Energy migration in conjugated polymers: the role of molecular structure

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Conjugated polymers undergo facile exciton diffusion. Different molecular structures were examined to study the role of the excited state lifetimes and molecular conformations on energy transfer. There is a clear indication that extended fluorescence lifetimes give enhanced exciton diffusion as determined by fluorescence depolarization measurements. These results are consistent with a strong electronic coupling or Dexter-type energy transfer as the dominating mechanism. The control of polymer conformations in liquid crystal solvents was also examined and it was determined that more planar conformations gave enhanced energy transfer to emissive low band-gap endgroups.

Keywords: Dexter energy transfer; Förster energy transfer; exciton diffusion; liquid crystals; conjugated polymers; sensors

1. Introduction

Our group has focused extensively on the use of energy migration in conjugated polymers (CPs) to create signal gain in chemical sensors (Zhou & Swager 1995*a*,*b*; Yang & Swager 1998). These methods have gained wide acceptance as a means of creating amplified sensory responses. However, a comprehensive fundamental understanding of the relative mechanisms of energy migration in these systems remains elusive. This inherent difficulty is a result of the fact that CPs have disordered dynamic conformations that produce variable electronic delocalization, both within a given polymer and between neighbouring polymers. To improve this situation, we are striving to design polymers with structures and properties to test directly the general mechanisms as well as create organizations that will facilitate the investigations of others. In this contribution, we discuss how the ability to design CPs with longer lifetimes can serve to test basic theories of energy migration in a very straightforward fashion. We also detail systems that can be organized to have extended electronic delocalization and well-defined conformations in liquid crystal solutions. These latter systems will serve to facilitate spectroscopic and theoretical analysis of these complex materials.

A thorough understanding of the mechanisms underlying energy migration in CPs is necessary to design its enhancement. The high efficiency of energy transfer in most conjugated systems (Devadoss *et al.* 1996; Ley *et al.* 1997) relative to systems with pendant chromophores (Guillet 1987; Byers *et al.* 1988; Kiserow *et al.* 1997; Levitsky & Webber 1998) suggests that strongly coupled electronic intrachain (Dexter-type) processes may increase transport in these systems over those provided solely by the dipole–dipole (Förster-type; Förster 1959) interactions that govern weakly interacting chromophores. Discrepancies between the two mechanisms allow the determination of which reigns over the ubiquitous energy migration in CPs.

As derived by Förster, the dipole–dipole approximation yields a transition probability (k_{ET})

$$k_{ET} = \frac{\kappa^2 J 8.8 \times 10^{-28} \text{mol}}{n^4 \tau_o R_{DA}^6},$$

where κ is an orientation factor; n is the refractive index of the medium; τ_o is the radiative lifetime of the donor; R_{DA} is the distance (cm) between donor (D) and acceptor (A); and J is the spectral overlap (in coherent units $\text{cm}^6 \text{mol}^{-1}$) between the absorption spectrum of the acceptor and the fluorescence spectrum of the donor. Therefore, a weakly allowed transition, as manifest in a long radiative lifetime, should discourage purely coulombic energy transfer.

Electron exchange effects contributing to energy transfer described by Dexter (1953) account for shorter-range processes which result from direct wave function overlap of interacting molecules. In this case, the transition probability is described by

$$k_{ET} = KJ \exp\left(\frac{2R_{DA}}{L}\right),$$

where K is related to specific orbital interactions; J is the spectral overlap; R_{DA} is the donor–acceptor distance; and L is the van der Waal radii distance between donor and acceptor. This process is often termed electron exchange or collisional mechanism because molecules must be almost within the van der Waals radii of each other to interact. In the specific case of CPs, the chromophores are directly conjugated, and therefore one might expect the Dexter mechanism to dictate the overall efficiency of energy migration, at least within a given backbone.

To determine the dominant energy migration mechanism in CPs, we are exploiting the oscillator strength independence of the Dexter mechanism in our investigations of isolated CPs in solution. The Dexter mechanism is in fact diametrically opposed to coulombic (Förster) energy transfer in this regard. To increase the coulombic energy transfer, one would target shorter radiative lifetimes (i.e. increase the oscillator strengths of D^* to D and A to A^* transitions) as indicated by its rate equation. However, because the electron exchange mechanism does not depend on the oscillator strength, longer lifetimes affected by less allowed transitions can serve to increase energy transfer by providing more time for the excitation to migrate before radiative decay.

We will describe herein how we have systematically reduced the oscillator strength in CPs to determine its effect on energy migration and demonstrate the widespread applicability of this approach. Structures with extended aromatic cores such as triphenylene, dibenzo[*g,p*]chrysene and benzothiophenes were incorporated into poly(phenylene ethynylene) (PPE) backbones (Yamaguchi & Swager 2001;

Tovar *et al.* 2002). In order to look more rigorously at the variations of effective conjugation pathways and their implications before and after chromophore cyclization, matched pairs of uncyclized and cyclized polymers were synthesized to assess the impact of rigidification and aromatization. The representative triphenylene- and thiophene-based systems afforded a more complete understanding of the interplay of rigidity, symmetrization, lifetime and energy migration in CPs. Collectively, all these systems provide further insight into the control of energy migration in CPs.

The conformational dependence of CPs on energy migration also remains a poorly understood problem. In electrical conductivity, greater planarization (delocalization) and strong interpolymer interactions are most important. As a first step to understand intramolecular energy migration in isolated CPs in dilute solution, we have designed structures that provide for high solubility and precise organizations in thermotropic nematic liquid crystals. In these solutions, the CPs exhibit purely chain-extended structures with high order parameters and planarized conformations. These systems present a highly regular conformation from which to study intrapolymer energy migration.

2. Results and discussion

(*a*) *Triphenylene-based PPEs*

To modify the excited state lifetimes in CP systems, we first incorporated triphenylene chromophores into a PPE backbone. Triphenylene has a well-known symmetrically forbidden groundstate transition (Berlman 1971) and hence exhibits a suppressed radiative lifetime. Although incorporation into a CP decreases the triphenylene's symmetry, it was likely that the strong aromatic structure influences the resulting photophysics. In order to determine the general trend, a family of triphenylene-based CPs was synthesized along with chemically similar CPs, lacking the triphenylene chromophore (figure 1; Rose *et al.* 2001). Polymers were size-selected by gel permeation chromatography to ensure comparison of similar chain lengths and the excited state lifetimes of resulting materials were measured in the frequency domain (Lakowicz 1999). All photophysical measurements were carried out in methylene chloride solutions.

Triphenylene incorporation universally extended the excited state lifetime of targeted PPEs when compared with similar PPEs without triphenylene (figure 2). In CPs where the excitation is more localized, the lifetime enhancing effect of the triphenylene component is more pronounced. An example is **5** consisting of a triphenylene monomer and a biphenyl monomer. Because biphenyl planarizes in the excited state, a large Stokes shift is observed in the resulting polymer. This process serves to localize the excitation and the radiative decay rates become more competitive with energy transfer. Consequentially, polymer **5**'s lifetime is about three times longer than its PPE analogue **5a**. This effect is mirrored in polymers **7** (60% 7.0 ns: 40% 1.3 ns)[1] and **15** (3.3 ns). The *meta* linkage in **7** and **15** disrupts conjugation, localizing the excitation. This results in some of the longest lifetimes

[1] Polymer **14**'s lifetime could only be modelled by a biexponential decay. This probably results from its short chain length. This is the only polymer synthesized that could not be satisfactorily modelled by a single component lifetime.
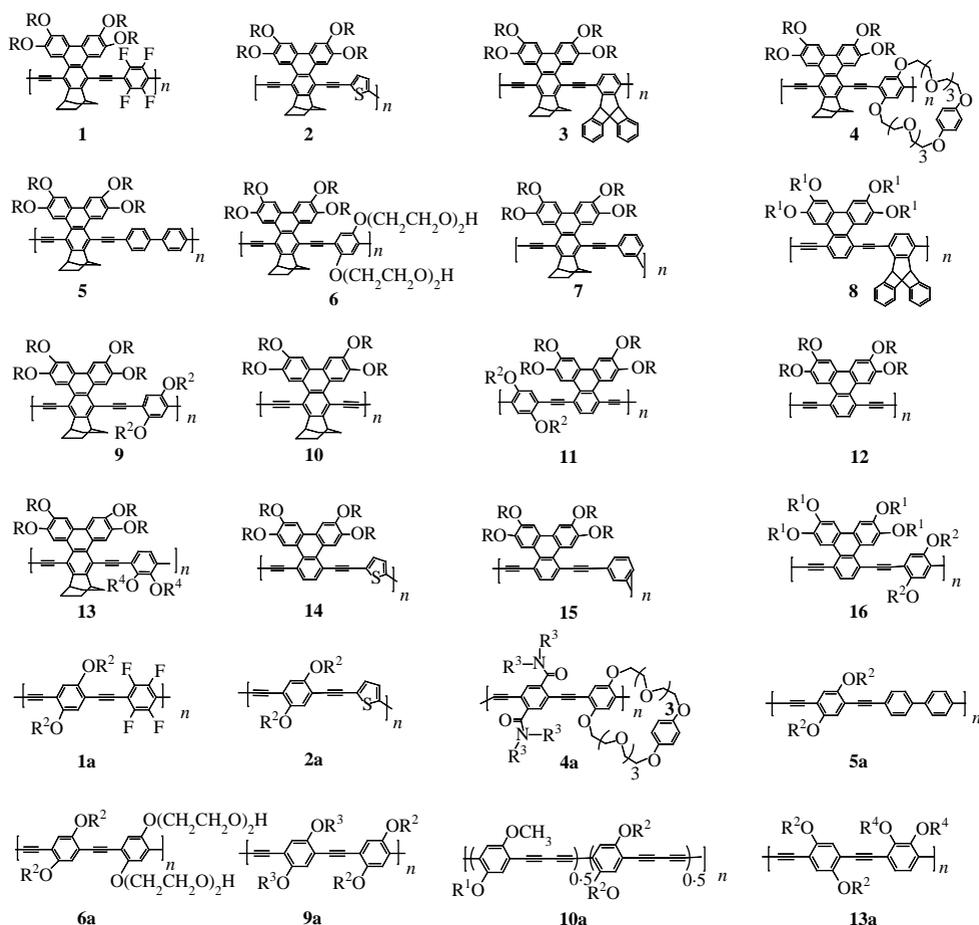
Figure 1. TPPE and model PPEs. R = 2-ethylhexyl; R^1 = n-decyl; R^2 = n-hexyldecyl; R^3 = n-octyl; R^4 = n-dodecyl.

in triphenylene-based PPEs (TPPEs). As expected, CPs with a larger triphenylene component demonstrate more pronounced lifetime enhancement. Homopolymers **10** and **12** coupling only the diactylede units and directly conjugating triphenylene monomers display lifetimes several multiples above that of their PPE analogue. In addition, electrostatic variation in TPPEs can lead to excited state interactions. In polymer **1**, an exciplex is probably formed between the triphenylene and its electron deficient tetrafluorinated comonomer. The very long excited state lifetime (4 ns) and broad, red-shifted emission spectra are clear indications of this phenomenon. The absence of these characteristics in its PPE analogue suggests the flat, electron-rich nature of triphenylene is necessary to induce exciplex formation. The electrostatic variation within the triphenylene materials can provide selection for an analyte with given energetics.

Polarization spectroscopy studies correlated suppressed radiative rates with energy migration enhancement. If migration between chromophores is slower in TPPEs as predicted by the Förster equation, the overall distance an exciton can cover will not be extended. However, the Dexter (1953) formulation makes no
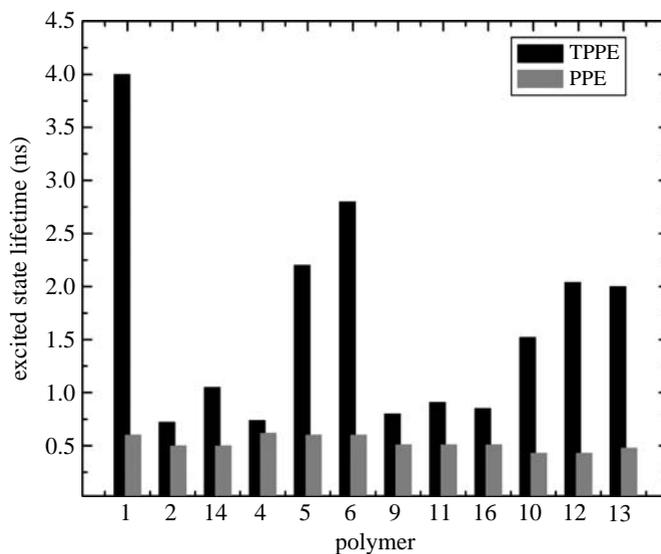
Figure 2. Lifetime comparison of TPPEs (black bars) and corresponding PPEs (grey bars). In all cases, TPPE excitations are longer lived.

such limitation as it describes energy transfer resulting from direct wave function overlap. Therefore, transition allowedness does not affect overall rates. Dexter transfer may therefore be the dominant mechanism in these systems.

All of the polymers studied are high molecular weight materials and can be considered rotationally static over the emission lifetime of the polymer. Therefore, energy migration is the major contributor to the fluorescence depolarization in our CPs; the exciton loses more of its initial polarization the more it diffuses along a disordered polymer chain (figure 3). The polarization value, P, was determined from the standard equation $P = (I_{vv} - GI_{hv})/(I_{vv} + GI_{hv})$, where I_{vv} and I_{hv} are the intensities of emissions detected parallel and perpendicular to the polarization vector of the incident light and G is an instrumental correction factor.

Aggregation of polymers can lead to high degrees of depolarization and spin cast films of closely related polymers exhibit higher degrees of depolarization than those observed in solution (Levitsky *et al.* 1999). As mentioned earlier, only **1** displayed features characteristic of aggregation with a red-shifted excimer-like emission and an anomalously long lifetime. The other polymers were designed with three-dimensional architectures and/or a large number of solubilizing alkoxy side chains to prevent interpolymer associations. These materials showed no evidence of aggregation in photophysical or gel permeation chromatography measurements over a range of concentrations in methylene chloride or THF solvent. Furthermore, our fluorescence depolarization measurements were conducted at dilute concentrations (approx. 10^{-6} M/repeating unit) to avoid reabsorption effects. As a result, polymer aggregation is probably not a contributing factor in our fluorescent depolarization measurements.

Concurring with lifetime data, depolarization is universally more pronounced in TPPEs. This trend is showcased in figure 4 wherein we compare TPPE depolarization with that of the corresponding PPE when excited at their
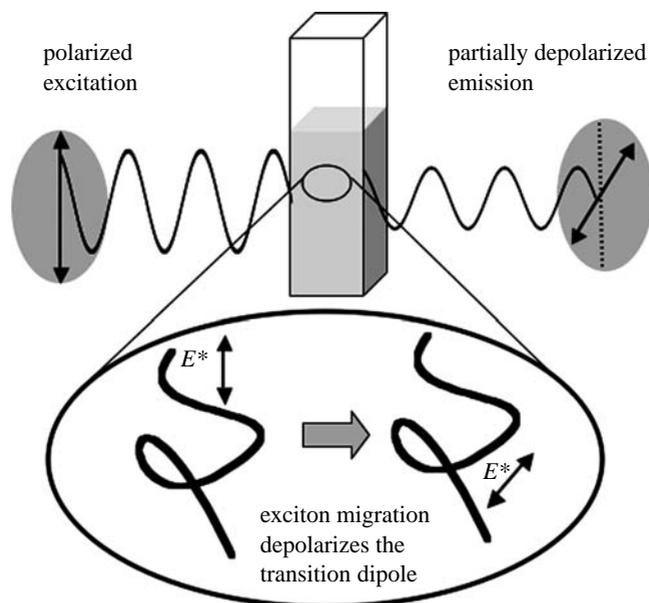
Figure 3. A simplified pictorial of depolarization due to energy migration in conjugated polymers (CPs). The excitation beam is vertically polarized and therefore only vertical transition dipoles are initially excited on the CP chain. Vertically polarized excitons on the polymer chain migrate. As they move over a disordered polymer chain, they lose their initial polarization. The emission of polymer is depolarized relative to the excitation beam. This amount of measured depolarization indicates the extent of energy migration in the conjugated polymer.
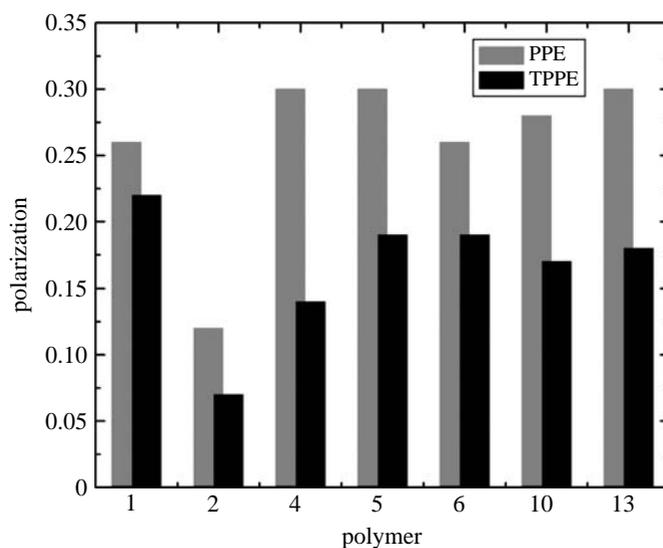

Figure 4. Polarization comparison of representative PPEs and TPPEs. Grey bars are polarization values for PPEs and black bars are polarizations for TPPEs. Both are excited at $\lambda_{\max}$ and in every instance, TPPEs exhibit greater depolarization, indicating more extensive energy migration.

respective absorption maxima. The TPPE's polarization behaviour underscores some important points. In the case of polymers **2** and **2a**, the kinked thiophene linkage results in a much greater depolarization than in other polymers studied. Greater polarization loss per migration step is expected in a kinked structure. Polymer **5**, with its localizing biphenyl monomer, retains one of the highest polarization values. The highest polarization value among TPPEs is observed in polymer **1**. The energy minimum formed by its exciplex probably quickly traps the wandering excitation, reducing energy migration. Collectively, these observations correlate expected trends in energy migration with observed polarization data, validating our assessment.

The full range of allowable excitation energies for a subset of polymers was investigated to separate depolarization owing to energy migration from that due to absorption/emission dipole alignment. Measurements were performed on materials selected for similar chain length, all above the small molecular weight regime. As excitation energy is increased, both the TPPEs and the PPEs display lower P values, consistent with population of higher energy excitons that readily lower their energy by migration to lower energy states. The decrease in emission polarization at higher energies may also be the result of exciting triphenylene localized transitions that have an angular displacement from the emission dipole. In this case, polarization would be expected to decrease more dramatically at certain intervals of wavelengths, not continuously over the range investigated. In TPPEs, a near linear decrease in polarization as a function of excitation wavelength (figure 5) is observed supporting energy migration as the major contributor to depolarization. Over all excitation wavelengths, the TPPEs consistently revealed lower P values. For TPPEs, the lowest attainable P values are a fraction of the P observed when exciting at $\lambda_{\max}$. In PPEs, however, this value is only about half, indicating that the radiative rate of emission limits the extent of energy migration. This limitation is overcome in the longer-lived TPPE systems as P values near zero are obtainable in most of the materials. Studies of polarization as a function of chain length support these conclusions. If the Förster mechanism dominated, then enhanced radiative rates in PPEs would encourage more extensive migration. This phenomenon is not observed, pointing to the Dexter mechanism as the dominant intramolecular energy transport process in these materials.

(b) Chrysene-based PPEs

We were concerned about the possibility that the persistence length of the TPPEs will be lower than the PPEs due to steric interactions between the ethynylenes and proximate aromatic CH bonds. If this was the case, a more coiled structure could be responsible for the more rapid fluorescence depolarization in the TPPEs. To address this concern, we have investigated polycyclic dibenzo[*g,p*]chrysene-based PPEs (CPPEs; figure 6) that lack any complicating steric factors and have a more rigid structure that should enhance the persistence length. The weakly allowed transitions and similar photo-physical properties of the CPPEs are similar to those observed in TPPEs (i.e. longer excited state lifetimes and more extensive energy migration; Berlman 1971). Absorbance and emission spectra (figure 7) reveal the weakly allowed groundstate transition of the dibenzo[*g,p*]chrysene monomer **17**. In contrast to
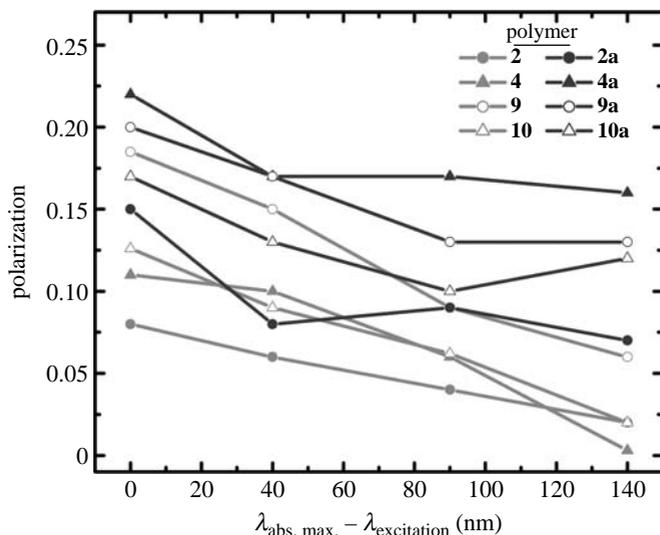
Figure 5. Polarization comparison as a function of excitation wavelength for TPPEs (grey lines) and PPEs (black lines). Polarization values truncate as excitation moves from λ_{max} in PPEs. In TPPEs, polarization continued to decrease with shorter wavelengths of excitation, indicating radiative rates are not competitive with energy migration as they are in PPEs.
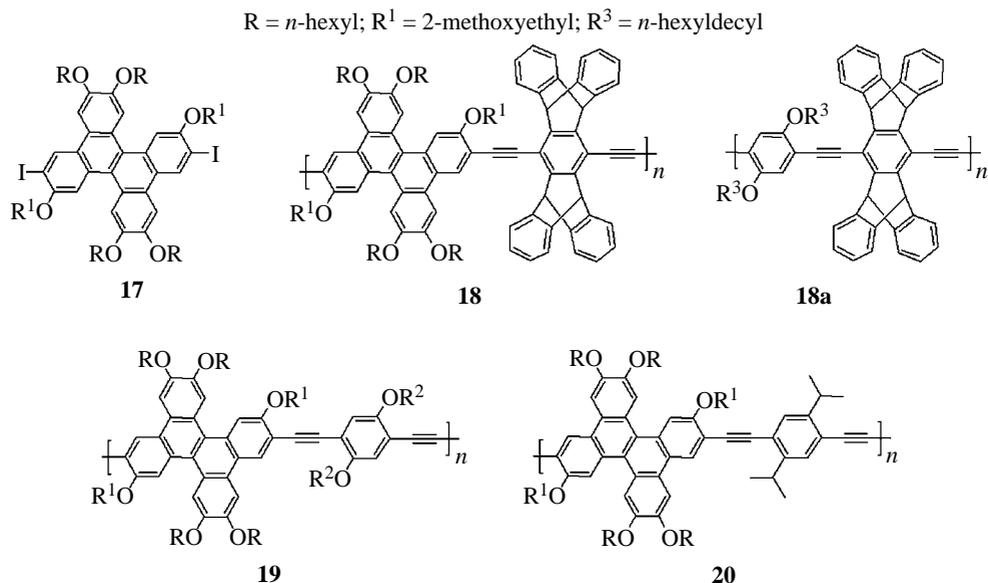
R = *n*-hexyl; R^1 = 2-methoxyethyl; R^3 = *n*-hexyldecyl

Figure 6. CPPEs.

the TPPEs, the weakly allowed transition is not entirely preserved upon polymerization; the lowest energy absorptions strengthen in the polymer spectra. It is likely that this intensity is due to greater π conjugation along the main chain, and the effect is desirable in that it will ensure that the transition moment of the emissive state is polarized along the chain axis. Despite the
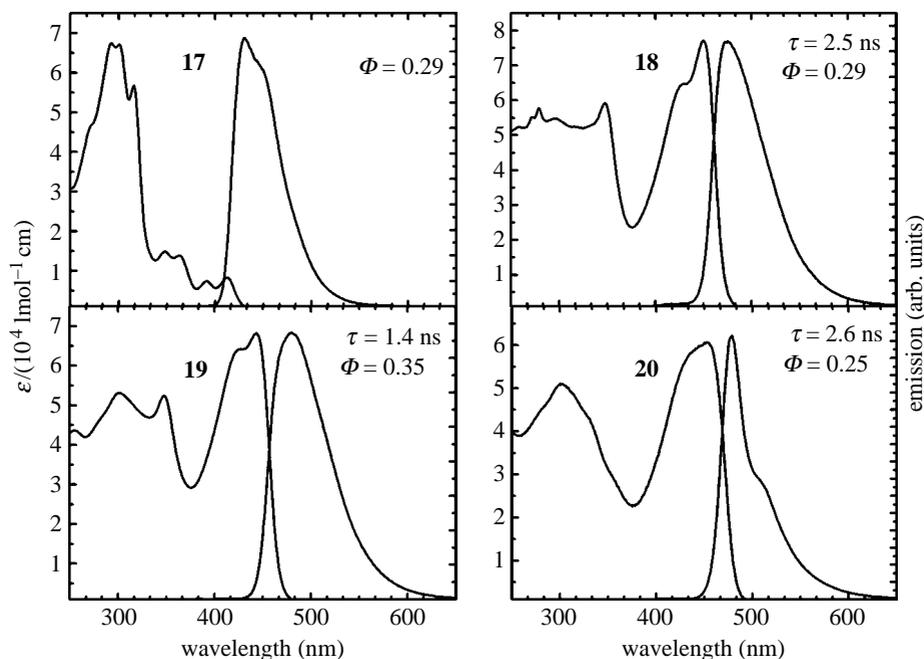
Figure 7. Absorption and emission spectra of **17–20**, dibenzo[*g,p*]chrysene monomer and polymers.

strengthening of these transitions, very long lifetimes are observed in these polymers. We compared lifetimes with PPE analogues of polymers **18** and **19** (**18a**, **9a**). PPEs have lifetimes several times shorter than those exhibited in the CPPEs as quantified in figure 7. We did not have the phenyl analogue for polymer **20** in hand; however, **20** has a longer lifetime (2.6 ns) than any PPE we have measured.

Polarization studies confirm enhanced energy migration in CPPEs. For all chain lengths and at all excitation wavelengths, CPPEs exhibited lower polarization values than their PPE analogues (figure 8). The degrees of polymerization given are approximate and were computed based on the number average molecular weights determined by gel permeation chromatography (THF solvent) relative to polystyrene standards. In most cases, the polarization values of CPPEs were about half of those in the corresponding PPEs. Polarization data as a function of excitation wavelength again discount dipole displacement as a main contributor to depolarization. As excitation energy is increased, both CPPEs and PPEs display lower P values, consistent with population of higher energy excitons that readily lower their energy by migration to lower energy states. In polymer **18**, a near linear decrease in polarization as a function of excitation wavelength (figure 8) is observed supporting energy migration as the major contributor to depolarization. In addition, the lowest attainable P values are a fraction of the P obtained when exciting at $\lambda_{\max}$. In **18a**, however, this value is only about half, indicating the radiative rate of emission limits the extent of energy migration. This limitation is overcome in the longer-lived CPPE system as P values near zero are obtainable. Because only very high molecular weights were the focus of this study, we observe very little change in polarization as a
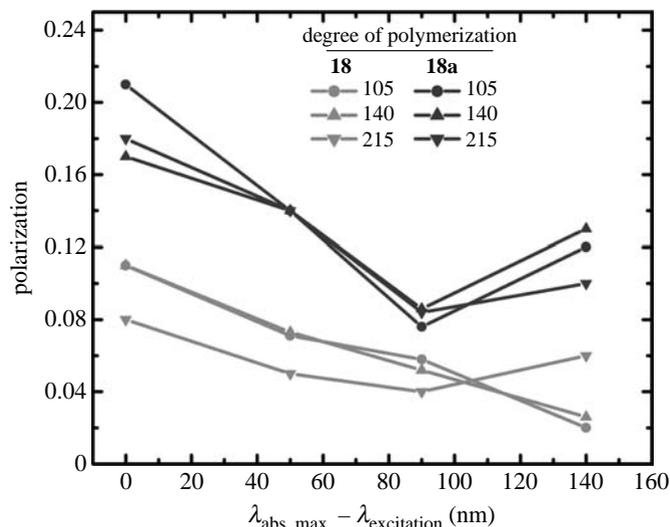
Figure 8. Polarization comparison as a function of excitation wavelength in **18** and **18a**.
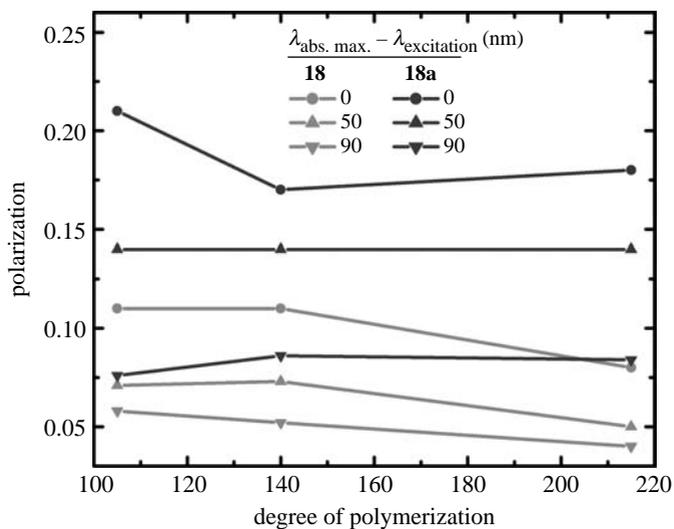

Figure 9. Polarization comparison of **18** and **18a** as a function of degree of polymerization for various excitation wavelengths.

function of chain length in **18** and **18a** (figure 9). However, a small decrease in polarization persists in **18** with increasing molecular weight while **18a** is insensitive. This indicates that radiative decay does not supersede energy migration in **18** even for the longest chain lengths.

Comparisons between **19** and **9a** were limited due to the fact that only relatively short chain lengths of **9a** were synthetically attainable. However, the trends observed in **18** along with the entire class of TPPEs are mirrored in this system as well. In all experiments, **19** exhibits greater depolarization (figure 10). As in the other materials, a decrease in polarization is observed with the increase in excitation wavelength; however, it levels off in **9a** while it continues to
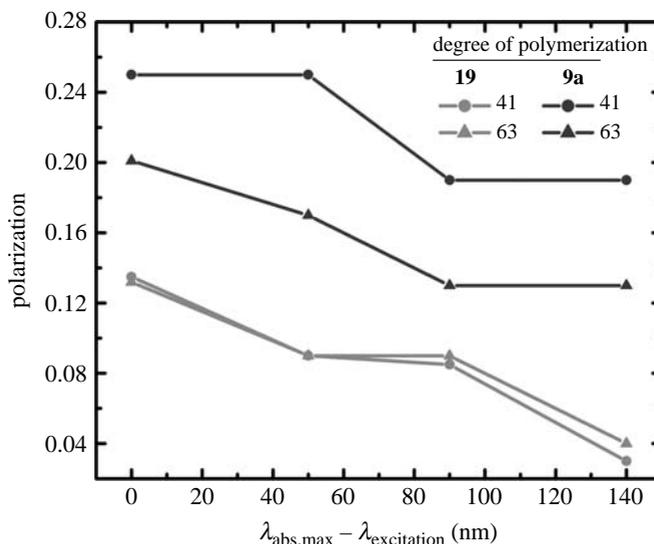
Figure 10. Polarization comparison as a function of excitation wavelength in **19** and **9a**.

decrease in **19**. This supports the assertion that energy migration is not truncated by radiative decay in CPPEs as it is in PPEs. Chain length studies in these materials are less straightforward. The polarization values are largely static for **19** over the limited range studied. This stability is most likely due to the high molecular weights of the isolated materials. The photophysical properties are well into the static regime, as is reflected in the polarization measurements.

(c) Thiophene-based model compounds and PPEs

Other polymers with pendant thiophenes (figure 11) further illuminate lifetime extension. Sulphur incorporation benefits material properties in part owing to the larger radial extension of its bonding. This promotes cofacial electronic interactions between stacked molecules that could enhance energy transfer. In addition, the facile functionalization of a thiophene monomer offers relatively efficient synthetic solutions to band-gap tuning, solubility and processability (Roncali 1997). We interrogated both a cyclized and a non-cyclized version of each model compound and polymer to assess the effects of imposed symmetry and rigidity. With both *meta* and *para* linkages represented, this family of polymers allowed us to explore effects of different degrees of aromatization as well as changes in conjugation pathways.

To predict the behaviour of these thiophene containing polymers, model compounds **21**, **22**, **23** and **24** provided systems with precisely defined conjugation lengths, allowing us to separate planarization effects from the effective conjugation length variations. The cyclized compounds **22** and **24** show a sharpening of vibronic structure concomitant with a decrease in Stokes shift as degrees of freedom are reduced (figure 12). The oscillator strength of the (0, 0) transition is significantly reduced in the *meta* system **24** ($\log \varepsilon = 3.63$) when compared with the *para* isomer **22** ($\log \varepsilon = 4.69$). This reduction is reflected in a disparity in lifetime (5.00 versus 1.12 ns, respectively) between the isomers.
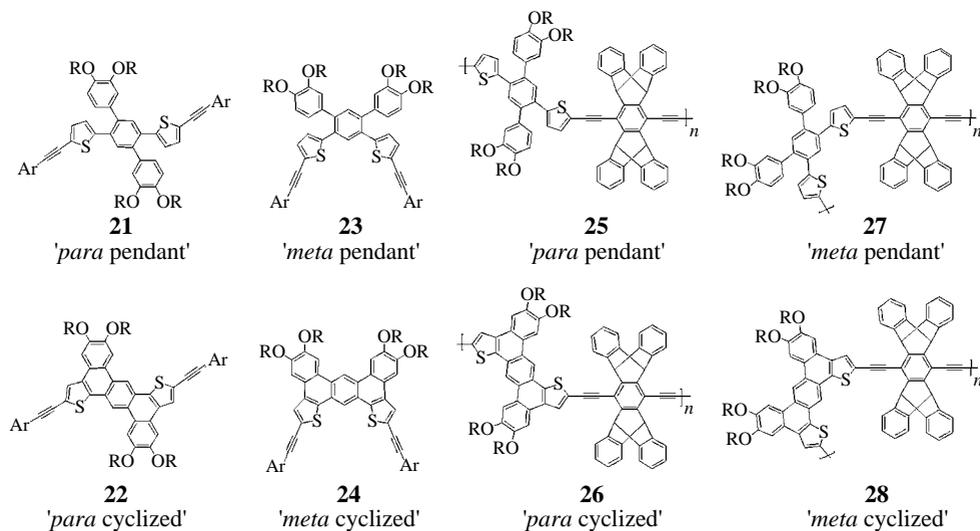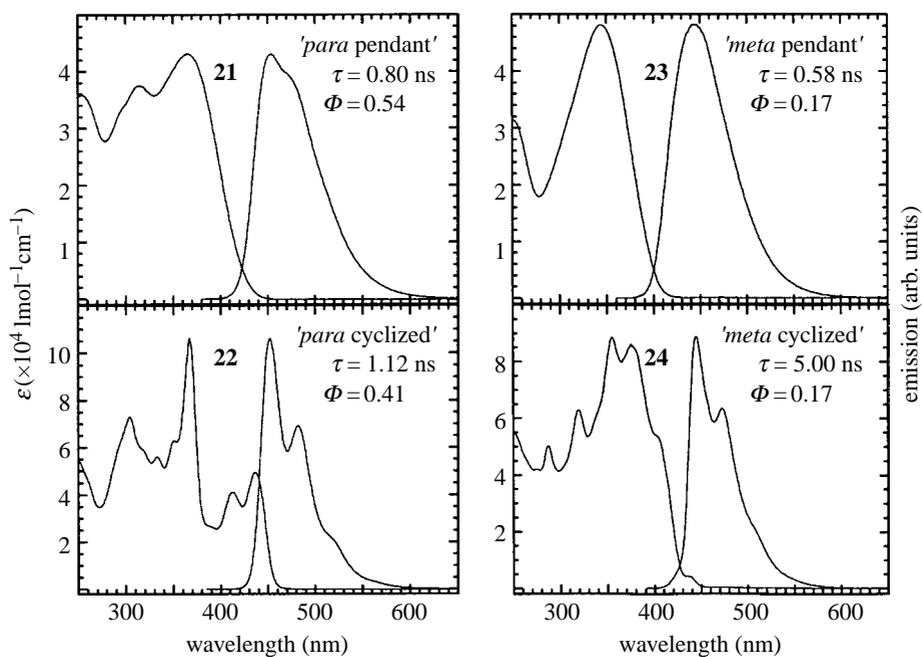
Figure 11. Thiophene-based model compounds and conjugated polymers.

Figure 12. Absorbance and emission spectra of **21**–**24**.

While a sharpening of emission spectra occurs, there is no significant wavelength shift in either system upon aromatization. This suggests that there is planarization in the excited state of **21** and **23** to allow for greater delocalization. The lifetime extension that arises from cyclization of each isomer is directly relevant to these studies. The *meta* system sees a ninefold increase (**23**: 0.58 ns; **24**: 5.0 ns) in lifetime. The lifetime increase in the *para* system is more modest (**21**: 0.80 ns; **22**: 1.12 ns).
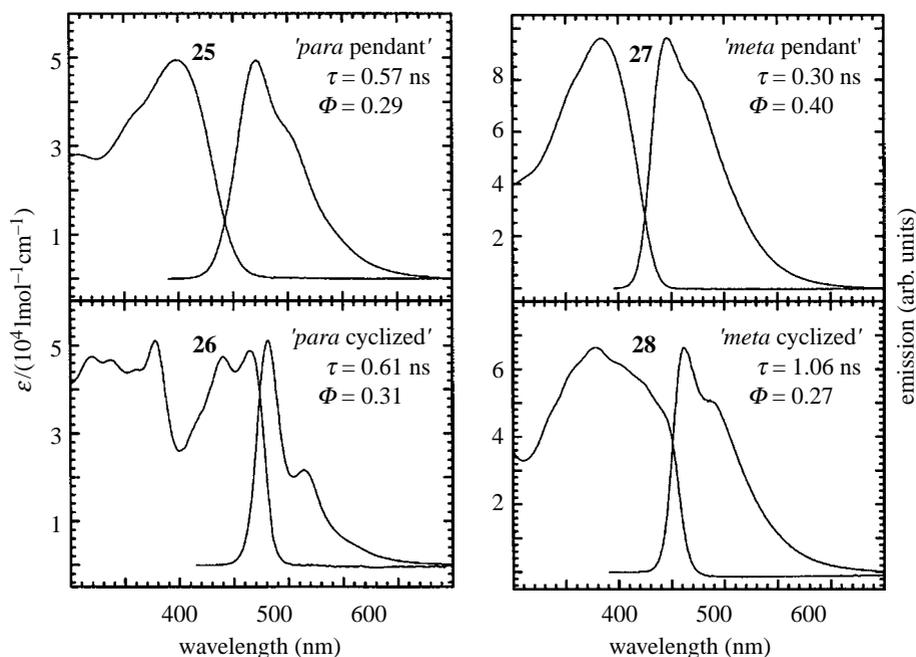
Figure 13. Thiophene polymer absorption and emission spectra.

Consistent with earlier systems, the photophysical properties of the model compounds are reflected in the corresponding polymers (figure 13). The absorption spectra of rigid, aromatized **26** and **28** display sharper vibronic structure and a decrease in Stokes shift when compared with the non-cyclized **25** and **27**. The *meta* polymer **28** displays a much lower oscillator strength at the band edge than its *para* analogue, also predicted by the model compound spectra. Aromatization effects only slight shifts in emission maxima in both the *para* and the *meta* systems. As in **21** and **23**, this may attest to excited state planarization in the flexible systems.

Lifetime trends in the model compounds are consistent with the related polymers. In concurrence with the diminished oscillator strength, the *meta* polymers **27** and **28** display a lifetime discrepancy (0.30 versus 1.06 ns, respectively) similar to that of their model compounds, **23** and **24** (0.58 versus 5.00 ns, respectively). The *para* polymers also mimic the model systems. However, in this case, the model compounds **21** and **22** exhibit comparable lifetimes (0.80 versus 1.12 ns, respectively) before and after cyclization. As a result, the *para* polymers share almost identical lifetimes (**25**: 0.57 ns; **26**: 0.61 ns). Both these examples correspond to the previously observed trend which suggests that monomer photophysics critically influences the photophysics of the resulting polymers.

The strengthening of b and-edge absorptions upon aromatization causes the spectroscopic polarization as an expression of energy migration to be more complex. We monitored polarization values for these materials by comparing polarization upon excitation at discrete differences between absorption maximum and emission maximum ($\Delta E = 0$, 50, 90, 140 nm). Population of higher energy sites on the polymer chain invariably leads to migration to lower energy sites before radiative decay. We accounted for this in the previous measurements by
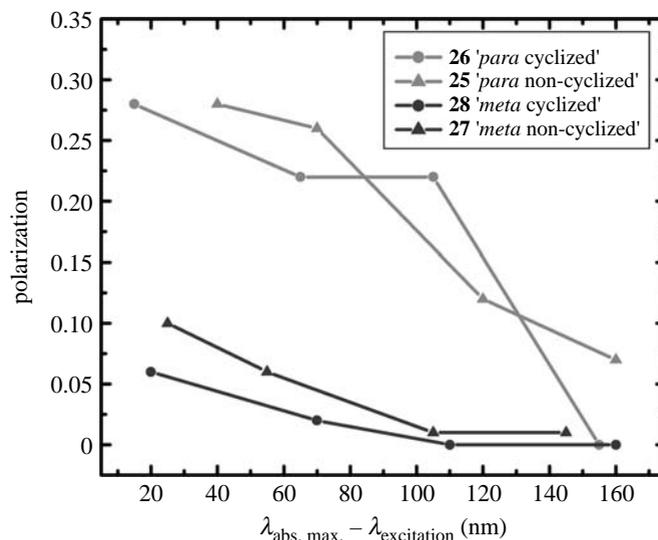
Figure 14. Polarization comparison as a function of excitation wavelength in **26**, **25**, **28** and **27**.
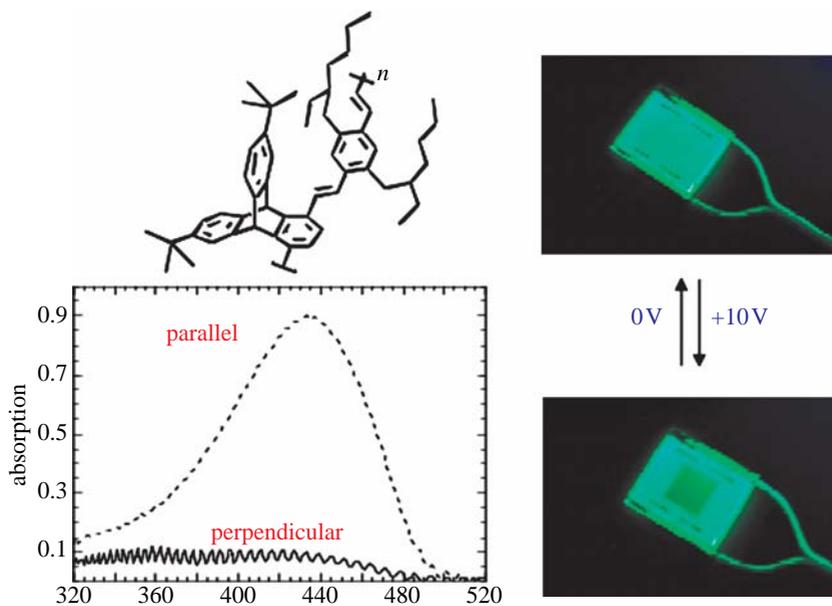

Figure 15. A nematic solution of the PPV shown. The absorption spectra reveal that the backbone is aligned and the response in a test cell indicates that it tracks the nematic director. Note that the polarized absorption reveals that the backbone is aligned parallel to the liquid crystal director.

comparing polarizations at varying differences from the absorption maximum. Polarization in the *para* isomers (figure 14) reveals that the cyclized system tends to decrease only at specific intervals of wavelengths. The more pronounced vibronic structure in this polymer reflects a more quantized energy distribution. Therefore, a dipole with different angular displacement can be excited as energy is

varied, contributing significantly to depolarization. In fact, polarization decreases rapidly at excitation wavelengths greater than 100 nm away from the emission maximum. This decrease coincides with a new manifold of states in the absorption spectrum, and hence simple local internal conversion from higher excited states will produce a dipole displacement that gives observed depolarization. The '*para* pendant' polymer **25** displays more expected behaviour, with a polarization decrease at each successive excitation wavelength. Interestingly, the polarization values are similar for both **25** and **26**. Although aromatization is formally increased in **25**, its lifetime is not affected and **25** and **26** register identical lifetimes. This similarity was expected because model compounds **21** and **22** demonstrate only a small variation in lifetime when compared with their *meta* counterparts, **23** and **24**. As anticipated, the *para* polymers also display almost identical lifetimes. Discounting the highest energy excitations as due to dipole displacement, polarization values in **25** and **26** are also roughly similar (figure 10). Together, these measurements suggest that energy migration is not enhanced without lifetime enhancement. It also underscores an important distinction: simply rigidifying the polymer backbone is not enough to extend lifetime and energy migration. One must carefully consider chromophore photophysics when attempting to impart these properties onto CPs.

Both *meta* systems, **27** and **28**, exhibit very low polarization values (figure 14) as expected from their poorly conjugated structure. A single hop along the twisted polymer backbone significantly decreases initial polarization. However, the cyclized version **28** exhibits the extreme of this effect, reaching near zero polarization values at higher excitation energies. This result is similar to the previous case wherein we cannot discount that at higher energies we are exciting states with dipole displacements. Nevertheless, it is most important to note for the lowest excitation energies, the cyclized isomer still exhibits lower polarization. This concurs with the observed lifetime disparity (**27**: 0.30 ns; **28**: 1.06 ns) facilitating energy migration. Cyclization in *meta*-substituted model compounds affords significant lifetime extension (**23**: 0.58 ns; **24**: 5.00 ns) mainly due to radiative rate suppression (**23**: 2.9×10^8; **24**: 0.34×10^8). This augmentation is transferred to the PPE backbone, resulting in longer lived excitations and enhanced energy migration. In this case, we again see that the excited state behaviour of polymers has been encoded by the choice of chromophores.

(*d*) *Aligned polymers for spectroscopic investigations*

We have studied and applied a new method for generating alignment of solutes in liquid crystals and polymers. The principle is based upon using rigid iptycene frameworks that promote specific orientations of solutes in order to minimize the amount of free volume in the composite structure. We have been interested in developing a liquid crystal strategy for creating highly organized CPs by dissolving them in a liquid crystal host (Smith *et al.* 1997).

We investigated nematic liquid crystalline solutions of highly emissive semi-conductive poly(phenylene vinylene)s (PPVs) and PPEs (Zhu & Swager 2002). The liquid crystalline solvent (a wide variety of nematics are acceptable) has the important feature that it creates an extended chain conformation that is highly aligned (order parameters range between 0.7 and above 0.8). As can be seen from simple switching studies in figure 15, the polymer can be reoriented with the
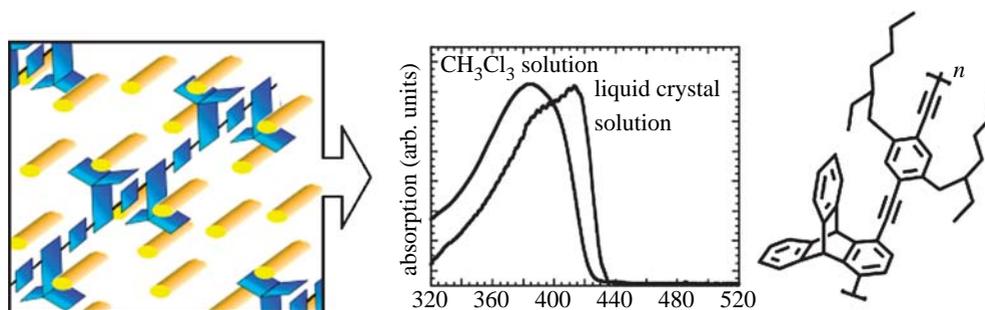
Figure 16. Comparison of the absorption spectrum of the PPE shown in methylene chloride and a nematic liquid crystal solvent. The liquid crystal imposes a planarized conformation that is responsible for the steep band edge and red shift of the absorption spectrum.
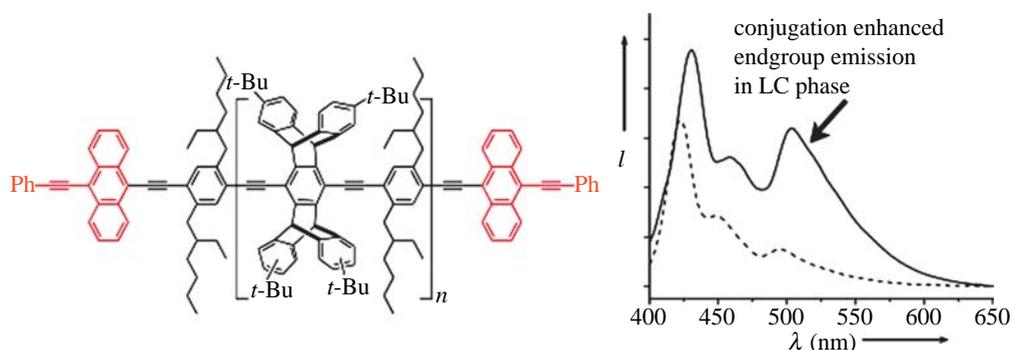

Figure 17. Fluorescence spectra of an endcapped polymer ($M_n = 24.5$ kDa, PDI$=1.7$) in the nematic LC phase at 25°C (solid line) and after heating the same solution into its isotropic phase at 60°C (dashed line). The emission at approximately 425 nm is from the bulk of the polymer and that over 500 nm is from the endgroups.

nematic host by application of electric fields. Additionally, the polymers have greatly enhanced conjugation lengths in nematic LC solutions. Methods to extend conjugation lengths in electronic polymers are critical to optimize their transport properties. An example of this effect is shown in figure 16, wherein a PPE in a liquid crystal solvent has an absorption spectrum that is red shifted and has an abrupt band edge, both of which suggest an extended conformation. The high order parameter, in this case 0.76, also reveals that the polymer is a chain extended conformation.

To develop a better understanding of energy processes, we have synthesized PPEs endcapped with lower energy anthracene trapping sites as shown in figure 17. Dissolving these materials in nematic liquid crystalline solvents allows for the study of the intrachain exciton migration rate under conditions of increased conjugation length and high alignment (Nesterov *et al.* 2005). These studies reveal that the order imposed by the nematic liquid crystal solvent increases the energy transfer efficiency, as determined by site-selective emission from lower energy traps at the polymer termini. This process is accompanied by a significant increase in the fluorescence quantum yield. These studies can also be

useful in preparing well-defined samples for time-resolved spectroscopy. Ongoing studies will further determine if the dominant mechanism of energy transfer is through the band structure (Dexter energy transfer) or a through-space dipolar interaction (Förster energy transfer).

3. Conclusions

The symmetrization and aromatization design principles pioneered with triphenylene-based PPEs were applied to novel molecular and polymeric systems. The consistent photophysical properties presented demonstrated lifetime extension in CPs is effected through deliberate chromophore design. Prior to the development and interrogation of these molecular systems, there had been no criteria for excited state lifetime extension in CPs. Because this lifetime extension can correlate with increased energy migration, the high self-consistency of these results suggests a universal platform has been developed with which to design better sensory materials.

Ongoing investigations of intramolecular energy migration can be studied by ultrafast spectroscopy on well-defined liquid crystal solutions of CPs. In this case, the conformation can be defined and hence better computational modelling of the behaviour should be possible.

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