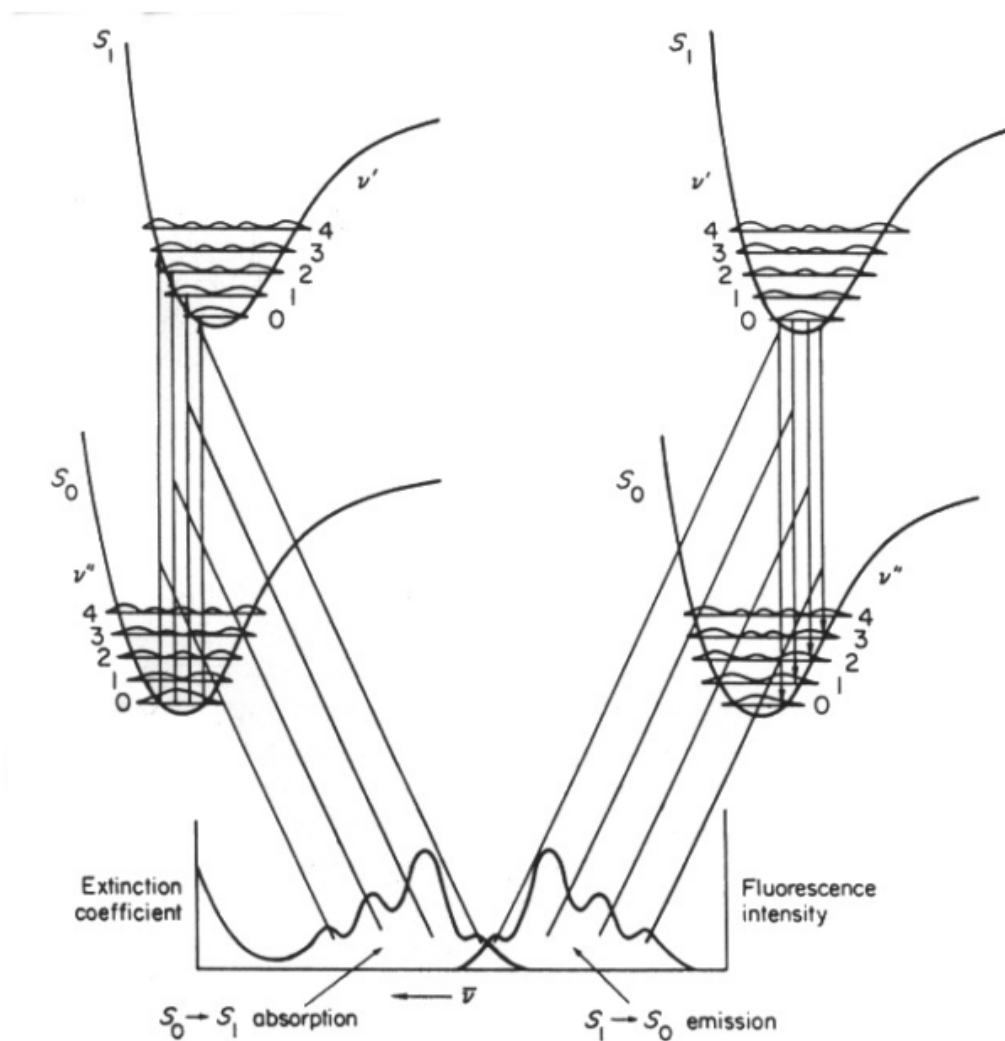


Figure 2.3: Simplified molecular potential curves illustrating vibronic transitions and the origin of the mirror image in the absorption and emission spectra. (Figure taken from Kearwell and Wilkinson 1969, p.108)

there is a progression of harmonic oscillator states, the vibrational levels of the ground and excited states are labelled by the quantum numbers ν' and ν'' in Figure 2.3. Transitions between two electronic states are usually accompanied by vibrational transitions, they are termed vibronic transitions [33]. The probability of a vibronic transition is proportional to $|M_{fi}|^2$, where M_{fi} the matrix element of the electric dipole operator D_e with

$$M_{fi} = \langle \phi_{\alpha'} | \mathbf{D}_e | \phi_{\alpha} \rangle \quad \text{and} \quad \mathbf{D}_e(\mathbf{r}) = -e \sum_i \mathbf{r}_i \quad (2.1)$$

where r_i is the position of i -th electron and the sum is over all electrons in the molecule. The total wave function ϕ_{α} is given by a simple product:

$$\phi_{\alpha} = \varphi_j(r, Q) \psi_{jm}(Q) \chi_s \quad (2.2)$$

where φ_j is the electronic wave function depending both on the electron coordinate r and the configuration coordinate Q . ψ_{jm} represents the vibronic wave function in the electronic energy state j and vibrational level m and χ_s is the spin wavefunction where s denotes the spin coordinates. To a first approximation, the dipole transition can be assumed to be independent of configuration coordinate Q due to the Franck-Condon principle, as well as independent of spin, which leads to a separation of the matrix element M_{fi} into one purely electronic, one purely vibrational part and one purely spin related term:

$$M_{fi} = D_{j'j}^e \langle \psi_{j'm'} | \psi_{jm} \rangle \langle \chi_{s'} | \chi_s \rangle \quad (2.3)$$

with the electronic transition dipole moment given by

$$D_{jk}^e = \int dr \varphi_j'^*(r, Q) D_e(r) \varphi_j(r, Q). \quad (2.4)$$

If any term in Equation 2.3 is zero, the transition would become forbidden, this leads to two major selection rules for absorption transitions [65]. A transition can be forbidden due to symmetry. Since the electric dipole operator D_e is a sum of odd operators, a transition is only allowed for φ_j and φ'_j with opposite symmetry, otherwise the transition is dipole-forbidden [54]. A detailed consideration of symmetry constraints requires the use of group theory. However, symmetry-forbidden transitions are often observed through coupling to vibrational modes, which is treated in depth in Section 2.1.4. In this case, the Born-Oppenheimer approximation breaks down [39]. The spin-related term dictates that transitions between states of different multiplicities are forbidden (spin-forbidden transitions), hence only singlet-singlet or triplet-triplet transitions are allowed. Nevertheless, spin-orbit coupling enables weak interaction between the wavefunctions of different multiplicities, for example this is the mechanism behind intersystem crossing.

The intensity of a vibronic transition from vibrational level m to m' between the electronic states $S_j \rightarrow S_{j'}$ is proportional to the Franck-Condon factor defined as

$$|S_{m'm}|^2 = |\langle \psi_{j'm'} | \psi_{jm} \rangle|^2 = \left| \int dQ \psi_{j'm'}(Q) \psi_{jm}(Q) \right|^2. \quad (2.5)$$

The vibronic transition is strong for significant overlap of the vibrational wave functions in the upper and lower levels. At low temperature, absorption only occurs from the lowest vibrational level. By approximating the molecular potentials with parabolic function and assuming the potential minima of the ground and excited state are separated by the configuration shift ΔQ , the Frank-Condon factor for a transition from the 0th vibrational level of the ground state to the

m th vibrational level of the excited state can be expressed as:

$$|S_{m'm}|^2 = \frac{S^m}{m!} \exp(-S) \quad (2.6)$$

where

$$S = \frac{k(\Delta Q)^2}{2\hbar\omega} \quad (2.7)$$

is the Huang-Rhys factor, $\hbar\omega$ is the phonon energy and k the force constant of the oscillator. Upon excitation, electrons relax down to the vibrational ground level by emitting excess energy as a phonon, hence emission always occurs from the lowest lying vibrational level, obeying Kasha's rule. Huang-Rhys factor is representative of the number of phonons emitted during the configuration relaxation process and $S\hbar\omega$ is the relaxation energy. The most prominent active phonon modes that couple to the electronic states are carbon-carbon stretching, ring breathing and torsions, which typically ranging from 1300 cm^{-1} to 1800 cm^{-1} . Both absorptions and emissions occur from the lowest vibrational level at low temperature, giving rise to the observed mirror image in the absorption and emission spectrum (Figure 2.3). The energy shift between the peaks of the fundamental absorption and emission bands is called the Stokes shift [54]. The transition between the lowest vibrational levels is the zero-phonon transition, since no phonon is involved in this case.

2.1.4 Herzberg-Teller intensity borrowing mechanism

In conjugated polymers, many electronic transitions are dipole forbidden due to symmetry, however, such transitions have nevertheless been observed experimentally and this phenomenon is attributed to vibrational induced transitions

and referred to as Herzberg-Teller vibronic coupling, intensity borrowing or intensity stealing [40]. This is particularly important for systems with rotational symmetry, such as benzene and porphyrin nanorings.

The transition moment $\mathbf{D}_{ev}$ for an electric transition between two vibronic states is given by:

$$\mathbf{D}_{ev} = \int \phi'_{ev}{}^* \mathbf{D}_e \phi''_{ev} d\tau_{ev} \quad (2.8)$$

where $\mathbf{D}_e$ is the electric dipole moment operator, ϕ'_{ev} and ϕ''_{ev} are vibronic wave functions of the upper and lower state respective, and the integral is over the entire electronic and vibrational coordinates. To satisfy the symmetry requirement for dipole allowed vibronic transitions, the integral in Equation 2.8 needs to contain the totally symmetric symmetry species [33]. Because $\mathbf{D}_e$ has the symmetry species of a translation, the condition follows:

$$\Gamma(\phi'_{ev}) \times \Gamma(\phi''_{ev}) = \Gamma(\phi'_e) \times \Gamma(\phi'_v) \times \Gamma(\phi''_e) \times \Gamma(\phi''_v) \supset \Gamma(T_x) \text{ and/or } \Gamma(T_y) \text{ and/or } \Gamma(T_z) \quad (2.9)$$

where $\Gamma(T_x)$, $\Gamma(T_y)$ and $\Gamma(T_z)$ are symmetry species of translations of the molecule. Symmetry species of a vibronic state $\Gamma(\phi'_{ev})$ can be separated into electronic $\Gamma(\phi'_e)$ and vibrational $\Gamma(\phi'_v)$ contributions irrespective of whether Born-Oppenheimer approximation holds [33].

Benzene is a well-studied example illustrating the Herzberg-Teller intensity borrowing mechanism. The hexagonal symmetry dictates dipole forbidden 0-0 transition between the ground state and S_1 of B_{2u} symmetry. However, substantial absorption is observed at 520 cm^{-1} above the true origin (0-0) due to coupling to an in-plane bending mode, ν_6 , of e_{2g} symmetry, as shown in Figure 2.4. Since:

$$B_{2u} \times e_{2g} = E_{1u} \quad (2.10)$$

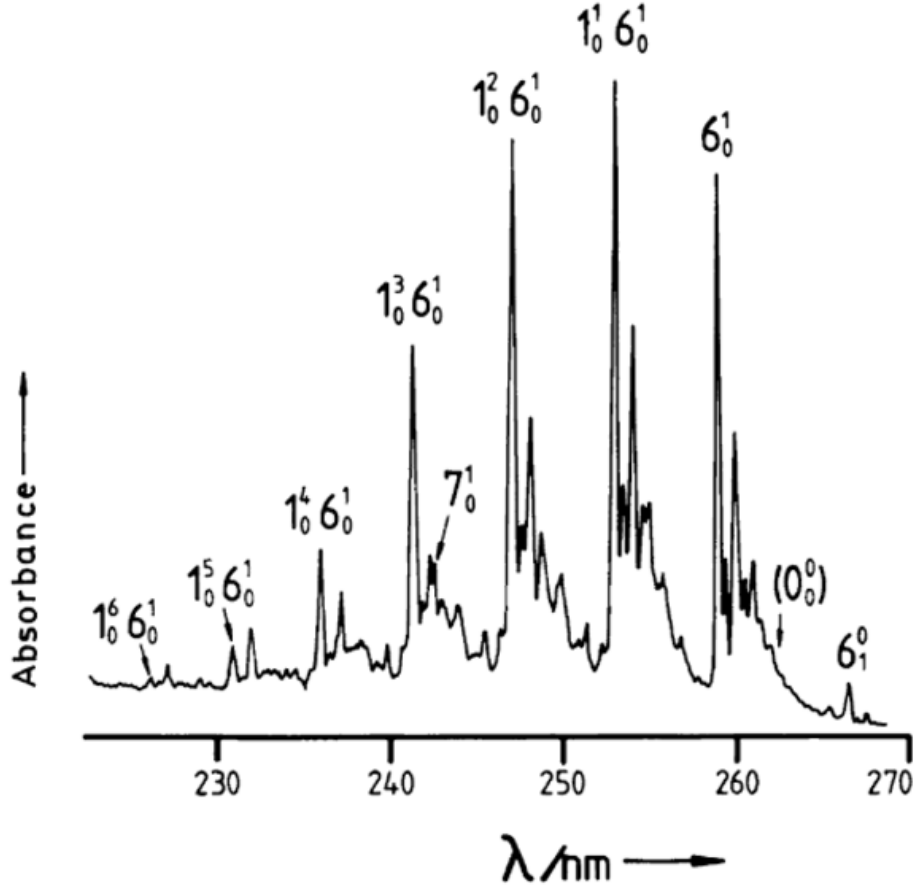


Figure 2.4: Absorption spectrum of benzene at room temperature and atmospheric pressure around 260 nm. 6_0^1 denotes transition coupled to vibration ν_6 from $\nu' = 0$ level in the ground state to $\nu'' = 1$ level in the excited state. Taken from Ref. [33].

and E_{1u} is a translational symmetry species of the D_{6h} point group of benzene, according to Equation 2.9 this transition is symmetry allowed. The progression observed in the absorption spectrum (Figure 2.4) originates from coupling to successive numbers of ν_1 of the totally symmetric ring breathing mode.

The original theory brought forward by Herzberg and Teller explained this phenomenon as due to breakdown of the Franck-Condon approximation [30]: When the vibrational overlap integral (Eq. 2.8) of the transition is non-totally symmetric, the electronic transition moment (Eq. 2.4) would not be indepen-

dent from vibrations. This theory is later further developed to include a second mechanism [33, 46] based on the breakdown of the Born-Oppenheimer approximation to include the impact of kinetic energy of the nuclei on the motion of the electrons. Both mechanisms are subject to the same selection rules, however, the quantitative effects differ depending on the dominating mechanism.

2.1.5 Non-radiative transitions

Upon excitation, several other relaxation channels, especially non-radiative transitions are possible beside fluorescence and subsequent vibrational relaxation described in the previous section. The possible processes are conveniently visualized in the Perrin-Jablonski diagram (Figure 2.5). The singlet states are denoted S_0 , S_1 , $S_2...$ and triplet states are T_1 , $T_2...$ each associated with a series of vibrational states.

A non-radiative transition is isoenergetic and is usually followed by vibrational relaxation to the lowest vibrational state. A non-radiative transition between states with the same spin multiplicities is referred to as internal conversion, whereas a transition between states with different spin multiplicities is called intersystem crossing [39].

Internal conversion from higher lying excited states S_n to the first excited singlet state S_1 occurs rapidly. Together with vibrational relaxation, the molecule usually arrives at the 0th vibrational level of the S_1 state on a time-scale of 10^{-13} – 10^{-10} s. Internal conversion from S_1 to S_0 however is less efficient due to much larger energy gap and occurs on a similar timescale as fluorescence. There are three competing de-excitation processes from the S_1 state: fluorescence, internal conversion and intersystem crossing.

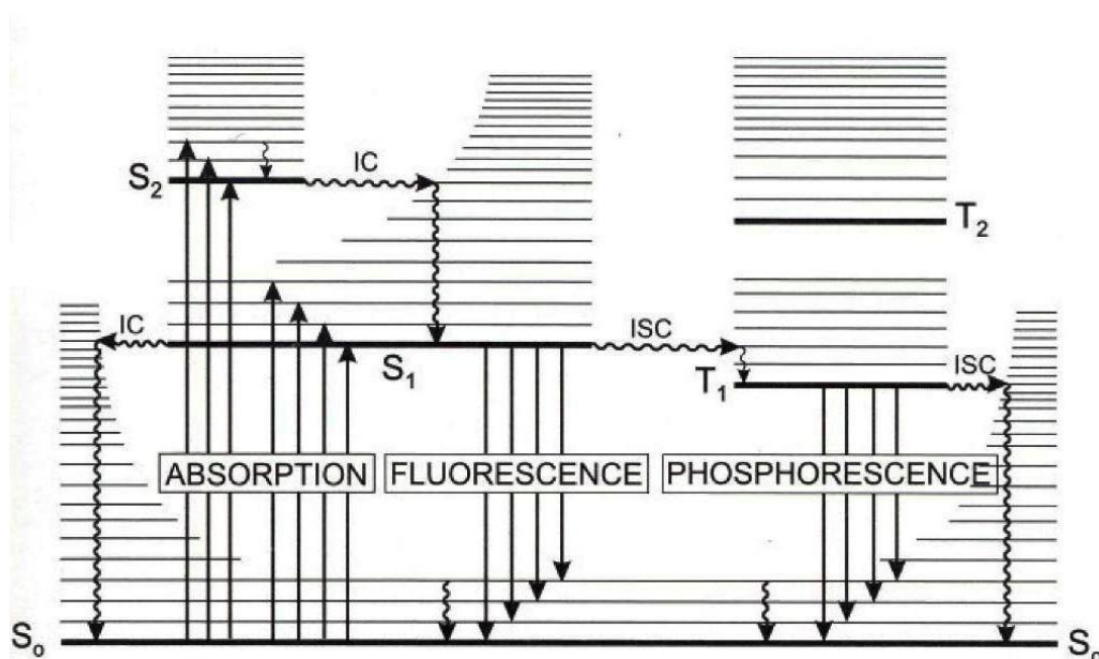


Figure 2.5: Perrin-Jablonski diagram illustrating possible radiative (wavy arrows) and non-radiative (straight arrows) transitions from singlet (S) and triplet (T) states: absorption, fluorescence, vibrational relaxation, internal conversion (IC) and intersystem crossing (ISC) followed by phosphorescence. Taken from Ref. [65].

Intersystem crossing occurs between states with different spin multiplicities, which is in principle forbidden by spin selection rule, but realized with strong coupling between the orbital magnetic moment and the spin magnetic moment on a time scale of 10^{-7} – 10^{-9} s. Spin-orbit coupling is stronger in the polymers containing heavy atoms, which makes intersystem crossing more favourable in such systems. Following intersystem crossing to the triplet T_1 state, spin-forbidden radiative de-excitation to S_0 can occur, which is enabled again by strong spin-orbit coupling. This transition is termed phosphorescence. Due to the long lifetime of the excited electrons in T_1 (10^{-6} – 1 s), intersystem crossing to the S_0 state and vibrational relaxation is favourable at room temperature. Phosphorescence can be more easily observed at low temperature and/or in a rigid medium. Because the lowest vibrational level of T_1 is usually lower than S_1 , the phosphorescence spectrum is located in a longer wavelength range compared to fluorescence spectrum [54, 65].

2.1.6 Radiative rate and quantum yield

The kinetics of a decay process in a conjugated molecule can be expressed using rate constants [38]:

$$k_{tot} = k_r + k_{nr}, \quad (2.11)$$

where k_{tot} is the total decay rate, k_r and k_{nr} are the radiative and non-radiative decay rate respectively. Non-radiative decay channels include internal conversion, intersystem crossing, non-radiative energy transfer to other molecules, in fact radiative decay often only represents a tiny fraction of the total decay processes. The lifetime τ obtained experimentally in time-resolved spectroscopy

is $\tau = 1/k_{tot}$, however, to compare the radiative behaviour across different molecules, we are often interested in the radiative rate, which can be obtained using the quantum yield ϕ :

$$\phi = \frac{k_r}{k_r + k_{nr}} = k_r \tau \Rightarrow k_r = \frac{\phi}{\tau}. \quad (2.12)$$

The quantum yield is defined as the ratio of the emitted photons to the number of absorbed photons. Experimentally, a relative approach can be adopted using a reference sample with known quantum yield ϕ_{ref} . By measuring the emission spectrum at excitation wavelength λ_{ext} and the absorbance A at λ_{ext} of both the sample and the reference compound, the quantum yield ϕ_{sample} is obtained:

$$\phi_{sample} = \frac{I_{sample}}{I_{ref}} \times \frac{A_{ref}(\lambda_{ext})}{A_{sample}(\lambda_{ext})} \times \phi_{ref} \quad (2.13)$$

where I_{sample} and I_{ref} are the integrated areas of the emission spectra for sample and reference compounds, respectively.

2.2 Excitation transfer

Upon creation of an exciton in a conjugated polymer, transfer of the excitation energy between different chromophores or sites within the material will follow and represent an important channel for energetic relaxation. We can distinguish between radiative and non-radiative energy transfer. Radiative energy transfer is the trivial case of re-absorption, where an exciton recombines emitting a photon, which is absorbed again by a remote chromophore in the sample. No interaction between absorbing and emitting sites is required here and the transfer distance is larger than the wavelength of the emitted photon. Non-radiative

energy transfer on the other hand is a photophysical process from a ‘donor’ chromophore in the excited state to an ‘acceptor’ mediated by dipole-dipole coupling or intermolecular orbital overlap [60] and occurs over much shorter distance, typically less than 100 Å [20, 21]. The energy transfer dynamics are different depending on the intermolecular coupling V and the excitation decoherence time τ_{decoh} , three cases can be distinguished [7]:

Strong coupling regime: $\hbar/V \gg \tau_{decoh}$. In the strong coupling regime between the chromophores, the exciton is delocalized over almost the entire system and the excited states of the system can be best described by a superposition of the exciton states of the individual chromophores [28, 39]. Energy transfer occurs coherently in a wavelike manner and oscillates back and forth between donor and acceptor sites over long distances, e.g. in a crystal. However, this regime is usually not valid for conjugated polymers.

Weak coupling regime: $\hbar/V \ll \tau_{decoh}$. In the weak coupling regime, the excited chromophore relaxes to its geometrical equilibrium before the energy transfer takes place. Excitations are localized at individual chromophore sites and transfer the energy to other sites in an incoherent manner. Once the exciton arrives at the acceptor, the strong vibronic coupling leads to energy relaxation to a lower vibrational state. A series of these individual energy transfers leads to a downhill incoherent hopping process through localized chromophore sites which is irreversible [7, 65]. A Förster type approach is engaged if the coupling potential contains only dipole-terms; if the coupling is only provided by exchange interactions, it is termed Dexter-type energy transfer process. Both mechanisms of energy transfer are described in detail later in this section.

Intermediate regime: $\hbar/V \sim \tau_{decoh}$. In the intermediate regime, an exciton may be delocalized initially after excitation, but quickly localizes through

various mechanisms. As a result, exciton may migrate rapidly along the polymer and the exciton diffusion can be described as an incoherent Förster type hopping process [36]. Excitation transfer dynamics between the donor and the acceptor is complicated comprising both coherent and incoherent behaviour [65].

In 1974 a generalized-master-equation theory of excitation transfer in organic solids was developed by Kenkre and Knox, in an attempt to unify all coupling regimes [37]. The theory suggests a description of the excitation transport as wavelike coherent motion for $t < \tau_{decoh}$ and as diffusive hopping transport for $t > \tau_{decoh}$.

2.2.1 Förster resonance energy transfer

J. and F. Perrin first developed the resonance energy transfer model [51, 52] which was later extended by Förster in 1946 [20, 21]. Förster resonance energy transfer is an interchromophore energy relaxation, mainly of Coulombic nature. Energy is transferred from an excited donor to an acceptor in the ground state without any mediator:



Therefore, it is referred to as a through-space mechanism. If the donor and acceptor are of the same species, it is called homotransfer, otherwise one speaks of heterotransfer. This transition is only possible between singlet-singlet states and also represents the primary mechanism of energy transfer for singlet transitions. The process occurs via a quantum-mechanical coupling between the electronic transitions.

In the model proposed initially by Perrin, the exciton is considered to be

delocalized over donor and acceptor and excitation oscillates coherently between donor and acceptor. The predicted interaction radii based on this model, however, are much larger than experimentally observed from luminescence depolarization measurements [19, 53]. Förster realized that the reason for the discrepancy lies within the strong vibronic coupling which was neglected. The condition for resonance transfer is only met for a short time during the transfer, before an excitation is relaxed rapidly to the lowest vibrational level resulting in an irreversible transfer process [19]. The energy transfer can be considered as discrete hopping process.

The quantum mechanical interaction between the donor and acceptor is approximated by the classical point-dipole model. By assuming the distance between donor and acceptor is large compared to their size, it is sufficient to only consider the contribution of the dominant dipole-dipole interaction. The Coulomb interaction energy is inversely proportional to R^3 , where R is donor-acceptor separation. The transition rate is derived using Fermi's Golden Rule and the time-dependent perturbation theory, taking into account the continuous energy distribution of the donor and acceptor states and is found to be inversely proportional to the sixth power of the separation R :

$$k_{FRET} = \frac{1}{\tau_D^0} \left[\frac{R_0}{R} \right]^6 = \frac{2\pi}{\hbar} |s V_{dd}|^2 J \quad (2.15)$$

where τ_D^0 is the excited state life time, V_{dd} is the dipole-dipole coupling approximation of the interaction, J is the overlap of absorption and emission spectra, s is the solvent screening factor and R_0 is the Förster critical radius given by:

$$R_0 = \left[\frac{9000 \ln 10}{128 \pi^5} \frac{\kappa^2 \Phi_D}{\tilde{n}^4 N} J \right]^{\frac{1}{6}} \quad (2.16)$$

with $\tilde{n}$ the refractive index of the solvent, N the Avogadro's constant, Φ_D

the photoluminescence (PL) quantum yield of the donor. κ is the orientation parameter and depends on the relative orientation between donor and acceptor dipoles:

$$\kappa = \boldsymbol{\mu}_D \cdot \boldsymbol{\mu}_A - 3(\boldsymbol{\mu}_D \cdot \mathbf{u}_{DA})(\boldsymbol{\mu}_A \cdot \mathbf{u}_{DA}) \quad (2.17)$$

where $\boldsymbol{\mu}_D$ and $\boldsymbol{\mu}_A$ are unit vectors of donor and acceptor dipole moments and $\mathbf{u}_{DA}$ is the centre to centre unitary vector of donor and acceptor. When donor and acceptor are separated by the critical Förster radius R_0 , resonance energy transfer is as likely to occur as any other de-excitation processes of the donor exciton. The major factors affecting the excitation transfer rate are absorption/emission spectra overlap, distance and dipole orientations between donor and acceptor.

2.2.2 Excitation transfer in an ensemble

Equation 2.15 describes the Förster resonance energy transfer for a single donor-acceptor pair. In praxis, however, a sample contains a large amount of donors and acceptors, hence the spatial distribution and the relative orientation of the donors and acceptors have to be considered. The average donor excitation probability is expressed as:

$$\overline{\rho(t)} = \exp\left(-\frac{t}{\tau_D} - \sqrt{\pi} \frac{c_A}{c_0} \sqrt{\frac{t}{\tau_D}}\right) \quad (2.18)$$

where τ_D is the donor lifetime, c_A the acceptor concentration, $c_0 = (\frac{4\pi}{3} R_0^3)^{-1}$ the *critical concentration*. Details to the derivation can be found in Ref.[55]. The first part in the expression is due to natural decay process and the second part can be attributed to the energy transfer process. The effective transfer rate

$K_{D \rightarrow A}$ for an ensemble of randomly distributed D-A chromophores in 3D thus can be written as:

$$K_{D \rightarrow A} = \frac{\beta}{\sqrt{t}} \quad \text{with} \quad \beta = \frac{1}{2} \sqrt{\pi} \frac{c_A}{c_0} \frac{1}{\tau_D}. \quad (2.19)$$

The ensemble averaged effective transfer rate is time-dependent, because donors located close to the acceptors transfer their excitations faster than the donors further away, leading to decreased transfer efficiency with time. This model has been investigated for many different conjugated systems, examples can be found in Ref. [11, 29, 48, 67].

2.2.3 Dexter mechanism

When orbitals on each of the donor and acceptor side are mixed with a molecular bridge, energy transfer can also happen via electron hole exchange interaction and the interaction strength decays exponentially with donor-acceptor distance. The *through-bond* interaction is a non-radiative process and typically occurs within 10 Å. Figure 2.6 illustrates the difference between Coulomb coupling and exchange coupling. For optically allowed transitions on donor and acceptor sites the Coulomb interaction is predominant, hence the exchange mechanism is mainly found for optically forbidden or only weakly allowed transitions, e.g. triplet-triplet transition [7, 14, 28, 39, 41].

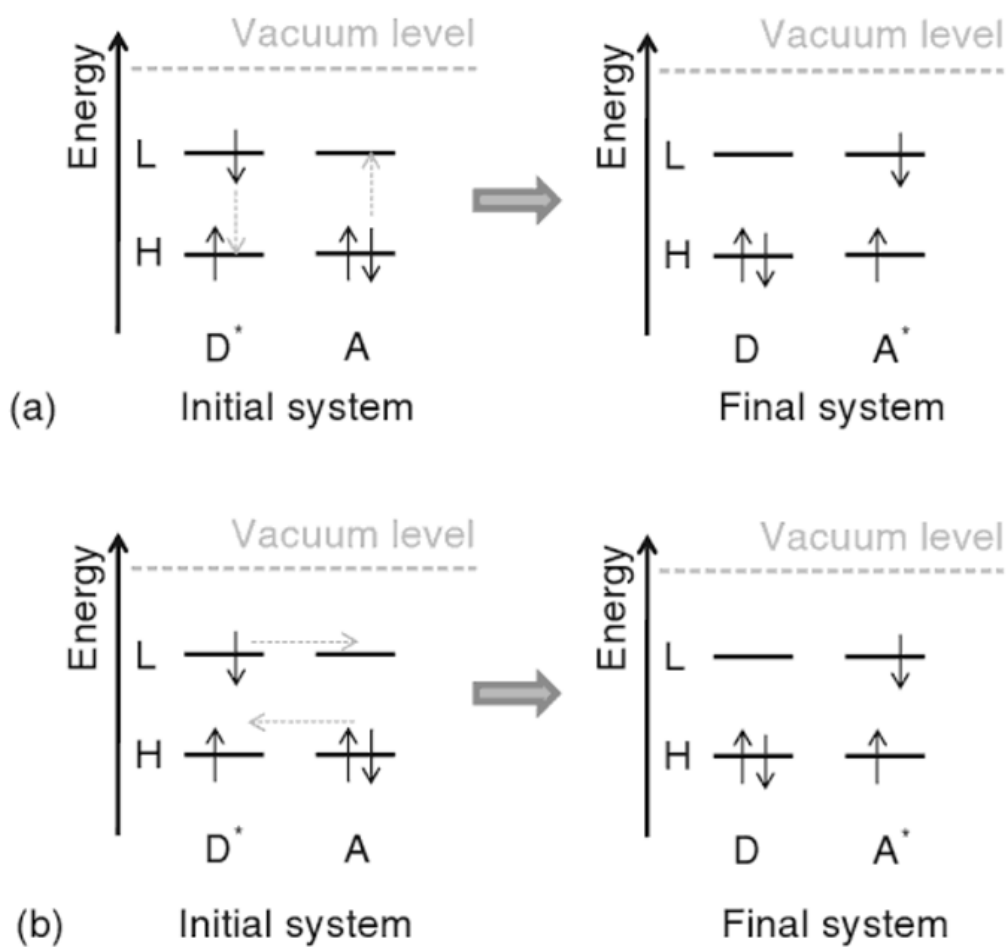


Figure 2.6: Illustration of a) Förster-type energy transfer by Coulomb coupling and b) Dexter-type energy transfer by exchange coupling. Figure taken from Ref. [39].

2.3 Polarization anisotropy

Fluorescence polarization measurements prove to be a great tool to investigate the dynamics of the excited states in conjugated polymers and can provide interesting insight into various properties such as shape, size and flexibility of the molecules, their energy transfer dynamics and relaxation processes. Most chromophores exhibit a preference in excitation polarization direction. When excited by linearly polarized light, chromophores with absorbing transition dipole moment $\mathbf{M}_A$ parallel to the electric field vector $\mathbf{E}$ of the incident light are most likely to be excited. The probability of excitation for each chromophore is proportional to $(\mathbf{M}_A \cdot \mathbf{E})^2$. When a sample containing a large amount of molecules of any orientation is excited, chromophores with absorbing transition dipole moments oriented closely to the direction of the electric field vector of the incident light are preferentially selected for excitation, this process is termed *photoselection* [65]. Fluorescence from the first singlet state then occurs with anisotropic polarization, because the excited population is anisotropic.

2.3.1 Excitation by polarized light

As emission from different chromophores in a sample is not phase dependent with each other, the total fluorescence intensity I_{tot} can be easily decomposed into three individual components I_x, I_y, I_z polarized along x -, y - and z -axis respectively of a cartesian coordinate system, with the sample positioned at the centre:

$$I_{tot} = I_x + I_y + I_z \quad (2.20)$$

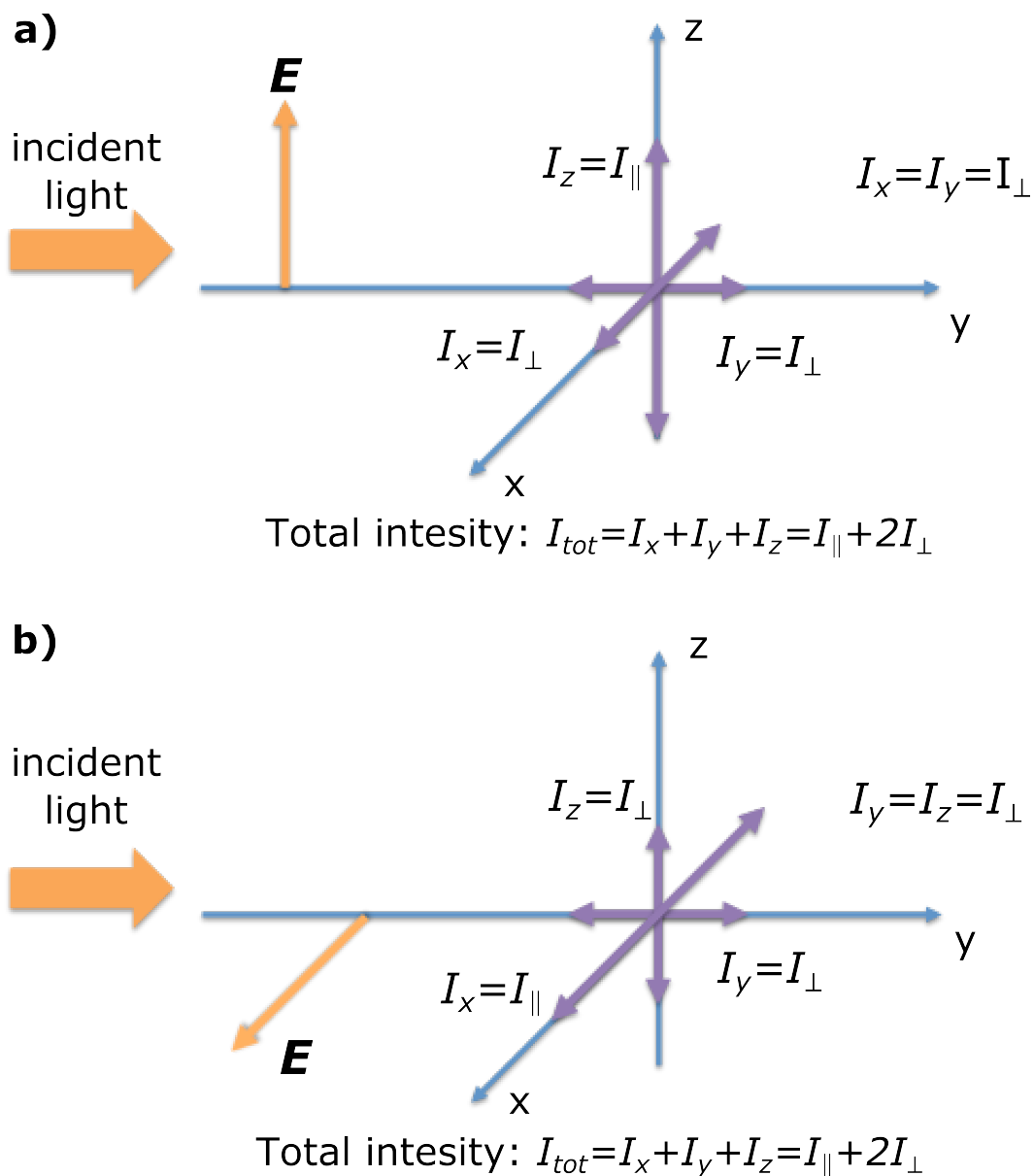


Figure 2.7: Fluorescence intensity components of a sample under excitation with (a) vertically polarized (b) horizontally polarized light. The sample is positioned at the centre of the coordinate system. Figure adapted from Ref. [65].

For vertically polarized excitation as depicted in Figure 2.7 a), the z -axis acts as axis of symmetry. $I_{\parallel}$ and $I_{\perp}$ denotes fluorescence intensity polarized parallel and perpendicular to the excitation polarization respectively. If we choose to detect along z -axis, only I_x and I_y components of equal size ($I_x = I_y = I_{\perp}$) can be registered due to emission characteristics of an electric dipole, therefore no information on the polarization anisotropy can be obtained. However, when detecting along the y -axis (or x -axis) this symmetry no longer exists. Intensity of emission polarized parallel to the excitation, $I_{\parallel} = I_z$, and perpendicular to the excitation, $I_{\perp} = I_x$ (or $I_{\perp} = I_y$), can be obtained separately. Together with Equation 2.20, the total intensity is given by:

$$I_{tot} = I_{\parallel} + 2I_{\perp}. \quad (2.21)$$

The same result holds for excitation polarized along the x -axis (as shown in Figure 2.7 b). The polarization anisotropy is then defined as:

$$\gamma = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + 2I_{\perp}) \quad (2.22)$$

In the up-conversion experiment used to experimentally determine anisotropy as described in Chapter 3, it is only possible to probe the vertically polarized emission component. In order to measure both $I_{\parallel}$ and $I_{\perp}$ the excitation polarization is rotated by 90° as in the case shown by Figure 2.7 b).

2.3.2 Additivity law of anisotropy

For a sample consisting of a number of different chromophores each contributing with a fraction $f_i = I_i / I_{tot}$ to the total emission intensity, the individual emission

anisotropy of any chromophore species can be written as:

$$\gamma^i = (I_{\parallel}^i - I_{\perp}^i)/(I_{\parallel}^i + 2I_{\perp}^i) = (I_{\parallel}^i - I_{\perp}^i)/I_i, \quad (2.23)$$

where I_i is the total emission from the species. When conducting experiments, the intensity measured from the ensemble of chromophores is the sum of their individual components: $I_{\perp} = \sum_i I_{\perp}^i$ and $I_{\parallel} = \sum_i I_{\parallel}^i$. Hence the anisotropy calculated from the measurement results is given by:

$$\gamma = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp}) = \frac{\sum_i I_{\parallel}^i - \sum_i I_{\perp}^i}{I_{tot}} = \sum_i \frac{I_{\parallel}^i - I_{\perp}^i}{I_i} \times \frac{I_i}{I_{tot}} = \sum_i f_i \gamma_i. \quad (2.24)$$

The total anisotropy of the ensemble sample is the weighted sum of the individual components. The additivity law proves useful when determining anisotropy for chromophores with more than one absorbing/emitting dipole moments.

2.3.3 Emission anisotropy of non-parallel transition dipoles

Consider a sample containing randomly oriented molecules excited by a laser pulse travelling along the y -axis and polarized along the z -axis as depicted in Figure 2.8. The orientation of the emission dipole moment $\mathbf{M}_E$ is defined by angle θ_E to the z -axis and the azimuthal angle ϕ . Because there is no phase relation between emission from different chromophores, the fluorescence intensity measured along the coordinate axis is proportional to the square of the projection of $\mathbf{M}_E$ onto each axis. Averaging over all possible orientations the intensity components are given by:

$$I_i \propto \overline{(\mathbf{M}_E \cdot \hat{\mathbf{i}})^2} \propto \overline{\cos^2 \theta_i} \quad (2.25)$$

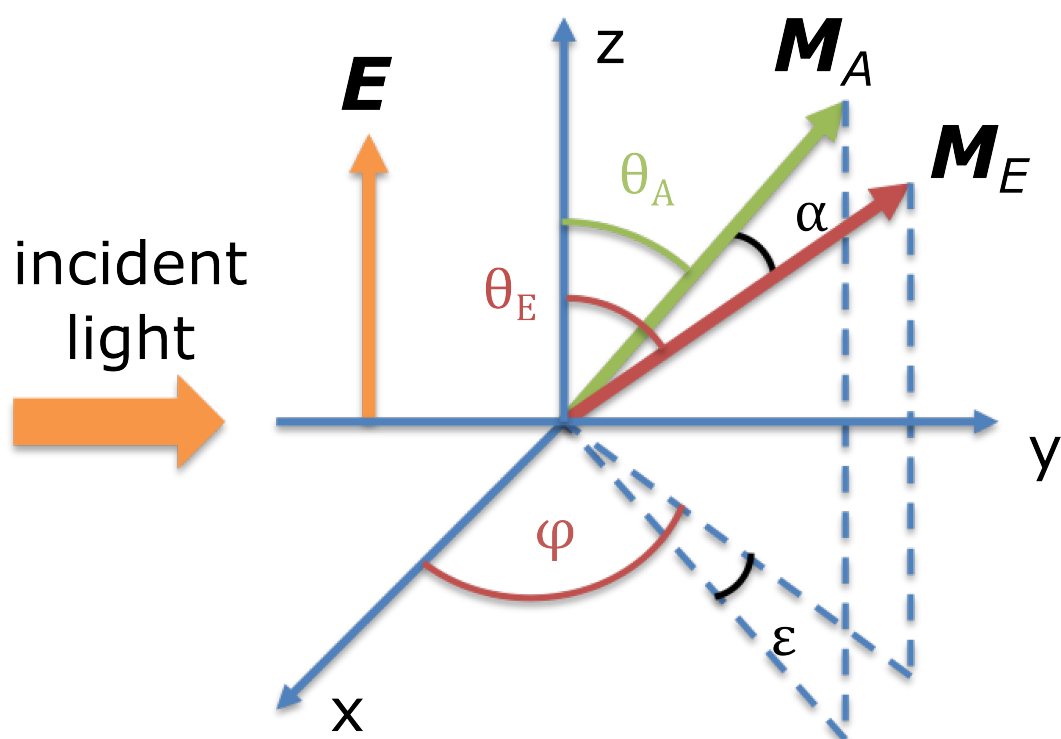


Figure 2.8: Angle notations of the non-parallel absorption (M_A) and emission (M_E) transition dipole moments in coordinate system.

where $i \in \{x, y, z\}$, $\hat{i}$ is the unit vector along each axis and θ_i is the angle of $\mathbf{M_E}$ with each axis. To simplify the expression, we define $\beta_i = \cos \theta_i$, then using the condition of axis symmetry $\overline{\beta_x^2} = \overline{\beta_y^2}$ and the trigonometric relation $\overline{\beta_x^2} + \overline{\beta_y^2} + \overline{\beta_z^2} = 1$, an expression for emission anisotropy can be obtained:

$$\gamma = \frac{I_{\parallel} - I_{\perp}}{I_{tot}} = \frac{I_z - I_y}{I_x + I_y + I_z} = \overline{\beta_z^2} - \overline{\beta_x^2} = \frac{3\overline{\beta_z^2} - 1}{2} = \frac{3\overline{\cos^2 \theta_E} - 1}{2} \quad (2.26)$$

As shown in Figure 2.8, an angle α is formed between non-parallel absorbing and emitting transition dipole moments. Using the spherical trigonometric relation:

$$\cos \theta_E = \cos \theta_A \cos \alpha + \cos \epsilon \sin \theta_A \sin \alpha \quad (2.27)$$

and substituting into Equation 2.26, the anisotropy is expressed as:

$$\gamma = \frac{3\overline{\cos^2 \theta_E} - 1}{2} = \frac{3\overline{\cos^2 \theta_A} - 1}{2} \times \frac{3\cos^2 \alpha - 1}{2}. \quad (2.28)$$

The average value $\overline{\cos^2 \theta_A}$ over all molecules is obtained by integrating over the unit sphere:

$$\overline{\cos^2 \theta_A} = \int \cos^2 \theta dx = \frac{3}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} \cos^4 \theta \sin \theta d\theta = \frac{3}{5}. \quad (2.29)$$

Substituting into Equation 2.28 we finally arrive at:

$$\gamma = \frac{2}{5} \frac{3\cos^2 \alpha - 1}{2} \quad (2.30)$$

Four special cases are of particular interest:

- For parallel absorbing and emitting dipole moments which are randomly oriented in 3D ensembles e.g. linear polymers $\alpha = 0$ hence $\gamma = 0.4$ [65].

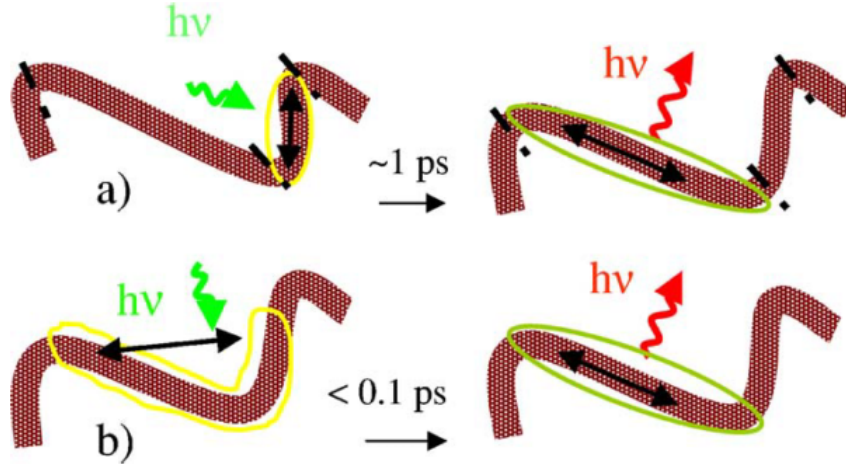


Figure 2.9: Orientation change of the transition dipole moments in the fully conjugated MEH-PPV due to a) excitation transfer and b) dynamic localization leading to depolarization. Figure taken from Ref. [59]

- For planar molecules with symmetry axis of order ≥ 3 and emission depolarized in the 2D plane, it follows from the additivity law of the anisotropy: $\gamma = \frac{2}{5} \frac{3\cos^2\alpha - 1}{2} = 0.1$. This is the ideal case for a porphyrin nanoring with simple ring structure and fully delocalized or depolarized excitation [49].
- If there is no preference in the direction of emission or absorption transition dipole moments, the emission is totally depolarized as in the case of fullerene due to its almost perfect spherical symmetry, hence $\gamma = 0$ [65].
- For molecules with perpendicular absorbing and emitting transition dipole moments $\alpha = 90^\circ$, hence $\gamma = -0.2$. This is the lowest anisotropy value possible [65].

The theoretical values are limiting cases, in reality however, there are many factors leading to depolarization on different timescales. Brownian motion can cause molecular reorientation which leads to depolarization [65]. It has been shown that excitation energy transfer can cause a dynamic depolarization pro-

cess on the time scale of picoseconds ($1 - 100$ ps). Upon excitation, exciton migrates to another segment on the molecule, resulting in a change of polarization direction of the emitting transition dipole moment [25, 26, 58]. This is depicted in Figure 2.9 a). In π -conjugated polymers, there is a strong coupling between the electronic transition and lattice vibrations. The nuclear framework undergoes strong geometric relaxation immediately upon excitation, leading to significant changes in carbon-carbon bond-length [15, 63]. The coupling of the exciton to nuclear modes forms a polaron and results in rapid contraction of the excited-state wave function, the delocalization length is reduced. This ultrafast process, termed by *excitonic self-trapping* occurs within 100 fs [5, 12] and may result in ultrafast depolarization [27, 59], as indicated in Figure 2.9 b). Furthermore, conformational disorder can distort the molecular geometry and cause a distribution of angles between absorption and emission transition moments, resulting in different anisotropy from that theoretically predicted.

2.4 Electronic properties in organic ring-like systems

2.4.1 Exciton model

For a simple illustration of the excitonic model in cyclic systems, we employ a model system consisting of N identical sites and the molecule at each site is described as a two level system. The ground state and the excited state are separated by an excitation energy E_0 . $|n\rangle$ denotes a state where only the n^{th} molecule is excited. The Hamiltonian can be written in terms of these

degenerate states as:

$$H = \sum_{n=1}^N E_0 |n\rangle \langle n| + \sum_{n=1}^N \sum_{m \neq n} V_{nm} |n\rangle \langle m|, \quad (2.31)$$

where V_{nm} denotes the interaction between excited molecules located on sites n and m . Due to this interaction, the localized wave function $|n\rangle$ is not an eigenfunction of the Hamiltonian. By diagonalizing the Hamiltonian, the eigenstates of the system, or the exciton states, are found to be linear combinations of the states $|n\rangle$:

$$|k\rangle = \frac{a}{\sqrt{N}} \sum_{n=1}^N e^{i2\pi k \frac{n}{N}} |n\rangle \quad (k = 0, \dots, N-1) \quad (2.32)$$

In the strong coupling regime, the degeneracy of the initial states is lifted by the interaction potential, which leads to the exciton band. In this ideal system, the magnitudes of the amplitudes over each site are equal, resulting in a fully delocalized state [14]. In the weak coupling limit however, excitations are fully localized at a single site.

2.4.2 Light-harvesting complexes in purple bacteria

The light-harvesting apparatus in purple bacteria cleverly exploits quantum mechanics, which enables a remarkably efficient photon absorption and energy transfer process [31]. Ever since the antenna complex LH2 was revealed in 1995, researchers have been driven to seek ways to mimic its fundamental features in synthetic and simplified systems. It is important to gain a solid understanding of the structure and energy transfer processes in the natural system as a reference, before exploring its synthetic counterparts.

Bacterial photosynthesis starts with the absorption of a photon by the light-

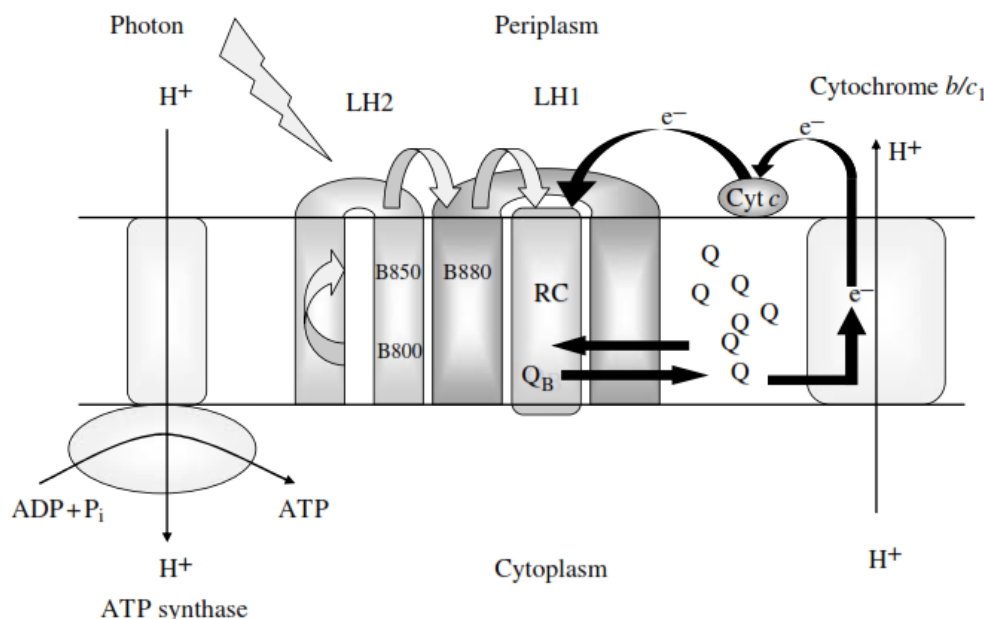


Figure 2.10: A schematic showing the photosynthetic membrane of a typical purple bacterium. Energy transfer paths are indicated in grey arrows and electron transport pathways in black arrow. Photons are absorbed in LH2, transferred to the reaction centre (RC) via LH1. The secondary electron acceptor ubiquinone (Q_B) are reduced in RC and the protons are transferred across the membrane resulting in trans-membrane proton motive force, which is used to generate ATP. Taken from Ref. [14].

harvesting (LH) antenna system, followed by a rapid and efficient energy transfer to the reaction centre (RC) [14]. The energy is ‘trapped’ here and is used to produce charge separation across the photosynthetic membrane by the primary redox reaction as shown in Figure 2.10 [24]. The purpose of LH apparatus is to increase the effective light absorption cross-section for each RC, which serves for an initial conversion of light energy into chemical energy.

2.4.2.1 Structures of light-harvesting apparatus

There are typically two types of LH antenna complexes in purple bacteria, the LH2 and RC-LH1 core complex. They are both integral membrane proteins con-

structed from similar building blocks: a small number of bacteriochlorophylla (Bchl*a*) noncovalently bound to apoproteins (called α and β) and carotenoids [43]. By being non-covalently attached to these proteins, the major absorption bands of Bchl*a* are red shifted by an amount depending on the specific arrangements. The red shifts provide a way to tune the pigments' absorption bands.

The Bchl*a* molecules in LH2 are present in two spectral forms, forming two concentric rings, B800 and B850 (a simplified illustration is shown in Figure 2.11). B800 consists of nine Bchl*a* molecules and absorbs at ~ 800 nm, the interaction between the Bchl*a* molecules are weak and they are generally considered as monomeric; B850 absorbs at ~ 850 nm and consists of 18 Bchl*a* arranged much closer to each other, they are strongly exciton-coupled [14, 24]. The reaction centre is surrounded by LH1, together they form the RC-LH1 core complex. LH1 only has tightly coupled Bchl*a* (B875) with strong absorption band at ~ 875 nm. LH2 complexes are arranged more peripherally around the core complex and the amount depends on the incident light intensity. Due to the different absorption band, a spectral and hence energy gradient is established to guide the absorbed energy towards the RCs [14].

2.4.2.2 Energy transfer paths

The first excited singlet state of a Bchl*a* molecule has a lifetime of a few nanoseconds [18], and the excitation is transferred from the LH antenna complexes to the RCs within this time window. The energy paths and the transfer time are illustrated in Figure 2.11. The fast energy transfer process is believed to originate from the cyclic symmetry and exciton delocalization [31, 70].

B800 $\rightarrow$ B800. The B800 Bchl*a* molecules are largely monomeric and the

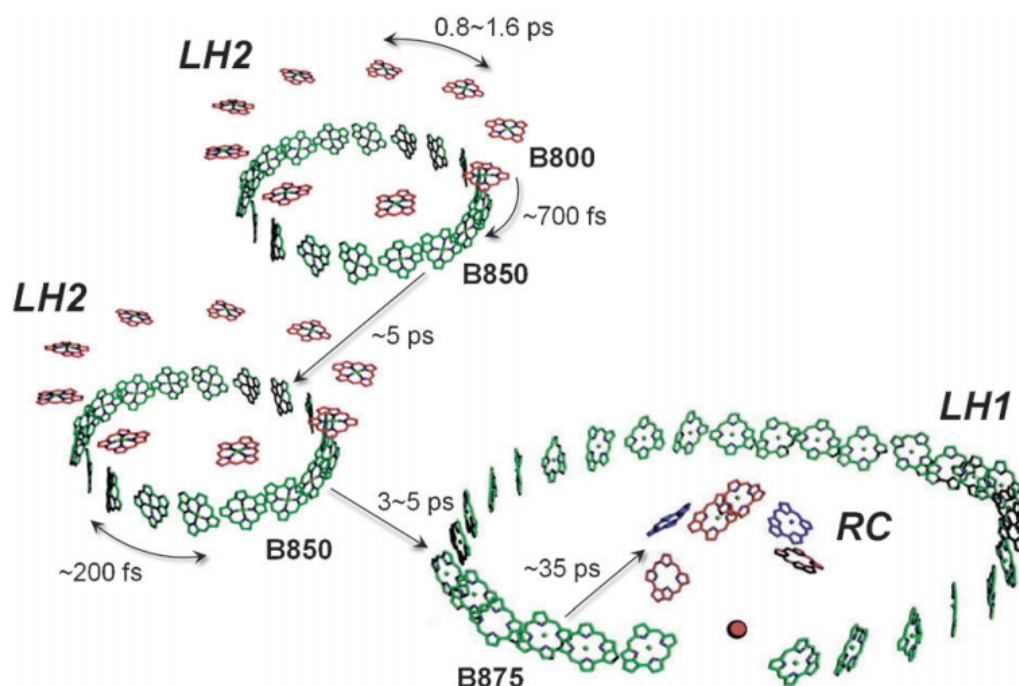


Figure 2.11: Schematic of LH2 and LH1-RC complex in purple bacteria and excitation transfer times of individual transfer processes. Taken from Ref. [70].

time constant of the hopping process between the Bchl a in the LH2 complex is predicted to be ~ 10 – 30 ps according to Förster model [69]. However, the excitation is found to be delocalized over 2 or 3 neighbouring Bchl a [66], this explains the slightly higher energy transfer rate obtained experimentally (~ 0.8 – 1.6 ps $^{-1}$) [70].

B800 $\rightarrow$ **B850** is a singlet-singlet exciton energy transfer and occurs with a rate constant 0.7 – 0.9 ps $^{-1}$ [70]. The simple point-dipole Förster theory predicts a much slower rate for a circularly arranged B850 rings and therefore proves to be an inaccurate model. The degree of excitonic delocalization is a matter of hot debate, reports ranging from a few Bchl a to at least half of the ring have been presented [71]. The acceptor in the energy transfer process is not a localized dipole, but a collective delocalized state [71]. Recent research has shown that

the generalized Förster theory, which takes the multichromophoric effects into account, combined with the disorder induced broadening of spectral overlap, allows a quantitative explanation of the fast $B800 \rightarrow B850$ transfer rate [4].

B850 $\rightarrow$ B850. After the excitation has reached the B850 ring, a collective excitonic state is created due to the strong coupling. This state is initially strongly delocalized over many Bchl a , then rapidly loses its coherence and becomes more localized due to various types of disorder (~ 50 fs) [16]. This results in a more localized state migrating around the ring on the 200–300 fs timescale [70]. The fast migration is the key to an efficient energy transfer process in the photosynthetic membrane. A direct consequence is energy transfer out of the ring occurring with equal efficiency at any position on the ring. Provided that the rings are positioned close enough to each other, irrespective of the overall intramembrane architecture, ‘ring’ to ‘ring’ energy transfers will occur efficiently for both LH2 $\rightarrow$ LH2 (~ 5 ps) and LH1 $\rightarrow$ LH1 [70].

B850 $\rightarrow$ B875. The singlet-singlet energy transfer from B850 of LH2 to B875 of LH1 is rather temperature independent and studies have shown that the energy transfer process takes between 2-5 ps [14]. LH1 complex has a similar structure as LH2 but a larger diameter. Because of the large degree of heterogeneity in the supramolecular complexes, the measured energy transfer rate is a crude average of many different transfer rates depending on which exact area of the membrane is involved during the energy transfer [14].

2.4.3 Synthetic Molecular Nanorings

Natural light-harvesting complexes have a remarkable efficiency in energy transfer as described in the last section. This has motivated many attempts to create

artificial light-harvesting systems based on e.g. J-aggregates, organic dyes, conjugated polymers and various nanoparticles [3, 13, 23, 44, 57, 61]. The main focus of this section is on nanorings based on conjugated polymers.

Fully conjugated macromolecules have the advantage of exhibiting a robust framework compared to the natural systems, which consist of a group of individual molecules loosely held in place by protein scaffold. Such synthetic systems are based on molecules such as phenyl, thiophene or porphyrin units, some examples are given here.

Synthesis of porphyrin wheels has been realized by bridging meso-meso directly linked discrete zinc(II) porphyrin dimers with 1,3-phenylene spacers. Wheels of variable size can be composed, the largest with 16 dimer units, which is comparable to the size of the LH1 complex. This approach mainly focuses on fast energy transfer via incoherent hopping on the time scale of picoseconds and exciton delocalization does not occur. [2, 34, 35, 68, 73].

Conjugated cycloparaphenylene is a simple and beautiful cyclic structure supporting delocalized excitations. Tretiak *et al.* have demonstrated that the exciton in the first excited state rapidly localizes via a self-trapping mechanism within 50 fs to extend over about 5 units [1, 22].

Using modified Sonogashira and McMurry coupling reactions, fully conjugated giant macrocyclic oligothiophenes have been synthesized. Kinked molecules have been utilized to bridge different segments of the ring. It has been shown that the electronic delocalization extends to about 18 units for a synthetic 30mer ring. The excited state lifetime is about 300 ps, much shorter than the 1 ns in the LH2 complex. However, the excitation transfer time is 40 fs, which is considerably faster compared to 700 fs in LH2 [17, 45].

π -conjugated butadiyne-linked cyclic porphyrin rings have been synthesized

using template-directed method developed by Anderson *et al.* Rings of different sizes ranging from 5 to more than 40 units were reported [42, 49]. The use of templates not only facilitates the creation of π -conjugated ring-like molecules, because the entropic and enthalpic barrier to cyclization is reduced and the necessity of a spacer to bridge over molecule segments vanishes, it also ensures efficient overlap of π -orbitals in the ring [32, 62]. The template can be knocked out of the porphyrin nanoring after successful synthesis and the ring shape would persist. A further advent of this method is the Vernier templating where smaller templates are used to direct the assembly of relatively large Vernier complexes. This approach enables synthesis of large macromolecule rings such as **c-P24** [47]. The absorption and emission spectral overlap is strong for the porphyrin nanorings. The large red shift in the emission spectrum of the porphyrin rings compared to the corresponding linear oligomers suggests a strong electronic delocalization. The red shift is larger in the more rigid templated ring due to the lack of symmetry distortions. A less pronounced red shift has also been observed in synthetic cyclic *para*-phenylacetylenes and cycloparaphenylenes. A close investigation of the depolarization confirms that the absorbing state of the porphyrin nanoring is indeed delocalized over the entire ring for rings up to about 12 porphyrin units [12, 49, 72]. Photophysical properties and exciton migration dynamics of a few porphyrin nanoring structures will be investigated extensively in the next three chapters.

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Chapter 3

Experimental Techniques

This chapter describes in detail the spectroscopic techniques used in this thesis to investigate the photophysical properties of porphyrin nanorings. The techniques can be broadly divided into two categories. Section 3.1 briefly deals with the steady-state techniques which are used to obtain absorption and emission spectra. These techniques are commonly established and commercially available tools are used. Section 3.2 is dedicated to an in-depth discussion of the fundamental principle and experimental implementations of the time-resolved spectroscopy techniques, namely time-resolved single photon counting (TCSPC) and photoluminescence up-conversion (PLUC) techniques.

3.1 Steady-state techniques

Porphyrin nanorings exhibit a strong Soret band in the near ultraviolet range of the absorption spectrum and a Q_y band in the near infrared range. All of the steady state absorption spectra presented in this thesis are recorded at room temperature for samples in solution using a PerkinElmer Lambda 1050 UV/VIS/NIR spectrometer with an operating range of 175–3300 nm. The light

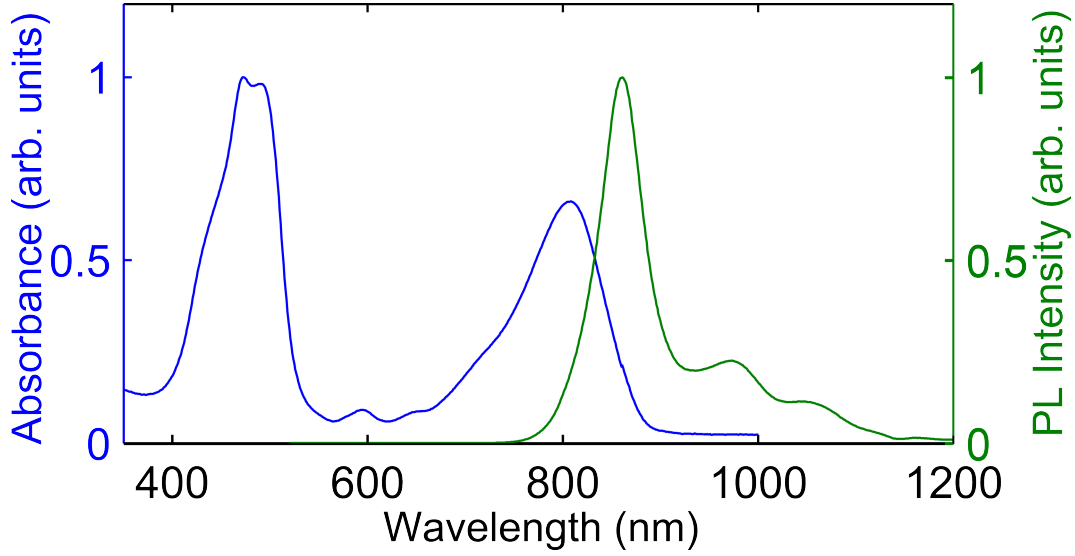


Figure 3.1: Normalized steady-state absorption (blue) and emission (green) spectra. The sample was a porphyrin ring based on 10 subunits in toluene/1% pyridine solvent. The emission was measured at 500 nm excitation.

intensities of the beam entering (I_{λ}^0) and leaving (I_{λ}) the sample are recorded. The transmittance $T(\lambda)$ and absorbance $A(\lambda)$ are obtained, which are defined as: $T(\lambda) = I_{\lambda}/I_{\lambda}^0 = 10^{-A(\lambda)}$. For a solution, the absorbance obeys the Beer-Lambert law: $A(\lambda) = \log \frac{I_{\lambda}^0}{I_{\lambda}} = \epsilon(\lambda)cl$, where $\epsilon(\lambda)$ is the extinction coefficient, c the molar concentration and l the light path length in centimeters.

The emission spectra of the nanorings exhibit a Stokes shift and are typically in the range of 700 – 1300 nm, well beyond the capability of the silicon CCD used in the PLUC setup. A Horiba FluoroLog fluorimeter is used to measure the steady-state emission spectra. A typical example of absorption and emission spectra is shown in Figure 3.1.

3.2 Time-resolved spectroscopy

Time-resolved photoluminescence spectroscopy is a powerful and versatile tool to investigate optical properties of conjugated molecules. After excitation by an ultrafast laser pulse, evolution of the fluorescence dynamics from the excited states can be studied with different temporal resolution and observation time windows. A common technique for lifetime measurements is time-correlated single photon counting (TCSPC) which offers high sensitivity and has the advantage of easy implementation because electronic time gating is used here. However, the time resolution of the TCSPC technique is fundamentally limited by the electronic components to tens of picoseconds, which is often orders of magnitude longer than the characteristic time scale of energy dynamics in organic semiconductors. A superior temporal resolution is provided by photoluminescence up-conversion which bypasses the limited time-resolution of the electronics and employs optical gating technique. Here the time resolution is limited by the width of the ultrafast laser and the thickness of the non-linear crystal used for gating the luminescence [1].

3.2.1 Time-correlated single photon counting technique

TCSPC is a picosecond spectroscopic technique to record low level light signals, it is a well-established, powerful analysis tool that uses pulsed lasers for lifetime measurement with picosecond time resolution. Its principle is based on repetitive, precise recordings of emitted single photons from the sample and their arrival times with respect to a reference signal. The light source is split into an excitation and a trigger pulse.

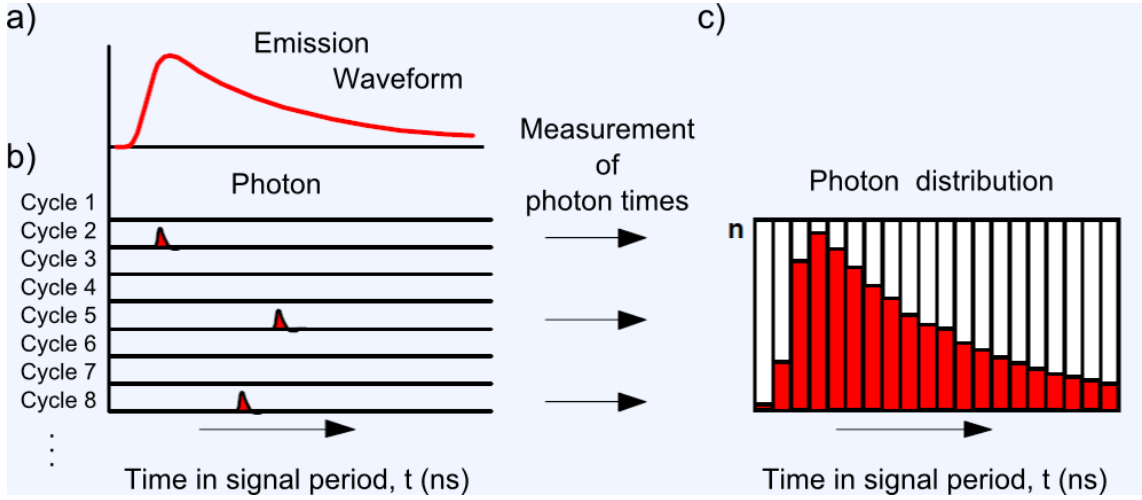


Figure 3.2: Principle of time-correlated single photon counting technique. Detailed explanation in the main text. Taken from Ref. [1].

If numerous fluorophores are excited simultaneously and many emitted photons are detected, the emission dynamics would take up a waveform as shown in Figure 3.2a) [1]. To reconstruct this waveform from individual photon detections using TCSPC, the excitation beam is kept at a low fluence such that less than one photon is emitted per laser pulse cycle, which is in the nanosecond to microsecond range depending on the laser source. Indeed the typical detection rate is 1 photon every 100 pulse cycles [1]. The emitted photon is registered by a sensitive detector such as a photomultiplier tube (PMT), micro channel plate (MCP) or single photon avalanche diode (SPAD). The time delay between excitation and the arrival of the photon is measured for each cycle (as shown in Figure 3.2b) and recorded in the histogram (Figure 3.2c) [1]. After a large number of cycles, many photons are detected and a distribution of the photon probability over the time in the laser pulse cycle builds up [2], which represents the fluorescence emission decay.

To measure the time delay between excitation and emission, specialized electronics are used and the system is designed to work in the reversed start-stop

mode. Upon detection of a single emitted photon at the detector the pulse of a time-to-amplitude converter (TAC) is started and the next photon in the gate pulse recorded at the PN diode stops the pulse. A signal proportional to the time between start and stop pulses is generated by the TAC. A delay line is used on the gate pulse to ensure that the optical path delays are matched between emission and gate pulses. Because only the first arriving photon in each laser pulse cycle can be detected due to the principle of the measuring process, the photon counting rate is limited to much less than one per cycle, usually 0.01 to 0.1 photons per signal period depending on the desired accuracy [1]. If multiple photons arrive and only the first (and fastest) is recorded, the decay curve will be distorted and biased to shorter decay time [1]. The reversed start-stop mode is vital for processing high excitation pulse repetition rate (80 MHz in the MaiTai laser). Since there are many laser pulse cycles without any emitted photons arriving, the TAC would need to be reset by some mechanism after each such cycle if not using the reversed start-stop mode. For a laser source with high repetition rate, this would result in resetting the TAC every few nanoseconds while the detection events take place with a rate which is one or two orders of magnitude lower [1].

The time resolution depends on the accuracy by which the time delay can be determined, therefore it is limited by the time-measuring electronics. The weakest component in terms of the timing uncertainties is usually the detector which sets the fundamental limit. Currently, the timing uncertainties of the different detectors range from hundreds of picoseconds down to tens of picoseconds [6]. The measurement range is the duration of one pulse cycle, e.g. for the MaiTai with 80 MHz this is 12.5 ns. The trade-off between a large measurement window and a short acquisition time enabled by a high repetition rate is the

key in choosing an appropriate frequency for the excitation pulse.

3.2.2 Photoluminescence up-conversion spectroscopy

3.2.2.1 Sum frequency generation

The photoluminescence up-conversion (PLUC) technique is based on a second order nonlinear effect induced in a non-centrosymmetric medium. Nonlinear optics effects are particularly important for high power laser pulses, as the linear dependence approximation of the polarization $\mathbf{P}$ on the applied electric field $\mathbf{E}$ breaks down and higher power terms can no longer be ignored. In linear optics we have:

$$\mathbf{P} = \epsilon_0 \chi \mathbf{E}, \quad (3.1)$$

where χ is the electric susceptibility. For polarization parallel to the electric field, the polarization P is split into the first-order linear term and a series of nonlinear terms:

$$P^{nonlinear} = P^{(1)} + P^{(2)} + P^{(3)} + \dots = \epsilon_0 \chi^{(1)} E + \epsilon_0 \chi^{(2)} E^2 + \epsilon_0 \chi^{(3)} E^3 + \dots, \quad (3.2)$$

where $P^{(n)}$ is the n th-order polarization, $\chi^{(n)}$ the n th-order nonlinear susceptibility and E the magnitude of the electric field. The second order nonlinear polarization $P^{(2)} = \epsilon_0 \chi^{(2)} E^2$ is responsible for the second harmonic generation (SHG) and sum-frequency generation vital in PLUC. The effect depends strongly on a large, non-zero $\chi^{(2)}$ which can only be achieved in non-centrosymmetric media. This is because inversion symmetry dictates polarization P to be unchanged upon inversion transformation and hence $\chi^{(2)} = 0$

follows¹.

Consider incident sinusoidal waves at frequency ω_1 and ω_2 with electric field amplitudes E_1 and E_2 respectively upon the medium, then the second order polarization takes the form [4]

$$\begin{aligned} P^{(2)}(t) &= \epsilon_0 \chi^{(2)} \times E_1 \cos \omega_1 t \times E_2 \cos \omega_2 t \\ &= \epsilon_0 \chi^{(2)} E_1 E_2 [\cos(\omega_1 + \omega_2)t + \cos(\omega_1 - \omega_2)t]/2 \end{aligned} \quad (3.3)$$

The second order nonlinear response generates two polarization waves at frequencies $\omega_s = \omega_1 + \omega_2$ and $\omega_1 - \omega_2$. Emission of light at frequency ω_s from the medium is called sum frequency generation: two incident photons at frequencies ω_1 and ω_2 are annihilated and a new photon at frequency ω_s is created; if $\omega_1 = \omega_2$, the sum frequency is twice the input frequency and this effect is called second harmonic generation (SHG).

To satisfy energy and momentum conservation two conditions have to be met:

$$\text{frequency matching : } \omega_s = \omega_1 + \omega_2 \quad (3.4)$$

and

$$\text{phase matching : } \mathbf{k}_s = \mathbf{k}_1 + \mathbf{k}_2, \quad (3.5)$$

where $\mathbf{k}$ is the photon wave vector. Phase matching condition arises from the fact that nonlinear effects are generally small and hence a high conversion efficiency needs to be achieved.

For nonlinear processes with a phase mismatch $\delta\mathbf{k} = \mathbf{k}_s - \mathbf{k}_1 - \mathbf{k}_2$ occurring at each point along the z-axis of a medium, the wave generated at $z + \delta z$ is not in phase with that generated at z . The sum-frequency waves generated along the z-axis are not able to add together coherently leading to low conversion

¹NB $\chi^{(2)}$ is a tensor in reality, $\chi_{ijk}^{(2)} = 0$ for all permutations of i, j, k for centrosymmetric crystals. A more rigorous derivation can be found in Ref. [3].

efficiency [3, 4]. Hence we require $\delta\mathbf{k} = 0$, which is accomplished with crystals of uniaxial birefringence. When a wave propagates in such a crystal, the refractive index is constant at n_o if the wave is polarized perpendicular to the optic axis (ordinary) and varies with incident angle θ to the optic axis ($n_e(\theta)$) for waves with component polarized parallel to the optic axis (extraordinary). By rotating the crystal, the incident angle θ can be tuned to satisfy the tight constraint of phase matching. The commonly used birefringent crystal for SHG and sum-frequency generation in PLUC is a β -BaB₂O₄ (BBO) crystal due to its large susceptibility value $\chi^{(2)} = 1.78 \text{ pmV}^{-1}$ and small absorbance down to 190 nm [5].

Because porphyrin rings have well-defined absorption spectra with a Soret band in the visible or near ultraviolet range, excitation into the Soret band is generated from the Ti:Sapphire laser fundamental (690 nm – 1040 nm) via SHG. Phase matching is satisfied for: $n_e^{2\omega} = n_o^\omega$ and is illustrated in Figure 3.3.

3.2.2.2 Principle of PL upconversion technique

The principle of PL up-conversion is illustrated in Figure 3.4. The laser pulse source is split into excitation and probe beams which are time correlated. At time $t = 0$ the sample is excited and the incoherent fluorescence at frequency ω_F is collected and focused onto the nonlinear crystal. After a delay time τ the probe pulse with frequency ω_P arrives at the crystal. The crystal is rotated to the phase matching angle θ for sum frequency generation (or up-conversion) for $\omega_F + \omega_P = \omega_s$. The signal at frequency ω_s usually lies in the ultraviolet range and occurs only if fluorescence and probe beams overlap temporally and spatially inside the crystal. The fundamental limit of the time resolution is set by the width of the probe beam, an optical gating is employed in this technique.

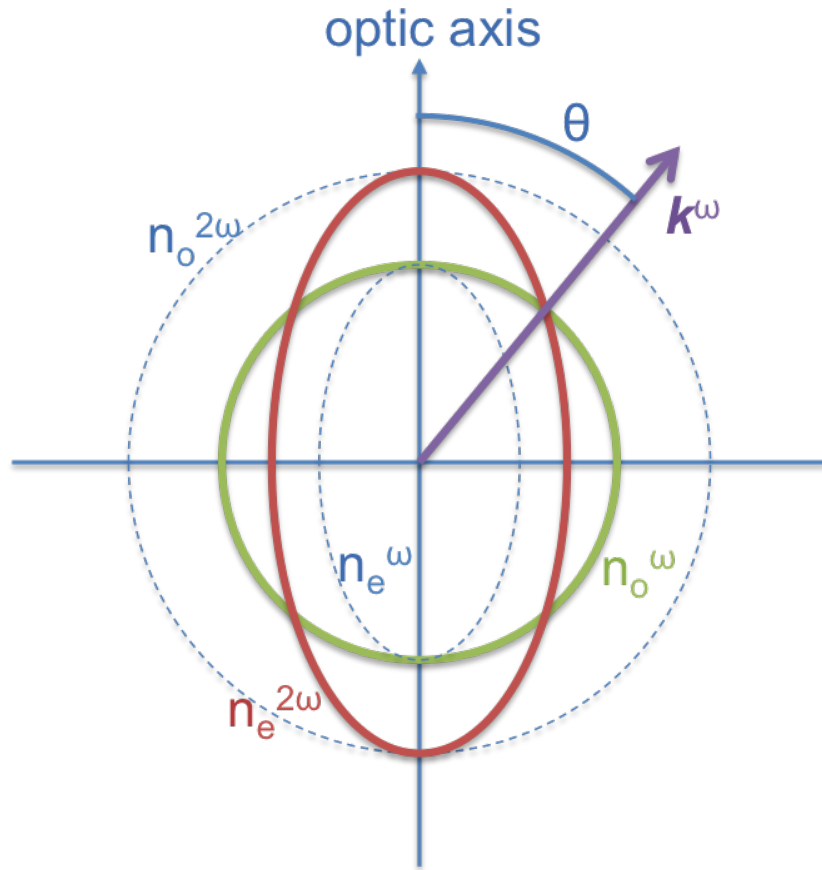


Figure 3.3: Refractive index indicatrices of a uniaxial birefringent crystal. Projected on the crystal plane, the refractive index surfaces for the ordinary polarization component $n_o(\theta)$ are circles, while $n_e(\theta)$ for the extraordinary component are ellipses. The indicatrices for the fundamental wave with frequency ω and second harmonic at 2ω are shown. Phase matching for SHG occurs at incident angle θ , where $n_e^{2\omega}(\theta)$ (red) intersects with $n_o^\omega(\theta)$ (green).

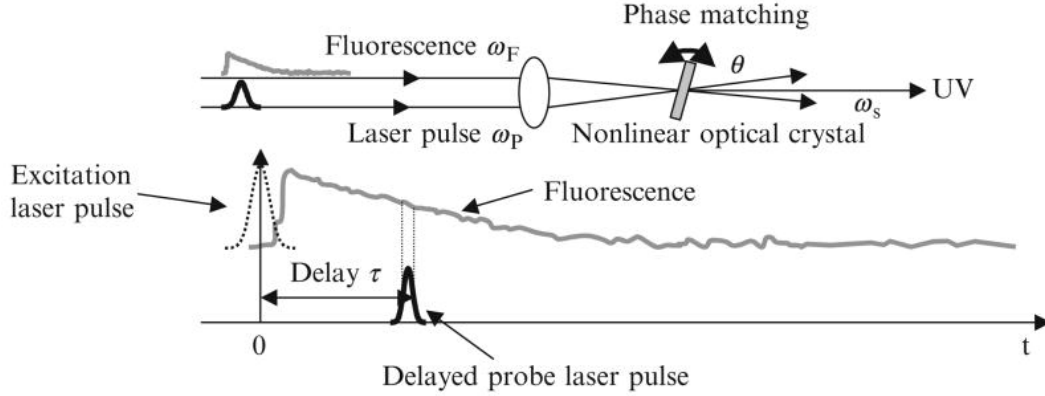


Figure 3.4: Schematic diagram illustrating the principle of photoluminescence up-conversion technique. Detailed description in the main text. Figure taken from Ref. [7].

The intensity of signal ω_s is proportional to the intensity of fluorescence. Hence by varying the time delay τ between the excitation and probe beams, time-dependent fluorescence decay profile can be inferred from the signal intensity. The strict constraint of the phase matching condition allows fluorescence photons from a small spectral range to interact with the probe beam at the given crystal angle, providing a good spectral resolution.

3.2.3 Experimental set-up

The experimental set-up of the photoluminescence up-conversion (PLUC) and TCSPC technique are illustrated in Figure 3.5 and a detailed description of the individual components are given in Table 3.1. Ultrashort laser pulses with pulse duration of 100 fs and repetition rate of 80 MHz in the wavelength range of 690 – 1040 nm are generated by a mode-locked Ti:Sapphire laser (MaiTai). The laser pulse is split into two beams when passing through the cube beam splitter (BS); one beam excites the sample and the other one acts as the gate for both

Table 3.1: Component list of the experimental system.

Component	Description
MaiTai	Spectra Physics Ti:Sapphire oscillator pulse duration 100 fs repetition rate 80 MHz
OPO	Radiantis femtosecond optical parametric oscillator pumped by mode-locked Ti:Sapphire oscillator tunability across 345 – 2500 nm
M-IR	Vis-IR mirror
M-UV	Vis-UV mirror
HWP1, HWP2, HWP3	Half-wave plate
BS	Beam-splitter
GT	Glan Thompson polarising prism
Stage 1	Translation stage
Stage 2	Sample stage
Stage 3	Rotation stage
L1, L2, L3, L4, L5, L6	Lens
P1, P2	Parabolic mirror
BBO 1, BBO 2	Barium borate crystal

the PLUC and the TCSPC techniques. The sample is usually in solution form and held in quartz cuvettes. The polarization and the power of the excitation beam is adjusted using the combination of a $\lambda/2$ -plate (HWP 3) and a Glan-Thompson polarizer. For excitation into the Soret band of the porphyrin rings, the excitation beam is frequency-doubled using a BBO crystal (BBO 1) and the fundamental wave is filtered out using a Glan-Thompson polarizer and a bandpass filter (Filter 1). For excitation wavelength between 500 – 700 nm, the optical parametric oscillator (OPO) is used, the output for SHG, signal and idler can act as excitation pulse and the fundamental is the gate.

For PLUC upon excitation of the sample, incoherent emission is collected by a pair of parabolic mirrors (P1 & P2) and focused onto the BBO crystal in the up-conversion box. The powerful gate beam passes through a Glan-Thompson polarizer and is always vertically polarized. The motorized delay stage (Stage 1) introduces a delay time τ with respect to the excitation beam before arriving at the BBO crystal to up-convert the vertically polarized component in the emission. The mixing angle between the gate beam and the PL cone at the crystal is 12° . The crystal (BBO 2) has a cutting angle of 30° and thickness 1 mm. Thicker crystal would result in higher conversion efficiency, but would also lead to temporal broadening due to dispersion and tightening of the phase matching condition. The crystal is rotated on the rotation stage (Stage 3) to meet the phase matching condition. The up-converted signal lies in the UV-range and is collimated by a pair of lenses (L5 and L6), dispersed in a monochromator (Jobin Yvon: Triax 190) and detected by a nitrogen-cooled charge-coupled device (CCD) (Jobin Yvon: Symphony) over a range of delay times τ . As $\tau = 100$ ps corresponds to ~ 3 cm on the optical bench, the measuring time window is limited to a few hundreds of picoseconds. By changing

the polarization direction of the excitation beam using the half-wave plate and the Glan-Thompson polarizer, either the parallel ($I_{\parallel}$) or the perpendicular ($I_{\perp}$) polarization in the emission with respect to the excitation beam can be selected for up-conversion. The time-dependent anisotropy can be calculated by $\gamma = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp})$. In order to achieve a good signal to noise ratio, the greatest challenge is to separate the up-converted signal from the PL (IR), gate (IR) and the frequency-doubled gate (UV) beam and this is managed by a carefully chosen combination of filters in front of the monochromator.

In the TCSPC experiment the gate beam is diverted to the PN diode which acts as the trigger; the BBO crystal is taken out and fluorescence photons are dispersed in the monochromator and registered at the silicon single-photon avalanche diode (SPAD), the detector for TCSPC.

3.2.4 Instrumental response function

Instrumental response functions (IRF) of the photoluminescence upconversion system were recorded using TiO_2 in water as a scattering material held in a cuvette, with the excitation wavelength set to 780 nm and detecting the elastically scattered light at 780 nm, gated by the 780 nm gate pulse to give upconverted photons at 390 nm. Excitation occurred through the front of the cuvette with respect to the collection pathway, i.e. the scattered light was collected in back-scatter geometry, identical to the configuration used for the nanoring photoluminescence. If the excitation pulse was polarized perpendicular with respect to the detection pulse polarization, no upconverted signal could be detected, because the sample does not absorb light at this wavelength but only scatters. Therefore, the two excitation polarization settings of (i) parallel and

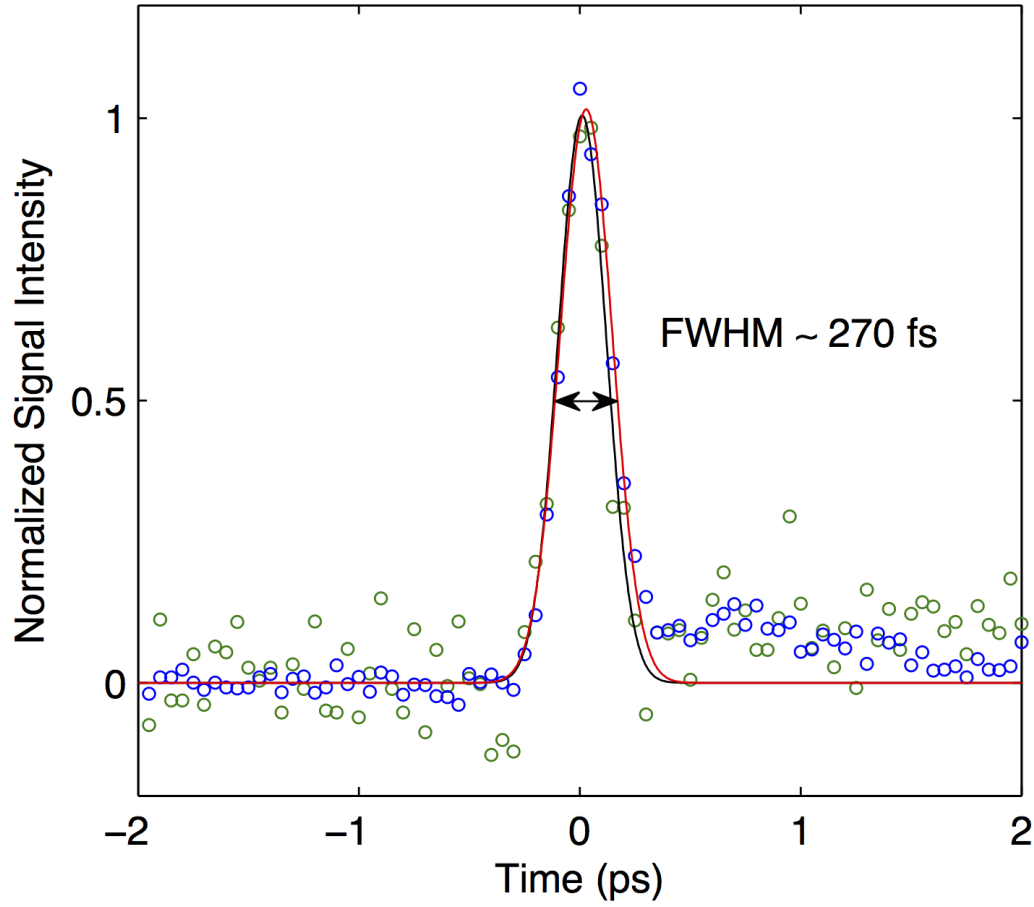


Figure 3.6: Normalized instrumental response function (IRF) of the photoluminescence upconversion system, measured with excitation at 780 nm polarized parallel (blue) and almost perpendicular (green) to the detection pulse polarization. Fitting to these IRF data is carried out using a Gaussian function for both parallel (red) and almost perpendicularly (black) polarized excitation pulses. The full width at half maximum is similar in both cases (270 fs).

(ii) 70° with respect to the detection pulse polarization were used to record the instrumental response functions, as illustrated in Figure 3.6.

Fitting to the IRF was carried out using a Gaussian model. From the fit to the data points, the centre of the peak and the full width at half maximum (FWHM) can be extracted. It is found that a temporal shift of 18 fs with a 50% error exists between the peak centres as a result of the walk-off effect in the Glan-Thompson polariser used to control the polarization of the excitation pulse. The actual temporal shift between the perpendicular and parallel polarized excitation pulses may be slightly (but insignificantly) larger. The FWHM of the Gaussian peaks are found to be 280 fs (7%) and 258 fs (13%) and hence the resolution limit of the upconversion system is about 270 fs.

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Chapter 4

Breaking the Symmetry in Molecular Nanorings

4.1 Introduction

Cyclic molecules can exhibit fundamentally different electronic dynamics compared to their linear counterparts due to the lack of chain end effects, high rotational symmetry and the presence of ring strain [33, 47]. The photophysical properties of cyclic molecules have been extensively investigated for a large number of systems ranging from small aromatic rings [4, 34] to large molecular complexes [46]. A recurrent key concept is exciton delocalization, which is known to lead to strong fluorescence suppression in cyclic molecular structures such as benzene [12, 41]. The high symmetry results in a dipole-forbidden lowest exciton ($k=0$) state, however, emission is weakly enabled by Herzberg-Teller intensity borrowing from allowed higher energy transitions through the involvement of vibrations with suitable symmetry [17]. Electronic delocalisation also plays a major role in the efficient energy transfer between adjacent antennae in natural light-harvesting complex 2 (LH2) based on chlorophyll units [7, 14], where the pigments are held loosely by protein scaffolds in circular structures [26]. Such designs of nature have inspired many attempts to create

synthetic nanoring analogues, for instance cycloparaphenylenes [1, 19], cyclic oligothiophenes [23], nanorings synthesized from phenylcarbazole units linked with phenylene-ethynylene-butadiynylene groups [2] and an extensive range of porphyrin arrays [18, 29, 32, 44].

While investigating electronic properties on structures with such high symmetry, an interesting question inevitably arises, namely how symmetry distortions influence the photophysical properties. When defects are introduced into cyclic molecular structures, the lowest dipole-forbidden exciton state may be mixed with higher lying states and some absorption into the lowest state becomes possible [25, 28]. As the distortion becomes more and more prominent, deviations from high rotational symmetry dominate and the fluorescence is no longer suppressed [25]. Symmetry breaking also plays an important role in structures found in natural systems, such as LH1 complexes containing a reaction centre (RC) at their centre, which can be divided into at least two distinct classes [7]. The first class is monomeric, consisting of only one RC surrounded by one cyclic LH1 complex, as found in *Rhodospirillum rubrum* and *Rhodospirillum rubrum palustris* [7]. However, while LH1 in *Rsp. rubrum* is believed to exhibit a highly symmetric ring-like structure [9], LH1 in *Rsp. palustris* displays a gap, providing a portal through which ubiquinone can transfer electrons across the boundaries of LH1, which is vital for photosynthetic processes [36, 37]. The second class of systems is dimeric, consisting of two circular RC-LH1 complexes as found in *Rhodobacter sphaeroides* [35, 40]. Such examples illustrate the urgent need for an understanding of how symmetry lowering in ring-like chromophore assemblies affects the electronic dipole transitions that control the absorption of light.

Previous studies have examined both experimentally and theoretically the

effects of conformational and dynamic disorder on cyclic system [6, 13, 22, 31, 39, 47]. However, investigations into the process of symmetry breaking based on ring-like compounds with geometrical defects require an excellent control over their structures. Fully π -conjugated porphyrin nanorings bound to wheel-like templates [15, 16] provide an ideal model system here: these nanorings have acquired a high level of rigidity through the butadiyne bridges and the template inside the rings; their initial excited states are fully delocalized over the entire ring [33]; and symmetry defects of varying extent can be introduced through modifications in synthesis.

In this study we examine five synthetic porphyrin nanorings with structures mimicking those of the natural RC-LH1 complexes described above. We investigate fully conjugated nanorings with and without defects, a nanoring featuring a gap due to broken conjugation, and systems consisting of two fused nanorings (see Figure 4.2). We reveal the effect of symmetry distortions on the electronic transitions in these systems, showing that as deviations from rotational symmetry increase, oscillator strength is transferred to the lowest ($k=0$) state. Concomitantly, the degeneracy of the dipole-allowed first excited ($k=\pm 1$) state is shown to be lifted, leading to an ultrafast polarization switching effect in the emission from strongly symmetry-broken nanorings.

4.2 Samples

Porphyrins are large, heterocyclic aromatic compounds consisting of four pyrrole units linked by methine bridges as shown in Figure 4.1. They are building blocks of the nanoring complexes investigated in this thesis. The synthesis and characterization of the nanoring complexes were carried out by Ludovic

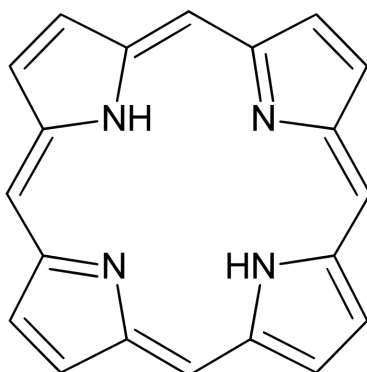


Figure 4.1: Chemical structures of a porphyrin.

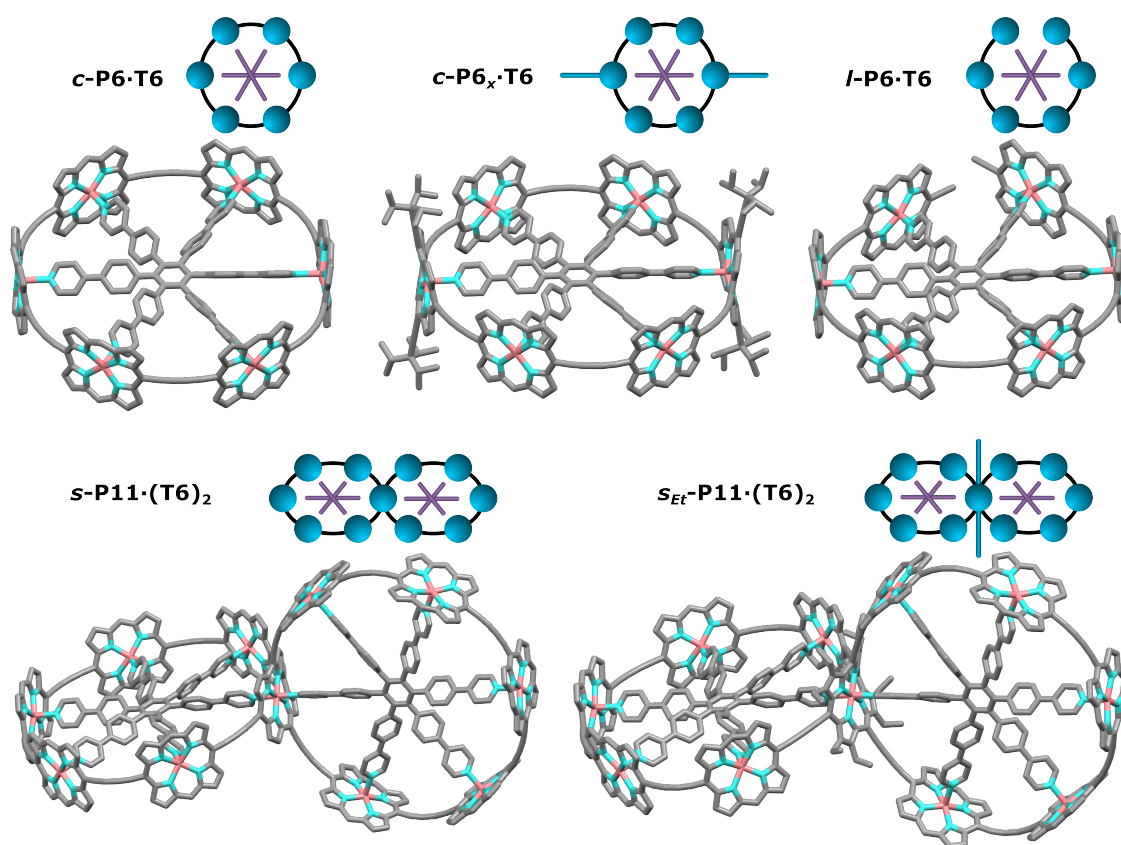


Figure 4.2: Chemical structures of the butadiyne-linked zinc porphyrin nanoring complexes investigated in this study. Carbon is indicated in grey, nitrogen in blue and zinc in red. The structures are generated using *HyperChem* with side chains omitted for clarity. Icons corresponding to each compound are shown on top of each structure.

Favereau from Anderson group in Organic Chemistry Department, University of Oxford. More details can be found in the literature reports [8, 10, 15, 38, 43]. Figure 4.2 shows the structures and simplified graphical representations of the five investigated nanorings consisting of zinc porphyrin units joined by butadiyne bridges. The six-legged (**T6**) templates inside all complexes bind to the porphyrin units thus maintaining a rigid ring-like shape for the nanorings, which is vital because it suppresses competing symmetry weakening from ring distortions.

The most highly symmetric compound **c-P6·T6** has a closed ring structure with six porphyrin units [42], comparable to the D_{6h} symmetry of benzene. For ring-like systems with six-fold symmetry, such as benzene, the energy-level structure can easily be visualized through the simple Hückel molecular orbital method for π -conjugated molecules. This approach postulates two non-degenerate ($k=0$, $k=3$) and two pairwise degenerate ($k=\pm 1$, $k=\pm 2$) exciton states. However, simple analysis of the transition dipole moments to these states reveals that only the two degenerate $k=\pm 1$ states of orthogonal polarization can carry significant oscillator strength. In particular, the transitions to the lowest ($k=0$) state can be visualized by the simple Kasha model [20] as dipole contributions summing to zero in a hexagonal arrangement. Therefore, once the molecule has relaxed into its lowest state, emission is expected to be strongly suppressed, as we have shown to be the case for **c-P6·T6** [42, 47].

Figure 4.2 also displays four other compounds whose symmetry has been reduced with respect to **c-P6·T6**. Here, **c-P6_x·T6** has a very similar structure, but with the minor modification that two opposite porphyrins have additional alkyne bridges with TIPS (triisopropylsilyl) end group attached, leading to reduced symmetry. Stronger deviations are introduced by **l-P6·T6** which

comprises a linear six-porphyrin chain bound to the **T6** template, and therefore features a “gap” in the π -conjugated backbone. The two spiro fused ring structures **s-P11·(T6)₂** and **s_{Et}-P11·(T6)₂** comprise 11 porphyrin units each and consist of two interlinked six-porphyrin nanorings with perpendicular template planes as shown in Figure 4.2, with the only difference being the ethyl side chains attached to the shared porphyrin unit in the centre of **s_{Et}-P11·(T6)₂** [8]. For all measurements reported, **l-P6·T6** was dissolved in toluene, while all other samples were prepared in toluene/1% pyridine solutions to avoid aggregation.

4.3 Results and discussion

4.3.1 Absorption and emission spectra

We proceed to investigate the impact of symmetry on the electronic properties of ring-like molecules by investigating the changes in absorption and emission of these five porphyrin nanoring systems, ranging from almost perfect six-fold symmetry, through modifications in structure, to ring structures with broken π -conjugation. As a first comprehensive insight into the energy level structure in these ring systems, Figure 4.3 shows the extinction coefficient spectra of the five compounds in the region of the Q_x-band. Extinction coefficient spectra over a wider range of photon energies, and emission spectra are shown in Figure 4.4. In contrast to zinc porphyrin monomers which display degenerate S₀-S₁ transitions at ~ 550 nm (Q-band) [3], the Q-band of the ring structures is split into Q_x and Q_y bands with polarizations parallel and perpendicular to the molecular backbone respectively and the Q_x band is significantly red-shifted to ~ 800 nm because of the increased conjugation length [6].

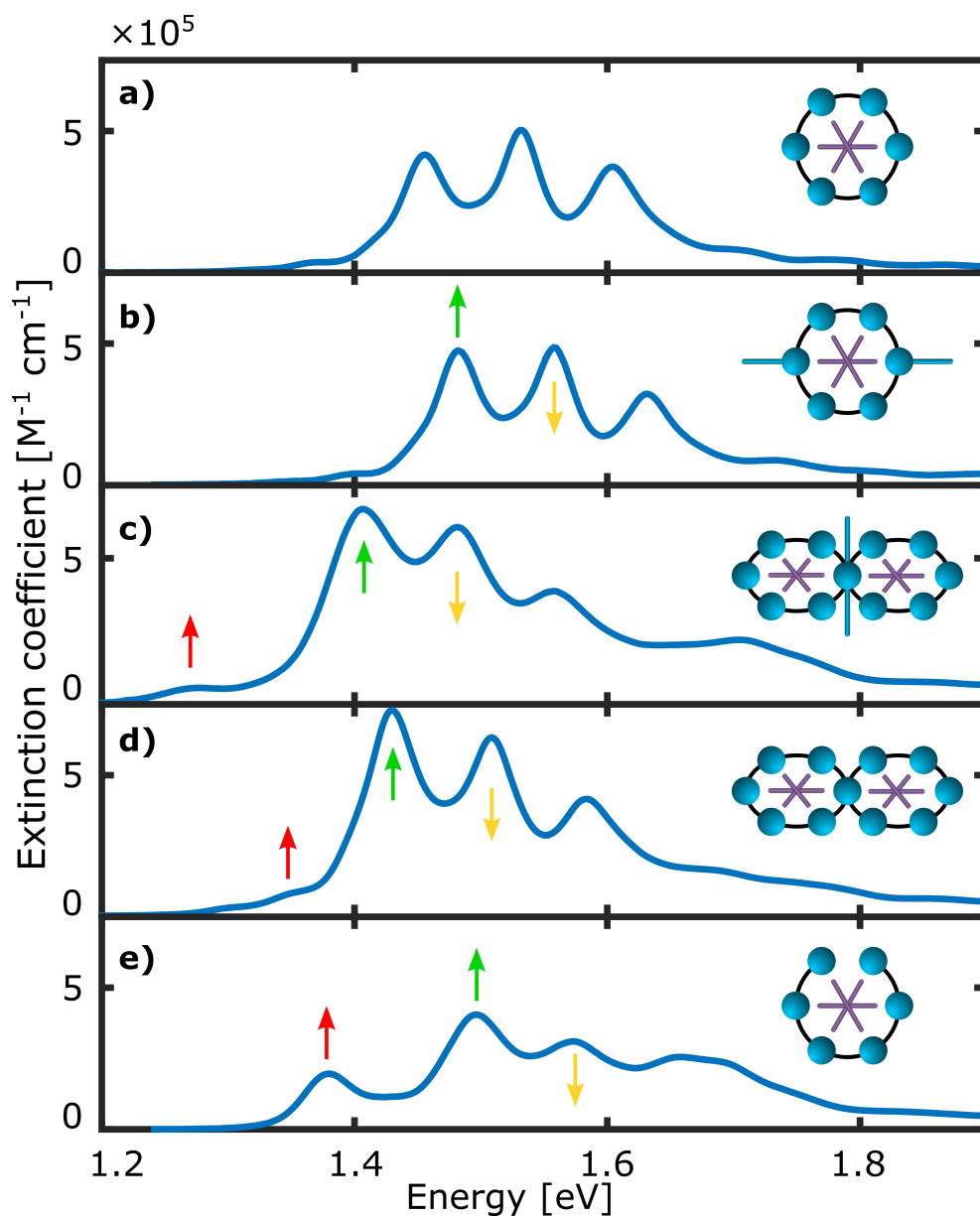


Figure 4.3: Extinction coefficient spectrum in the region of the Q_x -band for a) *c*-P6·T6, b) *c*-P6_x·T6, c) *s*_{Et}-P11·(T6)₂, d) *s*-P11·(T6)₂ in toluene/1% pyridine and e) *l*-P6·T6 in toluene. Arrows indicate the trend in peak intensity ratios for each compound in comparison to *c*-P6·T6.

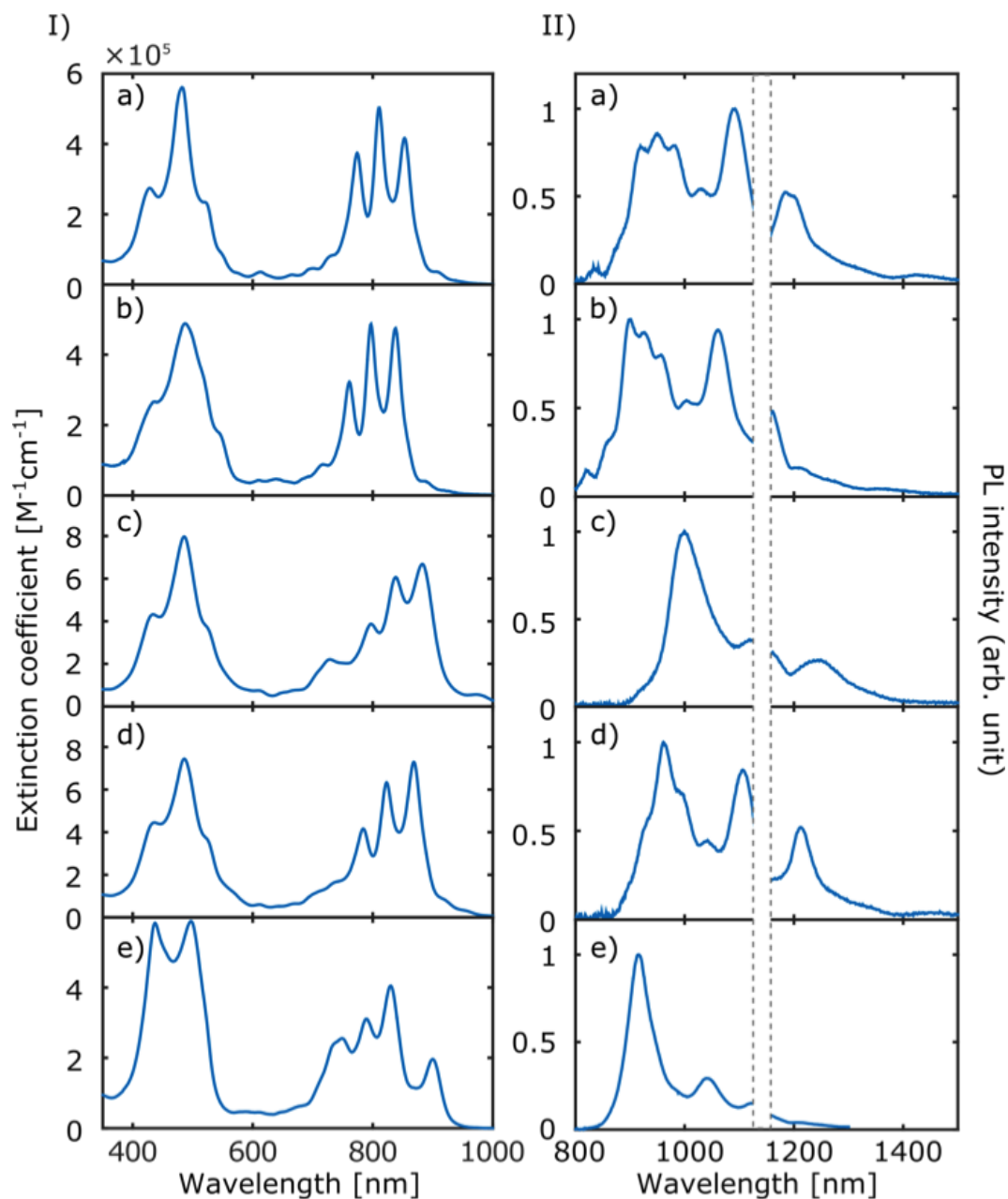


Figure 4.4: Extinction coefficient (I) and PL intensity (II) spectra of a) $c-P6_x \cdot T6$, b) $c-P6_x \cdot T6$, c) fused ring with ethyl, d) fused ring and e) $l-P6 \cdot T6$. Data points between dotted lines in PL intensity spectrum are excluded because of solvent absorption effects.

For the most highly symmetric molecule, **c-P6·T6**, the extinction coefficient spectrum shows three distinctive strong peaks with approximately equal energy difference. We have previously shown that excitations in this system are fully delocalized over the entire ring [42, 47]. Therefore, the simple Hückel model should hold as described above, and only the lowest allowed $k=\pm 1$ exciton state carries significant oscillator strength. As we have previously discussed [42], the multiple peaks most likely arise from vibrational contributions, with the approximate 75 meV energy spacing between the three main peaks tentatively supporting an interpretation in terms of Frank-Condon vibronic progression within an adiabatic Born-Oppenheimer framework. As the symmetry is lowered for the other nanorings systems, two effects can be clearly observed in the extinction coefficient spectra. First, new features appear at the low-energy end (1.2–1.4 eV) of the spectra, that grow in intensity (red arrows in Figure 4.3) as symmetry distortions become more severe. We propose that such deviations from six-fold symmetry may lead to oscillator strength being transferred to the lowest ($k=0$) exciton state. For the ring with broken π -conjugation (**l-P6·T6**) this low-energy peak rises to considerable strength (Figure 4.3e) suggesting a strongly-allowed transition to the $k = 0$ state becomes possible. This phenomenon has analogies with observations in the natural RC-LH1 complexes from *Rps. palustris*, which features a gap in the LH1 ring [36] that enhances absorption contributions for the $k=0$ state. Concomitant with these changes, the distortions from six-fold symmetry appear to also affect the peak intensity ratio of the three strong peaks visible in all extinction spectra. Compared to **c-P6·T6**, the first peak in the series, as indicated with green arrows in Figure 4.3, gradually rises with respect to the second peak as symmetry constraints are lifted. This effect may derive from higher-energy vibronic progressions of the emerging $k=0$ state overlapping

Table 4.1: Photoluminescence lifetime τ , quantum yield QY , radiative rate Γ_r and non-radiative rate Γ_{nr} for the five compounds.

Molecule	τ [ps]	QY	Γ_r [ns ⁻¹]	Γ_{nr} [ns ⁻¹]
c-P6·T6	627	0.7%	0.010	1.60
c-P6_x·T6	682	1.3%	0.019	1.45
s_{Et}-P11·(T6)₂	271	0.5%	0.020	3.73
s-P11·(T6)₂	343	0.8%	0.024	2.90
l-P6·T6	364	2.3%	0.064	2.69

with the $k = 1$ features, and is therefore most likely of similar origin.

4.3.2 Radiative decay rate and symmetry breaking

To ascertain whether a particular lowering of the nanoring symmetry indeed leads to the emergence of a dipole-allowed lowest ($k=0$) state, we further probed the emissive properties of these molecules, following excitation into the Q_x-band. While for a rotationally symmetric molecule, transitions from the $k = 0$ exciton state are dipole forbidden within the Franck-Condon approximation, weak emission is possible via Herzberg-Teller intensity borrowing through joint electronic-vibrational transitions that match the symmetry of the higher-lying allowed ($k=1$) transition [42]. A weakening of symmetry constraints however, is expected to relieve the strict selection rules on the $k = 0$ state leading to additional Franck-Condon emission.

To investigate such effects, we therefore measured the radiative emission rate of all molecules, which reflects the oscillator strength in the $k=0$ state into which the system rapidly relaxes following excitation. For this purpose, the fluorescence lifetime was measured using TCSPC (an example is shown in

Figure 4.5) and the quantum yield was obtained by comparing the fluorescence spectrum integral and the absorbance at the excitation wavelength against that of a reference standard, as described in Chapter 3. From these independent measurements, the radiative (Γ_r) and non-radiative (Γ_{nr}) rate contributions were evaluated, as listed in Table 4.1. It can be seen that the increasingly severe deviations from ring-like symmetry introduced along the group of molecules lead to a gradual increase in their radiative emission rates. The strongest enhancements are seen for ***l*-P6·T6**, for which Γ_r increases more than six-fold with respect to ***c*-P6·T6** as the π -conjugation is broken, resulting in efficient emission that suggests strong Franck-Condon allowed transitions. The spiro-fused rings, show weaker increases, with the radiative rate more than doubling in comparison to the six-fold symmetric ***c*-P6·T6**. The weakest effects are seen for ***c*-P6_x·T6** which may be partly because a C_2 -type symmetry reduction alone is not expected to lead to oscillator strength being transferred to the $k=0$ state [21, 36].

In contrast and as expected, no correlation between non-radiative decay rates and molecular symmetry is observed. The fluorescence lifetime of ***s*_{Et}-P11·(T6)₂** is particularly short, which is caused by stronger non-radiative decay channels (Γ_{nr} , Table 4.1) possibly introduced by the presence of the ethyl side chains attached to the shared porphyrin unit.

We proceed by establishing a quantitative correlation between such reduced-symmetry enhancements in radiative rates, and the changes in the absorption features discussed above. Figure 4.6 shows the correlation between (a) the absorption intensity of the $k=0$ state and (b) the intensity ratio of the first two main peaks, plotted against the radiative emission rate for each of the five compounds. To capture the contributions to the absorption into the emerging $k=0$

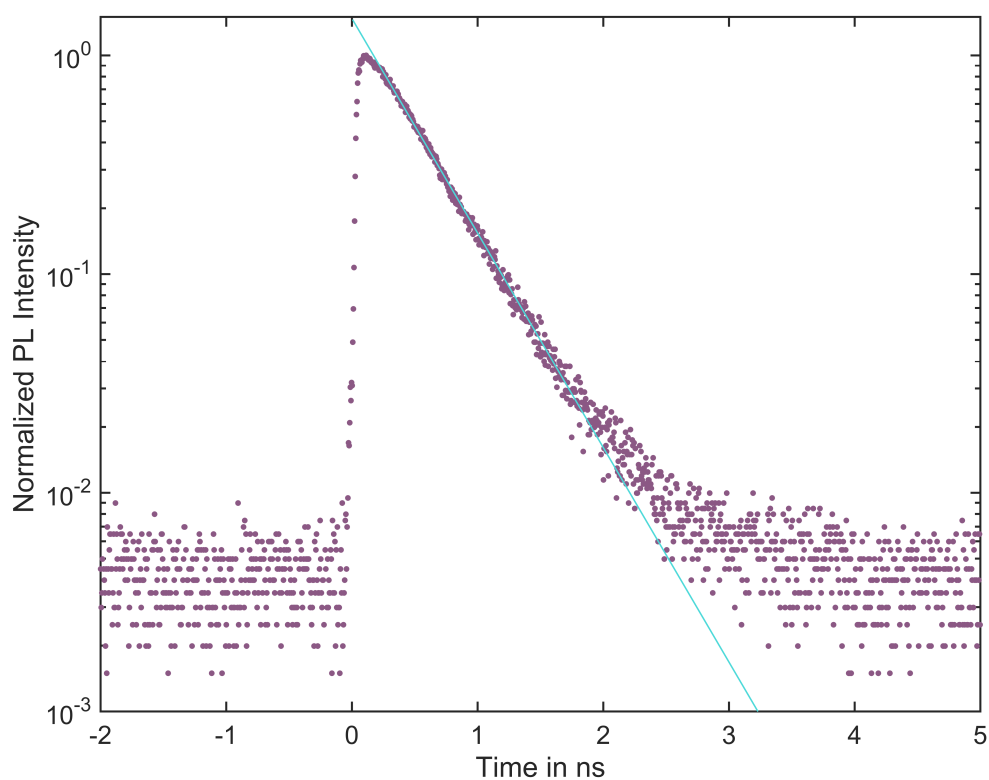


Figure 4.5: Normalized time-resolved PL dynamics of ***c*-P6·T6** measured using TCSPC (purple) with excitation at 500 nm and emission was detected at 910 nm. The lifetime was extracted by fitting a single exponential function to the PL dynamics (cyan).

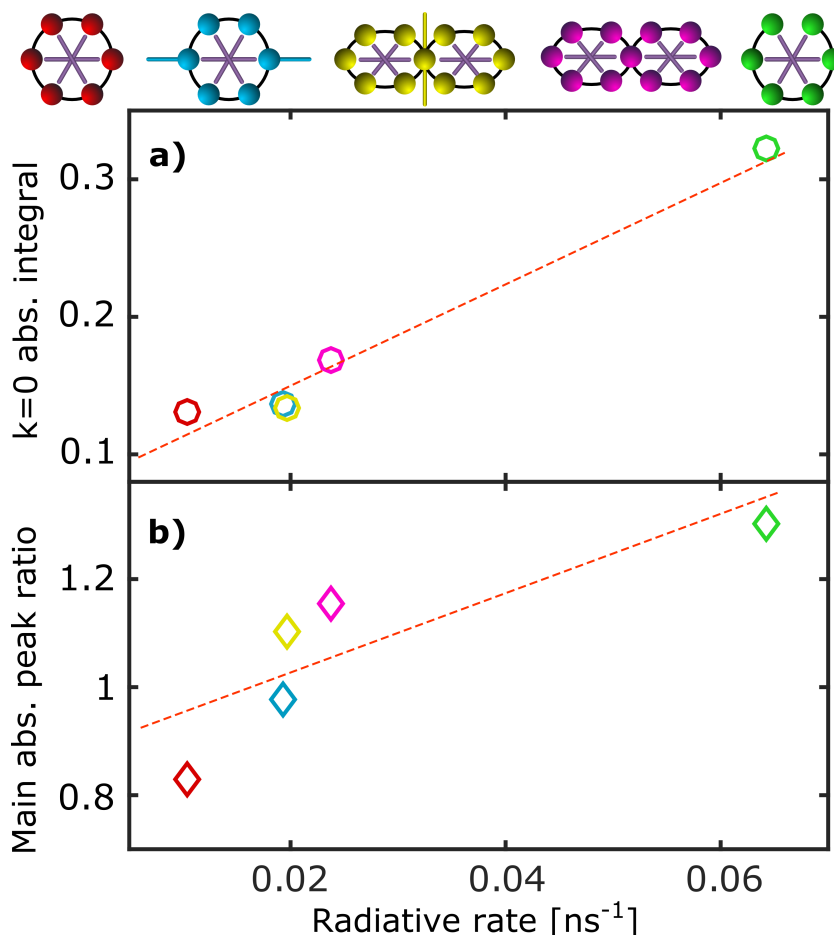


Figure 4.6: Analysis of the extinction coefficient spectra for the nanoring complexes $c\text{-P6}\cdot\text{T6}$ (red), $c\text{-P6}_x\cdot\text{T6}$ (blue), $s_{Et}\text{-P11}\cdot(\text{T6})_2$ (yellow), $s\text{-P11}\cdot(\text{T6})_2$ (magenta) and $l\text{-P6}\cdot\text{T6}$ (green) in relation to their radiative emission rates. a) Spectrally integrated extinction coefficient of the emerging low-energy ($k=0$) peak, determined by integration of the spectra shown in Figure 4.3 up to a full-width-half-maximum below the first main peak, and given in relation to the integral over the full spectrum of the Q_x -band. b) Intensity ratio of the first two peaks in the main ($k=\pm 1$) peak series of the extinction coefficient spectrum. Each data point corresponds to a ring complex with the colours depicted matching that of the icons above the graphs representing the structure. Dashed lines are guides to the eye highlighting the strong correlation between the parameters, but do not imply a particular functional dependence.

state (indicated by red arrows in Figure 4.3) the extinction coefficient spectrum was integrated over the low-energy wing up to a full-width-half-maximum below the first main peak associated with the $k = \pm 1$ state (marked with yellow arrows). This integration limit ensures that the contribution from the allowed $k = \pm 1$ state is largely excluded from the integration result. To facilitate accurate comparison between the five compounds, the above calculated integral is expressed as a fraction of the extinction coefficient spectrum integral over the entire Q_x -band. Figure 4.6a shows excellent correlation between the emergence of a partially allowed $k = 0$ feature in absorption, and an enhancement of the radiative emission rate. In particular, the lowest state is most strongly suppressed in the most highly symmetric **c-P6·T6**, and most strongly enhanced in the ring with broken π -conjugation, with the other three compounds falling in between, as would be expected. We note however that even the highly symmetric **c-P6·T6** appears to feature some small transition moment to the $k = 0$ state. This could be partly because Herzberg-Teller intensity borrowing can augment the absorption of Frank-Condon forbidden states (as in benzene [12]) but also partly because some disorder may exist through interaction with the solvent environment. In addition, Figure 4.6b demonstrates clear correlation between the intensity ratio of the strongest two peaks in absorption (green and yellow arrows in Figure 4.3) and the radiative rate of the molecules. As discussed above, these intensity ratios are therefore most likely caused by underlying higher-energy replica of the $k=0$ state overlapping with the $k=\pm 1$ peaks, and therefore derive from similar origins and are subject to similar changes as the symmetry of the ring-like molecules is lowered.

4.3.3 Photoluminescence polarization anisotropy

Apart from a transfer of oscillator strength to the lowest ($k=0$) excitonic state, a lowering of the ring symmetry can also lead to a lifting of the degeneracy of the allowed $k=\pm 1$ states [21, 25]. Since the two $k=\pm 1$ states carry orthogonal polarisations, such effects may conceivably be detected in polarization anisotropy spectroscopy, as described in details in Chapter 3. We have measured the ultrafast photoluminescence anisotropy dynamics for these systems, which reflect the polarization memory loss of the compounds following excitation with a polarized light pulse [45], the results for ***l*-P6·T6** are shown as an example in Figure 4.7a). The samples were excited using a range of wavelengths between 740 nm (1.68 eV) and 830 nm (1.49 eV) through the Q_x -band in the region of the three main peaks in the absorption spectrum to allow clear separation from the detected emission. The PL anisotropy γ was evaluated from the PL intensity components polarized parallel ($I_{||}$) and perpendicular ($I_{\perp}$) to the excitation polarization, according to $\gamma=(I_{||} - I_{\perp})/(I_{||} + 2I_{\perp})$ [5]. As reported in previous studies [33, 47], the PL anisotropy assumes a particular value within the time-resolution (270 fs) of the system, indicating ultrafast exciton delocalization and rapid relaxation in these systems (see Figure 4.7). This initial PL anisotropy value remains constant over the next tens of picoseconds as this timescale is too short for molecular reorientation in solution that can cause additional polarization memory loss [6]. To obtain a representative value for the PL anisotropy as a function of excitation wavelength, eight PL intensity values were independently recorded at 5 ps delay for each polarization direction, averaged and the equation above was applied. Figure 4.8 shows the value of this initial polarization anisotropy γ as a function of the excitation wavelength, for ***c*-P6·T6**, ***c*-P6_x·T6**

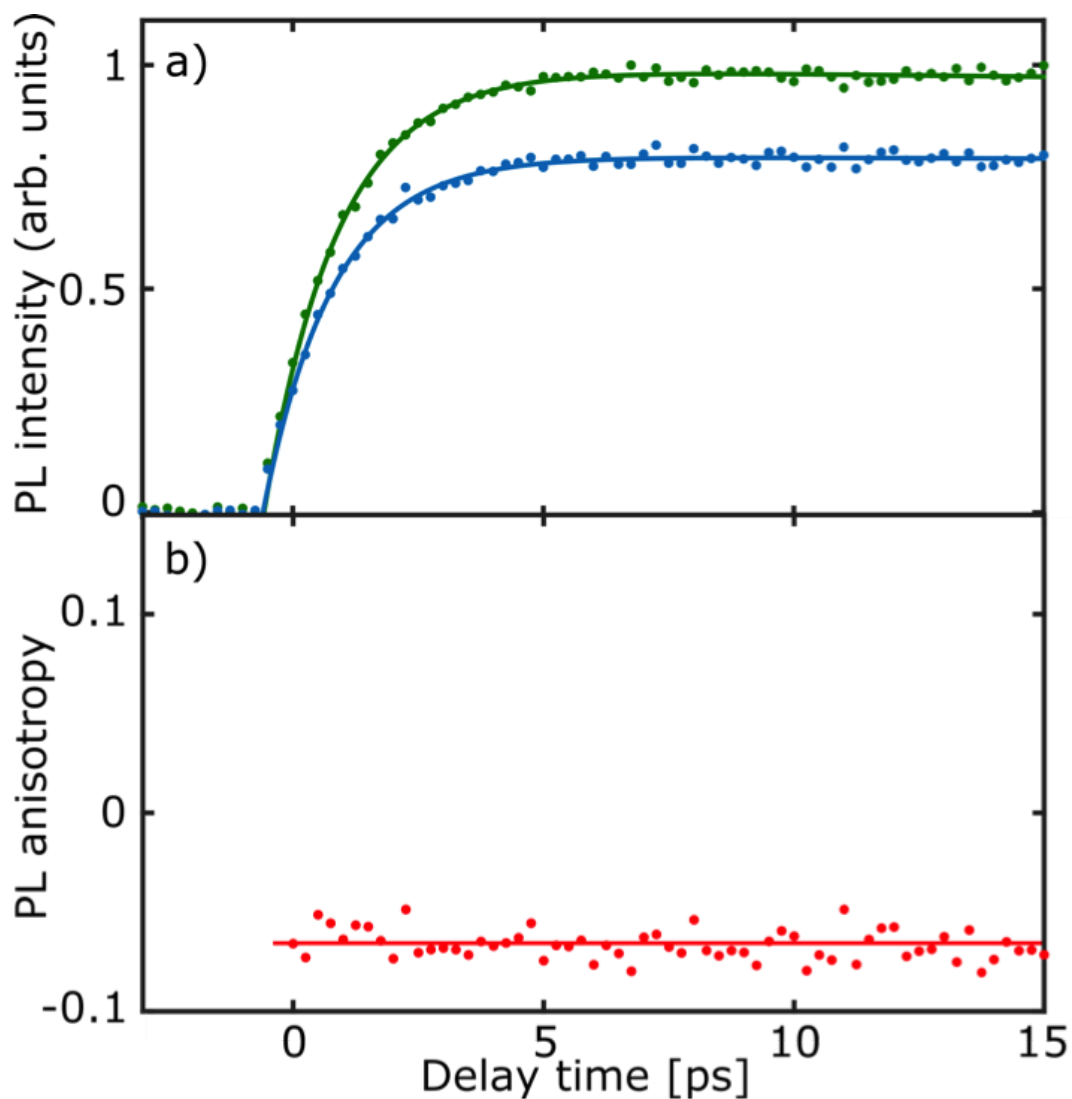


Figure 4.7: a) Time-resolved PL dynamics of ***l*-P6-T6**. The sample was excited by 810 nm pulses polarized either parallel (blue dots) or perpendicular (green dots) to the detection polarization and the PL at 915 nm was detected. b) PL anisotropy dynamics of ***l*-P6-T6**. The lines serve as a guide to the eye.

and ***l*-P6·T6**. Corresponding studies for the fused rings were not conducted since γ is very close to zero for these systems because of exciton delocalization across the orthogonal ring planes, as reported previously [8], and therefore any additional depolarization effects would be hard to discern. Figure 4.8 reveals that the initial PL anisotropy values for ***c*-P6·T6** and ***c*-P6_x·T6** are unaffected by the choice of excitation wavelengths and assume values close to 0.1. Such dynamics are expected for complete polarization memory loss in the 2D ring plane [24] which can be induced by absorption into the two degenerate (or near-degenerate) $k=\pm 1$ states with orthogonal polarization in the ring plane, that will be followed by exciton relaxation into the $k=0$ state [11, 33]. For ***l*-P6·T6**, on the other hand, a strikingly different dependence of γ on excitation wavelength is observed (Figure 4.8). For excitation at 740 nm, the anisotropy is 0.1, similar to the value displayed by the two more symmetric nanoring compounds. However, as the excitation wavelength increases, γ decreases and reaches -0.1 at 830 nm. A negative anisotropy value suggests that a significant fraction of the emitting dipole moments are perpendicularly polarized to the absorbing transitions [27, 30, 45]. We can rule out unintentional excitation of the Q_y state of the porphyrin monomers (polarized perpendicular to the ring plane) as a cause, because the excitation energies employed here are substantially lower than the transition energy of the Q_y state visible in absorption (2.1 eV).

4.3.4 Energy level model

We propose that the polarization switching observed in ***l*-P6·T6** is caused by the lifting of the degeneracy of the $k=\pm 1$ levels in this system, for which the symmetry is substantially lowered as a result of the clear break in conjugation.

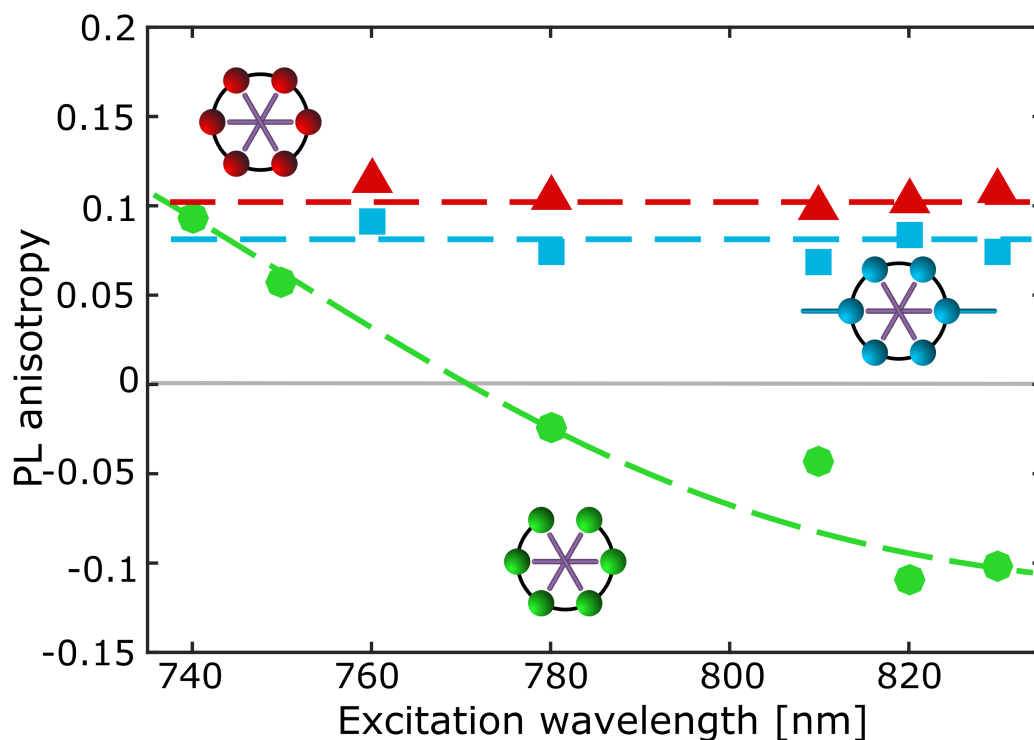


Figure 4.8: Initial value of the PL anisotropy following excitation with a short (100 fs) light pulse for *c*-P6·T6 (red), *c*-P6_x·T6 (blue) and *l*-P6·T6 (green). Dashed lines serve as a guide to the eye. Anisotropy values have been calculated using the PL intensity polarized parallel and orthogonal to the excitation pulse, averaged over the first 5 ps following excitation, during which these intensities do not vary.

Figure 4.9 illustrates the mechanism which explains our experimental observations. Highly rotationally symmetric systems such as **c-P6·T6** absorb light through the degenerate $k = \pm 1$ states that are orthogonally polarized. Following an ultrafast relaxation to the $k = 0$ state, Franck-Condon forbidden emission from this state takes place via weak Herzberg-Teller coupling. As there is no preferred excitation polarization direction nor a net emission dipole moment in the nanoring plane, the polarization memory is completely lost in this 2D plane resulting in $\gamma = 0.1$. However, for **l-P6·T6** the lowered symmetry lifts the degeneracy of the $k = \pm 1$ states, and results in the creation of new higher-lying states (labelled as $k = 1, 2 \dots$ in Figure 4.9) with transition dipoles of well-defined orientation with respect to the symmetry plane. These changes are accompanied by a strong recovery of Frank-Condon allowed transitions from the lowest excited state, as discussed above and examined in natural light-harvesting complexes [21, 25, 28]. As indicated in Figure 4.9 this scenario creates a well-defined relation between the orientation of the dipole moment associated with the lowest ($k = 0$) state and those of the non-degenerate higher-lying states, with some combinations being parallel, and others orthogonal. In particular, the conjugation break in **l-P6·T6** causes the lowest ($k = 0$) state wavefunction to have a lobe (probability density maximum) at the ring side opposite to the break, leading to a net dipole moment in the x -direction (here we take the y -direction to lie within the mirror-symmetry plane). Such deviation from a fully delocalized (i.e. no nodes) wavefunction in the $k = 0$ state of the highly symmetric **c-P6·T6** thus transfers oscillator strength to the ground state of **l-P6·T6**, in accordance with the observed recovery in radiative rate. The higher-lying $k = 1$ state of **l-P6·T6** has some analogy with the degenerate $k = 1$ state of the symmetric **c-P6·T6** as its nodes fall onto the symmetry plane, and it is

hence less perturbed by the conjugation gap than the orthogonal $k = -1$ state. Therefore, the observed polarization switch in ***l*-P6·T6** can be understood in terms of an initial excitation into non-degenerate higher-lying states, such as the $k = 1$ state with polarization along the y -direction, followed by relaxation into the $k = 0$ state that is associated with a dipole moment in the orthogonal x -direction. Strictly speaking, orthogonal absorbing and emitting transition dipole moments should yield $\gamma = -0.2$ whereas collinear dipole moments result in $\gamma = 0.4$ for randomly oriented molecules in solution [45]. However, contributions from higher-lying ($k \geq 1$) states and their vibrational progressions are broadly overlapping (clearly separate features are not discernable in the absorption of ***l*-P6·T6** – see Figure 4.3). Hence in reality, anisotropy values between -0.1 and 0.1 are observed for the range over which the excitation wavelength is varied (Figure 4.8). However, the strong observed variation of polarization anisotropy from negative to positive values as the excitation energy is tuned through the higher-lying excitation band provides clear evidence that severe symmetry lowering in such systems leads to a lifting of the degeneracy of the ring-like $k=\pm 1$ states, creating a series of states with well-defined transition dipole moments.

4.4 Conclusion

In conclusion, π -conjugated six-porphyrin nanorings with various distortions to the cyclic structures have been investigated to explore the influence of symmetry lowering on their photophysical properties. We have demonstrated that as symmetry distortions increase in severity along the series of structures, oscillator strength is transferred to the transition into the lowest ($k=0$) state, which is

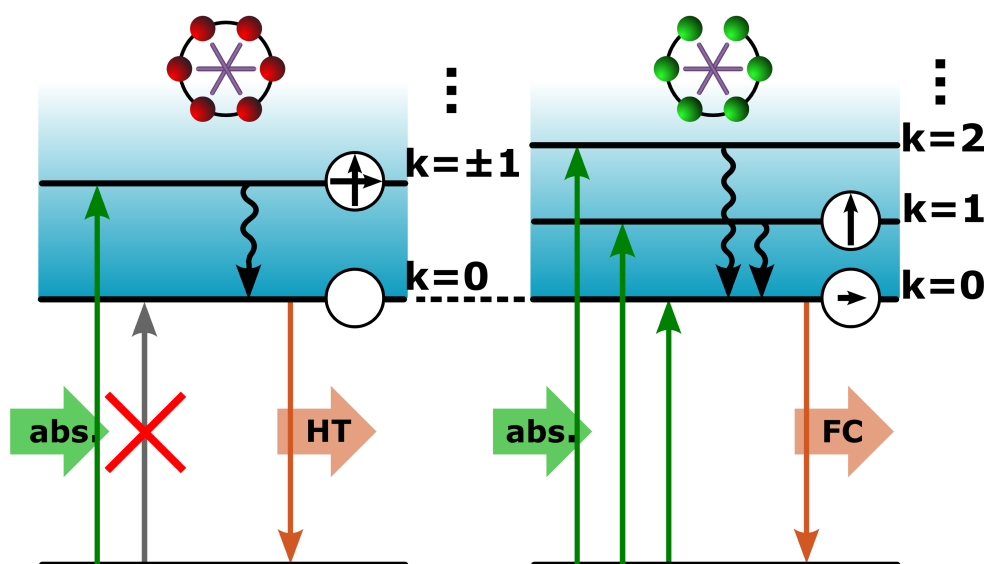


Figure 4.9: Schematic diagram illustrating the splitting of the $k=\pm 1$ level leading to the observed trend in PL anisotropy for ***l*-P6·T6**. For the highly symmetric ***c*-P6·T6**, Herzberg-Teller effects activate transitions from the $k=0$ state to the ground state via vibrational levels (not shown) while for ***l*-P6·T6** with broken π -conjugation, such transition may become directly Frank-Condon allowed.

Franck-Condon forbidden in the fully 6-fold rotationally symmetric rings. The associated increases in oscillator strength were shown to correlate with gradually emerging $k=0$ absorption features at the lower-energy end of the absorption spectra, and changes in intensity ratio of higher-lying overlapping absorption peaks. Thus symmetry plays a vital role in influencing and correlating absorptive and emissive properties of ring-like molecules, which we have been able to capture quantitatively. Furthermore, we have revealed through time-resolved photoluminescence anisotropy probes, that strong symmetry breaking, induced e.g. through full breaks in conjugation, lifts the degeneracy of the $k=\pm 1$ states found in highly symmetric ring assemblies, instead creating a series of states with well-defined transition dipole moments. We note that these findings have direct relevance to ring like complexes found in natural light harvesting systems, which have a rich diversity of geometrical structures. Here, chromophores can be arranged in circular, elliptically deformed or array arrangements, exhibit a gap or form dimeric structures. However, comparable investigations of the impact of structural symmetries on photophysical properties is challenging in such biological systems, as the chromophores are held loosely together and interact significantly with their environment. Our study therefore highlights the outstanding potential of using synthetic biomimetic porphyrin nanorings as model systems to investigate the effect of symmetry and geometric arrangement on the fundamental nature of the light-harvesting states.

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Chapter 5

Structure-Directed Exciton Dynamics in Templated Molecular Nanorings

5.1 Introduction

The rotational symmetry breaking effect has been investigated extensively in Chapter 4 on rings consisting of six porphyrin units, which exhibits a rather planar conformation due to its small size. In a recent advance, Vernier effects were exploited to direct synthesis of large porphyrin nanorings by using multiple smaller templates [20]. Vernier templating not only proves to be a powerful new strategy to construct large nanorings, but also renders shape-persistent structures with diverse geometries [8]. Exciton delocalization and emission depolarization processes are expected to be strongly affected by the change of geometry in the structures [36]. Conformational effects on photophysical properties have been examined extensively using both experimental [2, 17] and theoretical methods [12] on a variety of conjugated polymer systems, such as PPV [9, 15], P3HT [1, 29] and dendrimers [26]. In particular, effects on polarization memory loss [8, 9] and energy transfer [7, 22] have attracted much attention.

In this chapter, the question of how deliberate distortion of a molecular

CHAPTER 5. STRUCTURE-DIRECTED EXCITON DYNAMICS IN TEMPLATED MOLECULAR NANORINGS

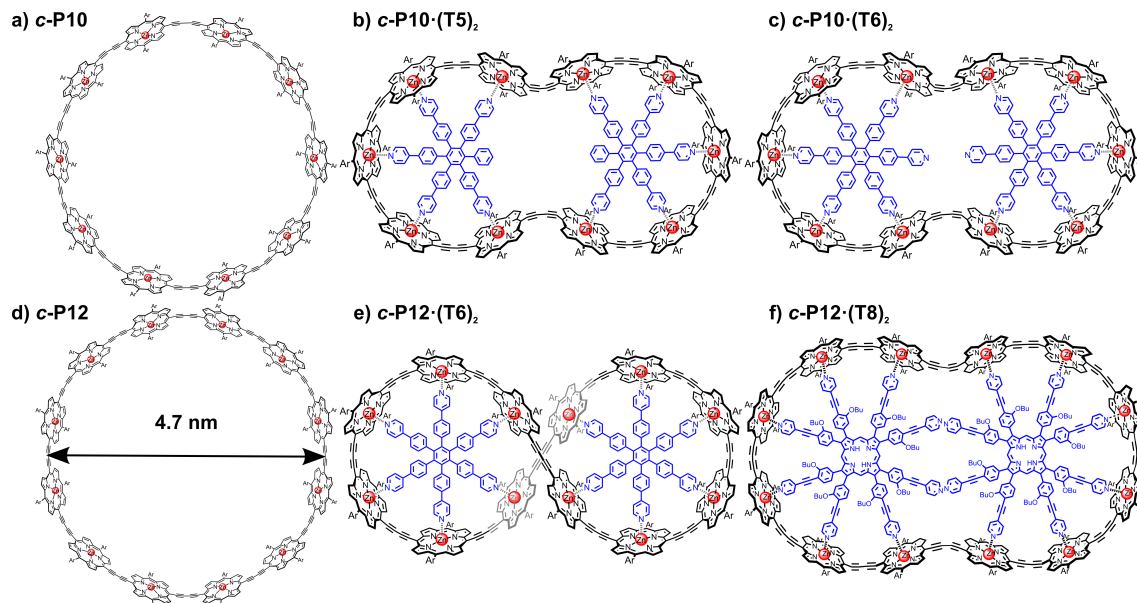


Figure 5.1: Chemical structures of the budadiyne-linked zinc porphyrin nanoring assemblies under investigation: (a) **c-P10**, (b) **c-P10·(T5)₂**, (c) **c-P10·(T6)₂**, (d) **c-P12**, (e) **c-P12·(T6)₂**, (f) **c-P12·(T8)₂**. Templates are indicated in blue, zinc atoms are denoted in red. All compounds have octyloxy side chains (Ar) which are omitted in the graphic for clarity.

nanoring influences the emissive properties of a molecule following excitation is addressed. We examine to what extent out-of-plane distortions of a particular nanoring topology affect the polarization memory of the transition dipole moment and whether such effects can be predicted by molecular mechanics simulations. In search for answers to these questions, a range of conjugated zinc porphyrin nanorings of similar size but different conformations are examined using ultrafast time-resolved spectroscopy and the results are compared to molecular dynamics simulations of ring structures.

5.2 Samples

The synthesis and characterisation of the nanoring templates and complexes were carried out by Dmitry Kondratuk from Anderson group in Organic Chemistry Department, University of Oxford. More details can be found in Ref. [13, 14, 20, 23, 27]. Figure 5.1 introduces the porphyrin nanorings under investigation, which comprise porphyrin units joined by butadiyne bridges. Through insertion of templates binding to the porphyrin units, a range of different molecular shapes are created with spatial extent on the nanometer scale. The nanorings without templates **c-P10** and **c-P12** only differ slightly in ring diameter and have almost identical conformation and absorption/emission spectra (see Figure 5.2). Both samples are prepared in toluene/1% pyridine solution to prevent aggregation. Templating changes the geometry considerably by rigidifying the nanoring into two smaller porphyrin “loops” and introducing significant out-of-plane distortions, such as bending and twisting. Molecular mechanics simulations (*vide infra*) show that **c-P10**·(**T5**)₂ and **c-P10**·(**T6**)₂ have similar structures, the main difference being in the shape of templates as shown in Figure 5.1(b)-(c). The angle between the mean template planes in **c-P10**·(**T5**)₂ is calculated to be $\theta = 72^\circ$. The twist in **c-P12**·(**T6**)₂ is even more pronounced and has the form of a figure-of-eight, with $\theta = 28^\circ$, as shown from crystal structure data in a previous study [20]. On the other hand, **c-P12**·(**T8**)₂ is planar and not expected to exhibit any substantial twist. These conformations have been deduced from molecular mechanics and dynamics simulation using *HyperChem*, which will be described later in detail. Samples with template complexes were prepared in pure toluene solution, as the templates would otherwise be displaced by competition with pyridine.

5.3 Results and discussion

5.3.1 Absorption and emission spectra

In order to gain basic insight about the photophysical and electronic properties of the nanorings, steady state absorption and emission spectroscopy was performed. The resulting spectra are compared in Figure 5.2. Zinc porphyrin monomers exhibit a strong $S_0 \rightarrow S_2$ transition at ~ 400 nm (Soret band) and a weaker $S_0 \rightarrow S_1$ transition at ~ 550 nm (Q-band) [5]. For the nanorings, π -conjugation extends through the butadiyne-bridges, lifting the degeneracy in both the lowest-energy Q band and Soret band of the porphyrin monomers. Transitions polarized parallel (Q_x) and perpendicular (Q_y) to the acetylenic backbone can therefore be observed (see Fig. 5.2). When the nanorings bind to the templates, Q_x is observed to be red-shifted with respect to the Soret band, while Q_y shows no considerable change (Figure 5.2(c)-(f)). In addition, a significant sharpening of features in both emission and absorption spectra can be observed for the templated complexes. Templates bring rigidity to the system; the molecules are less prone to inter-porphyrin torsional motions and the molecular backbone may be planarized [8], resulting in the observed red shift of Q_x . The four templated nanorings hence exhibit similar spectral features.

5.3.2 Photoluminescence intensity and polarization anisotropy dynamics

PL upconversion under ambient condition was performed to reveal the extent of emission depolarization following photoexcitation with a linearly polarized laser

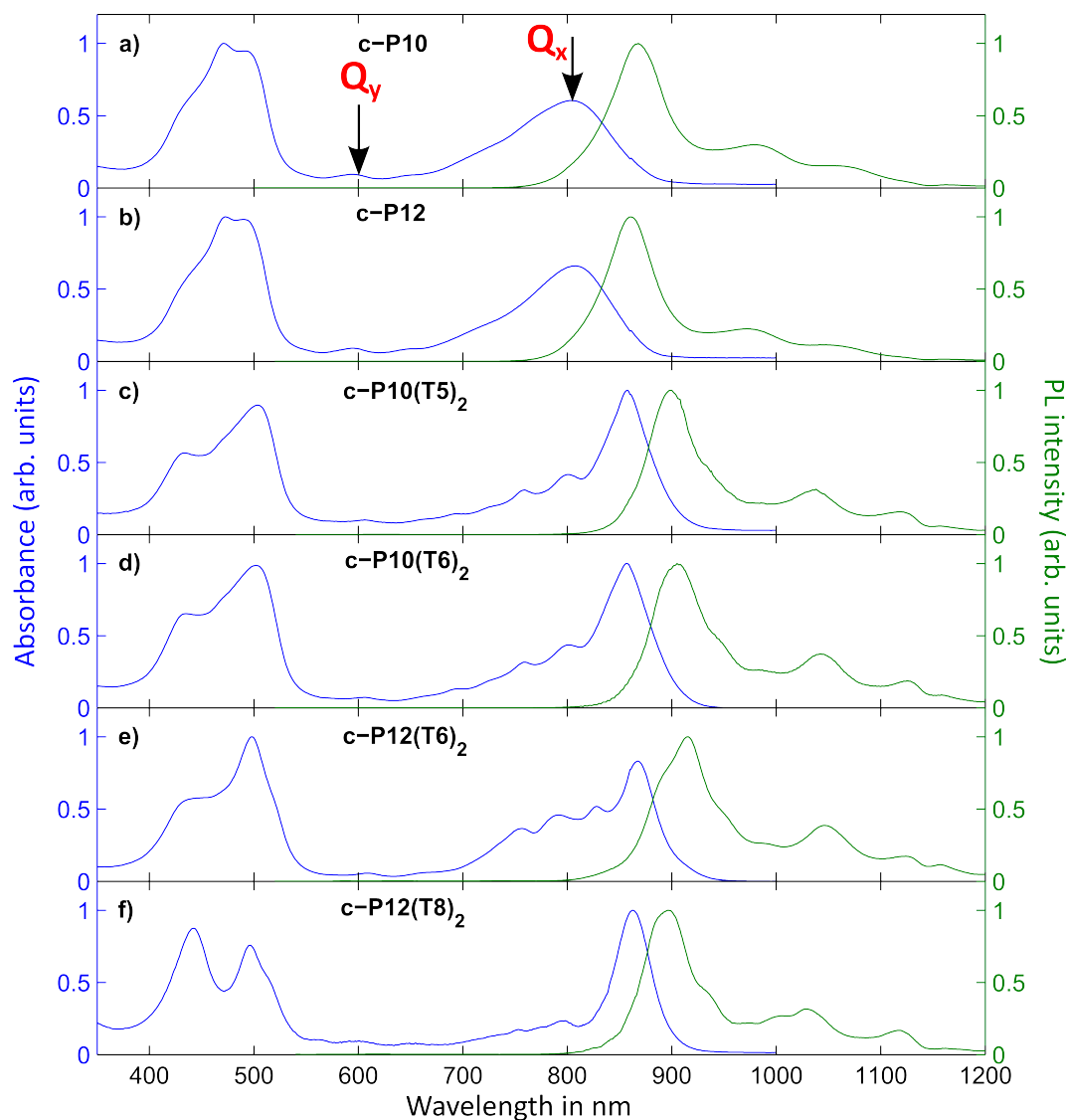


Figure 5.2: Normalized steady-state absorption (blue lines) and time-integrated photoluminescence (green lines) spectra at 295 K for (a) **c-P10** (b) **c-P12** in toluene/1% pyridine and (c) **c-P10·(T5)₂**, (d) **c-P10·(T6)₂**, (e) **c-P12·(T6)₂** and (f) **c-P12·(T8)₂** in toluene solution. The emission spectra were recorded after excitation at 520 nm (Soret band). The Q_x and Q_y transitions are indicated by red arrows.

pulse. The templated nanorings were excited at 820 nm and the rings without templates at 760 nm, with emission being monitored at the peak wavelength for each nanoring. To avoid PL quenching via exciton-exciton annihilation [11], the excitation fluence was kept low ($0.08 \mu\text{Jcm}^{-2}$). Figure 5.3 depicts the time-dependent PL of **c-P12** and **c-P12·(T6)₂** over the first 15 ps after excitation with a pulse polarized either parallel ($I_{\parallel}$) or perpendicular ($I_{\perp}$) to the polarization of the detected emission. For **c-P12**, the PL intensity remains constant over the experiment time window after the onset of the signal at $t = 0$, whereas **c-P12·(T6)₂** shows a slight decaying trend, in agreement with the shorter lifetime obtained using TCSPC (shown in Table 5.1).

Selective excitation near the Q_x band of a rigid butadiyne-bridged porphyrin oligomer is expected to result in an excited state with a transition dipole moment along the molecular backbone [8]. In the absence of any depolarization mechanisms, emission will occur in the same polarization direction as the absorption, and for a randomly oriented distribution of such molecules in solution, an initial anisotropy value of 0.4 is expected [21, 34]. However, for a complete depolarization of the transition dipole moment within the 2D plane, as may be the case for the rings without templates, a PL anisotropy value of 0.1 should be found [21, 34]. Other effects, such as out-of-plane distortion, could further lower the value towards zero [34].

Figure 5.4 shows the temporal dependence of the anisotropy $\gamma(t)$ for a number of the investigated nanoring topologies. For all nanoring topologies investigated, the anisotropy is found to be static over the first 20 ps after excitation, within the temporal resolution of 270 fs. These dynamics were recorded for excitation near the middle of the Q_x band. It is possible that excitation near the band edge (~ 900 nm) may lead to creation of localized states that have

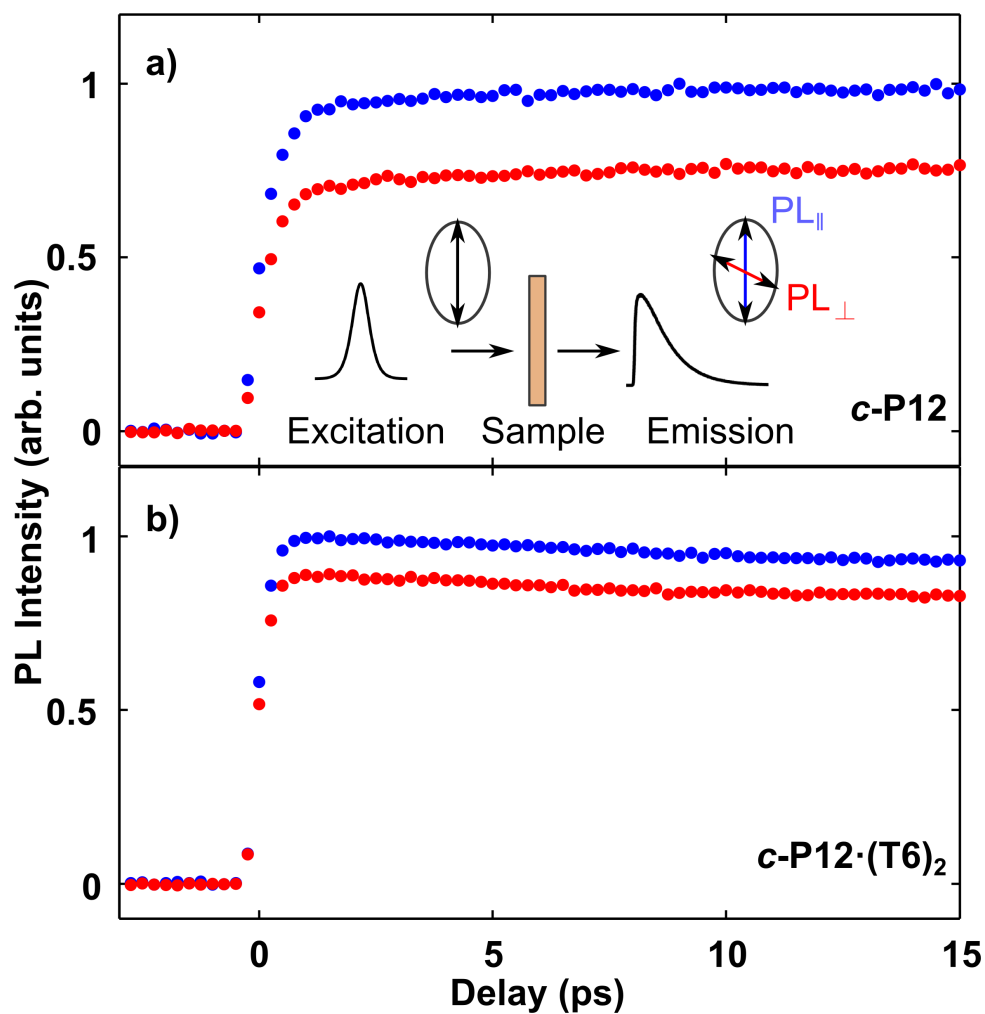


Figure 5.3: Time-resolved PL dynamics of (a) **c-P12** in toluene/1% pyridine (concentration 0.2 mM) and (b) **c-P12·(T6)₂** in toluene solution (concentration 0.4 mM). Samples were excited by excitation pulse polarized either parallel (blue dots) or perpendicular (red dots) to the detection polarization, as illustrated in the inset.

higher anisotropy and/or slower PL depolarization [36], however we are unable to probe such effects here. These transients therefore indicate that while an initial ultrafast depolarization process may occur within the first hundred femtoseconds after excitation, slower effects such as molecular reorientation are absent over these time scales [8]. The values extracted in this way for the initial PL anisotropy γ are listed in Table 5.1 for all molecules investigated. These values have been independently determined multiple times at 5 ps after excitation, and an overall accuracy of ± 0.02 was achieved. The untemplated rings **c-P10** and **c-P12** display anisotropy values around 0.1, as expected for a complete memory loss in the 2D plane and in the absence of significant out-of-plane distortions of the rings [36]. For all templated rings on the other hand, a significant reduction of γ below the value of 0.1 was observed.

These results suggest that the excitation can access any segment on the rings, both templated and untemplated, within the first few hundred femtoseconds after excitation. Such dynamics may be accounted for by either of two different mechanisms. In the first possible scenario, excitons are initially fully delocalized over the entire ring in the absorbing state [8, 33], but may subsequently self-localize following geometric relaxation [3, 4, 6, 30, 31, 32]. In the second scenario, the absorbing state is only delocalized over a subset of monomers, but excitons are subject to ultrafast energy migration along the ring within hundred of femtoseconds and thus beyond the time-resolution of the upconversion system, similar to observations reported in LH2 antenna complexes [19]. It has recently been shown that as the size of untemplated porphyrin nanorings increases, a shift from the former to the latter scenario may gradually occur [28, 36].

We find that the measured anisotropy values below 0.1 for the templated

nanorings can be explained by the presence of significant out-of-plane distortions. Molecular dynamics simulations discussed in detail below show that the measured γ is closer to zero for nanoring topologies with larger distortions. As illustrated in Figure 5.4, the rigid planar **c-P12**·(**T8**)₂ has an appreciably higher anisotropy ($\gamma = 0.07$) than the other three templated nanorings which are found to display significant out-of-plane distortions.

5.3.3 Molecular dynamics simulation

To quantitatively examine the distortions present in the different nanoring topologies, molecular dynamics simulations were conducted for the templated nanorings with side chains using *HyperChem*. The starting configurations were energy-minimized geometries (at 0 K) calculated using a modified form of *HyperChem*’s MM+ forcefield. Additional bond stretch, angle bend and torsion terms were added to describe metalloporphyrins [24, 25], alkynes [10] and butadiynes [16].

Molecular dynamics simulations were conducted assuming ambient vacuum at two constant temperature, 300 K and 600 K. Simulations ran in time steps of 1 fs for a time window of 500 ps, which gave a representative average. Since the templates are fairly rigid, it can be assumed that distortions mainly originate from motions between two template planes where two fundamental motions can be distinguished: twisting and bending, as illustrated in Figure 5.5. The corresponding angles α and β are introduced in the figure to quantitatively describe the deviation of the structure from a planar conformation. All starting configurations hold $\beta(0) \sim 0^\circ$. The distortion angles of the conformations in the 500 ps simulation window at 300 K are plotted as a histogram and the results

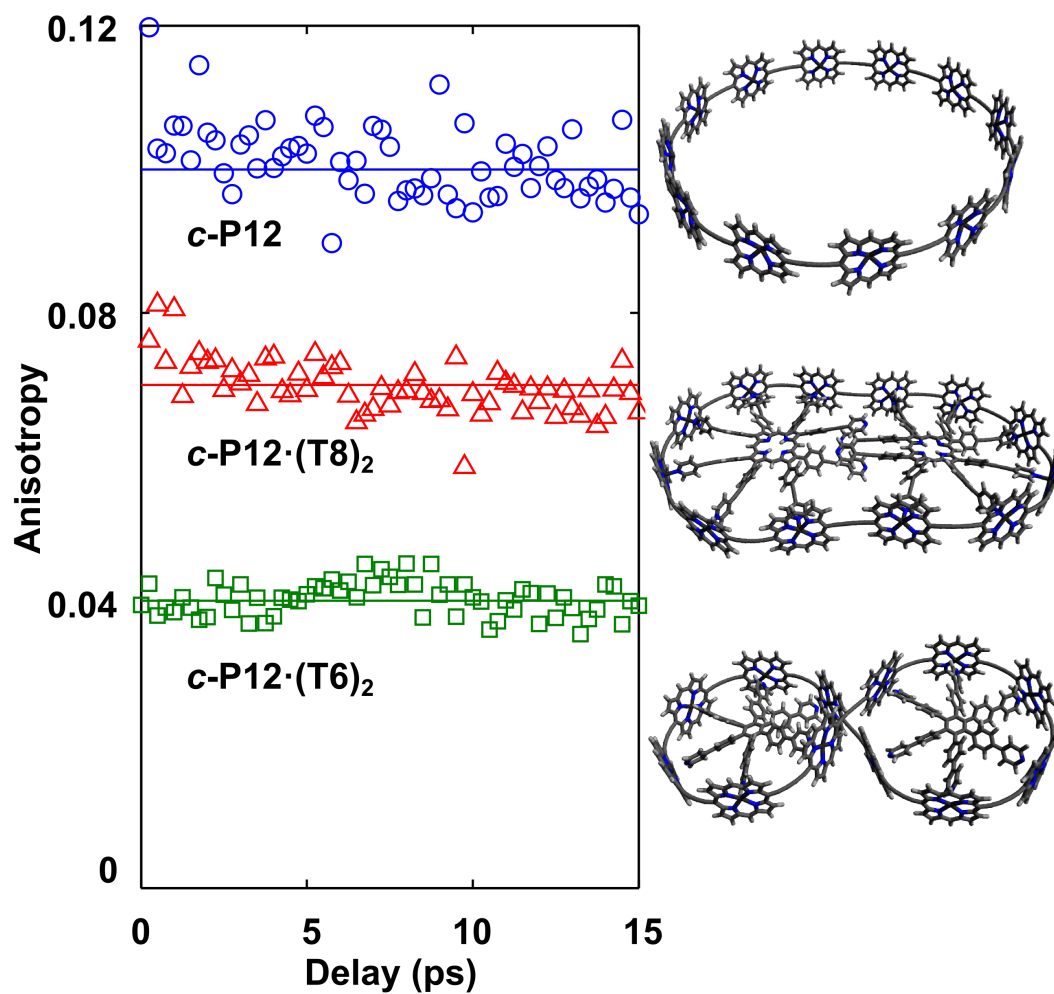


Figure 5.4: PL polarization anisotropy as a function of time after excitation at 820 nm for **c-P12** (blue circles, detection at 872 nm), **c-P12·(T8)₂** (red triangles, detection at 904 nm) and **c-P12·(T6)₂** (green squares, detection at 914 nm). The structures shown on the right are energy minimized geometries calculated using a modified form of MM+ forcefield in *HyperChem*. Side chains are not shown in the diagram but were included in the simulations.

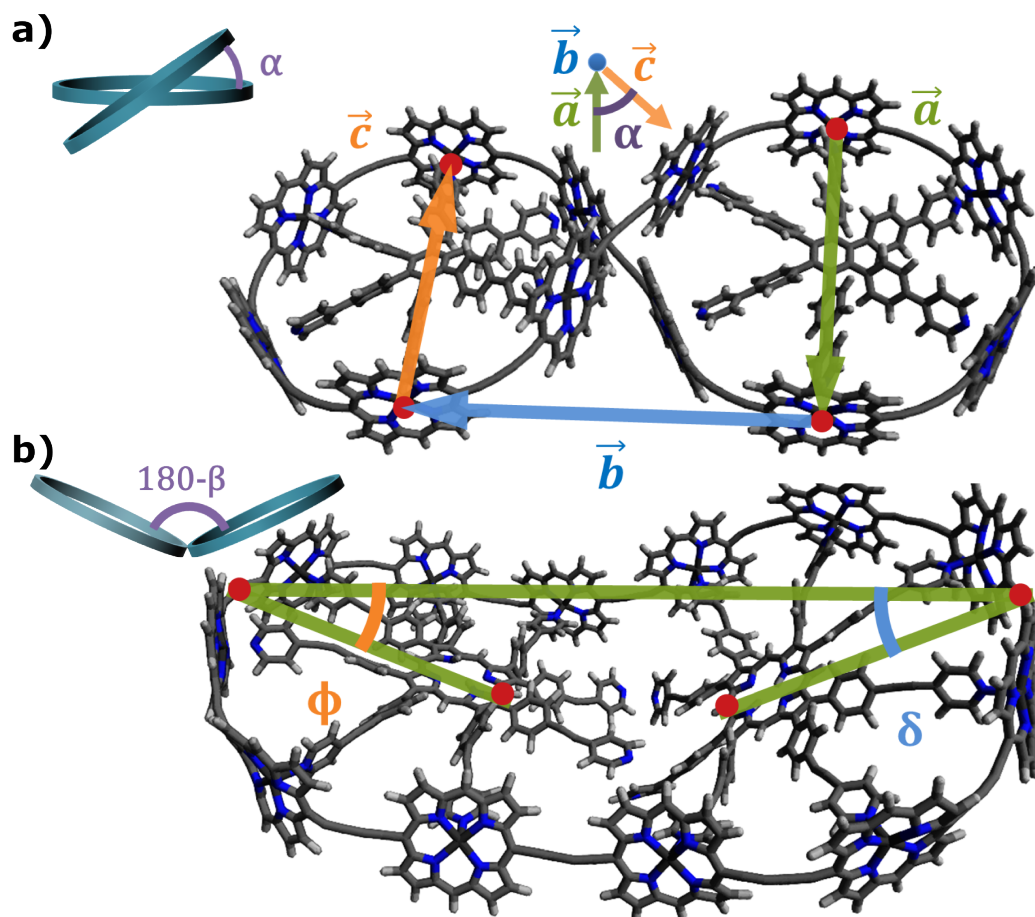


Figure 5.5: Definition of the distortion angles. (a) The twisting angle α between two template planes is defined using **c-P12·(T6)₂** as an example. Four atoms on the porphyrin ring (red) are chosen to form three vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$, with $\vec{a}$ and $\vec{c}$ lying approximately parallel to each other when the molecule does not exhibit any twist. α is the torsional angle defined by the four atoms and is the angle between the planes formed by $\vec{a}$, $\vec{b}$ and $\vec{b}$, $\vec{c}$. α represents the twisting angle from a planar position. (b) The bending angle β is illustrated using **c-P12·(T8)₂** as an example. Four atoms (red) are chosen as shown. Two angles ϕ and δ are calculated, where $\beta = \phi + \delta$ describes the deviation from a planar position. Simulations were carried out with octyloxy side chains, which are omitted in the diagram for clarity.

are summarized in Figure 5.6, with the root-mean-square (RMS) values listed in Table 5.1. Due to the nature of the simulations and the ambiguity in defining the distortion angles, these results only provide a good estimate of the overall trend. It is remarkable that compared to the bending angle β , the spread in the twisting angle α is generally much narrower and the RMS remains closer to the energetically optimized values, which indicates that in the molecular dynamics, thermal energy has a greater influence on the bending motion than the twisting motion. **c-P10**·(**T5**)₂ and **c-P10**·(**T6**)₂ show large out-of-plane distortions in twisting (around 65°) as well as bending motion at 300 K, consistent with the experimentally observed low PL anisotropy values of $\gamma = 0.05$. **c-P12**·(**T6**)₂ and **c-P12**·(**T8**)₂ both show similar distributions in α around $\sim 25^\circ$, much lower than for the templated **c-P10** topologies in comparison and in good agreement with structures obtained from crystallographic investigations [20]. These simulations explain the only slight decrease in γ from 0.1 to 0.07 experimentally observed for **c-P12**·(**T8**)₂. However, **c-P12**·(**T6**)₂ has a much lower PL anisotropy, which can be accounted for by its large bending angle similar to **c-P10**·(**T5**)₂ and **c-P10**·(**T6**)₂. In contrast, **c-P12**·(**T8**)₂ remains rigid: β is narrowly distributed around the planar starting conformation. Simulation results at 600 K are summarized in Figure 5.7(a)-(d), with the root-mean-square (RMS) values listed in Table 5.1. A broader angle spread in the twisting angle α is observed compared to the simulation results at 300 K, commensurate with what would be expected from the additional energy available.

In summary, the molecular dynamics simulations reveal that the templates provide an effective means to control the nanoring structure, as can be seen in the narrow distribution in Figure 5.6 as well as in the close resemblance between RMS values at 300 K and the energetically optimized values at 0 K for

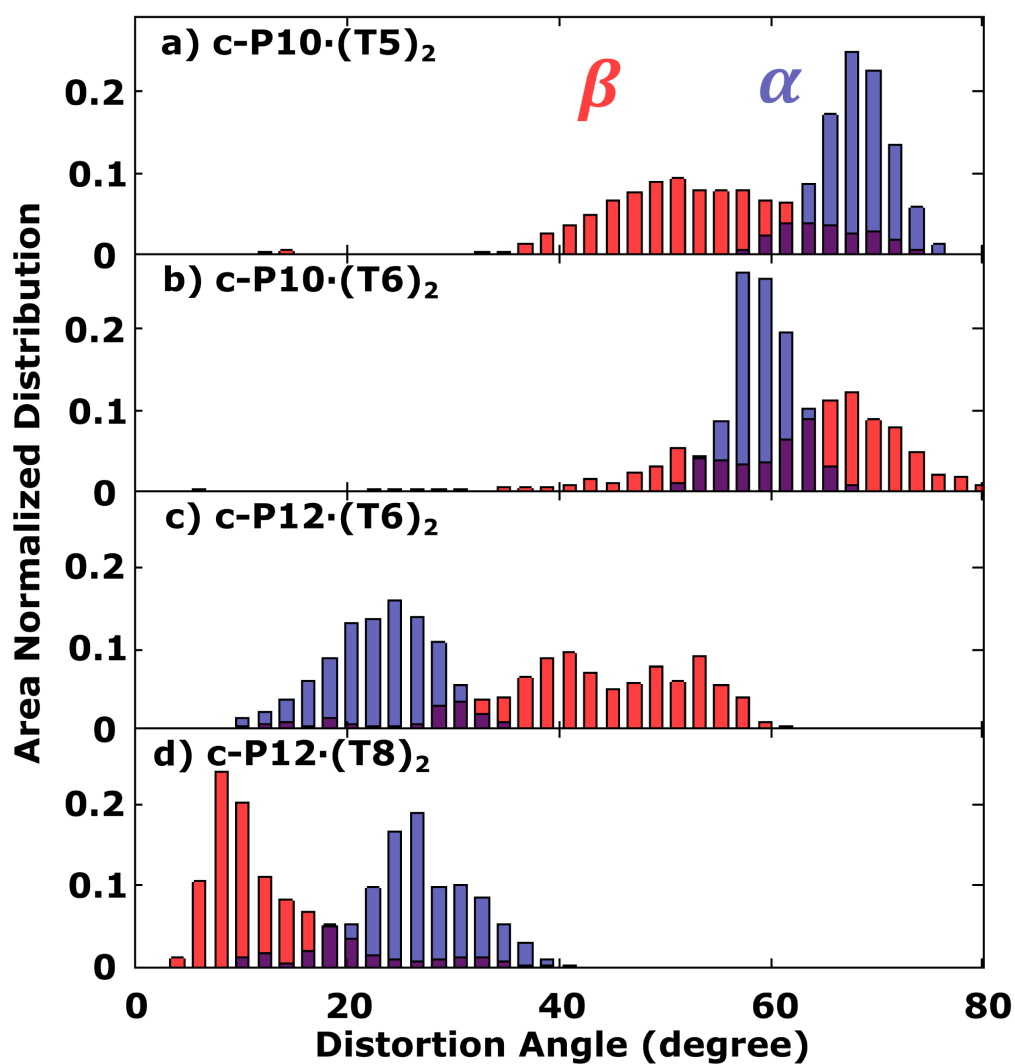


Figure 5.6: Area normalized histogram of twisting angle α (blue) and bending angle β (red) for (a) $c\text{-P10}\cdot(\text{T5})_2$, (b) $c\text{-P10}\cdot(\text{T6})_2$, (c) $c\text{-P12}\cdot(\text{T6})_2$, (d) $c\text{-P12}\cdot(\text{T8})_2$. Molecular dynamics simulation carried out using *HyperChem* at 300 K for 500 ps, as described in detail in the text.

Table 5.1: Experimentally obtained PL lifetimes τ and anisotropy γ values for all nanorings under investigation; as well as the root-mean-squared values of the distortion angles α (twisting) and β (bending) obtained for the templated rings from molecular dynamics simulation at 300 K and 600 K using *HyperChem*. Using a simplified model based on the results from *HyperChem* as described in the main text, simulated anisotropy values γ_s are given.

	Molecule	$\tau \pm 5\%$ (ps)	$\gamma \pm 0.02$	γ_s	$\sqrt{\langle \alpha^2 \rangle}$	$\sqrt{\langle \beta^2 \rangle}$
	c-P10	683	0.11	0.10	—	—
	c-P12	792	0.10	0.10	—	—
Simulation at 300 K	c-P10·(T5)₂	471	0.05	0.03	68°	54°
	c-P10·(T6)₂	463	0.05	0.03	60°	62°
	c-P12·(T6)₂	448	0.04	0.06	24°	44°
	c-P12·(T8)₂	543	0.07	0.08	27°	14°
Simulation at 600 K	c-P10·(T5)₂	—	0.05	0.06	48°	30°
	c-P10·(T6)₂	—	0.05	0.05	56°	39°
	c-P12·(T6)₂	—	0.04	0.06	36°	34°
	c-P12·(T8)₂	—	0.07	0.09	17°	18°

all nanorings. Furthermore, a good correspondence is evident between simulated conformations and measured PL anisotropy: the more pronounced the out-of-plane distortions in both twisting and bending motions, the further the anisotropy is found to be lowered from 0.1.

5.3.4 PL depolarization modelling

To link the value experimentally obtained for the PL anisotropy with the calculated molecular structures, simple simulations were performed using a distributed point-dipole model [18, 34, 35]. The porphyrin units in each nanoring are assumed to be arranged in two smaller circles around each template as a result of the template’s rigidity, with their transition dipole moments aligned

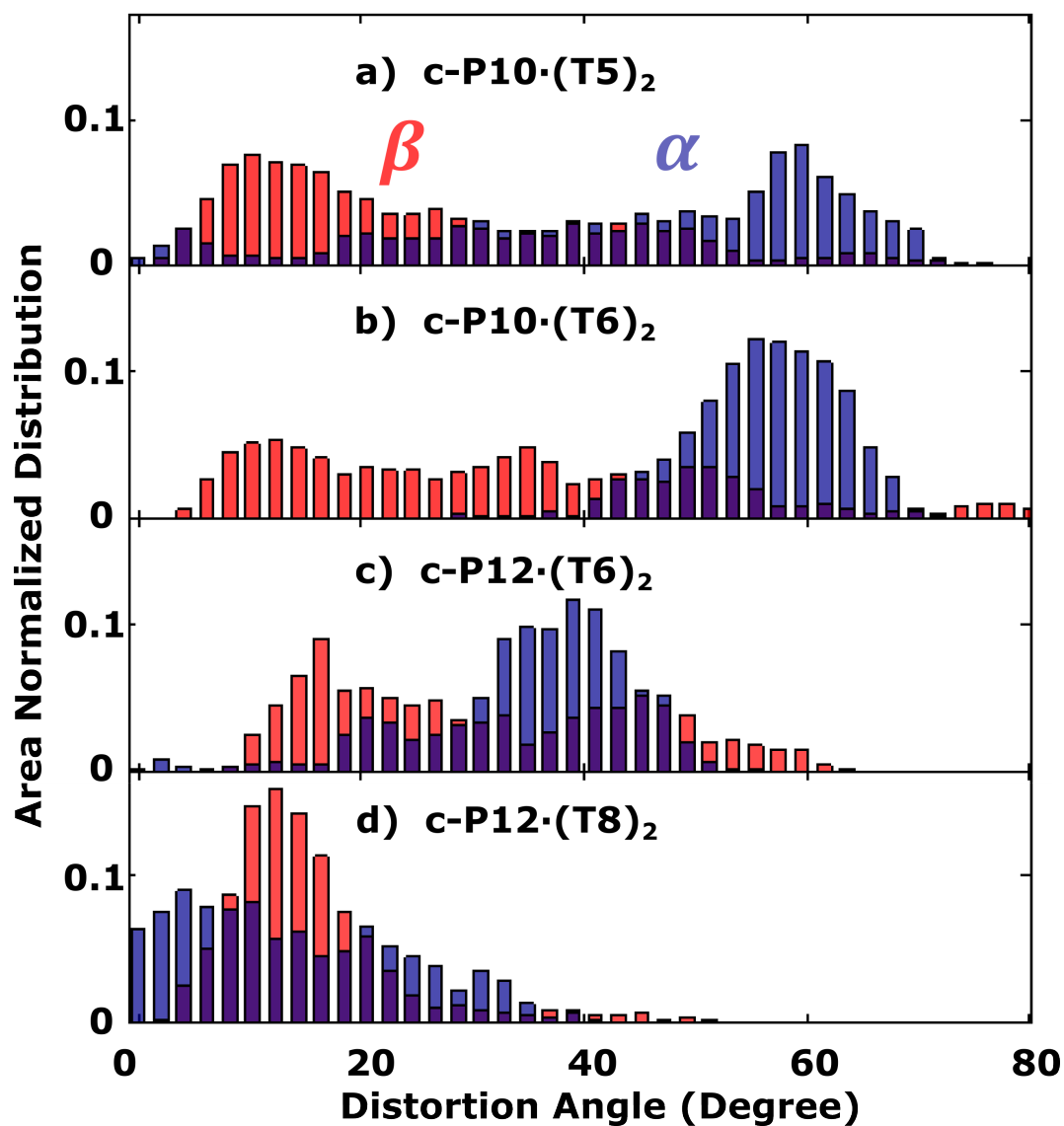


Figure 5.7: Area normalized histogram of twisting angle α (blue) and bending angle β (red) for (a) $c\text{-P10}\cdot(\text{T5})_2$, (b) $c\text{-P10}\cdot(\text{T6})_2$, (c) $c\text{-P12}\cdot(\text{T6})_2$, (d) $c\text{-P12}\cdot(\text{T8})_2$. Molecular dynamics simulation carried out using *HyperChem* at 600 K for 500 ps, as described in detail in the text.

along the molecular backbone, as shown in Figure 5.8. The angle between the two template planes in the calculation is taken to be the RMS values simulated by *HyperChem* at 300 K. For simplicity, further assumptions have been made: 1. The initially excited and the emitting states are discretized to extend over one monomer at a time. This is justified, because the observed anisotropy dynamics is static due to fast depolarization process (< 300 fs) which suggests that all sites are visited with similar probability. Hence the calculated anisotropy value based on averaged contributions from individual sites is not affected by delocalization length in such a circular arrangement; 2. The dipole moments are aligned tangentially to the circle which the porphyrins are forming; 3. Each monomer has equal probability of absorbing and emitting a photon. Therefore, the calculated average based on contributions from individual monomers will yield representative results, independent of the extent of exciton wavefunction delocalization. The polarization anisotropy is then calculated using [34]

$$\gamma_s = \frac{1}{5}(3 \langle \cos^2 \kappa \rangle - 1), \quad (5.1)$$

with the only parameter being κ , the angle between absorbing and emitting dipole moments. Excitation can access any segment of a nanoring, and so each monomer can act as absorbing or emitting site with equal probability. Therefore, angles between dipoles of any two porphyrin monomers on the rings are considered and the average of γ is calculated according to equation 5.1. Even though this model is rather simplified and primarily focuses on the effect of bending and twisting distortions on the PL anisotropy, the results agree well with the experimental findings. The calculated anisotropy γ_s are listed in Table 5.1. The results based on molecular dynamics simulations at 300 K lie within the error range of the experimental values. The calculated PL anisotropy

based on the simulations at 600 K is not affected to a large extent and yield similar results. This correspondence confirms that the out-of-plane distortion is in fact the major contribution causing the lowered anisotropy value from 0.1. The modelled values tend to be slightly lower than the experimental values, but are surprisingly close, given the simplicity of the model.

Deviations between experimental and simulated values may arise because simulations were carried out assuming vacuum conditions (screening of intermolecular interactions arising from the solvent was not taken into account) and because of some variation with the molecular mechanics potential chosen. In addition, a more complete description of exciton depolarization dynamics ought to include effects such as exciton localization dynamics [3], e.g. to sites that are preferred through specific local geometries. However, the good agreement between the experimental results and the simple simulation performed here ultimately results from the intimate link between the topology of the molecule to the polarization directions its emitting state can explore.

5.4 Conclusion

π -Conjugated nanorings containing 10 or 12 porphyrin units have been investigated to explore the influence of molecular topology on exciton dynamics and polarization memory loss. It is found that excitations can access any part of the templated nanorings, despite their twisted conformations, thus showing similar exciton dynamics to their more planar untemplated counterparts. Time-dependent ultrafast spectroscopy reveals that all nanorings exhibit static PL anisotropy transients within the first 20 ps after excitation, but with an anisotropy much lower than the value of 0.1 found for untemplated rings. Molec-

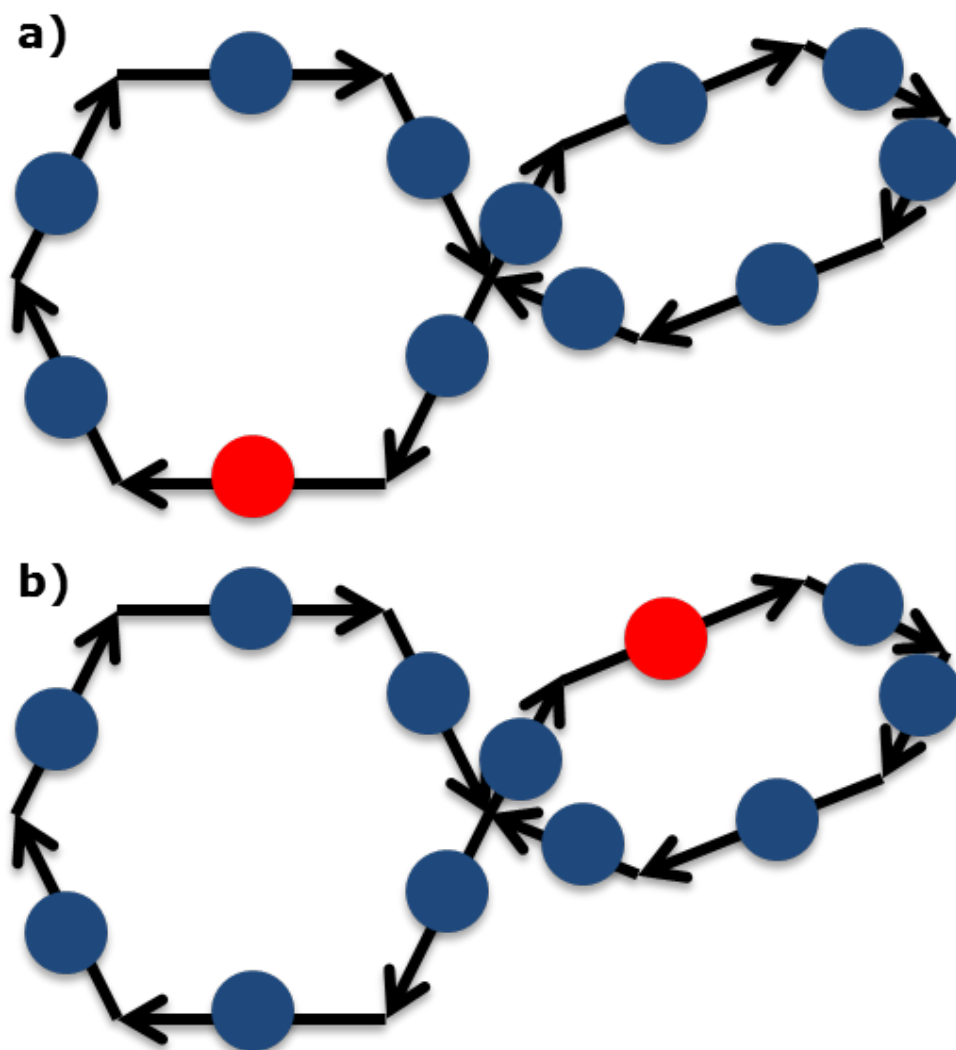


Figure 5.8: Oscillator distributions on nanorings assumed for PL anisotropy modelling: Circles denote porphyrin monomers and the arrows represent transition dipole moments. Porphyrin units are arranged in two smaller loops lying on two planes defined by the templates. (a) Initially excited state (red); (b) emitting state.

ular dynamics simulations show that this phenomenon can be fully explained and well described by the out-of-plane distortions of the rings from a planar conformation. Numerical simulations of the PL anisotropy taking into account such distortions yield values that correlate well with the experimentally obtained results. In summary, template-directed synthesis not only plays a vital role in the synthesis of large porphyrin rings, but it also rigidifies the nanorings and introduces a means to control their geometric structures while maintaining excellent π -conjugation. These findings open exciting new possibilities for fast and directional energy transfer in nanoscale molecular structures.

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Chapter 6

Energy Migration within Porphyrin Nanoring Complexes

6.1 Introduction

In Chapter 5 conformational effects of fully conjugated porphyrin nanorings with diverse symmetry were examined. In this chapter, time-resolved spectroscopy techniques are engaged to study molecular complexes which comprises two conjugated nanorings: Russian doll complex consisting of two covalently-linked concentric nanorings of different size and nanotube consisting of two same sized porphyrin rings conjugated in the direction to the template plane. These are intriguing systems to study directional excitation flow within the complex. Synthesis of π -conjugated macrocycles demonstrating ultrafast energy migration mimicking the natural photosynthetic light-harvesting (LH) complexes have attracted much attention [2, 3, 4, 6, 8, 11]. The Russian doll complex in particular has a structure similar to the light-harvesting complexes described in Section 2.4.2, where energy is funnelled efficiently from the LH1 complex to the reaction centre (RC), which is nested inside the LH1 ring. As these synthetic complexes are fully conjugated opposed to loosely held together by protein scaffold, they have a longer delocalization length and a more rigid structure than

their natural counterparts. Because the high energy transport efficiency derives from exciton delocalization, these synthetic macrocycles are perfect model systems to study the ultrafast energy migration processes.

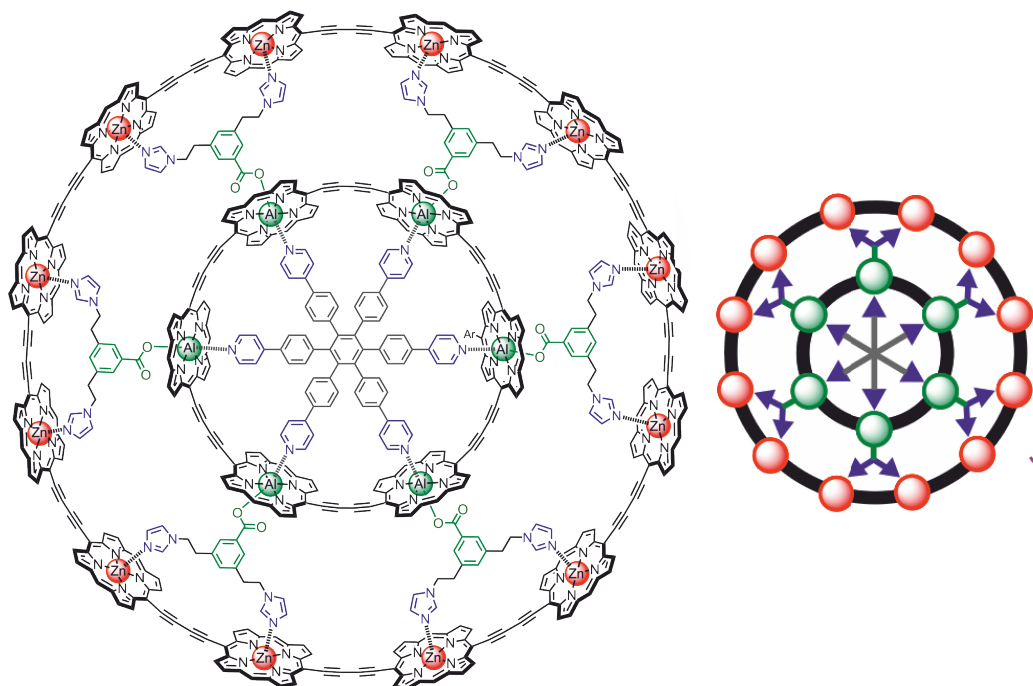
6.2 Samples

6.2.1 Russian doll complex

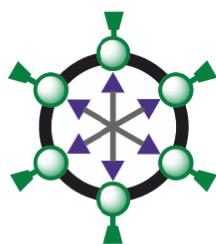
The self-assembled Russian doll complex is a concentric π -conjugated macrocycle consisting of an outer 12-porphyrin nanoring with zinc(II) centres and an inner 6-porphyrin nanoring with aluminium(III) metal centres; the chemical structure is shown in Figure 6.1a). A six-legged template **T6** is nested inside the 6-ring which gives the complex stability. The Y-shaped ligand **L1** was found to be a suitable bridge between the inner and outer rings, it contains two imidazole groups to bind the zinc-porphyrin nanoring, and a carboxylate to bind aluminium. The synthesis and characterization of the compound are carried out Sophie Rousseaux, Organic Chemistry Department of University of Oxford; more information can be found in Reference [7, 9].

Possible energy migration between the concentric rings in the Russian doll complex was probed. For this purpose, three compounds were used as reference samples for photophysical investigations. **T6·c-P6·(Ar'CO₂)₆** is the aluminium 6-ring with template capped with carboxylate ligands **Ar'CO₂** (Figure 6.1b)) and **c-P12·(Bn-L1)₆** is the outer aluminium 12-ring with 6 benzyl-protected **L1** ligands. The third reference compound is a 1:1 mixture of **c-P12·(Bn-L1)₆** and **T6·c-P6·(Ar'CO₂)₆** and is called *control mix*. All the compounds were prepared in chloroform solution.

a) Russian doll



b) $\text{T6} \cdot \text{c-P6} \cdot (\text{Ar}'\text{CO}_2)_6$



c) $\text{c-P12} \cdot (\text{Bn-L1})_6$

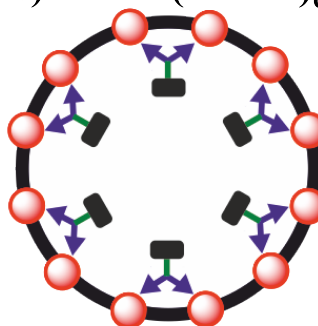


Figure 6.1: a) Chemical structure and representation of Russian doll complex $\text{T6} \cdot \text{c-P6} \cdot (\text{L1})_6 \cdot \text{c-P12}$. Meso-aryl side groups are omitted for clarity. $\text{T6} \cdot \text{c-P6} \cdot (\text{Ar}'\text{CO}_2)_6$ b) and $\text{c-P12} \cdot (\text{Bn-L1})_6$ c) are acting as reference sample for photophysical investigations.

6.2.2 Porphyrin nanotube

The nanotube ***t*-P12** consists of 12 zinc-porphyrin units, each of which is directly π -conjugated to its three neighbours. The chemical structure is shown in Figure 6.2a); it was experimentally realized using template-directed synthesis starting from readily accessible porphyrin dimers. Sample preparation and characterization were carried out by Patrik Neuhaus and Arjen Cnossen from Anderson group in Organic Chemistry Department, University of Oxford. More information can be found in Reference [5, 9]. The nanotube under photophysical investigation in this study has two six-legged templates in each of the two rings and the calculated 3D structure is depicted in Figure 6.2b). It can be considered as two conjugated cyclic six-ring ***c*-P6·T6** stacked on top of each other and coupled through the staves by forming six porphyrin dimers. The z-direction is defined to be along the staves of the nanotube and the template plane is in the xy-plane, as denoted in Figure 6.2b). Naturally, ***c*-P6·T6** acts as a suitable reference sample for photophysical investigations to probe possible energy migration between the ring plane and the staves. All samples were prepared in chloroform solution.

6.3 Results and discussion

6.3.1 Russian doll complexes

6.3.1.1 Absorption and emission spectra

The absorption and fluorescence spectra of the Russian doll complex were compared with those of reference compounds (in chloroform at 295 K), to explore

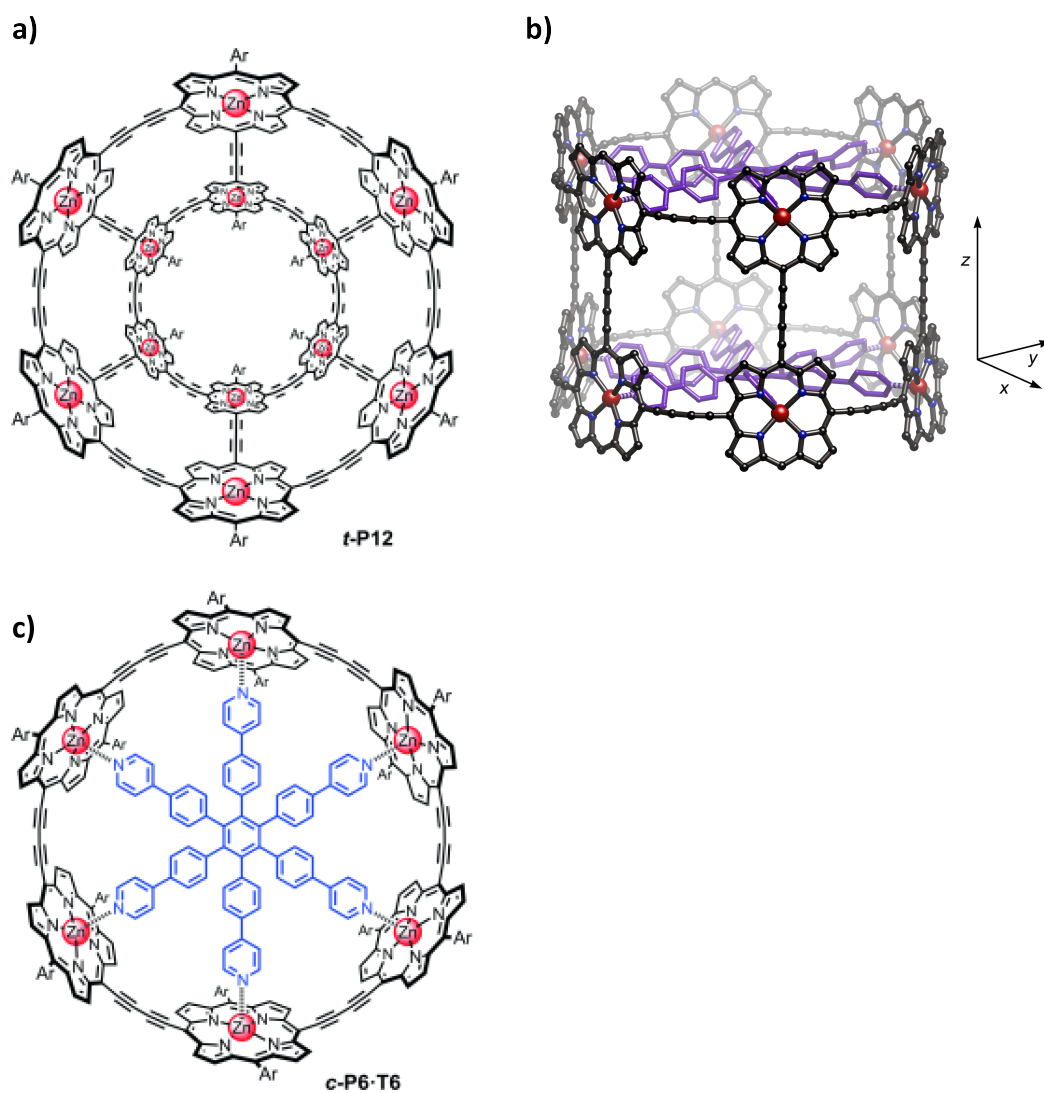


Figure 6.2: a) Chemical structure of the nanotube **t-P12** without the templates. b) Calculated 3D structure of the nanotube **t-P12**·(**T6**)₂, side chains are omitted for clarity. Calculation is conducted using *HyperChem* in MM2 force field. c) Chemical structure of the compare sample **c-P6**·**T6**.

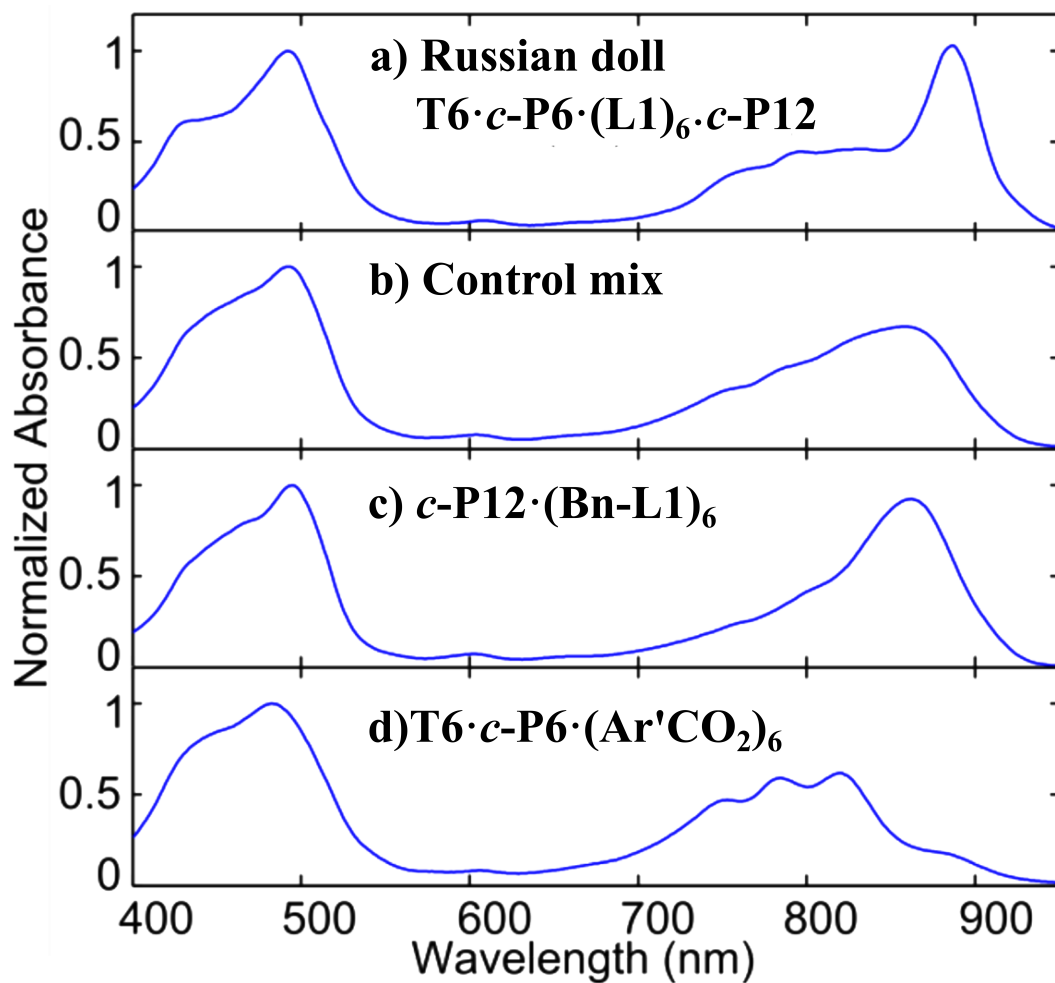


Figure 6.3: Normalized steady-state absorption spectrum of a) Russian doll complex $T6 \cdot c-P6 \cdot (L1)_6 \cdot c-P12$, b) Control mixture, 1:1 $c-P12 \cdot (Bn-L1)_6$ and $T6 \cdot c-P6 \cdot (Ar'CO_2)_6$, c) $c-P12 \cdot (Bn-L1)_6$, (d) $T6 \cdot c-P6 \cdot (Ar'CO_2)_6$ recorded at 295 K in chloroform.

the interactions between the two nanoring components.

All of the samples under investigation show a strong Soret band (400–550 nm) and a split Q band with dipole transitions polarized parallel (Q_x around 850 nm) and perpendicular (Q_y around 600 nm) to the molecular backbone. The Q_x band for the **c-P12·(Bn-L1)₆** complex is red-shifted compared to **T6·c-P6 · (Ar'CO₂)₆** due to an increased conjugation length (Figure 6.3c-d)) [12]. The absorption spectrum of the control mix consists of the sum of the contributions from its components, **c-P12·(Bn-L1)₆** and **T6·c-P6 · (Ar'CO₂)₆**, whereas the Russian doll shows a further red-shift and sharpening in the Q_x band (Figure 6.3a-b)), which indicates that the component in the Russian doll is held in a more rigid conformation [10].

The same effect is evident in the fluorescence spectra shown in Figure 6.4, which were measured at room temperature using a Horiba FluoroLog fluorimeter for excitation in the Soret band at 500 nm. The fluorescence maxima of **T6·c-P6 · (Ar'CO₂)₆** and **c-P12·(Bn-L1)₆** are observed at 897 nm and 917 nm, respectively. Both components contribute to the fluorescence in the control mix. As a result, the peak intensity of the control mix lies in between at 910 nm. The fluorescence spectrum of the Russian doll peaks at 928 nm, further red-shifted from **c-P12·(Bn-L1)₆**, because the complex is more rigid than its unbound constituent components.

6.3.1.2 Quantum yield

The fluorescence quantum yields is a key indicator of the emission property and it is calculated from the fluorescence intensity integrated over the entire spectrum and the absorbance at the excitation wavelength, with linear hexamer used as reference sample ($QY = 28\%$) [12]. The key results are listed in Table 6.1 [12].

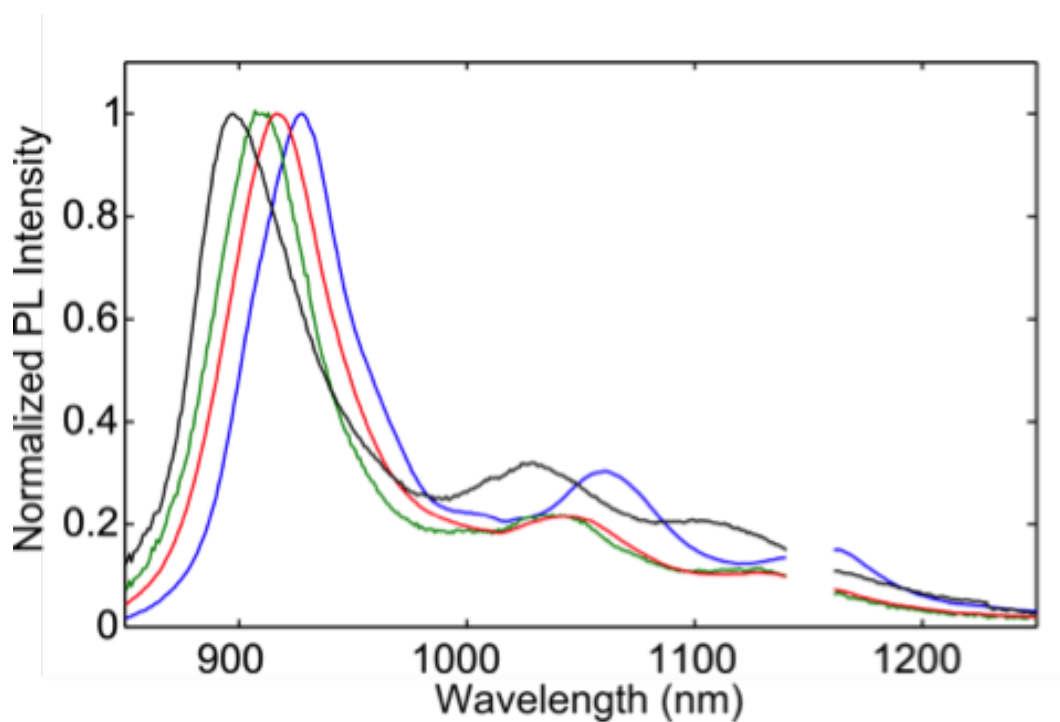


Figure 6.4: Normalized time-integrated emission spectrum of Russian doll complex (blue), control mixture (green), $c\text{-P12}\cdot(\text{Bn-L1})_6$ (red) and $\text{T6}\cdot c\text{-P6}\cdot(\text{Ar}'\text{CO}_2)_6$ (black) excited at 500 nm. Data in the gap are omitted for clarity due to self-absorption of the solvent.

Table 6.1: Quantum yield values of the samples under investigation.

Sample	Quantum Yield
Russian doll complex	2.4%
Control mix	5.4%
c-P12·(Bn-L1)₆	8.4%
T6·c-P6 · (Ar'CO₂)₆	2.1%

The quantum yield of **T6·c-P6 · (Ar'CO₂)₆** is lower than that of **c-P12·(Bn-L1)₆**, which is consistent with previous studies that have shown more strongly suppressed emission for smaller nanorings for which the excitonic wavefunction was delocalized over most of the ring [6, 12]. Both components contribute to the fluorescence efficiency of the control mix, which lies in between, at QY = 5.4% (with excitation at 500 nm). For the Russian doll molecule QY = 2.4%, the quantum yield is higher than that of **T6·c-P6 · (Ar'CO₂)₆** which could be attributed to energy transfer from the inner **c-P6** ring to the outer **c-P12** ring. This is the first indication of possible energy migration within the Russian doll complex.

6.3.1.3 Energy migration within a Russian doll complex

To examine fluorescence from different chromophores in the compounds, the PL excitation spectrum is explored and the results are shown in Figure 6.5.

The control mix comprises two emitting species, and for each emitter the PL excitation is proportional to its absorption spectrum. While the absorption spectrum of the control mix is a sum of the contributions from the two components according to their amount, the fluorescence intensity also depends on the quantum yield of each component. As the quantum yield of **c-P12·(Bn-L1)₆** is much higher than that of **T6·c-P6 · (Ar'CO₂)₆**, the excitation spectrum

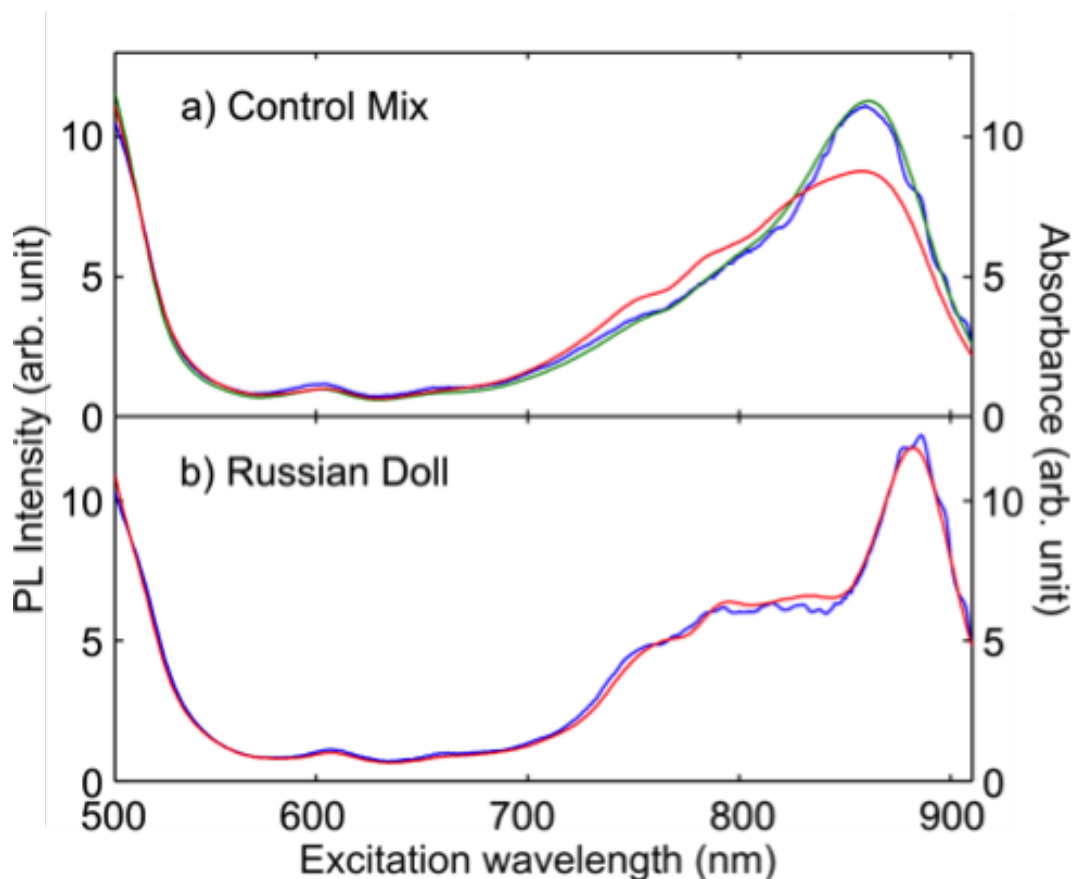


Figure 6.5: A comparison between the fluorescence excitation spectra detected at 920 nm (blue) and the absorption spectra (red) for a) control mix and b) Russian doll complex. The green curve in a) is a simulation of the excitation spectrum calculated from the excitation-dependent fluorescence intensity using the absorption spectra of $c\text{-P12} \cdot (\text{Bn-L1})_6$ and $\text{T6} \cdot c\text{-P6} \cdot (\text{Ar}'\text{CO}_2)_6$, weighted by the fluorescence quantum yields of the components.

of the control mix is not expected to be proportional to its absorption spectrum. For the control mix, the calculated excitation spectrum based on the measured absorption spectra and the quantum yield of **T6·c-P6** · (**Ar'CO₂**)₆ and **c-P12**·(**Bn-L1**)₆ agrees well with the experimentally determined excitation spectrum, as shown in Figure 6.5a). The absorption spectrum deviates from the excitation spectrum, especially at the red-edge of the Q_x band, as a result of the different fluorescence quantum yields of the components that make up the mix. For the Russian doll, the excitation spectrum matches well with the absorption spectrum (Figure 6.5b)), indicating that the whole complex acts as a single emitter, even though there are distinct features in the absorption spectrum arising from the different ring components. Evidently, there is energy transfer between the two porphyrin rings in the Russian doll complex.

To examine further evidence supporting intramolecular energy migration in the Russian doll complex, excitation dependent fluorescence decay dynamics were studied using the TCSPC technique, and the fluorescence lifetime was extracted by fitting the experimental data to a single exponential decay model. The dependence of the fluorescence lifetime on the excitation wavelength was examined at two different excitation wavelengths for the Russian doll and the control mix as shown in Figure 6.6. The fluorescence lifetimes of **T6·c-P6** · (**Ar'CO₂**)₆ and **c-P12**·(**Bn-L1**)₆ are 455 ps and 376 ps respectively, detected at 760 nm (not shown). Their lifetimes are independent of detection wavelength as expected. The measured fluorescence lifetime for the control mix varies with increasing detection wavelength from around 450 ps to 420 ps as the contribution from **T6·c-P6** · (**Ar'CO₂**)₆ and **c-P12**·(**Bn-L1**)₆ to the fluorescence changes. The fluorescence lifetime of the Russian doll, on the other hand, shows no dependence on detection wavelength, indicating that the emission orig-

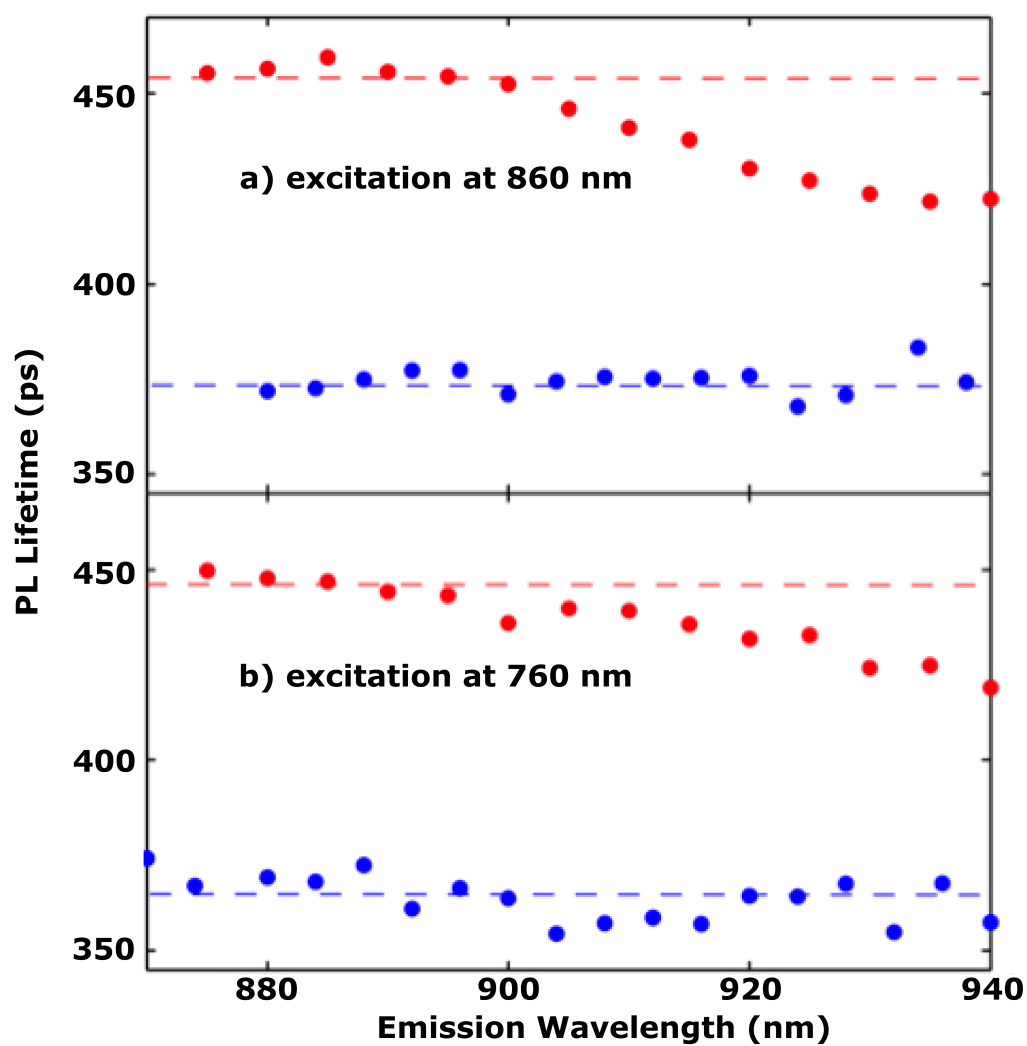


Figure 6.6: Emission wavelength dependent fluorescence lifetime of the Russian doll (blue) and the control mix (red) with excitation at a) 860 nm and b) 760 nm.

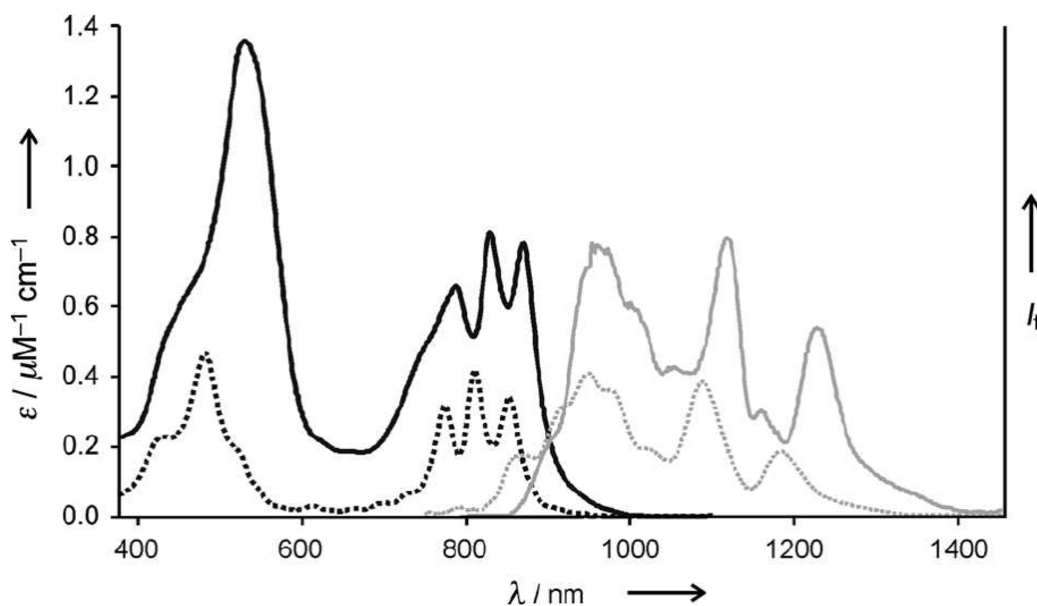


Figure 6.7: Absorption (black) and fluorescence (gray) spectra of $t\text{-P12} \cdot (\text{T6})_2$ (continuous line) and $c\text{-P6} \cdot \text{T6}$ (dashed) recorded in chloroform.

inates from a single emitter. The mean fluorescence lifetime of the Russian doll is 364 ps when detected at 760 nm and 375 ps when detected at 860 nm. A comparison of the individual component lifetimes suggests that the emitting species in the Russian doll is most likely the outer zinc 12-ring. The emission profiles of the aluminium 6-ring and zinc 12-ring overlap significantly, which makes it difficult to study the energy migration dynamics in this system, but it is clear that excitation is transferred efficiently from the $c\text{-P6}$ component to the outer $c\text{-P12}$ component within the 40 ps time-resolution of our instrumentation.

6.3.2 Molecular nanotube

6.3.2.1 Absorption and emission spectrum

The absorption and fluorescence spectra of ***t*-P12·(T6)₂** are compared with those of ***c*-P6·T6** in Figure 6.7. Both compounds show similar split absorption and emission bands, indicating that they have similar electronic structures, with emission from a dipole-forbidden first excited state becoming partially allowed through Herzberg-Teller coupling with higher excited states [9]. The absorption and emission maxima of ***t*-P12·(T6)₂** are red-shifted by approximately 300 cm⁻¹ relative to those of ***c*-P6·T6**, reflecting the greater conjugation in the larger π -system.

6.3.2.2 Ultrafast time-resolved PL spectroscopy

Ultrafast time-resolved fluorescence spectroscopy using the PLUC technique reveals strong coupling between the components of the nanotube. Figure 6.8 shows the fluorescence dynamics of ***t*-P12·(T6)₂**, excited at 830 nm and 742 nm, with excitation polarized perpendicular or parallel to the detection polarization. The time-dependent fluorescence anisotropy γ at these two wavelengths, derived from the data in Figure 6.8, shows no change over 0–15 ps after excitation (Figure 6.9). The average anisotropy on excitation at 830 nm is 0.07, which is similar to that recorded for ***c*-P6·T6** [9, 12] and close to the theoretical value of 0.1 for an excited state delocalized over a two-dimensional ring as demonstrated in Chapter 3. This indicates that in ***t*-P12·(T6)₂**, absorption at 830 nm is associated with transition dipoles in the template plane of the six-porphyrin rings, and that emission occurs from an excited state that is delocalized over the entire ring in the xy plane. However, at shorter excitation wavelengths,

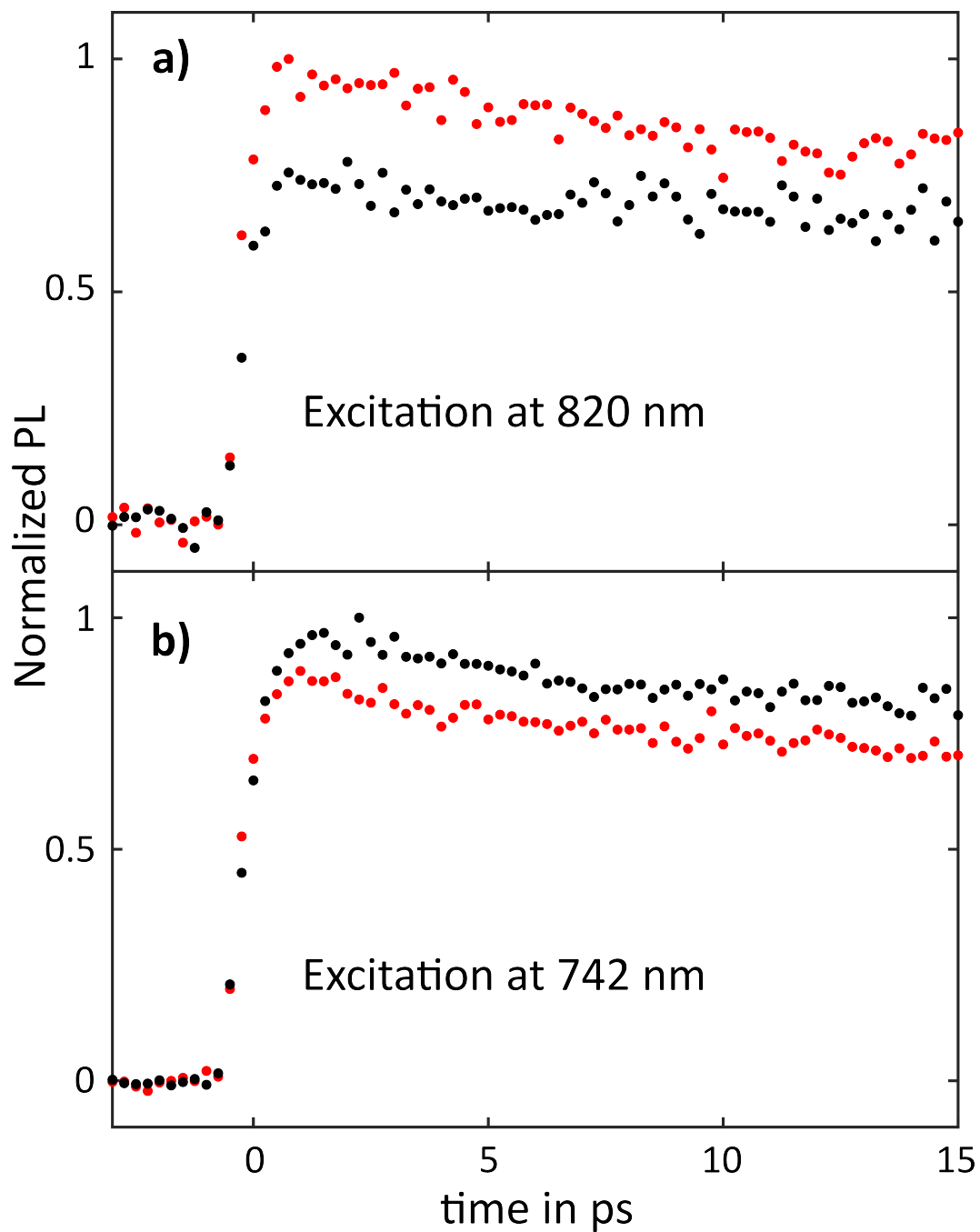


Figure 6.8: Time-resolved PL decay of $t\text{-P12}\cdot(T6)_2$ excited at a) 820 nm and b) 742 nm. Emission was detected at 941 nm and excitation laser pulse was either polarized parallel (red) or perpendicular (black) to the emission.

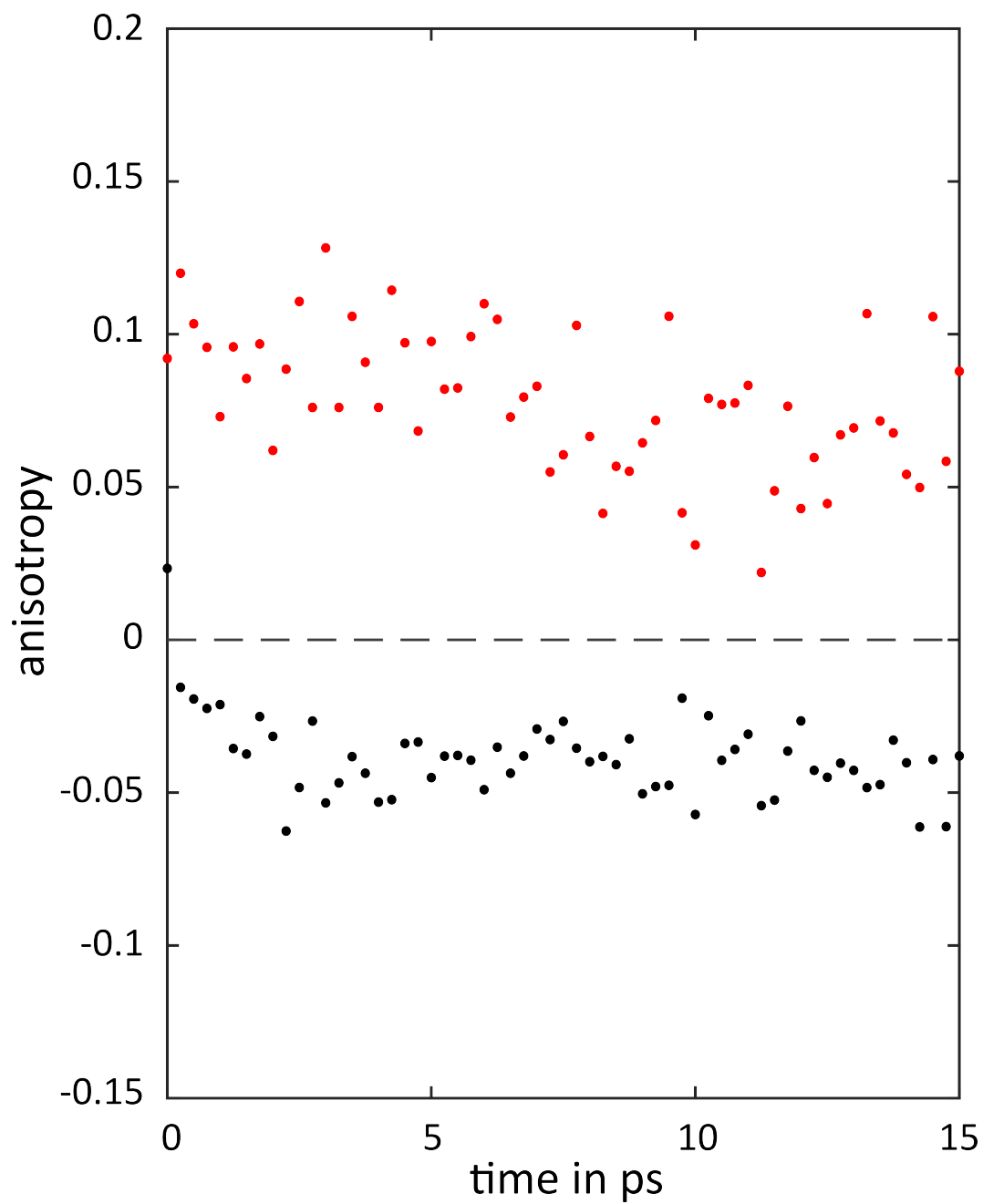


Figure 6.9: PL anisotropy dynamics of $t\text{-P12}\cdot(T6)_2$ for excitation at 820 nm (red) and 742 nm (black).

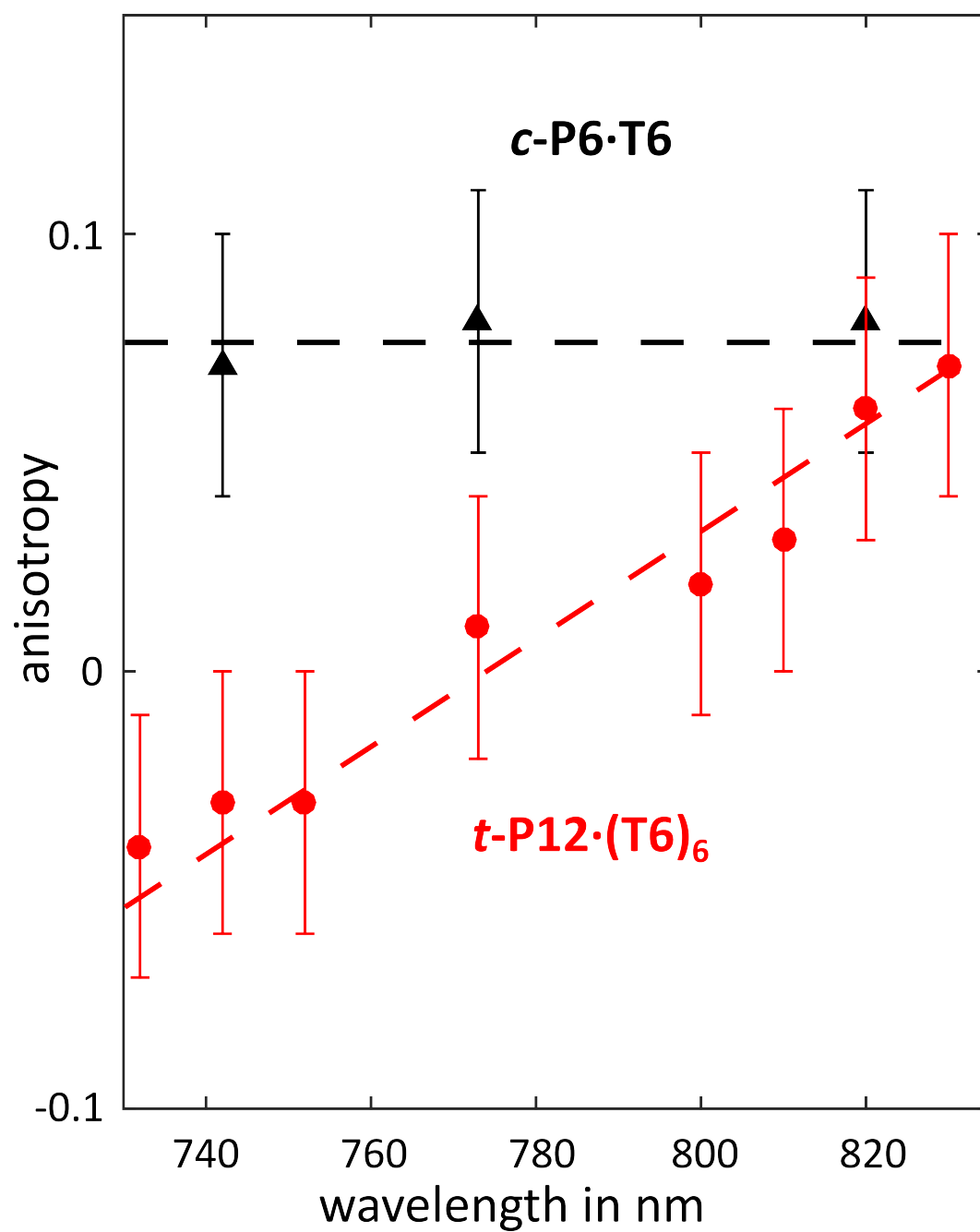


Figure 6.10: PL anisotropy for *t*-P12·(T6)₂ and *c*-P6·T6 measured over a range of excitation wavelengths. Dashed lines act only as guides to the eye.

the anisotropy decreases, becoming negative and reaching a value of -0.04 at 742 nm , whereas the fluorescence anisotropy of **c-P6·T6** is independent of the wavelength (Figure 6.10). The most likely explanation for this behaviour is that for excitation at 742 nm , light is absorbed by transitions associated with the z-polarized butadiyne-linked porphyrin dimer staves of the barrel to former higher excited states that emit from the xy-polarized ring-like state. This interpretation is further supported by the observation that the porphyrin dimer [1] has a Q_y band at 705 nm . If the absorption by **t-P12·(T6)₂** at 742 nm was entirely z-polarized, with emission only from a state polarized in the xy-plane, then the anisotropy would be -0.2 (see Chapter 3). The value of -0.04 reflects the presence of overlapping absorption bands at 742 nm , both the ring-like states in the xy-plane and the z-polarized states along the staves are excited. Migration of electronic excitation from the z-polarized staves to the xy-polarized state takes place faster than the 270 fs time resolution of the experiment.

6.4 Conclusion

In summary, energy migration within the porphyrin nanoring complex has been investigated using time-resolved spectroscopy techniques on two samples of different structures: Russian doll complex consisting of two concentric rings and a porphyrin nanotube which comprises two conjugated six-rings stacked on top of each other and coupled along the direction perpendicular to the ring plane. For the Russian doll complex, despite the significant overlap in the emission spectra of the individual rings which increases the difficulty to study the energy migration dynamics, we have been able to arrive at a definite conclusion. Comparison of fluorescence emission spectra with absorption spectra shows that the

Russian doll complex behaves as a single emitter and TCSPC reveals that its PL lifetime is independent of excitation wavelength, even though the absorption spectrum shows clear features of both ring components. Comparing the lifetime of the Russian doll complex with the lifetime of the individual ring components, it can be concluded that excitation migrates efficiently from the outer 12-ring to the inner 6-ring within the time resolution of the system (40 ps). The porphyrin nanotube also exhibits energy migration within a single molecule. Excitation dependent anisotropy probed by PLUC provides evidence of fast energy migration from the staves of the tube to the templates plane within 270 fs time resolution. The findings in these studies demonstrate that by engineering the structures of the porphyrin nanoring complexes, fast and directional energy migration can be facilitated. This is a vital step towards realizing efficient energy transfer in synthetic systems mimicking natural light harvesting complexes.

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Chapter 7

Conclusions and Outlook

In this thesis, electronic processes in porphyrin nanorings of various sizes, conformations and structures have been investigated using ultrafast spectroscopy such as TCSPC and the up-conversion technique. π -conjugated porphyrin nanorings are interesting systems as they possess well-defined structures that can readily be controlled and because they support highly delocalized excitations. They serve as excellent model systems for cyclic molecular structures such as natural light-harvesting complexes. The impact on the photophysical properties, e.g. radiative rate, polarization memory loss due to geometrical and conformational changes are investigated, as well as possible energy migration. This chapter gives a summary of the results and provides an outlook for future work.

Chapter 4 examines the rigid templated cyclic six porphyrin ring as the rotational symmetry is gradually lifted. To this effect, a series of modified nanorings are required: a six porphyrin ring with D_{6h} symmetry, a ring with extra side groups at two opposite porphyrin sites and hence reduced symmetry, a complex with two interlinked rings and a porphyrin ring with broken π -conjugation. It was found that as symmetry distortions increase in severity along the series of structures, an enhancement of radiative emission strength occurs, which derives from a transfer of oscillator strength into the lowest ($k = 0$) state. For

molecules with cyclic symmetry the $k = 0$ state is dipole forbidden due to symmetry constraints. As the symmetry is lowered, the constraint becomes less stringent, resulting in a strong recovery of Frank-Condon allowed transitions from the $k = 0$ state, which manifests in an increased radiative rate as well as emerging features in the absorption spectra. Concomitantly, the degeneracy of the dipole-allowed first excited ($k=\pm 1$) state is lifted and a series of new non-degenerate higher lying states with transition dipole moments of well-defined orientation are created. Upon excitation into higher lying states, the exciton relaxes quickly into the $k = 0$ state, which has a weak transition dipole moment due to the broken symmetry and fluorescence emerges from the $k = 0$ state. For absorbing and emitting states with orthogonal transition dipole moments, an ultrafast polarization switching effect in the emission is expected, which was observed for the strongly symmetry-broken nanorings.

Chapter 5 has concentrated on the conformational effects on exciton delocalization and emission polarization in porphyrin rings with 10 and 12 units. Vernier templating enables synthesis of large porphyrin nanorings with diverse topologies. Rings consisting of two smaller loops with various degree of twisting and bending ranging from almost planar to a figure-of-eight conformation were examined and compared with rings without templates. Experiments revealed that templated systems were more rigid and less prone to inter-porphyrin torsions leading to a planarized molecular backbone. However, excitation can access any segment on the ring within the first few hundreds of femtoseconds, independent of the conformational effect. This can be explained either by complete delocalization of the absorbing state over the entire ring, or ultrafast energy migration around the ring within the time resolution of our instruments. Furthermore, Chapter 5 has demonstrated that while porphyrin rings without

templates exhibit emission anisotropy as we would expect from complete depolarization in a 2D plane, further polarization memory loss in the templated nanorings is caused by out-of-plane distortions associated with twisting and bending in their topologies. Theoretical anisotropy values based on molecular dynamics simulations agree well with the experimental results.

Chapter 6 presented an investigation into energy migration within two porphyrin complexes: a Russian doll complex with two concentric covalently-linked porphyrin rings consisting of 12 and 6 units, and a nanotube with two six porphyrin rings coupled along the direction perpendicular to the ring plane. The Russian doll complex was found to act as a single emitter, despite having spectral features in the absorption spectrum attributable to both individual ring components of the complex. Excitons migrate efficiently within 40 ps from the inner ring to the outer ring component, which is energetically favourable. A similar structure is found in natural light-harvesting complex, here however, energy is funnelled from the outer LH1 ring to the reaction centre in the middle. Energy migration was also found to occur within the porphyrin nanotube. By exciting perpendicularly to the ring plane, effectively exciting the conjugated dimers, emission polarized in the plane of the ring components was recorded, leading to polarization switching. Excitons migrate rapidly from the staves of the nanotube to the ring plane within 270 fs of our instrument resolution.

After examining energy migration within a molecular complex, an interesting topic for further investigation would be inter molecular energy transfer between different porphyrin ring sites. Efficient energy transfer is sustained in light-harvesting complexes, excitation energy is transferred from a cyclic bacteriochlorophylls array B850 to another B850 in a neighbouring LH2 complex with the rate constant of 5 ps^{-1} . The highly symmetric cyclic structure and

exciton delocalization are believed to play a key role in the high energy transfer efficiency. Given the resemblance to the natural light-harvesting system in size and structure and the high degree of exciton delocalization, it would be interesting to find out whether a similar energy transfer dynamics is present between porphyrin rings. A suitable system for such investigation could be a 2D array of porphyrin rings with a small number of quenching sites. PL dynamics can be probed using ultrafast spectroscopy techniques. Excitations created at one porphyrin ring site can either relax to the ground state with emission of a photon, or transfer to a quencher site followed by non-radiative decay, or to another porphyrin ring site. The energy transfer dynamics between two sites can be described by incoherent Förster type energy transfer and the consecutive hopping from site to site can be modelled using Monte Carlo simulation as a random walk.

π -conjugated porphyrin nanorings are fascinating and promising synthetic molecules with many possibilities. Compounds with new and increasingly complex structures are being created and their photophysical properties are certainly worth investigating.