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Molecular Control of Luminescence from Poly(3-hexylthiophenes)[†]

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ABSTRACT: Photoluminescence (PL) from poly(3-hexylthiophenes) (P3HT) possessing various degrees of regioregularity has been studied. Wavelengths of maximum absorption and emission are blue-shifted for polymers possessing increasing head-to-head (HH) content due to steric interactions between adjacent thienyls. These repulsive forces are partially relieved in the excited state. Stokes shifts increase with increasing HH dyad content, reflecting the greater relief from conformational strain. Quantum yields of fluorescence from polymer solutions increase with decreasing head-to-head dyad content of the polymer due to a larger conjugation length, higher rigidity, and consequently, a decrease in nonradiative, torsional-mode shunt processes (intramolecular decay manifolds). In contrast, quantum yields of thin films of the polymers are largest for the less planar configurations containing significant fractions of head-to-head dyads. Low quantum yields associated with planar conjugated structures can be explained by classical concentration quenching effects which arise from nonemissive excimer complexes (intermolecular decay channels). The results are correlated with the quasi-one-dimensional band model.

Introduction

The photophysics of soluble, processable poly(3-alkylthiophenes) have been extensively studied.[1] Such polymers luminescence because the quasi-one-dimensional nature of the delocalized π-system renders the polymer backbone relatively stiff. Individual chains in polymer solutions possess relatively large Mark–Houwink constants, supporting their rather stiff nature.[2] Quantum yields of luminescence however are far from unity. The manner in which the excited chain dissipates energy by radiative and nonradiative modes is still poorly understood due to the fact that transport and trapping of electronic excitations in polymeric materials must take into account complex interactions between adjacent rings, chain defects, intermolecular forces, and aggregation states.

Photoluminescence (PL) studies on various conjugated polymers have revealed the existence of dominant nonradiative channels which accounts for low quantum yields.[3] Kaneto and co-workers attributed PL from stretched films of polythiophene to intrachain exciton decay,[4] and a recent study using optically detected magnetic resonance (ODMR) revealed three intrinsic radiative channels, namely, one intrachain "distant" polaron recombination and two triplet polaronic-exciton decays.[1d,5]

In this paper we focus upon the role of molecular structure on the photophysics of the conjugated polymers. It is well-known, for example, that regioregularity and steric interactions in poly(3-alkylthiophenes) can control their intrinsic electronic and physical properties.[6] In support of this we have illustrated that head-to-head dyad configurations in such polymers lead to amorphous polymers with lower effective conjugation lengths and lower electronic conductivities in the oxidized state. This is primarily due to the increased repulsive interactions between the alkyl side chain and the sp^2 lone pair on the sulfur, which forces the backbone out of coplanarity (Figure 1). Photophysical examination of polymers with different head-to-tail (HT) and head-to-head (HH) dyad ratios allows investigation of the influence of structural order/disorder, and hence conjugation length, on luminescence. The work complements previous studies on the effect of structural ordering in poly((2-methoxy-5-(2-ethylhexoxy)-p-phenylene)vinylene) on photoluminescence for which ordering was introduced by mechanical stretching.[7] In the present study we show how the polymer chain can be engineered at a molecular level to provide a variety of intrinsically disordered structures.

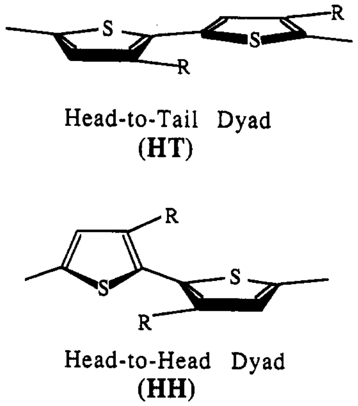

Figure 1. Illustration of twisted and coplanar conformations of head-to-head (HH) and head-to-tail (HT) dyads.

Experimental Section

Samples of poly(3-hexylthiophene) were prepared by chemical oxidative coupling using FeCl$_3$ or by polycondensation of 2,5-diiodothiophene via the Grignard route. A full description of the syntheses and physical characterization are given in ref 6f. The polymers were extensively purified prior to use. The configurational content of the dyads was determined by ^{1}H NMR as previously described.[6f] The following notation of polymers is used throughout this paper. P3HT (80% HT) comprises 80% head-to-tail dyads and 20% head-to-head dyads; P3HT (60% HT) comprises 60% HT dyads and 40% HH dyads; and P3HT (50% HT) comprises 50% HT dyads and 50% HH.

Photophysical studies were performed on polymers dissolved in CHCl$_3$ or cast onto glass or sapphire substrates from CHCl$_3$ solutions. The optical density of polymer solutions was <0.1 at their absorption maxima. Film thicknesses were $\sim$300 nm. Steady state luminescence was measured on a LS-100 spectrofluorometer (Photon Technology International Inc.). UV–vis absorption spectra were recorded on a Perkin-Elmer Lamda 3A spectrophotometer. Quantum yields of fluorescence were determined using 9,10-diphenylanthracene [ϕ_{fl}(hexane) = 0.54] and rhodamine B [ϕ_{fl}(ethanol) = 0.69) as standards.[8] For determining quantum yields of thin films 9,10-diphenylanthracene ($<10^{-3}$ M) in poly(methyl methacrylate) (ϕ_{fl} = 0.83) was used as the standard.[8] Quantum yields of films are quoted in vacuo, while solutions were purged with O$_2$-free nitrogen.

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Table I. Dyad Configuration and Molecular Weight of Poly(3-hexylthiophenes)

polymer notation	HT dyads,[a] %	HH dyads,[a] %	M_n[b]	MWD[b]
P3HT (80% HT)	80	20	40000	2.3
P3HT (60% HT)	60	40	3000	1.6
P3HT (50% HT)	50	50	4000	1.7

[a] Determined by ^{1}H NMR. [b] Determined by gel permeation chromatography.

Results

Photoluminescence. Several samples containing different ratios of configurational dyads were studied. Their molecular weights and configurational composition are given in Table I. Their wavelengths of maximum absorption and emission in the UV–vis region are tabulated in Tables II and III. Polymers P3HT (60% HT) and P3HT (50% HT) were of considerably lower molecular weight than P3HT (80% HT). Absorption and emission data obtained for higher molecular weight P3HT (60% HT) and P3HT (50% HT) samples ($M_n \sim 6500$) were virtually identical to their lower molecular weight analogs. Similarly, spectra of low molecular weight P3HT (80% HT) ($M_n \sim 9500$) were identical to those of high molecular weight polymers, indicating that the spectral difference between samples was due to configurational tendencies and not due to differences in molecular weight.

The absorption and emission spectra of polymer solutions and polymer films are shown in Figures 2 and 3. The wavelength of absorption and emission spectra are consistent with extensive π-electron delocalization. Spectra of samples containing larger fractions of HH dyads are significantly blue-shifted due to the two alkyl–sulfur lone pair repulsive interactions.

In the solid state, the polymers show absorption profiles similar to those of their solution analogs but the former are shifted to longer wavelengths. The increase in λ_{max} is indicative of an increase in conjugation, and the result of stabilization of the coplanar state via face-to-face van der Waals contacts between neighboring chains. This stabilization is less pronounced for polymers with high HH dyad content due to their more twisted, sterically hindered structure. This is supported by X-ray diffraction data, which show P3HT (50% HT) as being virtually amorphous and devoid of intermolecular order.[6f] P3HT (80% HT) on the other hand is semicrystalline, packing in a cofacial arrangement. Photoluminescence spectra, which we attribute to fluorescence due to its short lifetime and similarity to emission from the singlet state, show features similar to those of the absorption spectra; i.e., spectra are broad and exhibit the same trend of shifting to longer wavelength as head-to-head dyad content decreases. The differences in maximum wavelength of emission between the three polymers is less than it is for absorption, e.g., for polymer solutions, $\Delta\lambda_{max}$ between P3HT (80% HT) and P3HT (50% HT) is 27 nm for absorption, whereas it is 13 nm for emission; for polymer films, the difference, $\Delta\lambda_{max}$, is 98 and 62 nm, respectively.

The apparently anomalous differences in $\Delta\lambda_{max}$ are explained in terms of changes in the nuclear geometry of the chromophore upon excitation: In the ground state, thienyl conjugated segments are largely aromatic in character, where the average interannular bond order is ~1.[9] Upon excitation to the Franck–Condon excited state, the nuclear geometry of the chromophore rearranges rapidly (<1 ps)[10] to a more stable configuration, i.e., the equilibrium excited state. In polythiophenes, this represents an increase in quinoid character, for which the interannular bond order is 2 (Figure 4). The quinoid form has an intrinsically higher degree of coplanarity and presumably enhanced neighboring π-orbital interaction. P3HT (80% HT), for which conjugated segments are the most rigid and planar in the ground state, thus assumes an even more rigid and planar form in the $^*S_1$ excited state. However, the change in coplanarity upon excitation is potentially less than that available for P3HT (50% HT), for which the ground state is considerable less coplanar. The fact that a larger red-shift for fluorescence is observed for P3HT (50% HT) implies that steric interactions between HH dyads are less repulsive in the excited state, enabling a more planar structure than what might be anticipated from ground state considerations.

The change in configuration to a more planar state and the energy dissipated during the lifetime of the excited state are manifest in the Stokes shift, which we take as the magnitude of the difference between the wavelengths of the absorption and emission maxima.[11] Data for various samples of P3HT are shown in Tables II and III. For P3HT (80% HT) the Stokes shift is smaller in solid samples compared to polymer solutions due to the increased coplanarity forced by intermolecular interactions in the solid. In contrast, P3HT (50% HT) exhibits a larger Stokes shift in the solid state. The latter may be attributed to an increased coplanarity in the $^*S_1$ state which enables interchain interactions and leads to the formation of a localized molecularly ordered center. It is important to point out that the intermolecular interactions which stabilize the coplanar configuration are largely absent in the S_0 state due to the twisted nature of molecular segments.

Quantum Yields of Fluorescence. Fluorescence quantum yields for the three polymer samples are given in Tables II and III. Our primary finding is solutions of polymers containing higher HH dyad content yield lower quantum yields of fluorescence (ϕ_{fl}) in solution, whereas in solid films quantum efficiencies increase with HH dyad content.

Intrinsically ϕ_{fl} is determined by the relative rate processes of nonradiative and radiative deactivation. For conjugated aromatic oligomers and polymers a source for nonradiative deactivation is low frequency, interannular torsional modes, which are dominant for twisted interannular configurations.[11] Torsional vibrations are expected to be dominant for poly(3-hexylthiophenes) in solution, particularly when coplanarity is prevented by steric factors such as those present in HH dyads. The twisted nature of these conjugated segments thus results in lower quantum yields than those possessing considerably more rigidity. Polymers possessing higher degrees of coplanarity and rigidity (i.e., P3HT (80% HT)) are less susceptible to deactivation via torsional vibrations. In addition the larger effective conjugation leads to larger dipole strengths and oscillatory strengths, shorter fluorescence lifetimes, and hence, larger quantum yields.

Quantum yields are 1–2 orders of magnitude smaller in the solid state, and in contrast to solution, P3HT (50% HT) exhibits a larger quantum yield than P3HT (80% HT). Both phenomena can be explained on a molecular level by invoking concentration quenching considerations, which are well documented for planar conjugated systems and occur when a planar ground state molecule is in close face-to-face proximity with a planar excited state molecule.[12] Under these circumstances the excitation energy is shared intermolecularly, forming a new excited state species which can deactivate radiatively or nonradiatively. The latter can be considered as a nonradiative intermolecular decay channel. X-ray diffraction studies indicate P3HT (80% HT) as being semicrystalline.[6f] Figure 5 illustrates the cofacial packing in coplanar segments. The

Table II. Spectral Properties of P3HT in Solution

polymer	absorption[a] λ_{max}, nm (energy, eV)	emission[b] λ_{max}, nm (energy, eV)	Stokes shift, eV	ϕ_{fl}[c]	ω_0/Δ_0[d]	γ[e]
P3HT (80% HT)	440 (2.82)	580, 614[f] (2.14, 202)	0.69	0.14	0.76	1.00
P3HT (60% HT)	420 (2.95)	572, 600[f] (2.17, 2.07)	0.78	0.12	0.73	0.87
P3HT (50% HT)	413 (3.00)	567, 600[f] (2.18, 2.07)	0.81	0.09	0.73	0.86

[a] λ_{max}. [b] $\lambda_{max}\lambda_{excitation} = \lambda_{max\ absorption}$. [c] Quantum yields of fluorescence. [d] Ratio of subgap energy level of band gap. [e] Calculated from eq 1. [f] Shoulder.

Table III. Spectral Properties of Thin Films of P3HT

polymer	absorption[a] λ_{max}, nm (energy, eV)	emission[b] λ_{max}, nm (energy, eV)	Stokes shift, eV	ϕ_{fl}[c]	ω_0/Δ_0[d]	γ[e]
P3HT (80% HT)	518 (2.39)	670, 714[f] (1.85, 1.74)	0.54	0.002	0.77	1.05
P3HT (60% HT)	432 (2.87)	608,[f] 643 (2.04, 1.93)	0.83	0.003	0.71	0.80
P3HT (50% HT)	420 (2.95)	608 (2.04)	0.91	0.008	0.69	0.72

[a] λ_{max}. [b] $\lambda_{max}\lambda_{excitation} = \lambda_{max\ absorption}$. [c] Quantum yields of fluorescence. [d] Ratio of subgap energy level to bandgap. [e] Calculated from eq 1. [f] Shoulder.

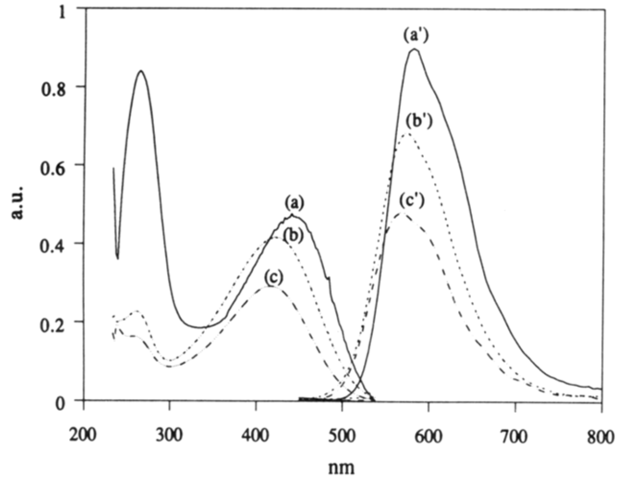

Figure 2. Absorption and emission spectra of poly(3-hexylthiophenes) in $CHCl_3$ at 298 K. Absorption spectra: (a) P3HT (80% HT); (b) P3HT (60% HT); (c) P3HT (50%) HT). Primed captions represent corresponding emission spectra.

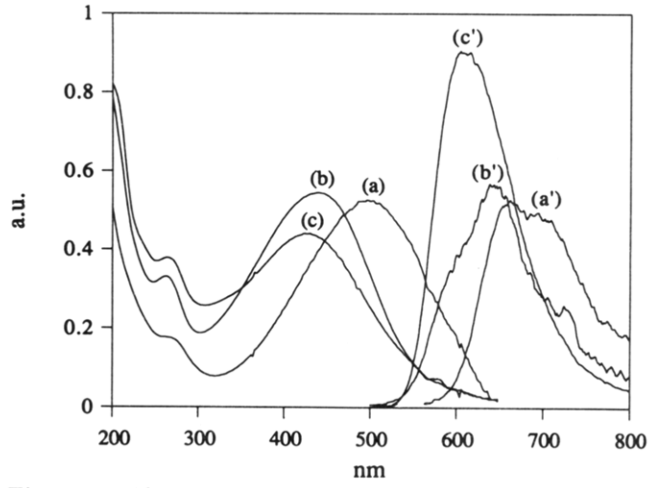

Figure 3. Absorption and emission spectra of poly(3-hexylthiophene) films at 298 K. Absorption spectra: (a) P3HT (80% HT); (b) P3HT (60% HT); (c) P3HT (50% HT). Primed captions represent corresponding emission spectra.

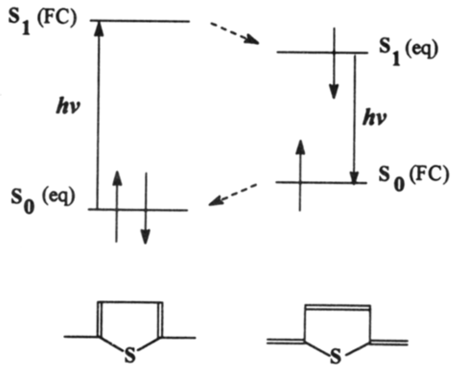

Figure 4. Energy diagram illustrating the change in nuclear configuration of conjugated thiophenes upon excitation. (FC) and (eq) represent Franck–Condon and equilibrium electronic states, respectively.

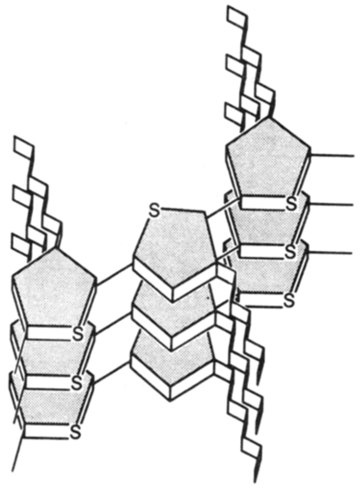

Figure 5. Simplified arrangement of coplanar conjugated segments (HT dyads) illustrating the cofacial stacking which facilitates excimer formation and intermolecular nonradiative decay of the excited state.

distance between stacked chains is 3.8 Å, which is similar to the distance required for excimer formation. Our data are consistent with formation of a nonemissive excimer since we observe a 2 orders of magnitude decrease in fluorescence in the solid state. It is worth noting that fluorescence from single crystals of polydiacetylene is completely quenched, and luminescence is only observed if the chains are deformed in some way.[13] Less coplanar polymers, e.g., P3HT (50% HT), are precluded from forming nonemissive excimers to the degree of nonplanarity exhibited by the molecules. In other words, as the dyads assume more twisted character, the cofacial distance increases and with it the likelihood of excimer formation diminishes. X-ray diffraction studies shows P3HT (50% HT) as being virtually amorphous and therefore relatively free of crystalline order. Even so quantum yields decrease from 9% to 0.8% on going from solution to solid. A viable explanation is that upon excitation the conjugated segment increases in coplanarity and is able to participate in excimer formation to a limited degree. The concept that intermolecular interactions are enhanced in the excited state is entirely consistent with the unusually large Stokes shift reported in the previous section.

Discussion. Much of our knowledge of the physics of π-conjugated polymers has derived from the one-electron continuum model,[14] which provides quantification and prediction of experimental parameters. Here we correlate the data obtained in this study with present theory since it provides an opportunity to define the role of molecular structure in terms of theoretical parameters.

Lattice relaxation in conjugated polymers has been described by Su and Yu.[15] In such a formalism, relaxation of the Franck–Condon excited state creates two electronic states from the band edges. The subgap between the two localized energy levels is given as $2\omega_0$ and represents a polaron-exciton. The band gap is defined as $2\Delta_0$. The emission spectrum for polythiophenes has been calculated using the Brazovskii–Kirova continuum model.[16] The number of phonon peaks in the emission spectrum is found to be sensitively dependent on the confinement parameter γ. Agreement of the observed emission spectra for polythiophene with the calculated spectra requires that γ is ~1, a value much larger than previous estimates, which have been in the range of 0.1–0.3 for polythiophene and ~0.4 for P3HT.[17] γ can be calculated from[1a,14b]

$$\gamma = (\omega_0/\Delta)\sin^{-1}(\omega_0/\Delta)/\sqrt{1-(\omega_0/\Delta)^2} \qquad (1)$$

Conjugated polymers often exhibit multiple phonon emissions (particularly at low temperature, and for highly planar, conjugated polymers). Under these circumstances, the zero-phonon electronic transition (E_{0-0}) represents the best estimate of 2Δ and $2\omega_0$. However, at higher temperature or with less-planar structures, vibronic structure and the zero-phonon transition are lost to the myriad of rotamers and their corresponding vibrational states. Diffuse absorption and emission spectra represent an ensemble of conformers, each possessing individual E_{0-0} transitions. Weighted averages of these transitions give rise to pseudoband edges which can be estimated from peak maxima. These are recorded in Tables II and III together with corresponding values of γ. It is recognized however that this method of assignment overestimates Δ and underestimates ω, thus yielding low values of γ.

As an indication of the relation of molecular structure to the confinement parameter the three samples show unequivocally for this class of polymer that the confinement of the polaron-exciton increases with increasing conjugation. The trend is consistent with previous studies in that decreasing disorder leads to increased delocalization in both the ground and excited states.[7] Apparently, even disordered polymers, e.g., P3HT (50% HT), can achieve considerable planarity in the excited state.

Conclusion

We demonstrate here tunability of intensity and wavelength of photoluminescence by controlling the molecular structure of poly(3-hexylthiophene). The photophysical study of this series of polymers in solution and in solid state provides an insight into intrachain and interchain nonradiative deactivation processes. In solution, where intermolecular deactivational pathways are negligible, low quantum yields are explained by deactivation through manifolds associated with interannular torsional vibrations, i.e., intrachain deactivation manifolds. These modes are enhanced for disordered or twisted structures such as those induced by HH configurational dyads. Intermolecular deactivation manifolds are evident in the solid state and become manifest at lower quantum yields of fluorescence. Although not exempt, twisted structures are less susceptible to intermolecular deactivation due to the inability of adjacent conjugated segments to achieve a cofacial arrangement. The localized excited regions in these systems would appear to be of higher molecular order than the ground state, as observed from the unusually large Stokes shifts in the solid state and low quantum yields. Excimer-type excited state complexes are nonemissive, providing an intermolecular route to deactivation of the excited state.

The results are particularly relevant to the study of electroluminescence from π-conjugated polymers since the spectral features of electroluminescence and photoluminescence are generally the same.[18] Both tunability and high intensity emission are primary goals for achieving technological applications of electroluminescent displays. Indeed, tunability of the latter has been recently demonstrated in substituted poly(*p*-phenylenevinylenes).[19]

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