Efficient Blue Luminescence of a Conjugated Polymer Exciplex

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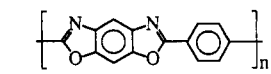
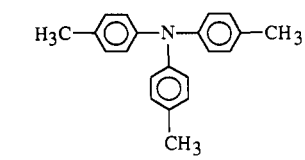
ABSTRACT: Efficient blue light emission is observed from a bilayer thin film of poly(*p*-phenylene-2,6-benzobis(oxazole)) (PBO) and tris(*p*-tolyl)amine (TTA) dispersed in the matrix of Bisphenol A polycarbonate. PBO thin films emit green light with the emission peak at 500 nm. The luminescence of PBO/TTA bilayer thin films (15–50 nm) has a peak at 474 nm and a factor of 3.4–4.2 increase in fluorescence quantum efficiency relative to PBO thin films. The steady state and time-resolved photoluminescence results suggest that the emission from PBO/TTA bilayer films originates from $(PBO^{-}TTA^{+})^{*}$ exciplex formation due to photoinduced electron transfer. The present results demonstrate that conjugated polymer exciplexes represent a new approach to blue luminescence as well as a means to enhance the solid state fluorescence quantum efficiency of conjugated polymers.

Conjugated polymers are currently of interest as optoelectronic materials for applications in areas such as light emitting diodes (LEDs),[1-9] photodetectors,[10] solar cells,[11,12] and electrophotographic photoreceptors.[13,14] Two of the many challenging problems in developing conjugated polymers for LEDs are (1) achieving high fluorescence quantum efficiencies (and ultimately electroluminescence device quantum efficiency) and (2) achieving spectrally pure blue luminescent polymers.[1-9] The difficulties in obtaining spectrally pure blue light emission from conjugated polymers are associated with both the usually large apparent Stokes shift between absorption and emission spectra and the inability to control or predict its value from molecular structure. Thus, although there are many conjugated polymers with a π–π^* transition energy of the order 2.8 eV or higher that would seem to be appropriate for achieving blue luminescence, the inability to predetermine the apparent Stokes shift throws off any prediction from the π–π^* transition energy. The large apparent Stokes shift in conjugated polymers originates from energy relaxation in the course of excitation energy migration among randomly distributed chromophores of different conjugation lengths.[15] The reported blue light emitting conjugated or nonconjugated polymers include poly(*p*-phenylene),[6] poly(alkylfluorene),[5] a polycarbonate derivative,[7] a copolymer of poly(*p*-phenylenevinylene),[8] and a block copolymer of poly(*p*-phenylene-2,6-benzobis(thiazole)).[9b] The problem of increasing the LED quantum efficiency has been addressed primarily through "device engineering" which includes varying the type of metal electrodes, the emitter thickness, the use of charge transport layers, and the use of random copolymers.[1-4] In an effort to understand the structural origins of efficient luminescence in polymers, our group has previously investigated polymer nanocomposites and polymer blends.[9b]

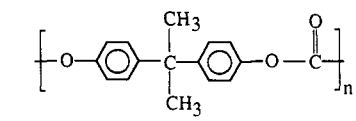
In this paper we explore a *conjugated polymer exciplex* as a new approach to enhancement of solid state fluorescence quantum efficiency and to blue luminescence in conjugated polymers. We recently suggested from solution studies that *sensitization*, whereby an excited conjugated polymer interacts with a suitable donor or acceptor molecule in its ground state and vice versa, many provide a means to enhance the luminescence quantum efficiency in the solid state.[9a] Here, we test this idea with bilayer thin films of the conjugated rigid-rod polymer poly(*p*-phenylene-2,6-benzobis(oxazole)) (PBO) and the donor molecule tris(*p*-tolyl)amine (TTA) dispersed in poly(Bisphenol A carbonate) (PC). It is found that PBO/TTA bilayer thin films exhibit bright blue luminescence (λ_{em} = 474 nm) whereas PBO thin films emit green light (λ_{em} = 500 nm) and TTA emits ultraviolet light (λ_{em} = 380 nm). Furthermore, the quantum yield of fluorescence of PBO/TTA thin films is a factor of 3.4–4.2 larger than that of PBO thin films.



PBO



TTA



PC

PBO thin films (~50 nm) for optical absorption spectra, photoluminescence (PL) spectra, and PL decay experiments were prepared by spin coating of an isotropic solution of the polymer in nitromethane containing aluminum(III) chloride ($AlCl_3$)[16] onto glass and fused silica substrates. The resulting coatings of the PBO/$AlCl_3$ complex were washed several times in deionized water and subsequently placed in a beaker of deionized water overnight to ensure complete decomplexation.[16] The films were dried in a vacuum oven for 6 h at 80 °C. The PBO/TTA bilayer thin films were prepared by spin coating of a solution of TTA/polycarbonate (40:60 by weight) in dichloromethane onto the PBO coated substrates.[17] These methods were similarly used to prepare PBO thin films of 15- and 80-nm thicknesses for photophysical measurements. The TTA/PC thin films containing 40 wt % TTA, hereafter referred to as TTA layers, were about 200 nm thick on top of the 50-nm PBO layer. The 15- and 80-nm PBO films were coated with 55-nm-thick TTA layers.

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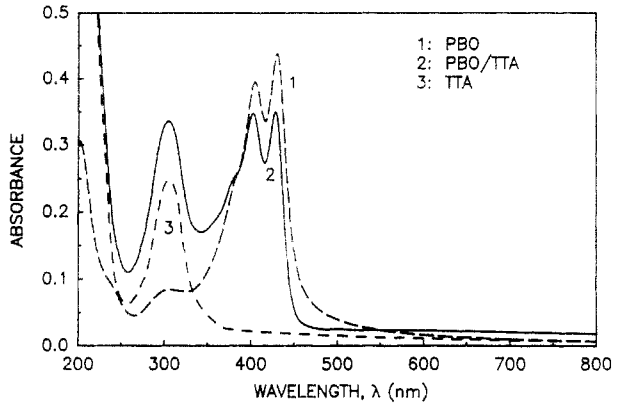

Figure 1. Optical absorption spectra of 15-nm PBO (1), bilayer PBO/TTA (2), and TTA (3) thin films.

All photophysical measurements were made at room temperature. UV–visible spectra were obtained on a Perkin-Elmer Lambda 9 spectrophotometer. Steady state photoluminescence studies were done on a Spex Fluorolog-2 fluorometer equipped with a DM3000F spectroscopy computer. The polymer films on glass slides were positioned such that the emission was detected at 22.5° from the incident beam. The relative PL quantum efficiency was obtained by comparing the integration of the emission spectra of PBO/TTA bilayers to those of PBO films. The steady state PL spectra were obtained with excitation at 380 nm.

Time-resolved photoluminescence decay measurements were performed by using the time-correlated single photon counting technique. The excitation system consisted of a mode-locked frequency doubled Nd:YAG laser (Quantronics Model 416) synchronuously pumping a cavity dumped dye laser (Coherent Model 703D) circulating rhodamine 6G. The dye laser pulses were typically 10 ps in duration at a repetition rate of 38 MHz. PBO and PBO/TTA samples were photoexcited at 380 nm. Time-resolved PL decay measurements were also done on the single-layer TTA/PC thin films (~200 nm) by exciting at 300 nm, the λ_{max} of TTA's lowest energy absorption band. The excitation at 300 nm was obtained by frequency doubling of the output of a dye laser (Rhodamine 6G).

Figure 1 shows the optical absorption spectra of thin films of TTA dispersed in the matrix of polycarbonate, PBO, and PBO/TTA. The absorption maximum (λ_{max}) of the lowest energy absorption band of the TTA films is 300 nm. The lowest energy absorption band of the PBO thin film has peaks (λ_{max}) at 401 and 427 nm, similar to its previously reported absorption spectrum.[18] The optical absorption spectrum of the PBO/TTA bilayer thin film shown in Figure 1 is composed of the component spectra. There are no new features or absorption bands in the spectrum of the PBO/TTA bilayer that may indicate strong interaction between PBO and TTA in the ground state. In particular, the TTA radical cation which absorbs strongly at 670 nm could not be detected. Figure 2 shows the excitation spectra of the same films whose absorption spectra are shown in Figure 1 and whose photoluminescence will be presented below; the excitation spectra are similar to the absorption spectra, and they do not reveal any evidence of ground state charge transfer complex formation between TTA and PBO. These results are in accord with the weak electron accepting properties of PBO in the ground state.

Figure 3 shows the photoluminescence (PL) spectrum of a PBO thin film excited at 380 nm. The PL spectrum has a peak at 500 nm, indicating green light emission. The

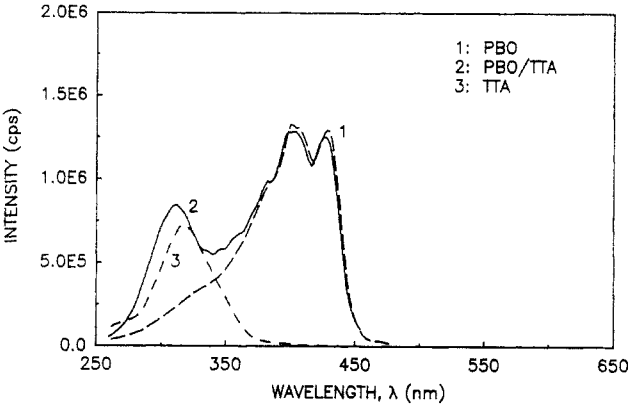

Figure 2. Excitation spectra of PBO (1), a PBO/TTA bilayer (2), and TTA (3) thin films. The excitation spectra correspond to the peaks of the emission spectra shown in Figure 3.

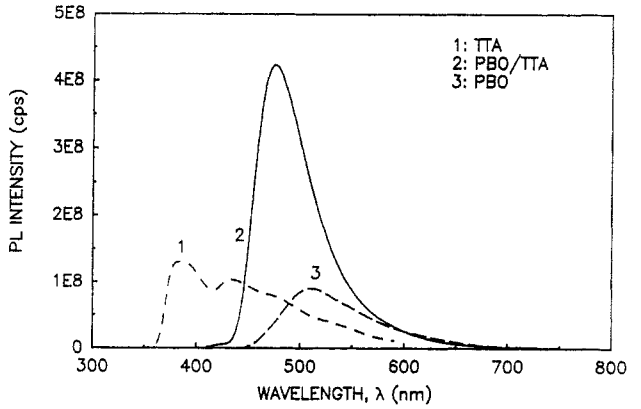

Figure 3. Photoluminescence spectra of a TTA thin film (1), a bilayer PBO/TTA thin film (2), and a PBO thin film (3).

PL spectra of PBO thin films excited at wavelengths in the spectral range 380–440 nm were identical with the one shown in Figure 3, suggesting that emission is from the same state. Although measurement of the absolute fluorescence quantum efficiency Φ_f in the solid state is very difficult,[19] we have estimated Φ_f relative to other conjugated polymers measured in our laboratory. PBO thin films are about 30% more fluorescent than poly(*p*-phenylenevinylene) and about a factor of 2 more fluorescent than the recently reported poly(benzobis(thiazole)–1,4-phenylene–bis(vinylene)) (PBTPV).[9a] The emission spectrum of the pure TTA layer shown in Figure 3 corresponds to excitation at 300 nm and has a monomer emission peak at 380 nm and an excimer emission at 432 nm. Excitation of the pure TTA layer at 380 nm shows a very weak emission at 440 nm that is at least a factor of 10 weaker in intensity compared to the emission from 300-nm excitation.

Also shown in Figure 3 is the PL spectrum of a PBO/TTA bilayer thin film excited at 380 nm. A highly intense blue emission with a peak at 474 nm is observed. The emission peak of PBO/TTA is blue shifted by 26 nm from the emission peak of the pure PBO. Most dramatic of all the differences between PBO/TTA and PBO is the factor of 3.4 enhancement of the fluorescence quantum efficiency of PBO/TTA compared to the pure PBO.

Time-resolved photoluminescence decay dynamics of PBO/TTA and PBO thin films confirmed the observed enhancement of the luminescence in PBO/TTA to originate from an excited state that is distinctively different from that of either component. The decay dynamics of PBO and of PBO/TTA excited at 380 nm were very different, as shown in Figure 4, reflecting the different excited states of the materials. The decay of PBO* showed

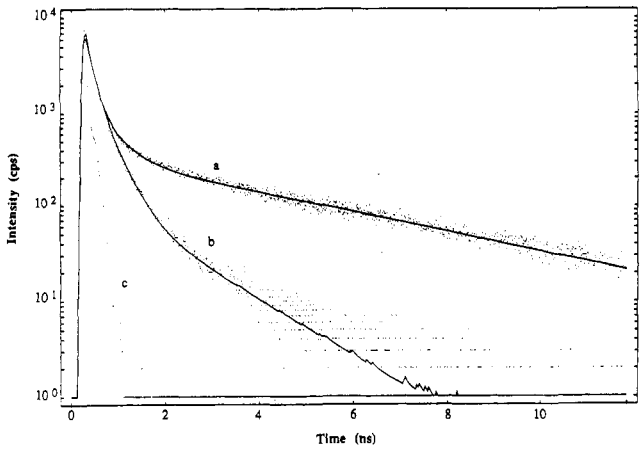

Figure 4. Time-resolved photoluminescence decay dynamics of a PBO/TTA bilayer (a) and a PBO thin film (b) excited at 380 nm. The pump response is shown in (c). The solid lines are nonlinear least-squares fits of the experimental data.

that the longest lifetime was 0.66 ns. However, the major component of the decay of the excited state associated with PBO/TTA had a lifetime of 4.6 ns. The TTA layer excited at 300 nm also exhibited a different decay dynamics with the major component having a lifetime of 2.9 ns.

Although the detailed photophysical processes in the PBO/TTA bilayer structure are yet to be fully investigated, the origin of the observed efficient blue luminescence of PBO/TTA is clearly due to the excited state interaction of the TTA molecule and PBO. As is well-known, electronically excited states are more easily reduced or oxidized than the corresponding ground states.[20] We expect the excited PBO molecule (PBO*) to be a good electron acceptor from the donor TTA in its ground state, leading to the formation of an *exciplex* of the conjugated polymer by photoinduced electron transfer: PBO* + TTA $\rightarrow$ (PBO$^-$TTA$^+$)*. Similarly, the PBO/TTA exciplex can also form by interaction of excited TTA with the ground state PBO: TTA* + PBO $\rightarrow$ (PBO$^-$TTA$^+$)*. The highly efficient blue light emission at 474 nm is thus from the (PBO$^-$TTA$^+$)* exciplex. The blue shift of the (PBO$^-$TTA$^+$)* exciplex emission from the PBO* emission reflects the different electronic structures of (PBO$^-$TTA$^+$)* and PBO and the possible reduced excitation energy migration, before recombination, in the PBO/TTA bilayer structure compared to that of the pure PBO thin film. The large enhancement of fluorescence quantum yield of the exciplex compared to the pure polymer reflects the different radiative lifetimes of the two excited states, (PBO$^-$TTA$^+$)* and PBO*. The exciplex emission characteristics, such as color and quantum efficiency, of PBO with other electron donors with different ionization potentials can be expected to be different from the present PBO/TTA results and hence other donors may provide a means to further tune the luminescence of the polymer.

Additional results supporting the interpretation of the luminescence of the PBO/TTA bilayer structure in terms of exciplex emission include the following. In separate charge photogeneration studies by xerographic photodischarge techniques employing the same TTA/PC layer on conjugated rigid-rod polymer thin films, we find virtually no dark decay, indicating that there are no trapped carriers due to band bending at the PBO/TTA interface prior to illumination. The emission spectra of PBO and PBO/polycarbonate thin films were identical, indicating that the polycarbonate plays no role in the observed photophysical behavior of the PBO/TTA bilayer. The PBO film thickness in the PBO/TTA bilayer was varied between 15 and 80 nm with illumination from the PBO and the TTA sides in steady state photoluminescence experiments. The quantum efficiency, relative to PBO, of the exciplex luminescence of the PBO/TTA bilayer illuminated from the PBO side varied with thickness: factors of 4.2, 3.4, and 2.5 for the 15-, 50-, and 80-nm films, respectively. The variation of the exciplex luminescence quantum yield with film thickness of the conjugated polymer is due to the varying absorption layer; the intrinsic absorption depth of PBO determined from its absorption coefficient is 40 nm, which suggests that the optimum PBO film thickness for the exciplex formation and luminescence in the bilayer thickness is 40 nm or less. These results suggest that the exciplex emission is from the PBO/TTA interface region.

The present results are, as far as we know, the first report on *exciplex luminescence of π-conjugated polymers* which has implications and significance for understanding and developing conjugated polymers as useful optoelectronic materials, including light emitting diodes and electrophotographic photoreceptors. Our results suggest that *exciplex formation* and *exciplex luminescence* may be important photophysical processes in organic electroluminescent devices which are commonly bilayer or multilayer structures.[21]

In summary, efficient blue light emission is observed from a bilayer thin film of poly(*p*-phenylene-2,6-benzobis(oxazole)) and tris(*p*-tolyl)amine (TTA) dispersed in the matrix of Bisphenol A polycarbonate. PBO thin films emit green light with the emission peak at 500 nm. The luminescence of PBO/TTA bilayer thin films (15–50 nm) has a peak at 474 nm and a factor of 3.4–4.2 increase in fluorescence quantum efficiency relative to PBO thin films. The steady state and time-resolved photoluminescence results suggest that the emission from PBO/TTA bilayer films originates from (PBO$^-$TTA$^+$)* exciplex formation due to photoinduced electron transfer. The present results demonstrate that conjugated polymer exciplexes represent a new approach to blue luminescence as well as a means to enhance the solid state fluorescence quantum efficiency of conjugated polymers. Our work on conjugated polymer exciplexes and their photophysics is continuing on PBO and other conjugated polymers.

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