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Communications to the Editor

First Observation of Phosphorescence from π-Conjugated Polymers

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Electronically excited states of π-conjugated polymers have been of significant experimental and theoretical interest over the past decade.[1] Recent discoveries of lasing, electroluminescence, and nonlinear optical activity of these materials will serve as an impetus for continued photophysical studies.[2] The majority of optical studies of nondegenerate ground-state π-conjugated polymers (i.e., those which possess benzenoid and quinonoid resonance structures) have been interpreted on the basis of polaronic and bipolaronic excitations. The existence of a triplet state has recently been invoked to explain a number of observed photophysical phenomena,[3] but information on this excited state is sparse. Particularly noteworthy is the absence of any report of direct emission from the triplet state of π-conjugated polymers or their oligomeric analogs,[4] although phosphorescence of α,ω-diphenylpolyenes, albeit in heavily-cation-exchanged zeolites, has been reported.[5]

In this paper, long-lived photoluminescence, at ~826 nm, is reported ($\tau_{1/e} \sim 15$ μs) for thin films of the processable, π-conjugated polymer, poly(3-hexylthiophene). Excitation of the π–π^* transition with 518-nm light ($S_0 \rightarrow S_1$) yields only very weak luminescence of 826-nm light, even at 18 K. The emission is enhanced, to the point where it can be observed at room temperature, when the excitation wavelength is 250 nm, but it is completely quenched by oxygen. This emission is attributed to phosphorescence, thus providing further evidence for the existence of a triplet state in π-conjugated polymers.[3] Upper-excited-state transfer (UEST)[6] leading to efficient population of the triplet state is believed to be responsible for the enhancement of phosphorescence using higher energy excitation. This is the first report of UEST in these polymer systems.

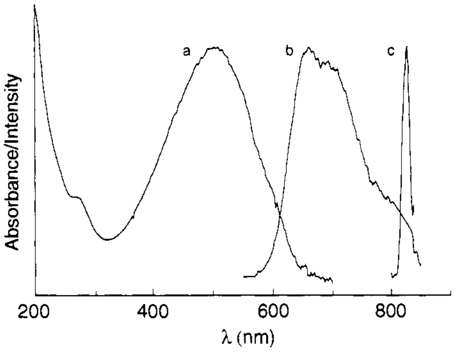

Figure 1. Absorption and emission spectra of poly(3-hexylthiophene) films. (a) Absorption at 298 K; (b) emission at 298 K, λ_{ex} = 518 nm; (c) emission at 18 K, λ_{ex} = 518 nm. For spectrum b, data were collected between 0 and 100 μs following the excitation pulse. For spectrum c, a 30-μs time delay was imposed before data acquisition. Spectra are normalized to peak height.

Several samples of poly(3-hexylthiophene) (P3HT) were used in this study. The samples differed in regiochemistry, morphology, molecular weight, and their synthesis. An account of their preparation and physical characterization is given elsewhere.[7] The properties described in this paper are consistent with all samples examined, although the temperature dependence of the long-lived emission varied with sample; temperature-dependent data will be published at a later date. Data for only one of these samples are presented. The polymer was prepared by oxidative coupling, possessed a number-average molecular weight of 40 000 with polydispersity 2.3, and was comprised of 80% head-to-head dyads and 20% tail-to-tail dyads. Thin polymer films (100 nm thick) were cast from oxygen-free-chloroform onto sapphire substrates. The substrate did not emit over the wavelengths studied. Sample impurities and instrumental artifacts were ruled out as a cause of the emission. Measurements of photoluminescence and emission lifetimes were performed on a PTI-LS100 fluorometer, which houses a pulsed xenon lamp excitation source, and were performed in the absence of oxygen, at 298 K, unless otherwise stated.

Figure 1a shows the typical broad absorption band of P3HT at 298 K. Figure 1b shows the corresponding emission spectrum ($\lambda_{ex} \sim 518$ nm). The emission exhibits a broad tail at low energy, presumably a result of emission from longer conjugated segments. Prompt fluorescence decays within 400 ps.[3d] When the sample is cooled to 18 K and data collection delayed by 30 μs following the incident light pulse, a weak, long-wavelength emission is observed at ~826 nm (Figure 1c). It is important to point out that the emission was very weak and cannot be distinguished in the presence of the much more intense prompt fluorescence. The decay of this emission is nonexponential but decreases by 1/e in 15 μs and disappears completely within 100 μs. The excitation spectrum of P3HT (λ_{em} = 826 nm) is considerably different from the absorption spectrum (Figure 2a). Irradiation with 250-nm light results in localized excitation of individual thienyl rings[8] and enhances emission at 826 nm (Figure 2b), compared to direct excitation of the π–π^* band ($S_0 \rightarrow S_1$). Furthermore, fluorescence of the π–π^* transition ($S_0 \rightarrow S_1$) was surprisingly absent, indicating the existence of a decay manifold which can compete with internal conversion to S_1.

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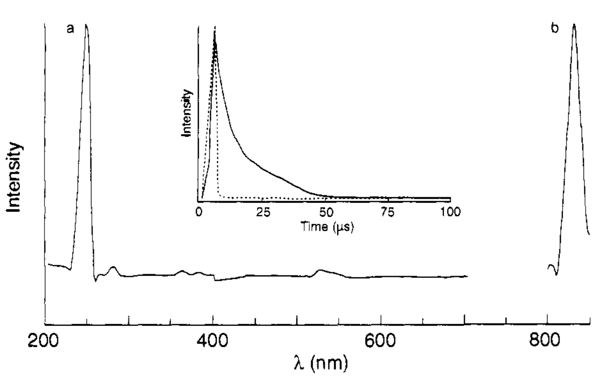

Figure 2. Excitation and emission spectra of poly(3-hexylthiophene) films at 298 K. (a) Excitation spectrum, λ_{em} = 826 nm; (b) emission, λ_{ex} = 250 nm. Data were collected between 0 and 100 μs following lamp pulse. Spectra are normalized to peak height. Inset: Decay profile of emission at 826 nm, λ_{ex} = 250 nm. Dotted line shows lamp pulse width.

Photoluminescence at 826 nm is attributed to a radiative, spin-forbidden $T_1 \rightarrow S_0$ transition, i.e., phosphorescence. The following scenario is invoked in order to explain the observed phenomena. The lifetime of the first excited singlet state is short (<0.4 ns), and the difference in energy between the S_1 and T_1 states is large. Consequently, population of T_1 via intersystem crossing (ISC) from S_1 is inefficient. Phosphorescence is, therefore, extremely weak when the $S_0 \rightarrow S_1$ excitation of the polymer is achieved with visible light. Excitation to a higher level singlet state (S_i) using 250-nm light, for example, affords an alternative route to T_1. From the observation that phosphorescence increases and fluorescence decreases when λ_{ex} is changed from 518 to 250 nm, upper excited-state transfer (UEST) is inferred, a process which facilitates intersystem crossing from higher lying singlets to higher lying triplets (T_j).[6] UEST is known to occur between higher energy states, since the difference in energy between singlet and triplet energy levels is often reduced and the rates of ISC substantially higher. Internal conversion (IC) of higher energy triplets populates T_1.[9] These processes are shown schematically below.

$$S_0 \xrightarrow{h\nu} S_i$$

$$S_i \xrightarrow{\text{UEST}} T_j$$

$$T_j \xrightarrow{\text{IC}} T_1$$

$$T_1 \xrightarrow{h\nu} S_0$$

The relatively narrow emission band is evidence for a localized triplet and is consistent with a recent optically detected magnetic resonance study (ODMR).[3a] This is further supported by phosphorescence of α-terthiophene, an oligomeric analog of polythiophene, which exhibits an almost identical emission profile (λ_{ex} = 250 nm) centered at 826 nm. Phosphorescence of α-bromoterthiophene is slightly red-shifted in comparison, but the intensity of phosphorescence is considerably larger, due to enhancement of ISC by the heavy-atom effect.

In conclusion, we report phosphorescence from π-conjugated polymers. The triplet is populated with greater efficiency via upper excited-state transfer. Since the triplet state of π-conjugated polymers may be intermediate of a number of photophysical and photochemical phenomena, e.g., photoinduced charge carrier generation[10] and photodegradation,[11] the observation and study of phosphorescence decay will play a valuable role in future research into these emerging materials.

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[9] Associating the emission with the spin-allowed $T_2 \xrightarrow{h\nu} T_1$ transition was ruled out since the latter would exhibit a much shorter lifetime.

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