

Conjugation Enhancement of Intramolecular Exciton Migration in Poly(*p*-phenylene ethynylene)s

Evgueni E. Nesterov,[†] Zhengguo Zhu, and Timothy M. Swager*

Contribution from the Department of Chemistry and Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received March 25, 2005; E-mail: tswager@mit.edu

Abstract: Efficient energy migration in conjugated polymers is critical to their performance in photovoltaic, display, and sensor devices. The ability to precisely control the polymer conformation is a key issue for the experimental investigations and deeper understanding of the nature of this process. We make use of specially designed iptycene-containing poly(*p*-phenylene ethynylene)s that display chain-extended conformations when dissolved in nematic liquid crystalline solvents. In these solutions, the polymers show a substantial enhancement in the intrachain exciton migration rate, which is attributed to their increased conjugation length and better alignment. The organizational enhancement of the energy transfer efficiency, as determined by site-selective emission from lower energy traps at the polymer termini, is accompanied by a significant increase of the fluorescence quantum yield. The liquid crystalline phase is a necessary requirement for these phenomena to occur, and when the temperature was increased above the nematic–isotropic transition, we observed a dramatic reduction of the energy transfer efficiency and fluorescence quantum yield. The ability to improve the exciton migration efficiency through precise control of the polymer structure with liquid crystalline solutions demonstrates the importance of a polymer's conformation for energy transfer, and provides a way to improve the energy transporting performance of conjugated polymers.

Introduction

The ability of conjugated polymers to function as gain media in electro-optical and sensory devices is dependent on the efficient transport of excited states (excitons) along the polymer chain. We have been specifically interested in facile exciton migration in conjugated polymers in general, and poly(*p*-phenylene ethynylene)s (PPEs) in particular, that allows energy absorbed over large areas to be funneled into traps created by the binding of analytes, resulting in signal amplification in sensory devices.^{1–3} The energy migration in conjugated polymers can occur both intramolecularly and intermolecularly. In the case of dilute solutions, the intramolecular process dominates in the form of a one-dimensional exciton random walk along isolated chains.⁴ Much higher efficiency can be reached in polymer aggregates and in solid films, where the energy migration occurs as a three-dimensional process by both intramolecular and intermolecular pathways. The interplay between these two pathways has received much attention in the literature, with the intrachain migration being sometimes considered slow and inefficient as compared to its interchain counterpart.⁵ However, recent experiments have shown that the

intramolecular exciton migration in isolated polymer chains may indeed be very efficient.⁶

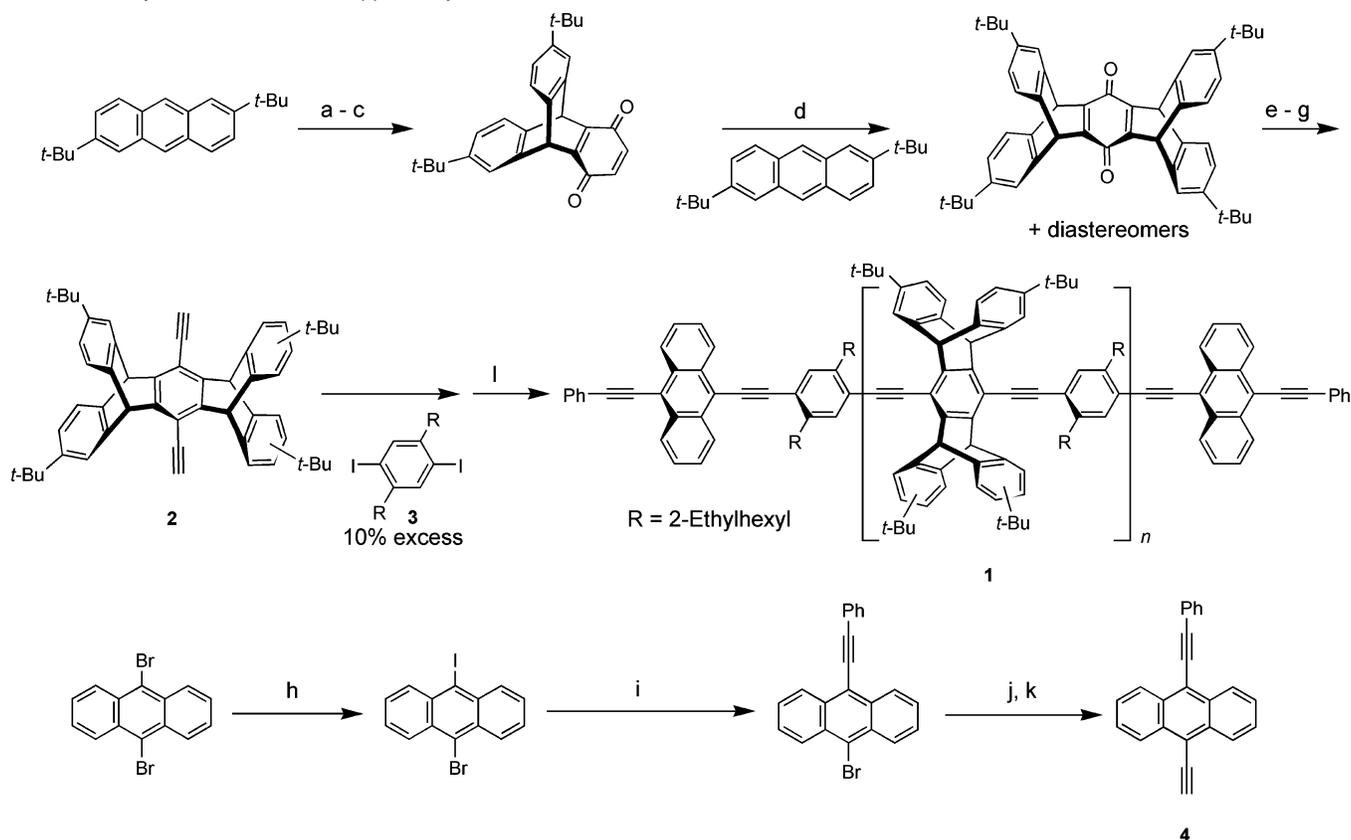
Emissive polymer films with modest to high quantum yields generally have limited electronic interactions between polymer chains, and in this case interchain energy migration is generally accepted to occur through the dipole–induced dipole mechanisms. The three-dimensional nature of energy migration in films usually leads to longer exciton diffusion lengths, but often is accompanied by formation of low-emissive intermolecular species, resulting in diminished emission quantum yields.⁷ A detailed understanding of intramolecular energy transfer in conjugated polymers is presently elusive and is complicated by the conformational complexities that are typically associated with conjugated polymers in solution and in thin films. An exception is a previous study^{4a} wherein the rate of energy transfer was investigated on PPEs assembled into discrete multilayers with precise control of polymer conformation and alignment. This study indicated that energy transfer was much

[†] Current address: Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803.

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Scheme 1. Synthesis of the End-Capped Polymer 1



^a Reagents and conditions: (a) *p*-benzoquinone, xylenes, reflux, 3 h; (b) concentrated HBr, AcOH, reflux, 10 min; (c) aqueous KBrO₃, reflux, 5 min, 65% over three steps; (d) AcOH, reflux, 66 h, 17%; (e) Me₃SiC≡CLi, THF, 0–25 °C, 16 h; (f) SnCl₂·2H₂O, acetone–AcOH, 25 °C, 24 h; (g) NaOH, MeOH–THF, 1 h, 49% over three steps; (h) *n*-BuLi (1 equiv), THF, –70 °C, 3 h, then add I₂, –70 to 25 °C, 12 h, 82%; (i) phenylacetylene (1 equiv), Pd(PPh₃)₄, CuI, *i*-Pr₂NH–toluene, 55 °C, 24 h, 73%; (j) Me₃SiC≡CH, Pd(PPh₃)₄, CuI, *i*-Pr₂NH–toluene, 80 °C, 36 h; (k) KOH, MeOH–THF, 25 °C, 40 min, 71% over two steps; (l) Pd(PPh₃)₄, CuI, *i*-Pr₂NH–toluene, 90 °C, 24 h, then add **4** (0.2 equiv), 90 °C, 12 h, 58%.

faster in the plane defined by each layer of the polymer chains as compared to the direction normal to the chains, thereby suggesting that intramolecular energy transfer is faster than the intermolecular process. Nevertheless, intermolecular energy transfer is often considered to be faster than intramolecular energy transfer because dipolar energy transfer mechanisms, known in small-molecule systems as Förster energy transfer, are assumed to be dominant. This assumption is largely based on the fact that through-space dipolar interactions scale as $1/R^6$, where R is the interchromophore distance, and hence in agglomerated weakly coupled systems the distances are shorter between effective chromophores on neighboring polymer chains, which favors interchain energy transport. However, when there is a strong electronic coupling between chromophores, as in extended systems like PPEs, there is also the possibility of facile energy transfer due to direct orbital overlap, which is generally referred to as the through-bond Dexter energy transfer mechanism.⁸

From the preceding discussion it is clear that energy transfer in conjugated polymers is complex and depends on the organization of the materials as well as their electronic structure. To gain a better understanding of the factors that control

intramolecular energy migration, we have devised methods for the study of isolated polymers in dilute solution with precise conformations. An important method in these investigations is to measure energy transfer in π -conjugated polymers that have low band gap termini. This approach, first demonstrated by one of us,⁹ has been used previously to investigate intramolecular energy transfer in isotropic solutions and amorphous films.^{5a,10} We report herein energy transfer studies on polymers dissolved in thermotropic nematic liquid crystals, and demonstrate that energy transfer is enhanced in ordered phases with chain-extended structures and increased π -conjugation. This level of control over polymer conformations has not been achieved previously, and has the potential to shed light on the relative importance of dipolar and Dexter mechanisms for intramolecular energy migration in conjugated polymers.

Results and Discussion

Synthesis of End-Capped Polymer 1. We synthesized the pentiptycene-incorporating PPE **1** (Scheme 1), end-capped with 10-(phenylethynyl)anthracenyl groups that create low-energy emissive traps.⁹ The efficiency of the exciton migration to the terminal groups can be evaluated by measuring their fluores-

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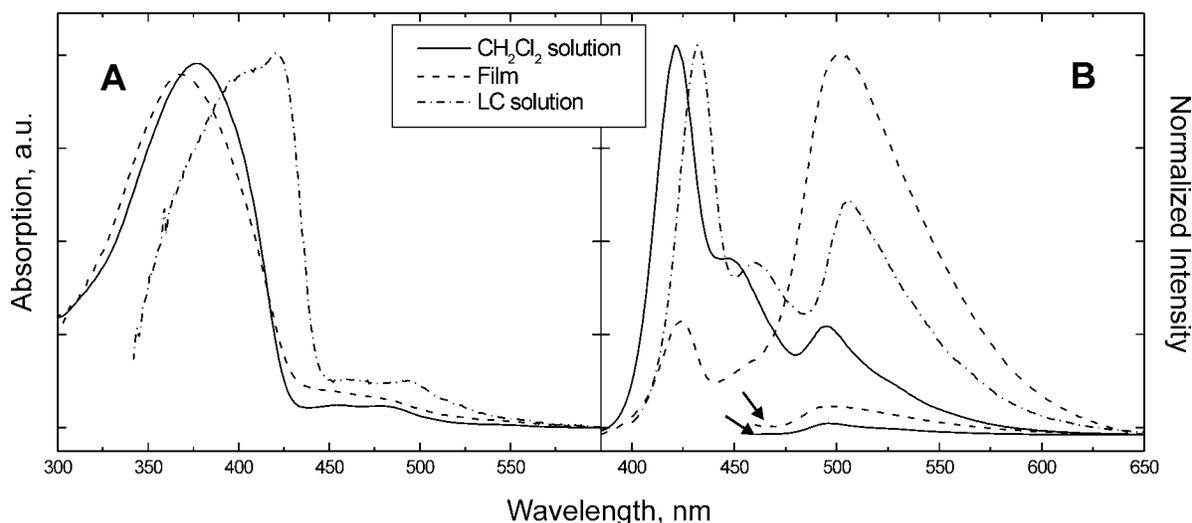


Figure 1. Normalized absorption (A) and emission (B) spectra of polymer **1**. Emission spectra were acquired upon excitation at 370 nm. Fluorescence quantum yields are the following: CH₂Cl₂ solution, 0.60; spin-cast film, 0.08; LC solution, 0.90. Extinction coefficients (at the PPE backbone maxima, per molar repeating unit): 13 000 (CH₂Cl₂ solution), 15 000 (LC solution). The lines marked with arrows correspond to emission spectra obtained at 450 nm excitation (direct excitation of the anthracenyl group).

cence intensity, with higher relative intensity corresponding to more efficient migration. The tetra-*tert*-butylpentiptcene units in the backbone of **1** limit interchain interactions in thin films,¹¹ and also promote the polymer's solubility in thermotropic liquid crystalline solvents.¹² In addition, the pentiptycene moiety has a substantial "internal free volume",¹³ which by design facilitates the polymers' alignment in nematic liquid crystalline media.¹⁴ Polymer **1** was prepared via a Sonogashira coupling protocol in two subsequent steps. The polymerization was carried out with 10% excess of diiodo monomer **3** to ensure that at the end of polymerization the polymer chain was terminated by iodine groups. The initially formed polymer was end-capped in situ by reacting with an excess of the acetylene reagent **4** (synthetic details are given in the Supporting Information). The polymer prepared by this procedure was analyzed by ¹H NMR and GPC and found to be completely end-capped (number-averaged molecular weight $M_n = 24.5$ kDa and a polydispersity index 1.69, according to GPC).¹⁵

Energy Transfer Studies. The UV/vis absorption spectrum of a dilute (0.005%) CH₂Cl₂ solution of **1** displays an intense absorption centered at 377 nm as well as a much weaker absorption at 466 nm, corresponding to the anthracenyl-based terminal groups (see Figure 1A). The polymer was found to be highly fluorescent in solution (quantum yield 0.60). The fluorescence spectrum parallels the absorption spectrum in that it consists of two bands (Figure 1B). The major band, centered at 420 nm, is characteristic for the emission from dominant PPE backbone, while the less intense band at 500 nm represents the end-group emission. When the solution is excited at 370 nm as shown in Figure 1B, essentially all of the light is absorbed by the PPE backbone, and hence the end-group emission is the result of intramolecular exciton migration. Under these condi-

tions, the efficiency of energy transfer is relatively low and was estimated by spectral deconvolution to be approximately 7%.¹⁶ The fact that the PPE is behaving as an antenna for the end groups is confirmed by the much weaker end-group emission observed when the anthracenyl group is excited directly at 450 nm with the same photon flux (Figure 1b).

We have recently demonstrated that dissolving iptycene-incorporating conjugated polymers in nematic liquid crystals (LCs) results in an increased conjugation length with the completely extended (uncoiled) polymer chains aligned along the LC director.¹⁴ The absorption spectrum of a dilute (0.05%) solution of the polymer **1** in 1-(*trans*-4-hexylcyclohexyl)-4-isothiocyanatobenzene (6CHBT, $T_m = 12.4$ °C, $T_{NI} = 42.4$ °C) at room temperature showed a dramatically red-shifted PPE backbone absorption band with a sharp maximum at 421 nm (bathochromic shift of ~44 nm as compared to CH₂Cl₂ solution, Figure 1A). The anthracenyl end-group absorption was also red-shifted, although to a lesser extent (~10 nm). Excitation spectra acquired under the detection of the anthracenyl end-group emission showed similar behavior, with the PPE-centered excitation band being significantly bathochromically shifted in the LC solution as compared to those in isotropic solution and thin film (Figure S2, Supporting Information). The fluorescence spectrum displayed a modest 10 nm red shift of both the PPE and the end-group emission bands, as compared to those of the isotropic CH₂Cl₂ solution (Figure 1B). Concomitant to these bathochromic shifts is a dramatic 5-fold increase of the efficiency of energy transfer (up to 36%) in the LC solution. This substantial enhancement of the energy transfer is accompanied by a large increase of the total fluorescence quantum yield, which is almost quantitative at 0.90 (cf. with the value of 0.60 for the isotropic CH₂Cl₂ solution).

These dramatic changes are the result of the highly uniform alignment of the polymer chains and the increased electronic

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 (15) The conclusion that **1** was completely end-capped was supported by comparison of an average degree of polymerization (DP) estimated using the ¹H NMR end-group analysis (~23) and the value obtained from the GPC analysis (~25), which are in excellent agreement with each other.

(16) We define the efficiency of energy transfer as a measure of the probability that an exciton formed on the PPE backbone is transmitted to the anthracenyl end group. It was estimated by comparing the emission spectrum of **1** to that of phenyl end-capped model polymer **5** at constant absorbance at the 370 nm excitation wavelength (see Supporting Information for more details).

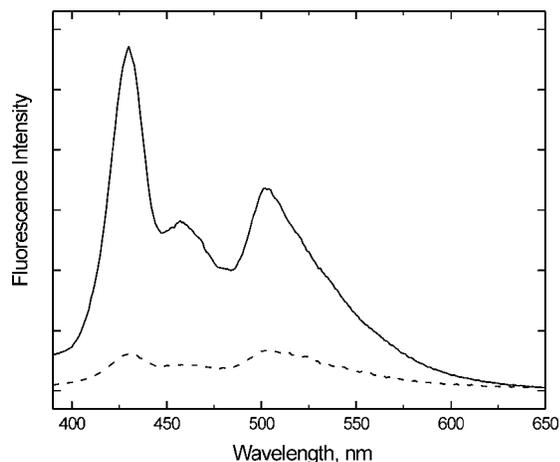


Figure 2. Polarized emission spectra of a LC solution of polymer **1** with the excitation light polarized parallel to the nematic LC director. The solid line shows the emission spectra acquired with the emission channel polarizer parallel to the polarization plane of excitation light (I_{\parallel}), while dashed line correspond to the spectrum obtained with the emission channel polarizer perpendicular to it (I_{\perp}). The latter spectrum is “G-factor” corrected. The fluorescence anisotropy ($(I_{\parallel}/I_{\perp} - 1)/(I_{\parallel}/I_{\perp} + 2)$) at 420 nm was calculated to be 0.79.

conjugation within the polymer backbone in the ordered LC phase. The fluorescence of the polymer in LC solution was found to be highly anisotropic, with the emission intensity being polarized parallel to the direction of the nematic LC director (Figure 2). In total, our observations are indicative of **1** exhibiting a chain-extended, highly conjugated planarized conformation in the nematic phase. The role of the pentiptycene structure is clearly evident when these results are compared to a recent report¹⁷ wherein LC solutions (possibly dispersions) of simple conjugated polymers were found to display broadened emission bands relative to those for CH_2Cl_2 solutions and exhibited modest polarization (fluorescence anisotropy ≈ 0.3). Such spectral broadening and low order parameters are indicative of a highly disordered polymer conformation (and potentially aggregation) in the LC solvent, in stark contrast to our results.¹⁸ The greatly enhanced conjugation length of **1** in the LC solvent is evident from the significant bathochromic shifts of the absorption and (to the lesser extent) emission spectra. The lower sensitivity of the emission wavelength to changes in the solvent is to be expected because energy transfer processes generally lead to domination of a conjugated polymer’s emission by minority low energy segments in the polymer chain.⁷ The high extent of the electronic conjugation in the polymer dissolved in the LC solvent is also clearly seen from comparing absorption spectra of **1** and the model polymer **5**, possessing the same backbone structure as **1** but with phenyl end-capping groups (Figure 3). Both spectra are very similar; however, the anthracenyl end-capped polymer **1** has an additional well-defined absorption maximum at the band edge (421 nm) which the polymer **5** does not show. The additional lower energy absorption peak is likely to originate from strong electronic coupling between the conjugated PPE backbone and the low band-gap terminal anthracenyl group. Regardless, the observed spectral

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 (18) It was recently demonstrated that the iptycene-incorporating conjugated polymers, if used as dopants, are capable of increasing the order parameter of nematic LCs due to the same “internal free volume” minimization effect (Araoka, F.; Shin, K.-C.; Takanishi, Y.; Ishikawa, K.; Takezoe, H.; Zhu, Z.; Swager, T. M. *J. Appl. Phys.* **2003**, *94*, 279–283).

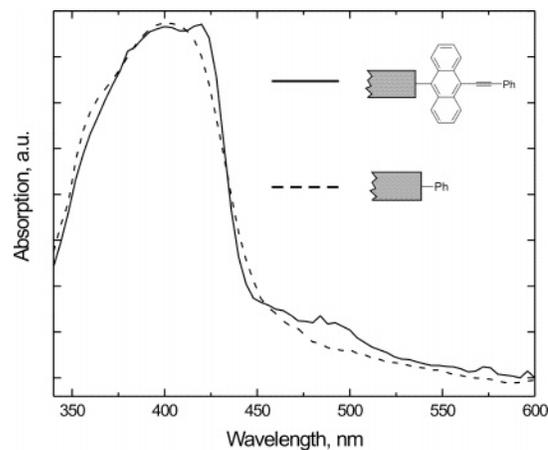


Figure 3. Comparison of absorption spectra of anthracenyl end-capped polymer **1** (solid line) and phenyl end-capped model polymer **5** (dashed line) in the LC solution.

shifts are too large to be simply a solvatochromic effect, and indicate a highly planarized polymer backbone conformation in the LC solution. This conclusion is in a good agreement both with our own previous results^{19a} and with the literature data obtained with PPEs,^{19b} as well as with small-molecule model systems.^{19c} On the basis of the experimental observation that at the low (0.005–0.05%) polymer concentrations in the LC solution the efficiency of energy transfer is concentration-independent, and the fact that we are dealing with a true, not aggregated, solution, one can safely rule out an intermolecular contribution to the increased energy transfer efficiency. Thus, the increased energy transfer to the terminal groups in the LC solution is attributed to the enhanced intrachain exciton migration. Of the two components of energy transfer, dipolar (Förster-like) mechanisms do not depend significantly on the electronic conjugation, while the Dexter through-bond exciton migration is expected to be greatly affected by the electronic conjugation.^{9,20} A strict deconvolution of the two mechanisms in this case is not possible; however, there are considerations that lead us to hypothesize that the Dexter mechanism may be more important than previously appreciated. The role of Dexter energy transport is further supported by our earlier studies²⁰ that revealed an enhancement in intrachain energy transfer with longer excited state lifetimes, a result that is in direct conflict with present theories which focus essentially exclusively on dipolar mechanisms.^{8c,21} Furthermore, earlier studies on singlet energy transfer over longer distances in conjugated donor–acceptor dyads revealed that this process cannot be satisfactorily described by using the Förster mechanism alone, without including the electron-exchange Dexter mechanism.²² In random coil conformations, intramolecular Förster-like energy transfer is thought to be facilitated by a reduction in the distance between the effective donor and acceptor chromophores. In the LC solution, **1** has a completely extended, effectively rigid-rod chain

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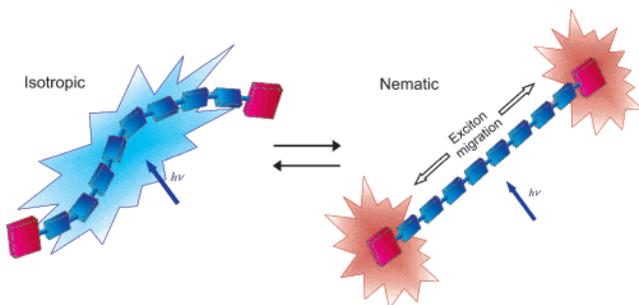


Figure 4. Simplified representation of polymer **1** in isotropic and LC solutions. In isotropic solution, the conformational disorder in the polymer backbone prevents efficient intrachain exciton migration, thus resulting in predominant emission from the PPE backbone. In nematic LC solution, the electronic conjugation on the straightened and planarized polymer chains is higher, which leads to the enhanced intrachain exciton migration toward the terminal groups with a concomitant increase in the termini's emission.

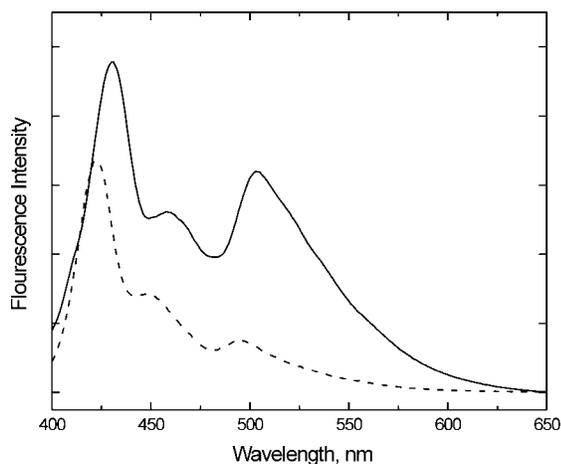


Figure 5. Fluorescence spectra of polymer **1** in the nematic LC phase at 25 °C (solid line) and after heating the same solution to its isotropic phase at 60 °C (dashed line).

conformation, in which the effective interchromophore distance is increased. In LC solution, dipolar energy transfer can also be enhanced by two additional factors: smaller Stokes shifts which will increase the spectral overlap integral,²³ and improved (more parallel) alignment of transition dipole moments.²⁴ This may increase the dipolar coupling between the effective chromophores required for the Förster-type mechanism. However, the $1/R^6$ distance dependence is a more dominating parameter. It appears likely that the facilitated energy transfer may result from an enhancement in the intrachain Dexter energy transfer, which results from the stronger electronic coupling along the polymer backbone in the ordered LC phase, and is weakened in the disordered isotropic solution (Figure 4). This critical dependence on the LC-induced order can further be simply demonstrated by heating the LC solution of **1** above its clearing point, when upon entering the resultant isotropic phase, **1**'s conjugation length was decreased (blue shift in the emission), and the energy transfer efficiency to the terminal groups was reduced to about 10% (Figure 5).

To rule out any possibility that intermolecular aggregation is responsible for the increased energy transfer to the end groups, we have investigated aggregates and thin films of **1**. In solid

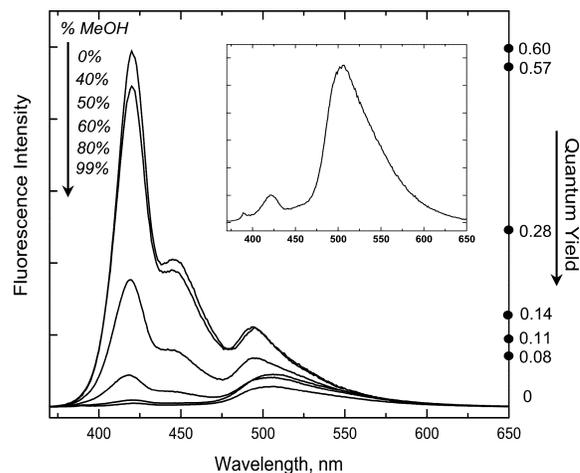


Figure 6. Fluorescence spectra of **1** recorded in chloroform–methanol mixtures with increasing fraction of methanol. Right vertical axis: Fluorescence quantum yield at each point. Inset: Magnified fluorescence spectrum in 99% methanol.

films, **1**'s fluorescence is almost completely dominated by the end-group emission, although the absorption spectrum showed no significant change from the solution spectrum (Figure 1). The high efficiency of exciton migration in this case is enhanced by intermolecular three-dimensional Förster energy transfer processes, resulting in the expected longer exciton diffusion length, as discussed earlier. However, this effect is accompanied by a significant drop of the fluorescence quantum yield (down to 0.08 as compared to 0.60 in dilute isotropic solution, and 0.90 in the nematic LC solution).

We also followed changes in the optical properties of the polymer **1** at different extents of aggregation. These studies are best performed by creating stable solutions of nanoscopic nonscattering particles, thereby allowing quantitative studies of the polymer optical properties in an aggregated state.²⁵ This is accomplished by the addition of methanol to a chloroform solution of the polymer **1**. These aggregates display no significant change in **1**'s absorption spectra, indicating that aggregation does not cause strong intermolecular electronic interactions between the PPE chains. The fluorescence spectra reveal a substantial decrease of intensity of both emission bands (Figure 6). We observe a rapid intensity decrease of the PPE backbone 420 nm band as the quality of solvent diminishes, accompanied by a much slower decrease of the 500 nm anthracenyl band. At very high methanol concentrations (above 80%), the fluorescence pattern (as well as the emission quantum yield) becomes similar to those of spin-cast films. In this strongly aggregated state, the 420 nm PPE-centered emission band drops to 0.7% of its initial intensity, while the intensity of the 500 nm anthracenyl-centered band decreases to only about 50% of its initial value. This differential quenching can be caused by more efficient energy transfer in the three-dimensional framework of aggregated state; however, it is also important to consider that the bulk of PPE and anthracenyl end groups exhibit dramatically different rates of nonradiative decay.²⁶ To deconvolute the effects of differential quenching, we obtained the emission spectra of **1** using direct excitation of the end groups

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at 450 nm (shown as the dashed lines in Figure 1b). This provided an “internal quantum yield standard”, enabling us to estimate the efficiency of the energy transfer. In solution, the direct excitation of the PPE backbone resulted only in 2-fold increase of the end-group emission intensity relative to that gained by direct excitation of the end groups. In thin films and in strongly aggregated poor solvent solutions, upon excitation at the wavelength of PPE-centered absorption we observe a much larger 18-fold increase in end-group emission intensity. This clearly indicates that the efficiency of energy transfer increases by an order of magnitude with the transformation from a one-dimensional (solution) to a three-dimensional thin-film/aggregated structure.²⁷

From the current studies, it can be concluded that intermolecular aggregation results in an overall decrease of the fluorescence quantum yield. The fact that we observed a substantial increase of the quantum yield in LC solution rules out aggregation as an explanation for the enhanced energy transfer. It is apparent that the more efficient energy transfer in nematic LC solutions is entirely the result of the improved intrachain energy transfer due to the conjugation enhancement. The increase of the polymer emission quantum yield in the LC solvent as compared to that in isotropic solutions is a remarkable observation which has no precedence. We can attribute it to an

(26) Because of the much larger size of the polymer backbone compared to the size of the terminating group, the rate of (collisional) quenching of an exciton in the backbone is expected to be much higher. This may result in nonproportional quenching of the emission, with the backbone emission displaying greater quenching.

(27) A statistical analysis (Montroll, E. W. *J. Phys. Soc. Jpn.* **1969**, 26 (Suppl.), 6–10) showed that in the case of an exciton random walk, the number of steps required for the exciton to find a trap decreases from $1/c^2$ for a one-dimensional array to $1/c$ for a three-dimensional network, where c is the concentration of randomly distributed traps. We believe this statistical reasoning to be critical if not dominant in the enhancement of exciton migration efficiency in the three-dimensional network.

effective rigidification of the polymer chains due to conformational restrictions imposed by the surrounding more highly organized LC medium. This should diminish vibrationally/rotationally coupled electronic deactivation processes, therefore reducing the rate of nonradiative decay. In addition, the organized LC environment reduces the rate of collisional deactivation (quenching) of the excited state by effectively “insulating” the polymer molecules.

Conclusions

We demonstrated that intrachain energy transfer in conjugated polymers can be enhanced in the nematic LC solutions as a result of the increasing electronic conjugation length. We have further shown that the reduction in conformational disorder in the nematic LC phase can give rise to greatly enhanced quantum yields. LC solutions provide a means to organize polymers into forms that optimize their performance and also can be used to study the effects of conformational order on their transport properties. This novel approach can be used in the design of new conjugated polymer-based sensing platforms that utilize facile intrachain exciton migration to improve their chemosensory performance without compromising the fluorescence efficiency.

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Supporting Information Available: Detailed synthetic procedures and additional experimental data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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