Enhanced Blue-Violet Emission from Poly(fluorene-*co*-thiophene) Host−Guest Systems

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ABSTRACT: Host−guest systems based on novel poly(fluorene-*alt*-thiophene) (PFT) polymers exhibiting enhanced solid-state blue-violet emission are presented. These polymers were synthesized via Suzuki polycondensation of 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) with 3,4-dibromothiophene and/or 2,7-dibromo-9,9-dihexylfluorene. The host is a UV-violet-emitting, alternating 3,4-linked poly(fluorene-*co*-thiophene), and the guests are poly(9,9-dihexylfluorene) (PDHF) segments, which are prepared by either blending or copolymerization. In both cases, blue-violet emission is observed in the solid state. The solid-state quantum yields of luminescence (Φ_{pl}) are determined. Blended and copolymer systems showed a pronounced difference: Φ_{pl} of blends were independent of polymer composition while copolymers were strongly composition-dependent. These differences are attributed to morphological differences, wherein blends are phase-segregated while the copolymer system are best described as solid solutions of the guest in the host. Copolymers gave up to 10-fold enhancement in the external quantum efficiency of electroluminescence compared to the case of PDHF.

Introduction

Conjugated polymers are of current interest in light-emitting devices (PLEDs) by virtue of their low operating voltage, wide viewing angle, fast video response, and cost-effective solution processability.[1] The efficiency and emission color of polymeric LEDs are generally related to the constituent emitting polymer's solid-state quantum yield of photoluminescence (Φ_{pl}) and emission wavelength, respectively. Polyfluorenes are of particular interest as the emitter in blue PLEDs because of their high device efficiency (over 20 lm/W) and operational lifetimes of 10 000 h (at 200 cd/m^2).[1] Solutions of poly(fluorene)s[2] display blue-violet emission with values of Φ_{pl} in the range of 0.7−0.8. However, in the solid state, red-tailing and a large decrease in the emission intensity are often observed which is attributed to fluorenone formation,[3] molecular aggregation, and/or excimer formation.[4] Red-tailing affects spectral stability, whereby an irreversible blue to green color emission is observed, or emerges, because of the eyes sensitivity to green light.

Several chemical modifications have been introduced with the aim of increasing the solid-state color purity of blue-emitting polyfluorenes. These include the attachment of branched alkyl,[5] aromatic groups,[6] or dendritic groups[7] at the 9- and 9′-positions of fluorene, hyperbranching,[8] blending,[9] increasing the polymer's molecular weight,[10] end-capping polymers with aromatic groups including postpolymerizable styrene end groups,[11] and the introduction of anthracene[12] or carbazole[13] on the backbone. However, there is room for considerable improvement in the solid-state Φ_{pl} and color purity, and alternative strategies are of great interest.

Host−guest systems are of interest in molecular based LED systems since it has been shown that device efficiency and operational lifetime are significantly enhanced.[14] Host−guest systems formed using polymer/dye,[15] polymer blend,[16] and copolymer[17] combinations have proven useful for enhancing the emission intensity in the solid state by isolating the emitting species. We recently reported a host−guest copolymer where the solid-state Φ_{pl} was dramatically increased by the self-formation of a solid solution of the emitting species.[17a] In this poly(9,9-dihexylfluorene-*alt*-thiophene) (PFT) polymer system, a 3,4-linked thiophene−fluorene host transfers electronic excitation energy to isolated 2,5-linked thiophene−fluorene guests. The color of this highly luminescent polymer varied from cyan-blue to green, depending on the guest concentration.

In this paper, the solution emission properties, i.e., blue color purity and quantum yield, of polyfluorenes in the solid state are attained using a self-forming host−guest system. Alternating thiophene-*co*-fluorene polymers were studied with molecularly kinked 3,4-linked thiophene and/or the molecularly linear 2,7-linked 9,9-dihexylfluorene, according to Scheme 1.

Experimental Section

General Synthesis of Poly(9,9-dihexylfluorene-*alt*-thiophene). Polymers were prepared by a Suzuki polycondensation according to previously reported methods.[18] To a flask containing a degassed solution of 3,4-dibromothiophene (0.26 g, 1 mmol), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (0.53 g, 1 mmol), and 2 mL of an aqueous solution of 2.4 M K_2CO_3 in freshly distilled THF (10 mL) was added 3 mol % of $Pd(PPh_3)_4$ (0.036 g, 0.03 mmol). The mixture was heated for 24−72 h at 80 °C in a sealed tube, diluted with $CHCl_3$, and washed with water. The organic phase was dried with $MgSO_4$, and the solvent was partially removed under reduced pressure. The remaining polymer solution was precipitated into a methanol solution. The polymer was collected and dissolved in chloroform and further purified via column chromatography (neutral activated alumina, 60−325 mesh, Fisher Scientific). Weight-average molecular weights (M_w) ranged from 5800 to 35 600 Da, and PDI values were 1.2−2.6. NMR: poly((3,4-thienylene)-2,7-(9,9-dihexylfluorene)), PFT: ^{1}H NMR (CD_2Cl_2): δ = 7.7−7.1 (8H, fluorene and thiophene), 1.7 (4H, β-CH_2), 1.05 (12H, CH_2), 0.70 (6H, CH_3) 0.55 (4H, CH_2). Poly(9,9-dihexylfluorene), PDHF: 7.88−7.37 (6H, fluorene), 2.16 (4H, β-CH_2), 1.13 (12H, CH_2), 0.81−0.75 (10H, CH_2 and CH_3). The NMR spectra of the hybrid polymers were a combination of signals from PDHF and PFT.

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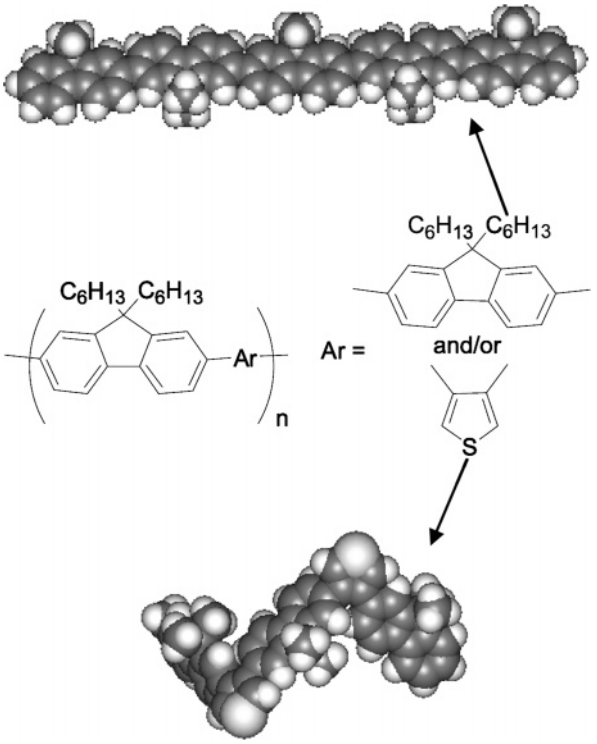
Scheme 1. Polymers Investigated and Their Corresponding Space-Filling Models (5 Units Long)



Materials. 3,4-Dibromothiophene (99%), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (97%), and tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) (99%) were purchased from Sigma-Aldrich Canada Ltd. and used as received. PEDOT (electronic grade Baytron P VP CH 8000) was purchased from H.C. Stark and used as received. THF was distilled prior to use.

Measurements. ^1H NMR spectra were recorded in CD_2Cl_2 on a 400 MHz Bruker AMX400 spectrometer. Chemical shifts were recorded in parts per million (ppm) and referenced to CH_2Cl_2 (δ 5.32). Molecular weights were measured by gel permeation chromatography (GPC) (Waters model 1515 isocratic pump) equipped with μ-Styrgel columns against polystyrene standards. Polymers (2 mg/mL) were eluted with tetrahydofuran (THF) using a flow rate of 1 mL/min and monitored with a UV−vis detector (Waters 2487). UV−vis absorption spectra were measured with a Cary 3E (Varian) spectrophotometer. Photoluminescence spectra were recorded with a Photon Technology International QuantumMaster model QM-1 equipped with an extra sample compartment containing an integrating sphere. For precise comparisons, both solution and solid-state absolute quantum yield of luminescence efficiencies (±10%) were obtained using an integrating sphere, as previously reported.[19] The excitation wavelength was 320 nm for all polymers, except for PDHF (370 nm). Solutions were deoxygenated with prepurified nitrogen prior to the fluorescence measurements, and the sample compartment was flushed with nitrogen for thin film measurements. Fluorescent spectra of the thin films, spin-cast from $CHCl_3$ on quartz, had an optical density of ~0.5. Spectra were recorded 22.5° normal to the incident light.

Polymer LEDs were based on the following structure: indium tin oxide (ITO) anode/PEDOT (140 Å thick)/polymer/magnesium:silver alloy (9:1) cathode (~1200 Å). The PEDOT layer was deposited at a rate of 2000 rpm, after filtering through a 0.45 μm PVDF filter on an ozone precleaned patterned ITO substrate. The polymer films were prepared by dissolving 8 mg of polymer in 1 mL of toluene, filtering through a 0.2 μm PTFE filter, and spin-coating (2000 rpm) on the PEDOT layer. A Mg:Ag cathode was formed by coevaporation of Mg and Ag at a rate of 4 and 0.4 Å/s, respectively. Deposition rates were controlled individually by quartz crystal monitors.

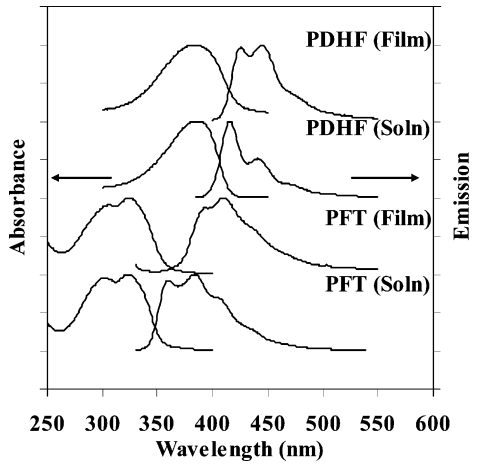


Figure 1. Solution and solid-state optical properties of PDHF and PFT.

Results and Discussion

Polymers were synthesized according to literature procedures via a Suzuki polycondensation method.[18] 9,9-Dihexylfluorene-2,7-bis(trimethyleneborate) were copolymerized with 3,4-dibromothiophene and/or 2,7-dibromo-9,9-dihexylfluorene, as depicted in Scheme 2. These polymers possessed a molecular weight ranging from 6000 to 35 600 Da, with synthetic yields ~80%. The polymers were soluble in common organic solvents, such as toluene, chloroform, tetrahydrofuran, and dichloromethane.

As background to the host−guest system, the optical spectra of poly((3,4-thienylene)-2,7-(9,9-dihexylfluorene)) (PFT) and poly(9,9-dihexylfluorene) (PDHF) are compared in Figure 1. Solution and film absorption spectra of PFT are blue-shifted compared to PDHF due to its kinked structure and lower effective conjugation length. Emission wavelengths are also blue-shifted: PDHF emission maxima are 417 and 424 nm for solution and film, respectively; the corresponding values for PFT are 383 and 410 nm.

Quantum yields of luminescence of PFT and PDHF solutions are 0.39 and 0.70, respectively: the lower yield of the former being due to its less rigid structure and heavy atom effect induced by the sulfur in thiophene.[20] Quantum yields of the corresponding films are much lower: 0.07 and 0.12, respectively. Since their emission wavelengths are red-shifted by 27 and 7 nm, respectively, compared to their solution spectra, it is evident the emitting segments exhibit enhanced coplanarity and/or aggregation in the solid state.[18]

A requirement for forming a host−guest emission system is the favorable overlap of the emission spectrum of the host with the absorption spectrum of guest. Examination of Figure 1 illustrates that the solid-state emission of PFT overlaps with the absorption spectra of PDHF. Thus, a polymer composite, prepared by either blending or copolymerization, based on a PFT host and a PDHF guest, should give rise to an efficient host−guest system.

Considering the molecular similarity between the PFT and PDHF, a polymer blend may be a feasible method for obtaining a host−guest system. Figure 2 illustrates the absorption and emission of blends at various concentrations. It is clear that the optical properties are dependent on the concentration of PDHF. That is, for blends with only ~4 wt % of PDHF, the primary emitting species is PDHF and exhibits struc-

Scheme 2. Polymers Synthesized with Various Feed Ratios

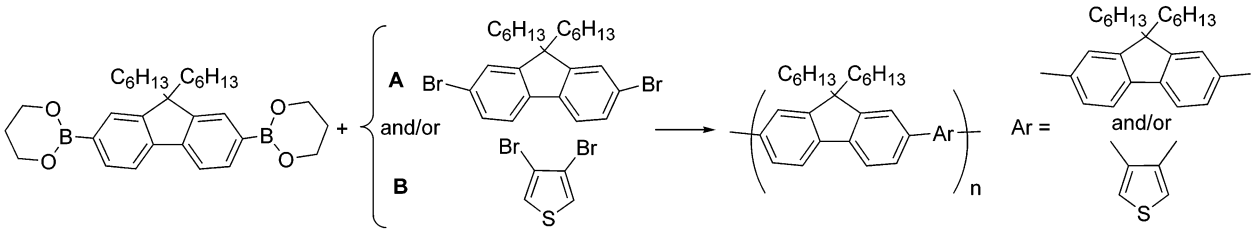


Table 1. Poly(fluorene-*co*-thiophene)s Prepared with Various 2,7-dibromo-9,9-dihexylfluorene (A) and 3,4-dibromothiophene (B) Feed Raios, and Their Corresponding Molecular Weights

Polymer	A	B	M_w	PDI
PFT	0.00	1.00	8132	1.31
PFT-0.05A	0.05	0.95	5838	1.18
PFT-0.1A	0.10	0.90	9168	1.36
PFT-0.15A	0.15	0.85	15, 836	1.61
PFT-0.2A	0.20	0.80	13, 292	1.54
PFT-0.35A	0.35	0.65	18, 863	1.69
PFT-0.5A	0.50	0.50	17, 530	1.69
PDHF	1.00	0.00	35, 607	2.56

tured emission occurring at 416 and 444 nm. Furthermore, at ~16% PDHF, the emission occurs primarily at 419 and 448 nm, again emanating from PDHF, with negligible emission from PFT, which indicates that blends should satisfy Förster energy-transfer requirements. With incorporation of 48% PDHF, the emission appears to originate from aggregated segments, having an emission maximum at 424 nm and the shoulder at 451 nm—as judged by its spectral similarity to aggregated PDHF. Analysis of the quantum yields of luminescence in Figure 3 uncovers only a small dependence on the concentration of the PDHF. The values are closer to solid-state values of PDHF (0.12) than to solution values (0.70), indicating that emission comes from aggregates of PDHF. From this, it can be inferred that polymer chains of PDHF are not molecularly dispersed in the PFT matrix but rather exist as phase-segregated aggregates. Therefore, the PFT/PDHF system appears to be a useful candidate to examine as host−guest copolymers to achieve a molecularly dispersed system of PDHF in PFT.

Several copolymers with various feed ratios of 9,9-dihexylfluorene-2,7-bis(trimethyleneborate), 3,4-dibromothiophene, and 2,7-dibromo-9,9-dihexylfluorene were prepared according to Scheme 2 and Table 1. Copolymers were prepared with the following ratios of 3,4-dibromothiophene:2,7-dibromo-9,9-dihexylfluorene: 0.95:0.05 (PFT-0.05A), 0.90:0.10 (PFT-0.1A), 0.85:0.15 (PFT-0.15A), 0.80:0.20 (PFT-0.20A), 0.65:0.35 (PFT-0.35A), and 0.50:0.50 (PFT-0.5A).

Two distinct absorption peaks are observed in both the solution and solid-state absorption spectra of the six copolymers, as shown in Figure 4: One occurs at a wavelength of ~322 nm and is due to PFT segments, while the other is a shoulder at ~368 nm due to PDHF segments. The ratio of the relative intensity of the absorption bands is correlated to the mass ratio of PDHF to PFT in the polymer and indicates that the hybrid copolymers are characterized by distinct polymer domains of PDHF and PFT.

Solution emission spectra are depicted in Figure 5a, where direct excitation of the PFT segment at 320 nm reveals two characteristic emission peaks for polymers

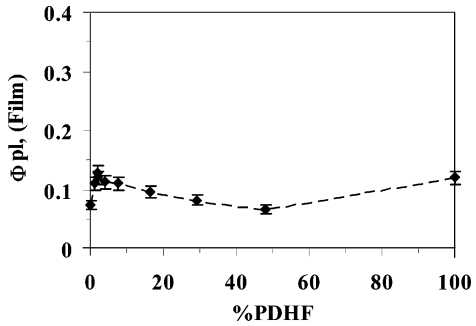


Figure 3. Quantum yield of luminescence of polymer blends as a function of PDHF concentration.

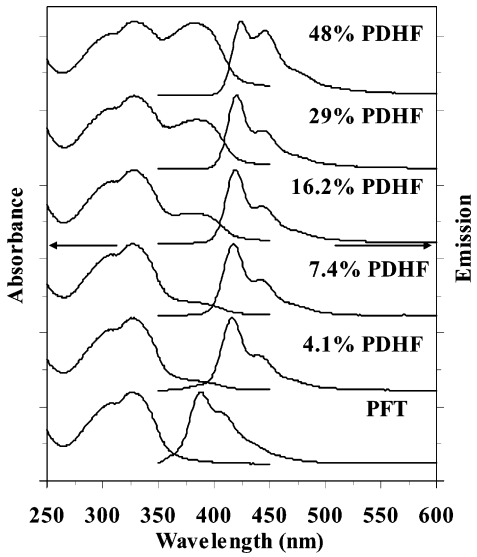


Figure 2. Solid-state optical properties of polymer blends.

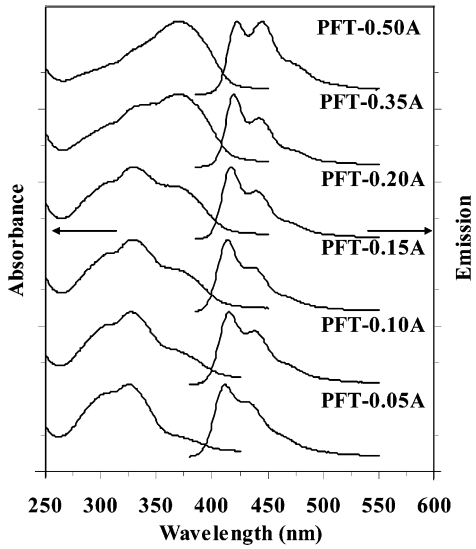


Figure 4. Solid-state optical properties of PFT copolymers with different feed ratios.

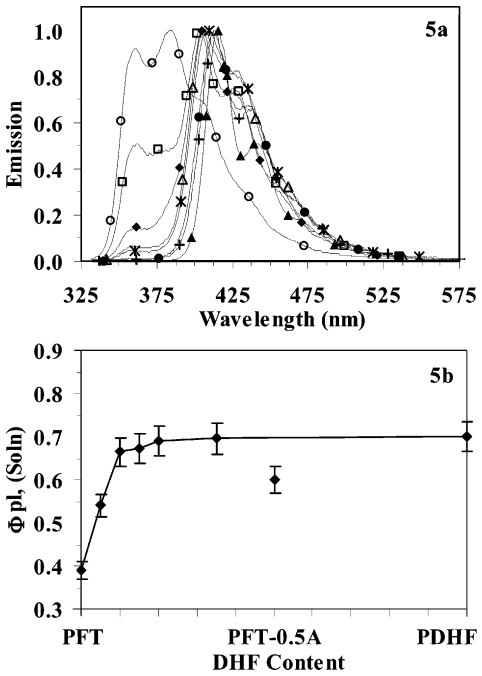


Figure 5. (a) Solution photoluminescence spectra of PFT copolymers: PFT (○), PFT-0.05A (□), PFT-0.10A (◆), PFT-0.15A (△), PFT-0.20A (★), PFT-0.35A (●), PFT-0.5A (+), PDHF (▲). (b) Quantum yield of luminescence as a function of DHF content.

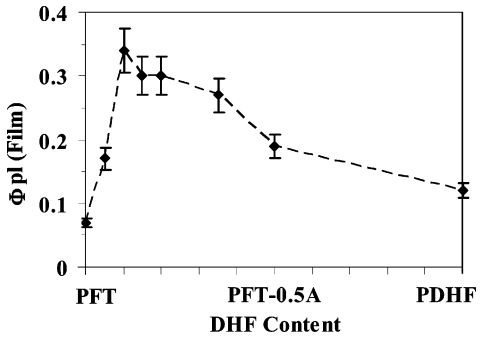


Figure 6. Solid-state quantum yield of luminescence of PFT copolymers with various feed ratios.

containing low 2,7-dibromo-9,9-dihexylfluorene ("A") content (up to about 20%): one corresponding to PDHF and the other to PFT. The fact that emission from a PDHF domain is observed implies that energy transfer from the PFT to the PDHF domains takes place; the fact that PFT emission is observed means that energy transfer is incomplete. Figure 5b displays Φ_{pl} as a function of copolymer composition. It is found that as the fluorene component increases, Φ_{pl} approaches that of pure PDHF, which also indicates the emission is dominated by PDHF emission.

Solid-state photoluminescence maxima vary from 412 nm (for PFT-0.05A) to 423 nm (PFT-0.5 A). PFT-0.05A emission is deep blue-violet in color, and PFT-0.5A is deep blue. In comparing emission profiles with those of PDHF and PFT (Figure 1), emission from the copolymers clearly emanates from PDHF units. With PDHF content $\geq$10% (PFT-0.10A), no emission is observed from PFT domains despite direct excitation of these domains with 320 nm light.

The solid-state quantum yields vary significantly, as shown in Figure 6. Φ_{pl} values are 0.07 for PFT, 0.17 with the incorporation of 5% of 2,7-dibromo-9,9-dihexylfluorene (PFT-0.05A), and 0.34 with additional 2,7-dibromo-9,9-dihexylfluorene. Φ_{pl} stabilizes (0.30−0.27) with incorporation of 35% 2,7-dibromo-9,9-dihexylfluorene but drops to 0.19, with further incorporation of the 2,7-dibromo-9,9-dihexylfluorene (PFT-0.5A). Φ_{pl} is only 0.12 for PDHF.

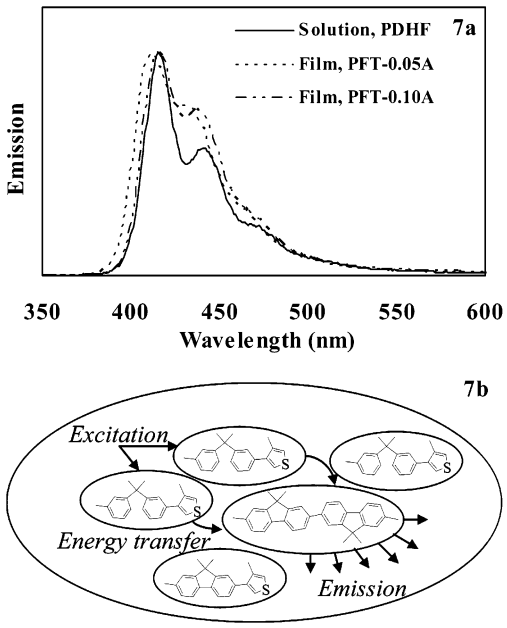


Figure 7. (a) Solution emission of PDHF with respect to film emission of PFT-0.05A and PFT-0.10A. (b) Energy-transfer mechanism.

The solid-state emission spectra of the five hybrid polymers are characterized by two peaks and a shoulder. The wavelength of maximum emission red shifts from 410, to 412, 414, 415, 417, 420, 423, and to 424 nm upon traversing the series PFT-0.05A to PFT-0.50A, which indicates that the emitting thiophene−fluorene copolymer becomes progressively more coplanar and aggregated with dihexylfluorene (DHF) content.

When the solution properties of PDHF are compared with the solid-state emission of the copolymers, the PFT-0.1A film emission spectrum is observed to be similar to the solution emission properties of PDHF. The solid-state PFT-0.05A spectrum is blue-shifted compared with PDHF, as depicted in Figure 7a. Furthermore, the solid-state quantum yield of luminescence of PFT-0.05A is similar to that of PFT (in the solid state), and its yield is lower than PFT-0.1A. This indicates that energy transfer from the PFT domains to the PDHF, as illustrated in Figure 7b, in PFT-0.05A is incomplete. PFT-0.1A displays the highest quantum yield of luminescence. A sharp decline in the quantum yields of luminescence with increasing DHF content was not observed, as in the case for copolymers of fluorene with 3,4- and 2,5-linked thiophene,[17a] most likely due to the alkyl chains on the fluorene emitter preventing molecular aggregation to some extent. Similarly, it was found in molecular based LEDs that the bulkiness of the guest emitter deterred aggregation.[22]

The dependence of quantum yield on the dihexylfluorene (DHF) content is clearly different for blends and copolymers. It is postulated that the DHF motifs in the copolymers are dispersed at the molecular level, while in the polymer blends distinct aggregated domains exist. The validity of this postulate may be examined by inspection of the energy-transfer efficiency. For efficient

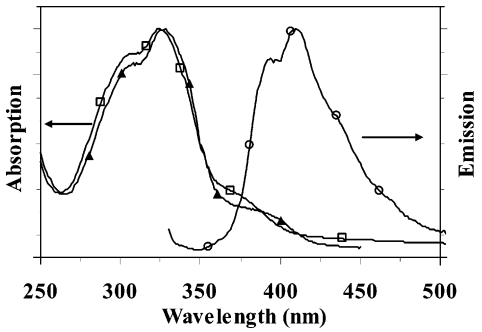


Figure 8. Absorption spectra of PFT-0.05A (□) and 7.1% PDHF blend (▲) and emission spectrum of PFT solid-state emission (○).

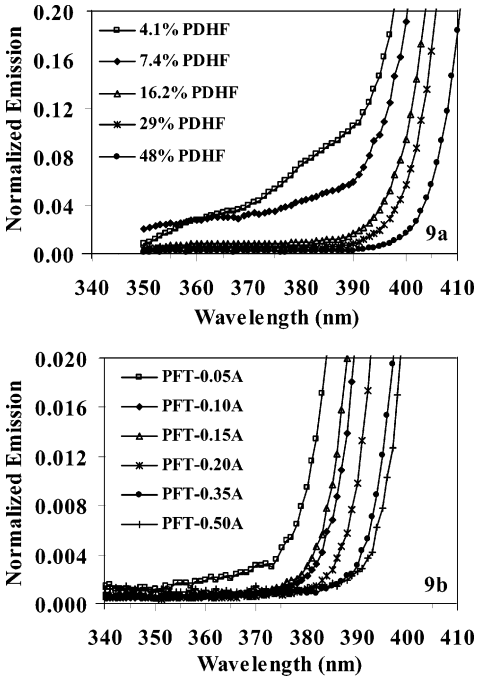


Figure 9. (a) Solid-state emission of polymer blends in the PFT region. (b) Solid-state emission of PFT copolymers from PFT domains.

energy transfer to occur, the absorption of the guest and the emission of the host must have significant overlap, and the distance between the donor and acceptor must be small (3−10 nm).[23] When comparing the absorption of the PDHF segment in PFT-0.05A and the 7.4% PDHF blend with the solid-state emission of the PFT (Figure 8), the overlap integral of the DHF segments—blends and copolymers—with the PFT emission is similar. Since the overlap integral is the same, the efficiency of energy transfer must be dependent on the distance between the donor and acceptor. Figure 9 shows an expanded view analysis of the emission region of the PFT domains in both the blend (Figure 9a) and copolymers (Figure 9b). Emission from the PFT segment, which indicates incomplete energy transfer, is at least an order of magnitude greater for the blend than for the copolymer. This confirms that energy transfer in the blends is less efficient and indicates that DHF units in the copolymers are solid-state solutions rather than phase-separated aggregates.

Light-emitting devices were fabricated from the copolymers described above. The devices had the following structure: ITO anode, poly(3,4-ethylenedioxythiophene)−poly(styrenesulfonate) (PEDOT) hole injection layer (140 nm), PFT polymer, Mg:Ag cathode (9:1; 100 nm), Ag encapsulation layer (300 nm). Structured electroluminescence is observed for all polymers, with emission maxima in the range of 415−426 nm, which are shown in Figure 10. Emission from PFT-0.05A occurs at 415 nm with a shoulder at 428 nm; emission from PFT-0.20A occurs at 417 nm with a shoulder at 444 nm; from PFT-0.35A, it occurs at 419 nm with a shoulder at 445 nm; from PFT-0.50A, 422 nm with two shoulders at 445 and 484 nm; and from PDHF it occurs at 426 nm, with shoulders at 446, 481, and 521 nm. Red-tailing was significantly reduced for the PFT copolymers compared to PDHF, thus providing an alternative method for obtaining color purity in blue-emitting polymers.

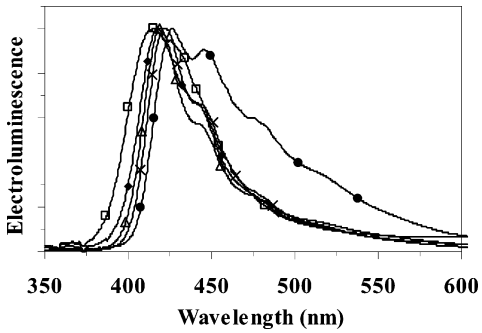


Figure 10. Electroluminescence of PFT copolymers: PFT-0.05A (□), PFT-0.20A (◆), PFT-0.35A (△), PFT-0.5A (×), PDHF (●).

Quantum yields of electroluminescence were generally quite low (external efficiencies: 1×10^{-4} for PDHF). With the addition of a 15 nm thick electron transport/injection layer (triphenyltriazine) between the polymer and the cathode,[24] the efficiency increased: the external quantum efficiency of PDHF was 1.3×10^{-3}; for PFT-0.5A, 7×10^{-3}; PFT-0.35A, 5.3×10^{-3}; PFT-0.20A, 1.1×10^{-2}; and PFT-0.05A, 1.1×10^{-3}. Copolymer content has a pronounced effect on the quantum yields of electroluminescence. Too high a DHF content decreases the quantum efficiency. However, with ≤5% DHF content, the quantum efficiency also drops. Furthermore, the host (PFT) efficiency was low ($<1 \times 10^{-4}$), with a high turn-on voltage of ∼11 V. This indicates that resistance to charge injection into the host is significant, and the device efficiency is injection limited at DHF contents ≤5%. Nonetheless, between 20 and 50% DHF content, the polymers exhibit a pronounced enhancement (up to 10-fold) in quantum efficiency. This enhancement has been observed in other host−guest based polymers and was attributed to isolating the emitting states.[17d]

An important attribute of blue-emitting luminescent polymers is spectral stability. The two leading theories for color instability in poly(fluorene)s are fluorenone formation[3] and aggregation.[4] The host−guest system presented here is a model system to investigate this effect since aggregation is reduced and the emitters are isolated. Thus, films were annealed and electroluminescence recorded at various current densities. These two experiment methods are depicted in Figure 11. Upon annealing the films at 140 °C for 2 h, a broad luminescence band evolves at ∼560 nm. The same band is observed in the electroluminescence recorded at different current densities. Instability in these poly(fluorene)s is therefore attributed to fluorenone formation,[3a] which may be minimized in combination with modified fluorene monomers and polymers.[3,5−7,10,11]

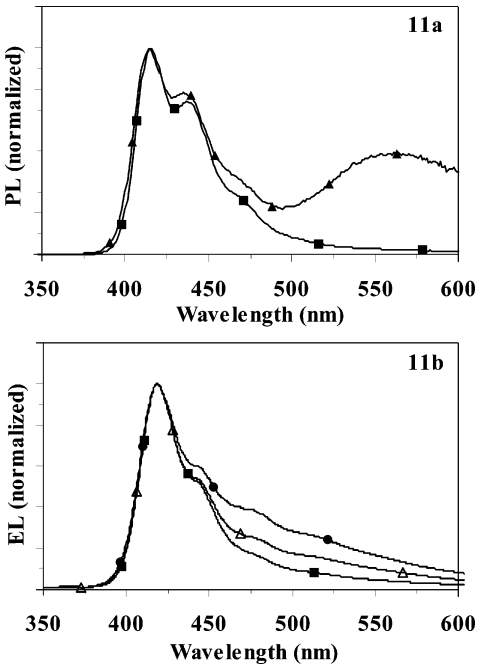


Figure 11. (a) Photoluminescence of PFT-0.1A before (■) and after annealing (▲). (b) Electroluminescence of PFT-0.35A at various current densities (25 mA/cm^2, ■; 50 mA/cm^2, △; 125 mA/cm^2, ●).

Conclusion

Host−guest systems were formed by both blending and copolymerization. Both these systems provided blue-violet emission; thus, a facile alternative route for increasing the blue color purity in blue-emitting PLEDs is presented. It was found that the copolymer yielded a 3-fold increase in the quantum yield of photoluminescence, while the blend gave a negligible increase in the quantum yield compared to that of the constituent polymers. These differences are attributed to differences in morphology. Electroluminescent yields were increased 10-fold. The polymer's photo- and electroluminescent properties mimicked PDHF with the additional attributes that the luminescent yields were much higher, and red-tailing was absent.

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