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Light-Emitting Diodes from Fluorene-Based π-Conjugated Polymers

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We report the synthesis of novel fluorene-based π-conjugated polymers and the investigation of their electroluminescent properties in organic light-emitting devices. We also report on the photo- and electroluminescence of materials of the same class whose synthesis was recently published. The alternated incorporation of phenylene or thiophene moieties in fluorene-based π-conjugated polymers leads to the tunability of the electroluminescent properties. The spectral emission varies from blue to green or yellow, depending on the composition of the copolymers. To enhance the luminous efficiency of the devices, the hole injection and hole transport into the polymer were improved by insertion of an insulating buffer layer and the incorporation of efficient hole transport material in the polymer. The insertion of a charge injection layer such as LiF and a hole transport layer such as *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1-biphenyl-4,4′-diamine significantly improves the electroluminescence efficiency of the diode from 4.5 to 125 cd/m^2.

Introduction

Since the first demonstration of efficient multilayer organic light-emitting devices (OLED) and the discovery of electroluminescence from polymeric materials,[1] there has been considerable interest in developing highly efficient, full color, flat panel displays.[2,3] Moreover, there is great interest in developing an efficient and stable blue OLED in order to obtain the three primary colors. Along these lines, several authors have recently reported blue light emission using polyfluorene derivatives.[4−7]

In addition to excellent luminescent properties, OLEDs also need adequate and balanced transport of both injected electrons and holes to allow an efficient recombination of these electrical charges in the luminescent chromophore. Due to their wide energy gaps, blue luminescent polymers usually have high oxidation potentials and low electron affinities. Because of these features, polymeric blue-light-emitting devices usually face charge injection difficulties for both types of charge carriers with the currently available anode and cathode materials. Therefore, it is often desirable to have a hole injection/transport layer adjacent to the anode and an electron injection/transport layer adjacent to the cathode, on both sides of an emitting layer, in order to improve device performance. However, the formation of such multilayer structures is, in general, difficult with polymeric materials. Since polymer thin films are typically spin-coated from solution instead of evaporated multilayers, the incorporation of different materials' functions can be achieved through a single step mixture and spin-coating.[6−9]

Along these lines, we report here the fabrication and characterization of light-emitting diodes from various fluorene-based conjugated polymers, namely, poly[1,4-(phenylene)-2,7-(9,9-dioctylfluorene)] (PPF), poly[1,1′-(4,4′-biphenylene)-2,7-(9,9-dioctylfluorene)] (PBPF), poly-[2,5-(thienylene)-2,7-(9,9-dioctylfluorene)] (PTF), poly[2,2′-(5,5′-bithienylene)-2,7-(9,9-dioctylfluorene)] (PBTF), poly[2,5-(3,4-ethylenedioxythienylene)-2,7-(9,9-dioctylfluorene)] (PEDOTF), poly[2,2′-(5,5′-di(3,4-ethylenedioxythienylene))-2,7-(9,9-dioctylfluorene)] (PdiEDOTF),

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10.1021/cm0001298 CCC: $19.00

Chart 1

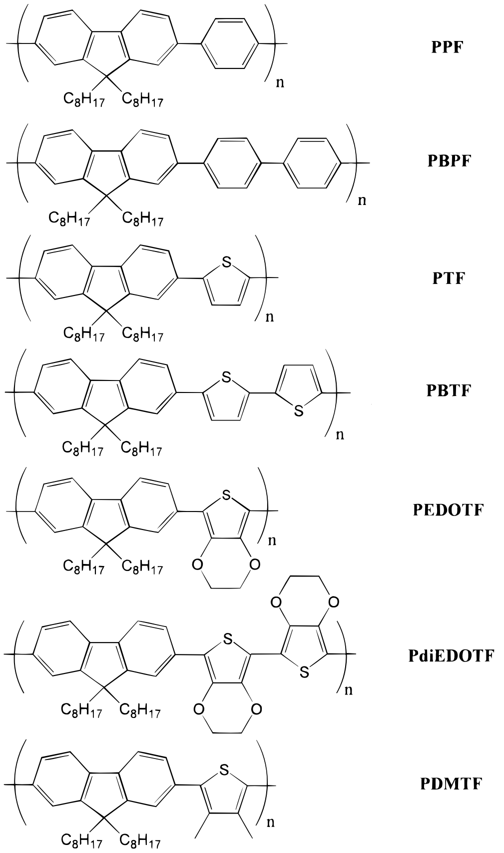
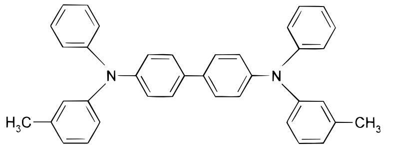


Chart 2



and poly[2,5-(3,4-dimethylthienylene))-2,7-(9,9-dioctylfluorene)] (PDMTF) (see Chart 1). Some of these polymers were blended with TPD (a hole transport material) in order to improve the recombination of the charge carriers. This new class of materials allows the fabrication of light emitting devices ranging from blue to yellow.

Experimental Details

Synthesis. Fluorene and 2,5-dibromothiophene were obtained from Aldrich Co. *N*,*N′*-Diphenyl-*N*,*N′*-bis(3-methylphenyl)-1,1-biphenyl-4,4′-diamine (TPD) (see Chart 2) was obtained from H. W. Sands Corp. 2,7-Dibromo-9,9-dioctylfluorene, 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene, and tetrakis(triphenylphosphine)palladium were prepared following already published procedures.[10,11]

2,5-Dibromo-3,4-dimethylthiophene (1).[12] To a solution of 3,4-dibromothiophene (Aldrich, 4.00 g, 16.5 mmol) in THF (15 mL) was added [1,3-bis(diphenylphosphino)propane] nickel(II) chloride (Aldrich, 89 mg, 0.17 mmol) and methylmagnesium bromide (Aldrich, 24.5 mL, 34.4 mmol, 1.4 M in toluene/THF 75:25). The reaction mixture was heated to 50 °C overnight and then poured into water with a few drops of 3 M hydrochloric acid to destroy the emulsion. The aqueous layer was extracted with diethyl ether, and the organic fractions were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure. To this crude product (1.86 g, 16.5 mmol) in $CHCl_3$ (90 mL) at 0 °C was added bromine (Aldrich, 1.80 mL, 34.8 mmol). It is important that the reaction proceeds in the dark to avoid any bromination of the aliphatic part of the molecule. The mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into water and then extracted with diethyl ether, and the organic fractions were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica gel, hexane) to provide 1.74 g (40%) of the title product as a colorless liquid. ^1H NMR (300 MHz, $CDCl_3$, ppm): 2.11 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 14.73, 107.30, 136.91.

2,5-Dibromo-3,4-ethylenedioxythiophene (2).[13] To a solution of 3,4-ethylenedioxythiophene (Bayer, 2.00 g, 14.1 mmol) in DMF (20 mL) was added NBS (Aldrich, 5.02 g, 28.2 mmol). The reaction mixture was stirred 1 h at room temperature. The resulting slurry was poured into water and then extracted with diethyl ether, the organic fractions were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure to afford a white solid. Mp: 94−95%. ^1H NMR (300 MHz, $CDCl_3$, ppm): 4.27 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 64.98, 85.86, 139.74.

2,2′-Di(3,4-ethylenedioxythiophene) (3).[14] Under a nitrogen atmosphere, in a 500 mL three-neck round-bottom flask, 10.0 g (70.0 mmol) of 3,4-ethylenedioxythiophene (Bayer) was put in 300 mL of dry THF. This solution was cooled at −78 °C. At this temperature, 29.0 mL of n-BuLi (2.5 M in hexanes, Aldrich) (72.5 mmol) was added dropwise during 30 min. This solution was stirred during 45 min, and 9.38 g (70.0 mmol) of $CuCl_2$ was then added. The reaction mixture was allowed to warm to 40 °C for 2 h. This solution was then dropped in approximatively 500 mL of cooled water. The desired greenish precipitate was collected by filtration. This solid was washed with pentane, dissolved in CH_2Cl_2, and filtered. The solution was dried with Na_2SO_4 and the solvent evaporated. The crude product was purified by flash chromatography on silica gel with CH_2Cl_2 as eluent. Evaporation under reduced pressure gave 2.74 g of the desired product (yield = 27.7%). Mp: 203 °C. ^1H NMR (300 MHz, $CDCl_3$, ppm): 4.23 (4H, m), 4.31 (4H, m), 6.26 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 64.47, 64.87, 97.41, 109.78, 136.92, 141.11.

2,2′-Dibromo(5,5′-di(3,4-ethylenedioxythiophene)) (4).[15] To a solution of 2,2′-di(3,4-ethylenedioxythiophene) (**3**, 0.445 g, 1.58 mmol) in DMF (2.5 mL) was added NBS (Aldrich, 0.575 g, 3.23 mmol) at 0 °C. The reaction mixture was stirred for 17 h, at room temperature. The resulting slurry was poured into water and then extracted with diethyl ether. The organic fractions were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure to afford a white solid (yield = 90%). Mp: 216−218 °C. ^1H NMR (300 MHz, $CDCl_3$, ppm): 4.31 (8H, s). ^{13}C NMR (75 MHz, $(CD_3)_2SO$, ppm): 64.87, 65.18, 84.87, 108.27, 136.41, 139.82.

Polymerization. All polymers were synthesized via palladium-catalyzed Suzuki couplings between dibromoaryl and diborolanylaryl compounds following already published procedures (yields = 85−90%).[10,11,16] The polymers were soluble in THF and $CHCl_3$. Characterization and ^1H NMR values for PPF, PBPF, PTF, and PBTF have already been reported elsewhere.[10]

PDMTF: ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.75 (2H), 7.49 (4H), 2.27 (6H), 2.03 (4H), 1.10 (24H), 0.84 (6H).

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Table 1. Physical Properties of the Copolymers

polymers	M_n[a] (kDa)	M_w/M_n	T_g[b] (°C)	T_m[b] (°C)
PPF	17.5	2.4	55	162
PBPF	15.0	2.2	70	265
PTF	6.8	1.6		217
PBTF	14.5	3.0	73	
PEDOTF	12.7	1.4	129	233,250
PdiEDOTF	6.6	1.9	105	
PDMTF	15.0	2.2	70	200

[a] Number-average molecular weights determined by GPC using polystyrene standards in THF. [b] Determined by DSC at a scan rate of 10 °C/min.

PdiEDOTF: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.8−7.4 (6H), 4.39 (8H), 1.94 (4H), 1.01s (24H), 0.74 (6H).

PEDOTF: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.75 (2H), 7.68 (4H), 4.46 (4H), 2.06 (4H), 1.10 (24H), 0.82 (6H).

All polyfluorene derivatives exhibit a number-average molecular weight (M_n) of about 7−17 kDa with a polydispersity index (M_w/M_n) of about 2 (Table 1).

Physical Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX300 or AMX400 in deuterated chloroform solution at 298 K. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography (SEC) with an HPLC pump using a Water 515 differential refractometer. The calibration curve was made with a series of monodispersed polystyrene standards in THF (HPLC grade, Aldrich). Differential scanning calorimetry measurements were made using a Perkin-Elmer (DSC-7) instrument calibrated with ultrapure indium, under a nitrogen atmosphere. The glass transition temperature (T_g) and the exothermic transition temperature (T_m) were measured at a scanning rate of 10 °C/min. About 10 mg of polymer was used for each sample. Cyclic voltammetry was carried out in a two-compartment cell with a Solartron potentiostat (model 1287) with platinum electrodes at a scan rate of 50 mV/s against a Ag/Ag^+ (0.1 M of $AgNO_3$) reference electrode with an anhydrous and argon-saturated solution of 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in acetonitrile (CH_3CN).

The organic light-emitting diodes were prepared on commercial ITO-coated glass substrates (Applied Films Corp.) with a sheet resistance of 30 Ω, and an ITO thickness of 120 nm. Before lithographic patterning, the ITO substrates were cleaned using cleanroom soap, acetone, and 2-propanol. The anodes were defined by etching the patterned ITO substrates in a solution of $HCl:HNO_3:H_2O$ (25:2:25). The patterned ITO substrates were treated in UV ozone for 10 min before spin-coating the polymer solution. The concentration of the chloroform solution was 6 mg/mL. The TPD was incorporated to the solution at a concentration of 20% w/w (TPD/polymer). The spin-coating speed was 1500 rpm during 50 s. Under these conditions, the average thickness of the films was 250 nm. The substrate was then loaded into the vacuum chamber. The device structure consisted of 250 nm of polymer (or polymer blended with TPD), 2 nm of LiF as the electron injection layer, and thermally evaporated aluminum and silver layers as a cathode. The thermal evaporation was carried out in an Edwards 306 autocoater equipped with a cryopump, using tungsten or molybdenum boats. All depositions were performed in high vacuum (2×10^{-7} Torr). A typical growth rate was 2 Å/s, and the substrates were held at ambient temperature. The active device area is 5.0×6.0 mm^2. The devices were encapsulated and then operated and characterized in air. The EL spectra and luminance were measured by using a Photo Research-650 SpectraColorimeter, and the current−voltage (I−V) characteristics were measured with a Keithley 236 voltage source measurement unit. The photoluminescence (PL) spectra were measured using a Spex Fluorolog 3 spectrometer. For fluorescence analysis in solution, the polymer concentration (based on the repeat unit) was about 10^{-6} M. For fluorescence analysis in the solid state, the polymer was cast from a solution or spin-coated on a quartz plate and placed at 45° with respect to the incident beam. The UV−visible absorption spectrum was recorded on a Hewlett-Packard diode-array spectrophotometer (model 8452A) or on a Cary spectrophotometer (model 50).

Table 2. UV−Visible Properties of Copolymers in the Solid State Evaluated on a Quartz Plate

polymers	λ_{abs} (nm)[a]	λ_{PL} (nm)[b]	λ_{PL} (nm)[c]
PPF	364	425, 443	420, 442
PBPF	365	424, 442	418, 440
PTF	438	490, 515	485, 512
PBTF	427	563	548
PEDOTF	444	495, 527	494, 526
PdiEDOTF	517	536, 574	532, 574
PDMTF	384	469	460

[a−c] Wavelength of the maximum of [a]absorption (cast film), [b]emission (cast film), and [c]emission (spin-coated film).

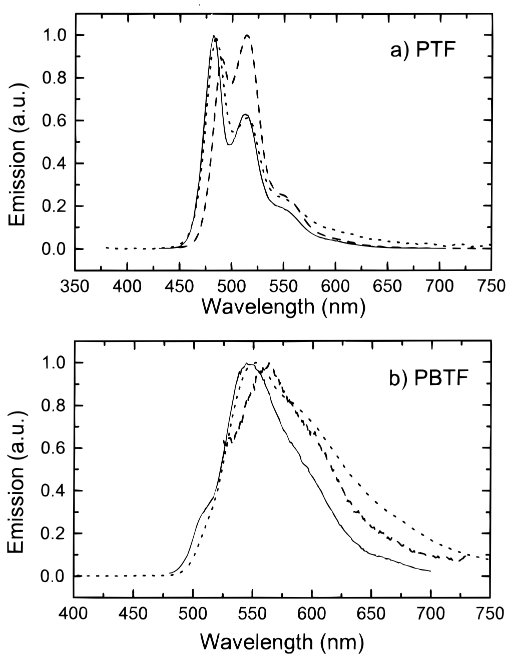

Figure 1. Photoluminescence spectra (PL) in the solid state from a spin-coated film (—) and from a cast film (- - -) and the electroluminescence spectra (.....) for (a) PTF and (b) PBTF.

Results and Discussion

Physical and UV−Visible Properties. The UV−visible absorption and photoluminescence (PL) properties are summarized in Table 2. Polymers containing thiophene moieties are red-shifted compared with those containing phenylene moieties. This is probably due to the more planar conformation of the backbone and a smaller band gap in the case of thiophene rings.[10] However, in the case of PDMTF, the addition of two methyl groups at the 3,4-positions increases the steric hindrance and leads to a more twisted conformation; this conformational effect can explain the larger band gap of this copolymer. It has been observed that the conformation of the polymer can change depending on the preparation of the film. No significant difference was observed between the PL spectra of cast and spin-coated films (Figures 1−4) except in the intensities of vibronic structures. There is a poor resolution of the PL spectra for PBTF and PDMTF. This behavior is probably due to the formation of excimers.[17]

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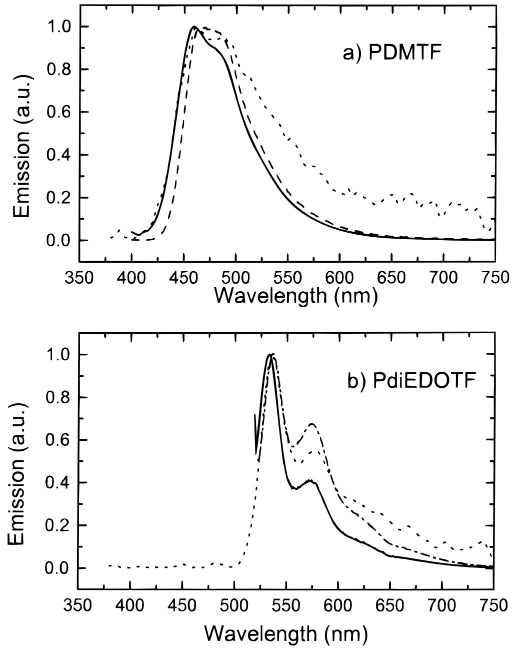

Figure 2. Photoluminescence spectra (PL) in the solid state from a spin-coated film (—) and from a cast film (- - -) and the electroluminescence spectra (.....) for (a) PDMTF and (b) PdiEDOTF.

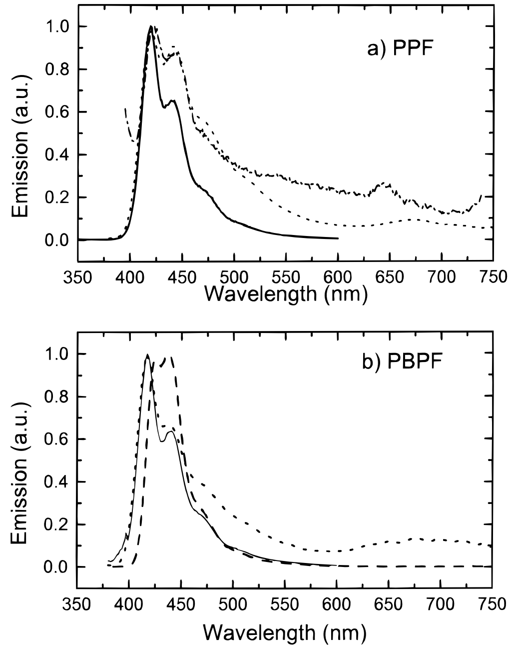

Figure 3. Photoluminescence spectra (PL) in the solid state from a spin-coated film (—) and from a cast film (- - -) and the electroluminescence spectra (.....) for (a) PPF and (b) PBPF.

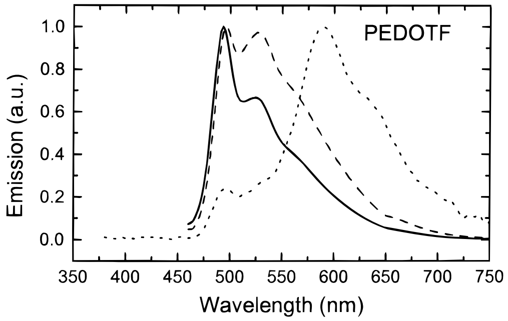

Figure 4. Photoluminescence spectra (PL) in the solid state from a spin-coated film (—) and from a cast film (- - -) and the electroluminescence spectra (.....) for PEDOTF.

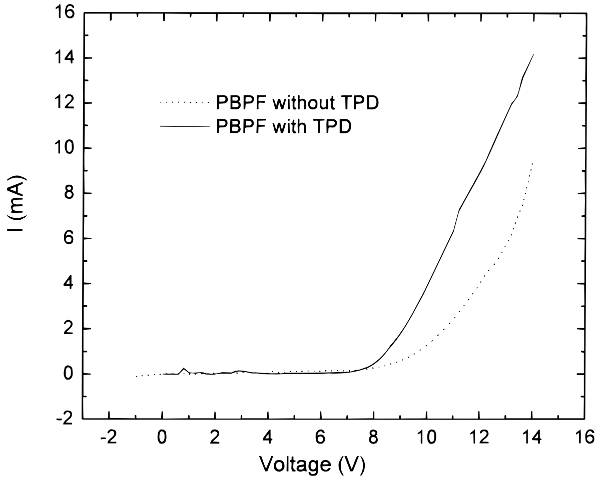

Figure 5. *I*—*V* curves of PBPF with TPD (—), and without TPD (.....).

The transition temperatures (T_g and T_m) vary depending on the nature of the copolymer units (Table 1). For example, PEDOTF has a considerably high T_g (129 °C) compared to the other polymers, due to the rigid EDOT unit. However, for PdiEDOTF, where a bithiophene unit is present, T_g goes down to 105 °C. This polymer does not show any exothermic transition. This behavior is also observed for PBTF, which also contains a bithiophene unit and has a relatively low T_g (73 °C). These properties can considerably influence the morphology of the polymers, which affects the luminescence properties. It has been shown[17] that too low molecular weight polymers display some excimer emission after annealing. In our case, the films were not thermally treated after coating. Although some copolymers do show excimer formation, the formation of excimers could not be related without a doubt to the lower molecular weight polymers.

Electroluminescence Properties. *Current*—*Voltage Characteristics.* All the samples studied show similar rectifying behavior in their current—voltage (*I*—*V*) curves (Figure 5). The turn-on voltage for these devices varies between 5 and 10 V. The *I*—*V* curve of blended samples shows no significant difference in comparison with the *I*—*V* curve of the unblended one. Naka et al.[8] have shown that the electroluminescence (EL) efficiency is improved when the TPD (hole transport material) ratio is around 20%. According to Bernius et al.,[18] unlike polyphenylenevinylenes, in which the holes seem to be the majority carrier, fluorene polymers and some copolymers seem to have electrons as the majority carrier. In our copolymers, hole transporters such as thiophene or phenylene units can change the balance of the nature of the carriers.

In the simplest configuration (anode/polymer/cathode), charge injection difficulties exist for both carriers (especially when aluminum is used as cathode material). There is a need to improve the injection on both sides of the devices. According to the oxidation and reduction

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Table 3. Oxidation (E_{ox}) and Reduction (E_{red}) Potential of the Polymers[a]

polymers	E_{ox} (V)	E_{red} (V)
PPF	1.76	−2.44
PBPF	1.50	−2.40
PTF	1.26	−2.40
PBTF	1.11	−2.34
PEDOTF	1.18	
PdiEDOTF	1.22	−2.73
PDMTF	1.35	

[a] Scanning rate 50 mV/s, electrolyte TEABF$_4$/MeCN, V vs SCE.

Table 4. Luminance Values for Various Devices at 17 V

	luminance (cd/m^2)		
polymers	no additives	with 20% TPD	with 20% TPD and LiF on ITO
PPF	2	18	35
PBPF		4.2	
PTF	2.1	8.2	
PBTF	4.5	18	125
PEDOTF	2.1		
PdiEDOTF	0.3	1.0	
PDMTF	0.5		

potentials (Table 3) it is probably easier in these copolymers to inject holes rather than electrons (reduction potential −2.4 V vs SCE). Under those conditions, the majority of holes may reach the cathode without contributing to the EL. However, the insertion of an ultrathin (2 nm) LiF layer between the polymer and the aluminum cathode increases the electron injection.[19] Few short circuits in the $I-V$ curves were observed with a thin layer of LiF but the lifetime of the devices was relatively short (less than 1 h).

The luminance varies strongly from one sample to another. It is well-known that the EL efficiency depends on the charge injection into the emitter. Although most of these copolymers were shown to be electroactive upon reduction and oxidation, they have different behaviors upon oxidation (Table 3). The presence of one or two thiophene units decreases the oxidation potential. The hole injection is therefore facilitated compared to the other copolymers. PBTF, with the lowest oxidation potential [1.11 V vs saturated calomel electrode (SCE)], has the highest luminance. Adding TPD increases the luminance of the device by a factor of 4 (Table 4). Moreover, for PBPF, the addition of 20% TPD made the measurement of the EL spectrum possible and a luminance of 4 cd/m^2 was found. The best results (quality of the film and luminance) were obtained for blended PBTF with a luminance of 18 cd/cm^2 at 17 V. Diodes with PBTF were found to be the most stable under those conditions and an enhancement of the lifetime with the incorporation of TPD was observed. PPF is a promising blue emitter, although the nonuniformity of the film can adversely affect the light emission.

To improve the performance of the diodes, a 1.5 nm LiF layer was inserted between the ITO and the PBTF or PPF layers. In the case of PBTF, the device has shown an increased lifetime (more than 2 h) with good stability and a remarkable improvement of the luminance up to 125 cd/m^2. Here, the thin LiF layer acts as an insulating layer that allows sufficient potential difference to be maintained between the ITO and the polymer for better hole injection into the polymeric emitter.

Electroluminescence Spectra. The EL spectra of all the polymers are nearly identical to the PL spectra of the spin-coated films, except for two polymers (PBPF and PEDOTF).

PBTF, PTF, PDMTF, PdiEDOTF. Devices made from PTF, PBTF, and PdiEOTF show a green emission (EL peaks at 480, 545, and 536 nm, respectively) (Figures 1a,b and 2b), whereas PDMTF emits a pale blue color (EL peak at 468 nm) (Figure 2a). Both EL and PL spectra show a maximum of intensity at similar wavelengths. This behavior indicates that the EL emission originates from the polymer itself and confirms that the EL spectrum is not modified by the addition of TPD at moderate concentrations.[8] However, we have observed that the shape of the EL spectra is broadened at long wavelengths compared with the PL spectra. One possible explanation that has been cited in the literature is that of the cavity effect[20] when there is an excess of injected electrons on the molecule. There is also the possibility that this shift is due to increased radiative decay from longer conjugated segments, with a smaller gap, in the EL relative to the PL processes. No dependence of the EL emission spectra on the applied voltage is observed in the measured range (8−17 V). These results exclude the possibility of exciplex formation at the interface regions, since the intensity of exciplex emission is usually voltage dependent.

PPF, PBPF, and PEDOTF. The devices made from PPF and PBPF show respectively a blue emission at 419 nm (Figure 3a) and a blue-violet color with a maximum emission at 416 nm (Figure 3b). However, a weak band appears around 680 nm for PPF and near 710 nm for PBPF. Very similar results have been recently reported by Heeger et al.[21] This weak band is probably due to an excimer and/or aggregate formation.[17,22] The former involves interchain interactions in the excited state, while the latter is associated with a ground-state interaction. However, previous spectroscopic studies[4,23] seem to favor the formation of an excimer. This excimer is not voltage-dependent. It is worth noting that this excimer in PPF is much weaker than that observed in poly[2,7-(9,9-dialkylfluorene)]s[5,21] and could lead to the design of pure blue-light-emitting polymers where formation of excimers is completely suppressed.

The PL spectrum of PEDOTF (Figure 4) is very different from the EL spectrum. The main peak at 494 nm in the PL spectrum almost disappears in the EL spectrum. At the same time, a new peak appears at 588 nm (pale yellow) which is assumed to be related to the formation of excimers. Further measurements will be necessary to get a clear understanding of the processes involved in these materials.

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In conclusion, we have demonstrated that the alternated incorporation of thiophene or phenylene moieties in fluorene-based π-conjugated polymers has permitted the preparation of tunable electroluminescent materials. PBTF seems to be a promising green emitter. Moreover, PPF shows blue emission, although a weak excimer band near 670 nm has been observed. The incorporation of LiF ultrathin injecting layers increases the efficiency of the device. We are not able at this point to state unequivocally whether electrons or holes are majority carriers, but the electroluminescence of the copolymers can be significantly enhanced by blending the copolymer with a hole-transporting material. Time-of-flight measurements should be conducted in order to elucidate this point. However, it is believed that further improvement of the electroluminescence could be achieved by enhancing and balancing the electron and hole transport.

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