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Articles

Red Electrophosphorescence of Conjugated Organoplatinum(II) Polymers Prepared via Direct Metalation of Poly(fluorene-*co*-tetraphenylporphyrin) Copolymers

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A series of novel soluble conjugated phosphorescent copolymers with tetraphenylporphyrin platinum(II) complexes inserted into the polymer main chain is synthesized through direct metalation of the metal-free polyfluorene-*co*-tetraphenylporphyrin copolymers with $PtCl_2$ in benzonitrile. Chemical and photophysical characterization confirms that platinum(II) was successfully incorporated into metal-free porphyrin in the copolymer backbone. The PL decay studies indicate that polyfluorene-*co*-tetraphenylporphyrin platinum(II) (PFO−PtTPP) is a triplet emitter. EL emission from the fluorene segment was completely quenched for copolymers with PtTPP content as low as 0.5 mol %. The PFO−PtTPP copolymers emit deep red emission. The highest external quantum efficiency of the devices based on the platinum(II) complex PFO−PtTPP1 (1 mol % PtTPP in copolymer) was 0.43% with emission peaking at 676 nm.

Introduction

OLEDs based on organic and polymeric phosphorescent materials have been absorbing researchers' intense interest due to their potential application in flat panel displays.[1−3] Nearly 100% of internal quantum efficiency (corresponding to the harvesting of all singlet and triplet states) can be achieved in small-molecule-based devices using metal-organic phosphor complexes based on Ir complexes.[4−6] The use of a triplet-complex-containing polymer as the triplet emitter is attractive since it allows LEDs to be made through varieties of high-resolution printing techniques without the utilization of shadow masks, which are typically a limiting factor for the realization of large-area high-density flat panel displays. Most work related to the design and syntheses of phosphorescent polymers was concentrated on Ir complexes incorporated into the polymer side chain via a pendant group as a ligand. Recently, considerable interest has been focused on platinum porphyrin complexes as red phosphorescent materials. One of the representative derivatives of porphyrin complexes, 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphyrine platinum (PtOEP), was the first highly efficient triplet emitter in PHOLEDs.[1] To use device processing by printing techniques for PLEDs, several groups reported phosphorescent polymer light-emitting diodes prepared by spin-coating of porphyrin-Pt complexes doped into a polymer host.[7−9] Excitations created in the polymer host were transferred to the platinum(II) porphyrin complexes and emit red light. However, the devices from blending with phosphorescent dyes doped into small molecule or a polymer host might result in phase segregation, which leads to fast decay of efficiency with an increase in current density. A possible solution to this problem is to introduce the phosphorescent dye into the polymer chain. There are only a few papers reporting the synthesis and characterization of phosphores-

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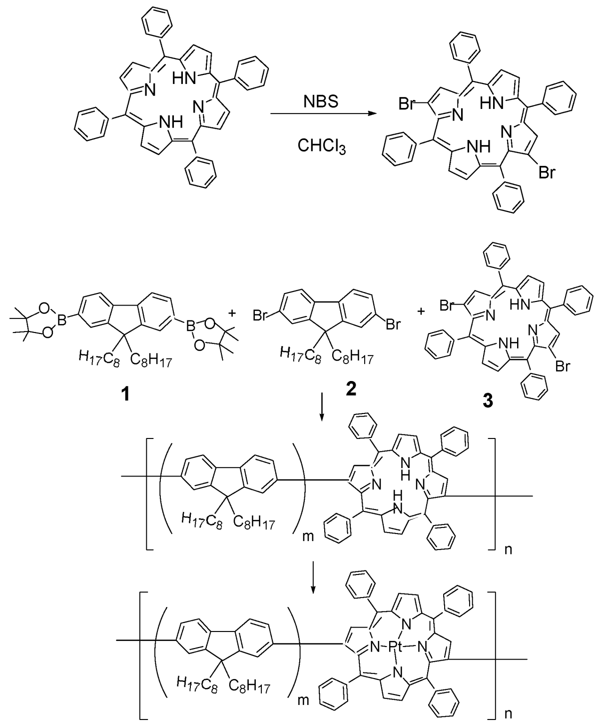
cent polymers containing porphyrin platinum complexes. Holmes-Smith et al.[10] reported luminescent electropolymerized porphyrin polymers for fast-response optical oxygen sensors. Several groups have designed and synthesized polymers containing metal or metal-free tetraphenylporphyrin (TPP) in polymers' main chain or side chain.[11−17] Jones et al.[12−15] have reported a series of conjugated polymers from metal-free tetraphenylporphyrin PPV or PPE units. Ballarin et al.[16] have synthesized polythiophene, bearing a porphyrin macrocycle in the β position, either free or complexed with Ni(II). Li et al.[17] have reported star-shaped porphyrins with four oligofluorene arms, the photoluminescent properties of which are being investigated. To our knowledge, no electroluminescent properties and device performance of these porphyrin-containing polymers have been investigated and reported.

In this paper, we report for the first time the synthesis and photo- and electroluminescent properties of copolymers containing tetraphenylporphyrin platinum(II) (PtTPP) complexes in the polymer main chain derived from direct metalation reaction of the copolymers from metal-free poly(fluorene-*co*-tetraphenylporphyrin), into which the platinum(II) was incorporated by post-polymerization metalation by using $PtCl_2$ in benzonitrile (structures in Scheme 1). In the resulting copolymers, the PtTPP complex unit and fluorene segments were covalently linked and each individual PtTPP unit is separated from both sides by fluorene segments, which may protect the porphyrin rings from aggregation. We expected that direct metalation of metal-free conjugated copolymers has certain advantages over the existing synthetic routes for preparation of copolymers containing metal-porphyrin complexes in the main chain. This method allows fine control of Pt complex content in the copolymer main chain, which is important in such energy-transfer systems. On the other hand, this method provides flexibility to shift from one metal ion to another with a single type of metal-free porphyrin copolymer. The photophysical and electroluminescent properties of the copolymers were also reported and compared with that of metal-free copolymers and a blend of PtTPP complexes with PFO homopolymers.

Results and Discussion

Synthesis and Characterization of Copolymers PFO−PtTPP. Conjugated copolymers PFO−TPP of different compositions were prepared using palladium-catalyzed Suzuki coupling reactions following the published procedure[18] (Scheme 1). The starting monomer molar ratios have been adjusted in order to investigate the effect of copolymer composition on the physical and optical properties. The comonomer feed molar ratios of DOF to TPP are respectively 99.5:0.5 (PFO−TPP0.5), 99:1 (PFO−TPP1), 95:5 (PFO−TPP5), 80:20 (PFO−TPP20), and 50:50 (PFO−TPP50). The actual composition of the TPP in the copolymer estimated from the results of elemental analysis (nitrogen and carbon) is slightly less than the feed ratio (Table 1). Both the low solubility of comonomer 2,13-dibromotetraphenylporphyrin (**3**) in toluene and the steric hindrance of the benzene ring in TPP are probably responsible for such a difference between the TPP feed ratio and composition in the copolymers. The actual TPP content in the copolymers PFO−TPP0.5 and PFO−TPP1 cannot be estimated by using elemental analysis due to the accuracy limit of the N analysis (±0.3%). The number-average molecule weights (M_n) of the synthesized copolymers were 6000 to 23 000 with a polydispersity index (M_w/M_n) from 2.1 to 2.6 (Table 1).

Scheme 1. Synthetic Route of Copolymer PFO−PtTPP



Platinum(II) was incorporated into TPP in the copolymer main chain by the reaction of the metal-free copolymers PFO−TPP of different composition with $PtCl_2$ dissolved in benzonitrile.[19] The obtained copolymer PFO−PtTPP containing the platinum(II) TPP complex in the polymer backbone is characterized by ^1H NMR spectra. The N−H proton signal at δ −2.54 ppm in the porphyrin disappeared when platinum(II) was inserted into the metal-free porphyrin in the copolymers. The ^1H signal in the benzene rings for the porphyrin platinum(II) complex in the copolymer shows

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Table 1. Molecular Weights of the Copolymers and Element Analysis

copolymer	$M_n/\times10^3$	M_w/M_n	DOF/TPP molar ratio		Pt content in copolymer PFO−PtTPP/%	
			feed composition	in polymers[a]	calcd values[b]	actual values
PFO−TPP0.5	23	2.2	99.5/0.5			0.30
PFO−TPP1	20	2.5	99/1			0.56
PFO−TPP5	22	2.1	95/5	97.8/2.2	1.08	1.11
PFO−TPP20	11	2.6	80/20	81.9/18.1	7.62	7.33
PFO−TPP50	6	2.5	50/50	56/44	15.01	14.77

[a] Calculated from results of elemental analysis. [b] Calculated according to the actual TPP content in the copolymer PFO−TPP used in the complexing reaction assuming 100% yield.

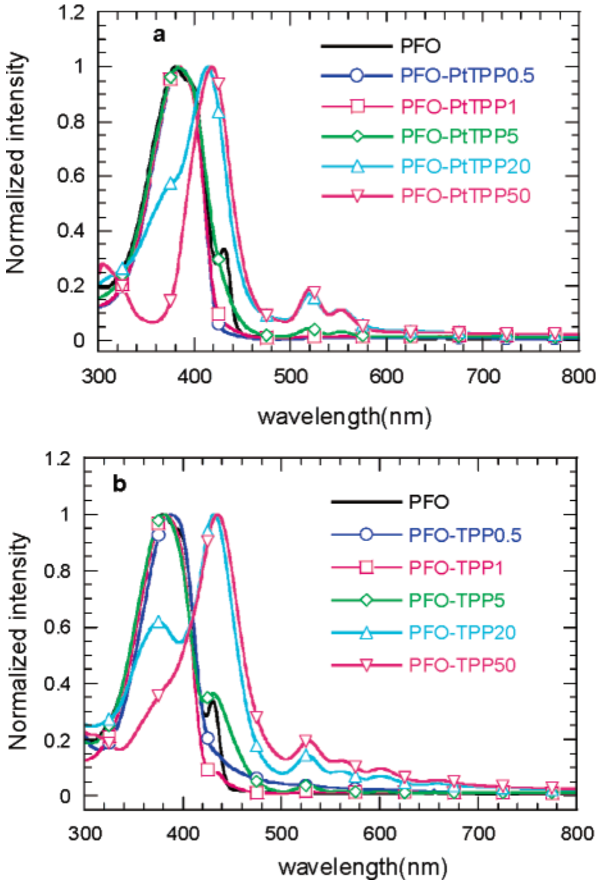

Figure 1. (a) UV−vis spectra of copolymer PFO−PtTPP in thin films. (b) UV−vis spectra of copolymer PFO−TPP in thin films.

a small upfield chemical shift compared with the ^{1}H signal for the metal-free tetraphenylporphyrin. The slightly upfield ^{1}H chemical shift results from π-back-bonding of platinum to porphyrin.[19] The actual platinum content in the copolymers PFO−PtTPP is measured by atomic absorption spectroscopy, and the results are listed in Table 1. The platinum(II) content was very close to that calculated according to the actual content of TPP unit in the pristine copolymer PFO−TPP (Table 1). This indicates that metalation reaction of $PtCl_2$ with PFO−TPP copolymer is quantitative in our experimental conditions.

Optical and Electrochemical Properties. Figure 1a shows the absorption spectra of copolymers PFO−PtTPP in film. For copolymers PFO−PtTPP0.5 and PFO−PtTPP1, the absorption feature is similar to that of a polyfluorene homopolymer (PFO) in which the absorption spectra consist of only one absorption peak at around 380 nm. The absorption peak responsible for PtTPP cannot be observed due to the low sensitivity of the spectrograph for such a low PtTPP content. The absorption peak appearing at ca. 380 nm in the film is consistent with that for PFO homopolymer (380 nm) (Figure 1a). This indicates that the incorporation of a small amount of PtTPP in the copolymers does not disturb the electronic configuration of the polyfluorene main chain. For the copolymer PFO−PtTPP5, two weaker absorptions with peaks at 519 and 552 nm, which obviously can be assigned to PtTPP absorption, are observed along with a 380 nm main absorption peak. For the copolymer PFO−PtTPP20, the intensity of the absorption peak at about 380 nm responsible for the fluorene segment decreased significantly. An intense absorption band centered at about 413 nm along with two weak absorption bands centered at about 519 and 552 nm became dominant. The 413 nm absorption is attributed to the porphyrin platinum(II) “Soret” band, and absorption peaks at 519 and 552 nm can be attributed to the Q-band, which is typical of porphyrin platinum(II) complexes.[19] For alternating copolymer PFO−PtTPP50 the absorption responsible for the fluorene segment at 380 nm disappears completely. Figure 1b shows the absorption spectra of metal-free copolymers PFO−TPP from which PFO−PtTPP copolymers were synthesized. As can be seen from Figure 1b, copolymers with low TPP content ($\leq$1 mol %) show similar absorption spectra characteristics for PFO homopolymers. Comparing Figures 1a and 1b, we note that for copolymers with PtTPP and TPP contents equal to or greater than 5 mol % the absorption peaks attributed to the tetraphenylporphyrin platinum(II) unit (Figure 1a) are blue shifted respectively about 18−19 nm for the “Soret” band and about 7 nm for the Q-band, in comparison with that for corresponding parent metal-free copolymers PFO−TPP (Figure 1b).

The electrochemical properties of the copolymers PFO−PtTPP were investigated by cyclic voltammetry (CV). Table 2 lists the electrochemical data for PFO−PtTPP copolymer films. For copolymers PFO−PtTPP20 and PFO−PtTPP50, we can record two oxidation waves. The onset of the first oxidation wave is 1.25 V for PFO−PtTPP20 and 1.16 V for PFO−PtTPP50. The onset of the second oxidation process is almost constant for all copolymers at about 1.35−1.36 V. Since the oxidation potential for polyfluorene homopolymer was observed typically at 1.4 V,[20] the second oxidation wave can be assigned to the oxidation process for the fluorene segments in the copolymers. The first oxidation wave

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Table 2. UV−Vis Properties and Electrochemical Properties of the Copolymers PFO−PtTPP and PFO−TPP Copolymers

copolymer	λ_{abs}/nm DOF	PtTPP (or TPP)	E_{ox}/V	E_{red}/V	HOMO/eV	LUMO/eV
PFO−PtTPP0.5	383		1.35	−2.20	−5.75	−2.20
PFO−PtTPP1	385		1.36	−2.23	−5.76	−2.17
PFO−PtTPP5	383	519, 552	1.36	−2.22	−5.76	−2.18
PFO−PtTPP20		413, 519, 552	1.25, 1.36	−2.20	−5.65	−2.20
PFO−PtTPP50		417, 519, 552	1.16, 1.35	−2.19	−5.56	−2.21
PFO−TPP0.5	387		1.34	−2.22	−5.74	−2.18
PFO−TPP1	382		1.35	−2.24	−5.75	−2.16
PFO−TPP5	382	430, 526, 561	1.33	−2.21	−5.73	−2.19
PFO−TPP20	375	432, 526, 561	1.15, 1.35	−2.20	−5.55	−2.20
PFO−TPP50		435, 526, 561	1.03, 1.34	−2.23	−5.43	−2.17

observed at 1.16−1.25 V in the copolymers can be attributed to the oxidation process for the PtTPP unit. When the PtTPP content in the PFO−PtTPP is less than or equal to 5 mol % in the feed, only the second oxidation (1.35−1.36 V) process responsible for the oxidation of the fluorene segment can be observed in the voltammogram. For all the copolymers PFO−PtTPP of different compositions, only one reduction process can be recorded. The onset of the reduction process is almost constant for all the copolymers at about −2.19 to −2.23 V, which can be assigned to the reduction process for the fluorene segments in the copolymers since the reduction potential for polyfluorene homopolymer was observed typically at −2.28 V.[20] HOMO and LUMO levels are calculated according to the empirical formulas $E_{HOMO} = -e(E_{ox} + 4.4)$ (eV) and $E_{LUMO} = -e(E_{red} + 4.4)$ (eV).[21] The resulting HOMO and LUMO levels are listed in Table 2. The HOMO level is almost constant for copolymers with PtTPP content less than or equal to 5 mol % and slightly decreases with increasing PtTPP content from 20 mol % to 50 mol % and becomes 5.56 eV for PFO−PtTPP50. The LUMO level is almost constant for all the copolymers at about −2.21 to −2.17 eV. The electrochemical properties of the metal-free copolymers PFO−TPP are similar to those of PFO−PtTPP. The first onset of the oxidation wave attributed to the oxidation process of the TPP unit for PFO−TPP20 and PFO−TPP50 appears at slightly decreased potential. This indicates that the incorporation of Pt(II) into porphyrin rings leads to the increased band gap, which is consistent with the blue shift of the absorption edge of PFO−PtTPP compared with the incorporation of corresponding pristine PFO−TPP copolymers (Table 2).

Photoluminescent Properties. PL spectra of copolymers PFO−PtTPP in thin film under 325 nm excitation of a HeCd laser are shown in Figure 2a. For all PFO−PtTPP copolymers of different PtTPP content, PL spectra in the solid film are dominated by red emission around 680 nm with a weak vibronic shoulder at 740 nm for copolymers with different PtTPP content, which is slightly red-shifted with increasing PtTPP content (within 5 nm). The 680 nm emission can be attributed to the emission of the PtTPP unit in the copolymers. For copolymers with PtTPP content less than or equal to 5 mol % in the feed (actual PtTPP content is 2.2 mol %, Table 1), a weak emission responsible for the fluorene segment at around 430 nm can be observed. The intensity of the 430 nm emission decreases significantly with increasing PtTPP content in the copolymers. Emission of the fluorene segment was

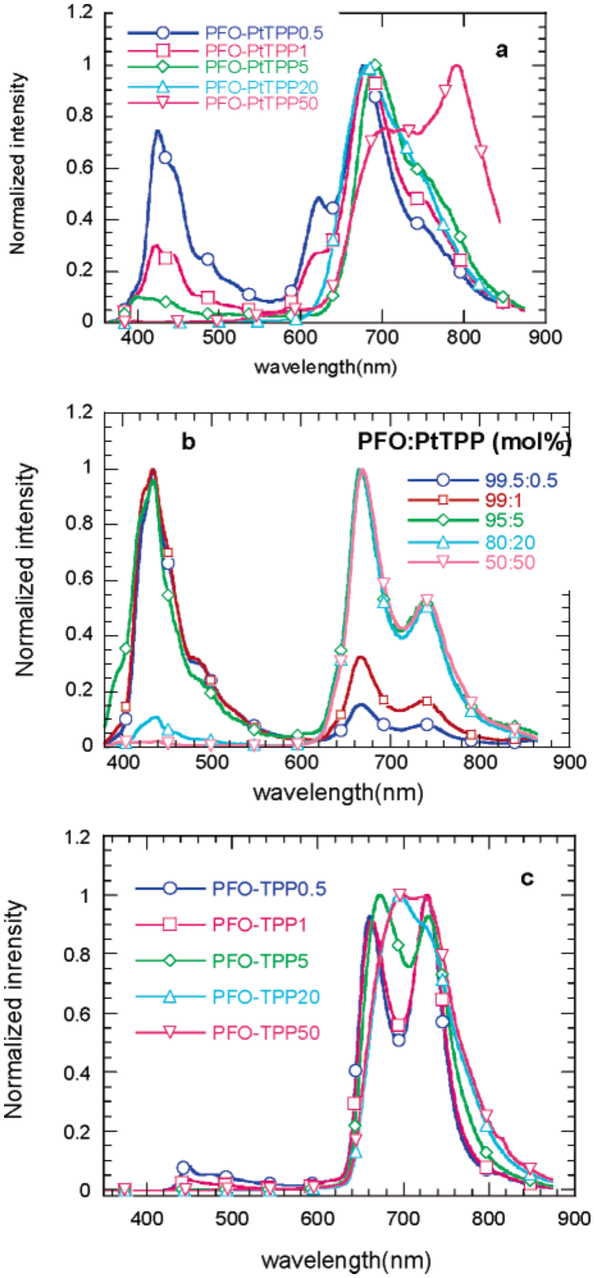

Figure 2. (a) PL spectra of complexes PFO−PtTPP in film under 325 nm excitation. (b) PL spectra of the blend of PFO and PtTPP (+PBD(40 wt %)) in film under 325 nm excitation. (c) PL spectra of copolymer PFO−TPP in film under 325 nm excitation.

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completely quenched for the copolymer when the PtTPP content reaches 20 mol % in the copolymer. This indicates that the efficiency of energy transfer from fluorene segments to the PtTPP unit increases with increasing PtTPP content. The emission spectra of the alternating copolymer PFO−PtTPP50 are quite different from copolymers of other composition. The emission peak was red-shifted to 717 and 790 nm with significantly higher intensity for the 790 nm feature. It is worth noting that in the blended films of PtTPP-doped PFO (+PBD (40 wt %)) (Figure 2b), host (PFO) PL emissions have been completely quenched only when the PtTPP dopant concentration is greater than 20 mol %. This indicates that energy transfer from host (PFO segment or polymer) to dopant (PtTPP unit or molecule) in the PFO−PtTPP copolymers is more efficient than in the blend of the same composition. However, we note also that dopant concentration required for complete quenching of the emission of PFO host polymers has been reported previously for PtOX-doped PFO[22] and PtOEP-doped PFO[23] blends at dopant concentration around 5 and 8 (wt/wt)%, respectively. For comparison, Figure 2c shows the PL spectra of metal-free copolymer PFO−TPP in solid film under 325 nm excitation of a HeCd laser. The main emission peak for metal-free porphyrin copolymers appeared at around 670 nm, which is around 10−20 nm more red-shifted than that of the metal-free TPP monomers respectively doped into a conjugated polymer host: 650 nm in polyfluorene[24] and 660 nm in MEH−PPV host.[25] By comparing Figure 2c with Figure 2a, it is worth noting that the incorporation of platinum ion into the porphyrin rings in the copolymers leads to a further red-shift by 10 nm for PFO−PtTPP in comparison with PFO−TPP. It is found that the emission from polyfluorene segments at around 430 nm was completely quenched for metal-free copolymers at a much lower TPP content (Figure 2c) than that for PFO−PtTPP (Figure 2a). For PFO−TPP0.5 and PFO−TPP1 copolymers the emission intensity of the fluorene segments is negligible (Figure 2c). The fluorene emission for copolymers with TPP content equal to or greater than 5 mol % is completely quenched. Since PtTPP is a triplet emitter and TPP is a singlet emitter (see below about lifetime measurement), the energy transfer for PFO−PtTPP copolymers that is much less efficient than that for PFO−TPP seems to indicate that the singlet−triplet crossing in the PtTPP is a limiting process in such an energy-transfer system.

To further investigate the energy-transfer process in PFO−PtTPP and PFO−TPP copolymers, we compare PL emission of these two types of copolymers in the solution. Figure 3a shows the PL spectra of copolymers PFO−PtTPP in $CHCl_3$ solution with the copolymer PFO−PtTPP concentration of 1×10^{-2} mol/L (by repeat unit) under 380 nm excitation taken by a Fluorolog-3 spectrometer (Jobin-Yvon) using 90° angle detection. In the $CHCl_3$ solution, all the copolymers show one PL emission peak at around 440 nm with clear vibronic structure, while there is no trace of emission peak responsible for the PtTPP unit even for PFO−PtTPP50. The fact that no energy transfer from the wide band gap PFO segment to the narrow band gap PtTPP unit occurred in the solution of this relatively high concentration (1×10^{-2} mol/L) clearly indicates that intramolecular energy transfer does not take place. On the other hand, this fact also indicates that interchain energy transfer in PFO−PtTPP is also weak. For comparison, PFO−TPP copolymer containing metal-free TPP shows significant energy transfer in the solution at very dilute solution of concentration 1×10^{-5} mol/L (Figure 3b). As can be seen from Figure 3b, all the PFO−TPP copolymers show clearly 685 and 727 nm emissions responsible for the TPP unit at this very dilute solution concentration. Except the alternating copolymer PFO−TPP50, where the fluorene 430 nm emission is completely quenched, the intensity of the PFO emission at around 430 nm decreases with the increase of TPP content in the copolymers and with the simultaneous increase in the intensity of red-emitting peaks. This fact indicates that the intramolecular energy transfer in metal-free copolymers PFO−TPP must be very efficient, in contrast with the fact that intramolecular energy transfer in PFO−PtTPP in solution is negligible. Figure 4a shows the concentration dependence of the PL profile of PFO−PtTPP1 (1 mol % PtTPP in copolymer). When

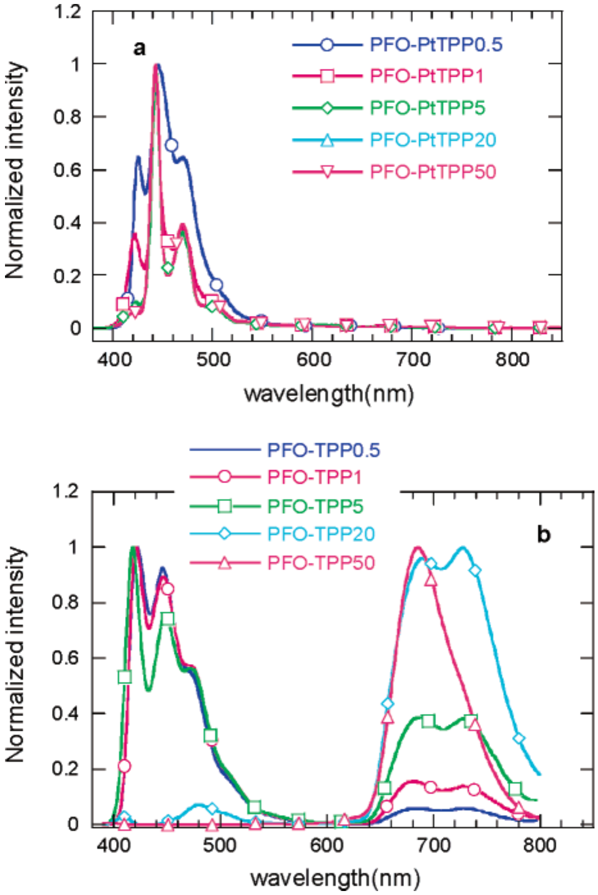

Figure 3. (a) PL spectra of copolymers PFO−PtTPP in $CHCl_3$ solution at 1×10^{-2} mol/L. (b) PL spectra of copolymers PFO−TPP in $CHCl_3$ solution at 1×10^{-5} mol/L.

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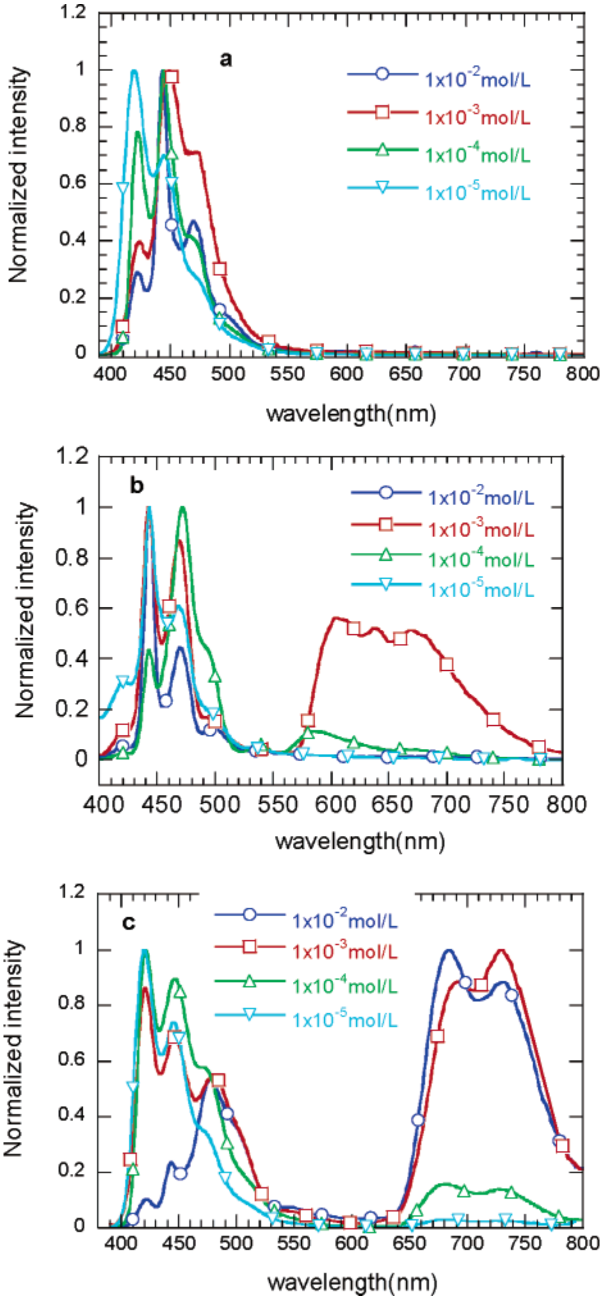

Figure 4. (a) Concentration dependence of PL profile of PFO−PtTPP1 in $CHCl_3$ solution. (b) Concentration dependence of PL profile of PFO−PtTPP50 in $CHCl_3$ solution. (c) Concentration dependence of PL profile of PFO−TPP1 in $CHCl_3$ solution.

Table 3. PL Properties of PFO−PtTPP and PFO−TPP Copolymers

copolymers + PBD (40 wt %)			copolymers PFO−TPP		
copolymer	λ_{PL}/nm	Q_{PL}/%		λ_{PL}/nm	Q_{PL}/%
PFO−PtTPP0.5[a]	437,675	1.23	PFO−TPP0.5	664, 726	9.33
PFO−PtTPP1[a]	437,680	1.29	PFO−TPP1	666, 727	7.1
PFO−PtTPP5	688	1.76	PFO−TPP5	675, 728	5.6
PFO−PtTPP20	698	1.15	PFO−TPP20	698, 726	2.4
PFO−PtTPP50	790		PFO−TPP50	700, 727	1.5

[a] With long-pass filter of 520 nm cutoff.

the concentration of PFO−PtTPP1 varied from 1 × 10^{-5} mol/L to 1 × 10^{-2} mol/L, the PL spectra show exclusively PFO emission. This fact indicates that the energy transfer from fluorene segments to the PtTPP unit does not take place in the range of tested solution concentration. Figure 4b shows concentration dependence of the PL emission for PFO−PtTPP50, which shows only very weak red emission responsible for the PtTPP unit in the copolymers at high concentration. Figure 4c shows concentration dependence of metal-free copolymer PFO-TPP1 in solution. In contrast to PFO−PtTPP1 and PFO−PtTPP50, the metal-free copolymer shows efficient energy transfer from the fluorene segment to the TPP units. The prominent red peaks appeared at the emission wavelength of 680 and 730 nm even at very dilute concentration (1 × 10^{-4} mol/L), and the intensity of red emission increases rapidly with increasing the solution concentration. Since the PtTPP monomer shows reasonable red porphyrin emission in the solution,[26] the extremely weak energy transfer from the host PFO segment to the PtTPP unit in the solution must be related to the change of chain conformation of PFO−PtTPP after incorporating platinum ions. We speculate that the incorporation of Pt(II) into PFO−TPP leads to the significant torsion between PtTPP and PFO planes, which prevent both intrachain and interchain interaction in PFO−PtTPP polymers. The synthesis of fluorene oligomer (dimer or trimer) substituting TPP and its Pt complex is in progress. Structural analysis of such compounds could help in the understanding of behavior of copolymers in this study. The results will be reported in the future.

The absolute PL efficiencies of PFO−PtTPP and PFO−TPP copolymers in thin film were measured in the integrating sphere by using 405 nm excitation of a UV diode laser (CrystaLaser CL-2000). To compare PL efficiency of red emission from PtTPP and TPP units, a long-pass filter with a cutoff of 520 nm (Edmund) was used to eliminate emission at around 430 nm from residue PFO emission for copolymer with low PtTPP content. PL efficiencies of PFO−PtTPP copolymers were determined to be around 1−2%, which are considerably lower than PL efficiencies for metal-free copolymers PFO−TPP of the same composition, 9.3% for PFO−TPP0.5 and 1.5% for PFO−TPP50, respectively, obtained with the same conditions (Table 3). Since the lowest triplet excited state of the PFO polymer or oligomer is approximately 2.1−2.3 eV,[27,28] higher than the triplet state of the PtTPP complex (ca. 1.9−2 eV),[29] triplet−triplet quenching of PtTPP emission by the PFO host segment is unlikely the case. We attribute the significantly lower PL efficiency for Pt-incorporated copolymers to the heavy metal (Pt) quenching effect. We also note that PL efficiencies of PFO−TPP copolymers obtained in this study are well consistent with those reported previously for TPP-doped PFO blended films (9.5% for 1% TPP doped into PFO[30] and 12.5% for 2.6% TPP doped into PVK blended film,[25] respectively).

Photoluminescence decay studies were carried out to estimate the lifetime of the excited states. Table 4

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Table 4. PL Lifetime of Copolymers PFO−PtTPP in Film (λ_{Em} = 700 nm) and Their Metal-Free Parent Copolymer PFO−TPP in Film Excited at 371 nm

copolymer	lifetime τ (μs)[a]	copolymer	lifetime τ (ns)[a]	
PFO−PtTPP5	7.70	PFO−TPP5	1.61 (680 nm)	1.52 (730 nm)
PFO−PtTPP20	2.45	PFO−TPP20	0.85 (700 nm)	0.83 (720 nm)
PFO−PtTPP50	0.24	PFO−TPP50	0.57 (690 nm)	0.60 (720 nm)

[a] Degassed by repeat evacuation in dry ice/acetone bath.

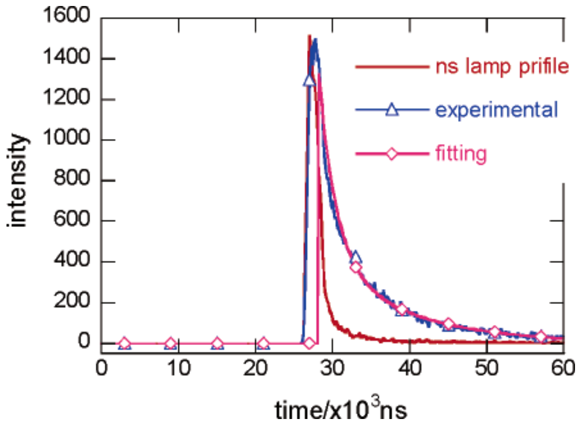

Figure 5. PL decay at 700 nm polymer emission peak for PFO−PtTPP5. The ns flash lamp profile shows the instrumental response.

summarizes the PL lifetime of these PFO−PtTPP and PFO−TPP copolymers with different compositions under the excitation of 371 nm. It can be seen from Table 4 that pristine metal-free PFO−TPP copolymers show a short lifetime on a nanosecond scale typical for the singlet state. However, the lifetimes of PFO−PtTPP copolymers were found to be in the microsecond range. For example, Figure 5 shows exponential decay characteristics of copolymer PFO−PtTPP5 containing 5 mol % PtTPP unit (λ_{em} = 700 nm). This profile was fitted by an exponential component resulting in the lifetime of τ = 7.7 μs. The long lifetimes of the excited states of these copolymers PFO−PtTPP containing a platinum(II) porphyrin complex clearly indicate their triplet nature. We note that these values of lifetimes are very close to what was reported for platinum porphyrin single crystals grown on a KCl surface (τ = 0.45 μs).[31] However, it is much shorter than those reported for the PtTPP complex (60 μs)[32] and other planinum porphyrin complexes.[8] The PL lifetimes of PFO−PtTPP reduced gradually with increasing the content of the PtTPP unit. We note that a similar dependence of lifetimes on the TPP content for the metal-free copolymers is observed also for the copolymers PFO−TPP (Table 4).

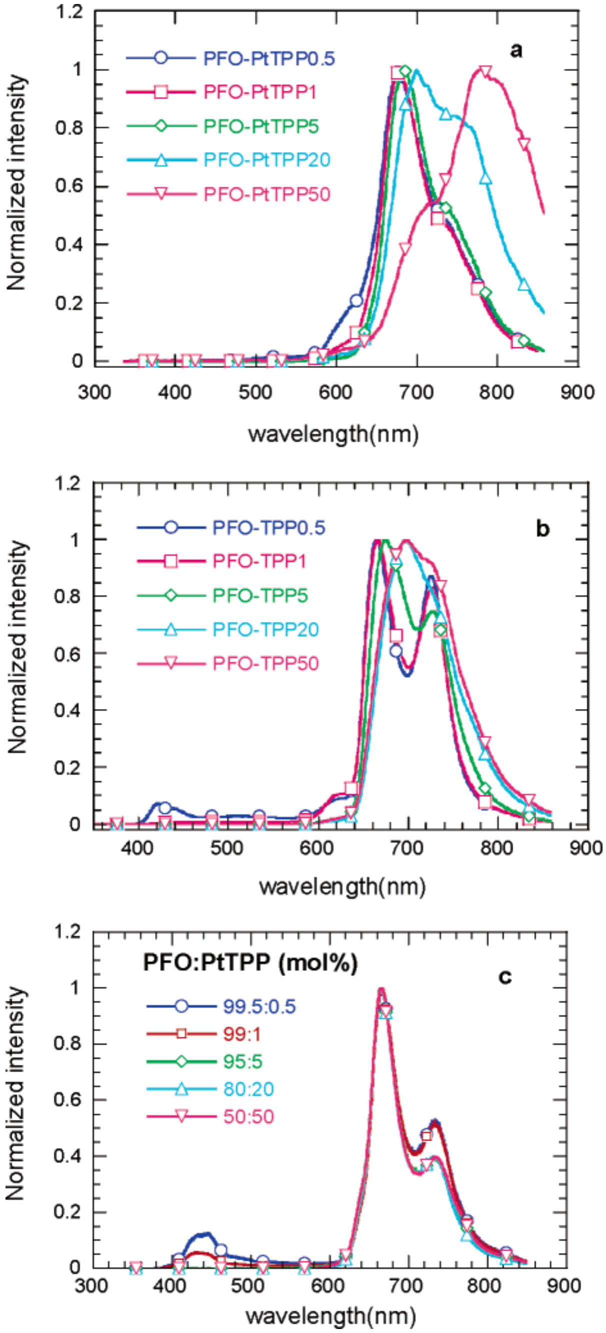

Figure 6. (a) EL spectra of complexes PFO−PtTPP in the device ITO/PEDT/PFO−PtTPP/Ba/Al. (b) EL spectra of copolymer PFO−TPP in the device ITO/PEDT/PFO−TPP/Ba/Al. (c) EL spectra of PtTPP-doped PFO blend in the device ITO/PEDT/PVK/PtTPP:PFO + PBD (40 wt %)/Ba/Al.

Electroluminescent Properties. Figures 6a and 6b show the EL spectra of the copolymers PFO−PtTPP and pristine metal-free copolymer PFO−TPP, respectively. The EL spectra of both copolymers are dominated by emission originating from PtTPP or TPP units. The fluorene emission is completely quenched for all copolymers except a small feature for the PFO−TPP0.5 device. The differences in PL and EL spectra at low doping concentration were attributed to the differences in recombination zone for photo and electric excitations.[28,32,33] However, Lane et al. pointed out that for the EL process the dominant emission mechanism in phosphorescent dye-doped PLEDs was charge trapping instead of Förster transfer followed by the recombination on phosphorescent complex molecules.[27] The dif-

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Table 5. Device Performance of Copolymers PFO−PtTPP

	electroluminescence[a]						chromaticity coordinates	
copolymer	$V_{\text{Turn on}}$	λ_{EL}/nm	V	mA/cm^2	cd/m^2	Q_{ext}/%	x	y
PFO−PtTPP0.5	15.2	677	18.2	28.06	26.1	0.31	0.63	0.34
PFO−PtTPP1	18.4	676	22.2	15.8	18.5	0.43	0.68	0.31
PFO−PtTPP5	14.5	682	21.3	29.90	14.2	0.16	0.69	0.30
PFO−PtTPP20	10.5	703	14.4	33.26	18.8	0.19	0.64	0.32
PFO−PtTPP50	10.2	780	15.8	35.45	13.8	0.13	0.60	0.35

[a] Device structure: ITO/PEDT/PVK/copolymer + PBD (40 wt %)/Ba/Al, active area 0.15 cm^2.

ferences in PL and EL spectra at low NBG loading of PFO−PtTPP and PFO−TPP copolymers indicate that the emission mechanism for photo and electric excitations is different. The dominant emission mechanism in these copolymers is charge trapping followed by the recombination on PtTPP and TPP molecules.

We also note that the EL emission profile of the copolymers PFO−PtTPP is different from that of metal-free copolymers PFO−TPP. The EL spectra of PFO−PtTPP show a single emission peak with depressed vibronic structure for the copolymer of low PtTPP content, resulting in much narrower emission. More interesting, with further increase in PtTPP content, the 0−0 main peak is significantly depressed and the intensity of the 0−1 peak increases with increasing the PtTPP content. For PFO−PtTPP50, the main emission peak moved to around 780 nm. Ariu et al.[34] has pointed out that the relative intensity of the lower-energy vibronic emissive states to the main electronic transition decreases with the enhancement of rigidity of the chain and with the increase in chain conjugation length. It is obvious that the conjugation length of PFO−PtTPP decreases with increasing PtTPP content in the copolymers, which leads to the line broadening of EL emission.

Table 5 lists the device performance of PFO−PtTPP. (4-Biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) was blended into PFO−PtTPP copolymers in order to increase the electron transport ability according to several previous reports.[4,35] The external EL efficiencies in device configuration ITO/PEDT/PVK/PFO−PtTPP+PBD(40 wt %)/Ba/Al vary with copolymer compositions. The external quantum efficiencies increase initially with the PtTPP content to the maximum for copolymer with 1% PtTPP content and then gradually decrease. The highest external EL quantum efficiency in such a device configuration was 0.43% with the luminance of 18.5 cd/m^2 at the current density of 15.8 mA/cm^2 for copolymer PFO−PtTPP1 with 1 mol % PtTPP. To determine the best concentration of PBD to optimize the device performance, we vary the ratio of PFO−PtTPP1 and PBD in wide range as shown in Figure 7. The results show that the ratio of PFO−PtTPP1 to PBD around 40:60 or 30:70 provides the best device performance over the other composition. For comparison, Table 6 lists the device performance of PFO−TPP containing metal-free TPP. The external quantum efficiencies of devices from the copolymers PFO−TPP are much less than that of copolymers PFO−PtTPP. Comparing Tables 5 and 6, we notice that turn-on voltage (defined as the voltage at which the light intensity rises to 0.1 cd/m^2) for devices from metal-free PFO−TPP copolymers are generally much lower than that for PFO−PtTPP; for example, PFO−PtTPP1 and PFO−TPP1 copolymers show turn-on voltages of 18.4 V (Table 5) and 10.1 V (Table 6), respectively.

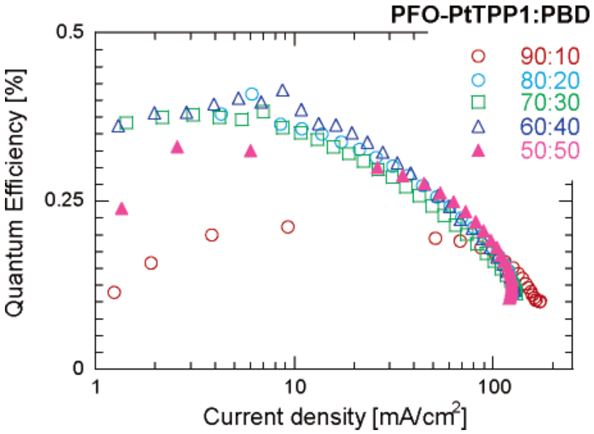

Figure 7. External efficiency−current density curve of devices with a blend of PFO−PtTPP1 and PBD.

Table 6. Devices Performance of Copolymers PFO−TPP

	electroluminescence[a]					
copolymer	$V_{\text{Turn on}}$	λ_{EL}/nm	V	mA/cm^2	cd/m^2	Q_{ext}/%
PFO−TPP0.5	5.0	665, 727	5.76	36.73	5.2	0.047
PFO−TPP1	10.1	667, 727	12.32	35.87	7.5	0.07
PFO−TPP5	6.0	674, 727	10.14	33.6	12.1	0.12
PFO−TPP20	4.9	696	5.94	43.07	4.5	0.035
PFO−TPP50	5.4	700	5.58	45.27	2.7	0.02

[a] Device structure: ITO/PEDT/ PFO-TPP/Ba/Al, active area 0.15 cm^2.

As we mentioned above, there were considerable reports on performance of phosphorescent devices from Pt complexes doped into a polymer host.[7,9,22,23] To compare the device performance of copolymers PFO−PtTPP and the PtTPP-doped PFO blend, devices from the latter with the same PtTPP content (molar ratio) as for PFO−PtTPP copolymers have been fabricated. Figure 6c shows EL spectra of devices from the PtTPP/PFO blend. Comparing with EL spectra (Figure 6a) of devices from PFO−PtTPP copolymers where PFO emission was completely quenched at 0.5 mol % PtTPP content, for the PtTPP-doped PFO blend, 430 nm emission was completely quenched only at a PtTPP content of 20 mol % or higher. More efficient energy transfer for copolymers might originate from strong intrachain energy transfer or less aggregation of PtTPP chromophores in the copolymer main chain. Devices from a PtTPP/PFO blend show device performance at a current density of about 30 mA/cm^2 (Table 7) compa-

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Table 7. Device Performance of a Blend of PFO and PtTPP

PFO:PtTPP (mol %) blend composition	electroluminescence[a]					
	$V_{\mathrm{Turn\ on}}$	λ_{EL}/nm	V	mA/cm^2	cd/m^2	Q_{ext}/%
99.5:0.5	16.2	665, 734	28.2	30.13	12.5	0.14
99:1	16.2	665, 732	28.8	31.44	22.5	0.24
95:5	16.8	666, 734	28.2	32.78	33.2	0.34
80:20	21.6	665, 731	33	26.67	40.3	0.89
50:50	5.4	666, 733	12.6	33.39	28.1	0.28

[a] Device structure: ITO/PEDT/PVK/PFO:PtTPP + PBD(40 wt %)/Ba/Al, active area 0.15 cm^2.

rable with those from PFO−PtTPP copolymers. Slightly higher efficiency has been observed for a device with 20 mol % PtTPP in PFO blend with an external efficiency of 0.89% at 26.67 mA/cm^2 and 40.3 cd/m^2. We note that devices from copolymers show much gentler efficiency decay than the devices from a PtTPP-doped blend with the increase of current density and with the increase in Pt complex content. Yang et al.[36] reported the maximum efficiency is 2.5% at 3.1 mA/cm^2 current density and the brightness is 28 cd/m^2 for the device performance with the structure as ITO/PEDT/PVK-PBD-PtOX (4 wt %)/Ca/Al, although when the current density increases to 60 mA/cm^2, the maximum efficiency decreases quickly to 0.79%. Although device efficiencies reached at this stage of experiment for PFO−PtTPP copolymers were not satisfactory, as we expected, it is not surprising considering extremely low PL efficiencies for these copolymers (only 1−2%, Table 3). Currently, the design and synthesis of PtTPP complexes incorporated into conjugated segments of different structure are in progress, which is aimed at the reduction of polymer aggregation as well as the increase in molecular weight of the copolymers. The results will be reported in forthcoming reports.

Conclusions

We have first synthesized the tetraphenylporphyrin platinum-containing copolymers PFO−PtTPP through direct metalation of the metal-free copolymers PFO−TPP with $PtCl_2$ in benzonitrile. Chemical and photophysical characterization confirm that platinum(II) is quantitatively incorporated into the polymer main chain. All the copolymers PFO−PtTPP emit a deep red color. The PL decay studies indicate that the emission of copolymers PFO−PtTPP is originated from the triplet state of the PtTPP complex unit. Photophysical properties were investigated to make a comparison with pristine metal-free PFO−TPP copolymers in solution and solid states. In contrast to efficient energy transfer of excitons from the fluorene segment to the TPP unit for metal-free PFO−TPP in solution, PFO−PtTPP shows extremely weak energy transfer in solution. This unique phenomenon must be related to the change of the chain conformation of PFO−PtTPP after incorporation of platinum ions. EL spectra of PFO−PtTPP and PFO−TPP copolymers are dominated by the emission originating from PtTPP or TPP units. The fluorene emission is completely quenched even for copolymers with PtTPP and TPP content as low as 1 mol %. The differences in PL and EL spectra of copolymers at low PtTPP and TPP loading indicate that the emission mechanism for photo and electric excitations is different. The dominant EL emission mechanism in these copolymers is charge trapping followed by recombination on PtTPP and TPP molecules. The highest external quantum efficiency was 0.43% with a luminance of 18.5 cd/m^2 and emission peak of 676 nm at a current density of 15.8 mA/cm^2 for 1 mol % PtTPP content in copolymer PFO−PtTPP with the device structure ITO/PEDT/PVK/PFO−PtTPP + PBD (40 wt %)/Ba/Al.

Experimental Section

Materials and Measurement. All reagents, unless otherwise specified, were purchased from Aldrich, TCI, and Acros and were used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 400 in deuterated chloroform solution. Number-average (M_n) and weight-average (M_w) molecular weights were determined by a Waters GPC 2410 in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. The elemental analysis was performed on a Vario EL elemental analysis instrument (Elementar Co.). Platinum(II) content in polymer complex was measured by atomic absorption spectroscopy on a Z-5000 Polarized Zeeman atomic absorption spectrophotometer. Cyclic voltammetry was done on a potentiostat/galvanostat Model 283 (Princeton Applied Research). UV−visible absorption spectra were recorded on a HP 8453 spectrophotometer. The PL quantum yields were determined in an IS080 integrating sphere (Labsphere) with 405 nm excitation of a UV diode laser (CL-2000, CrystaLaser). PL spectra in the film were taken by an Instaspec IV CCD spectrophotometer (Oriel) under the 325 nm line of a HeCd laser. PL spectra of the copolymer solution were obtained on a Fluorolog-3 spectrometer (Jobin-Yvon) using 90° angle detection. Time-correlated single photon (TCSPC) fluorescence studies of the copolymers PFO−TPP were performed using an Edinburgh Instruments LifeSpec-PS spectrometer. The LifeSpec-PS comprises a 371 nm picosecond laser (PicoQuant PDL 800B) operated at 2.5 MHz and a Peltier-cooled Hammamatsu microchannel plate photomultiplier (R3809U-50). Emission lifetimes of the copolymers PFO−PtTPP were measured with an Edinburgh FL-920 spectrometer. The excitation source was a nanosecond flash lamp operating under an atmosphere of H_2 gas (0.40−0.50 bar, 1.2 ns fwhm, 40 kHz repetition rate), whose output was filtered through a monochromator prior to sample excitation. All fluorescent lifetimes were determined from the data using the Edinburgh Instruments software package.

LED Fabrication and Characterization. Polymers were dissolved in *p*-xylene and filtered through a 0.45 μm filter. A mixture of PtTPP and PFO in an amount corresponding to the same molar ratio as in PFO−PtTPP copolymers in *p*-xylene solution were prepared and filtered before use. Poly(3,4-ethylenedioxythiophene) (PEDT, 60 nm) doped with poly(styrenesulfonic acid) (PSS) (Batron P 4083, Bayer AG) was spin-coated onto the patterned indium tin oxide (ITO) coated glass substrates followed by drying in a vacuum oven at 80 °C for 8 h. A thin film of electroluminescent polymer (about 90 nm) was coated onto the anode by spin casting inside a drybox. A thin layer of Ba (4−5 nm) and subsequently 200 nm layers of Al were vacuum-evaporated subsequently on the top of an EL polymer layer under a vacuum of 1×10^{-4} Pa. Current−voltage ($I-V$) characteristics were recorded with a Keithley 236 source meter. EL spectra were recorded on an Oriel Instaspec IV CCD spectrograph. Luminance was measured by a PR 705 photometer (Photo Research). The external quantum efficiencies were determined by a Si photodiode with calibration in an integrating sphere (IS080, Labsphere).

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Synthesis. 2,7-Dibromo-9,9-dioctylfluorene (**1**) and 2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**2**) were prepared following the already published procedures.[18]

2,13-Dibromotetraphenylporphyrin (3).[37] NBS was added into the solution of tetraphenylporphyrin in $CHCl_3$ at room temperature. The solution was refluxed for 2 h and cooled to room temperature. The whole mixture was condensed and poured into methanol. The precipitated material was recovered by filtration through a funnel. The crude product was purified by column chromatography on silica gel (eluent cyclohexane/benzene, 1:1) and further recrystallized from CH_2Cl_2/methanol to give the title compound (yield: 33%) as a brown solid. Mp > 300 °C. Anal. Calcd for $C_{44}H_{28}N_4Br_2$: C, 68.30; H, 3.63; N, 7.25; Br, 20.69. Found: C, 68.08; H, 3.86; N, 6.98; Br, 21.08. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.91(2H), 8.84 (4H), 8.23 (8H), 7.76 (4H), 7.74 (8H), −2.92 (2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 134.55, 134.30, 128.86, 128.35, 128.07, 127.06, 126.79, 120.20.

Synthesis of Copolymers PFO−TPP Containing Metal-Free TPP. All copolymers containing metal-free TPP were synthesized from **1**, **2**, and **3** via palladium-catalyzed Suzuki coupling reaction following the published procedure.[18] Yield: 64−76%. The resulting copolymers were soluble in common organic solvents (toluene, chloroform, and tetrahydrofuran). The results of elemental analysis of nitrogen and carbon for each copolymer were used for calculation of actual copolymer composition. Anal. Found: for PFO−TPP0.5: C, 77.34, N, <0.3; for PFO-TPP1: C, 88.16; N, <0.3; for PFO-TPP5: C, 88.49; N, 0.31; for PFO-TPP20: C, 87.60; N, 2.33; for PFO-TPP50: C, 86.44; N, 4.98. Because of the low sensitivity of the element analysis instrument, the N content in copolymers PFO−TPP0.5 (TPP in the feed is 0.5 mol %) and PFO−TPP1 (TPP in the feed is 1 mol %) cannot be recorded. NMR results: for PFO−TPP50: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.84 (4H), 8.75 (2H), 8.24 (8H), 7.78 (4H), 7.75 (8H), 7.50 (4H), 7.32 (2H), 1.99 (4H), 1.25 (24H), 0.83 (6H), −2.54 (2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 150.61, 142.74, 142.30, 140.81, 138.64, 136.72, 135.87, 134.83, 130.14, 127.76, 126.29, 124.42, 121.16, 119.75, 118.63, 54.97, 39.82, 31.84, 30.53, 29.52, 24.71, 22.68, 14.10.

Synthesis of Platinum(II)-Containing Copolymers PFO−PtTPP by Direct Metalation of Copolymers PFO−TPP.[19] The copolymer PFO−TPP was added into the $PtCl_2$ solution in benzonitrile preheated at 100 °C for 1 h in an argon atmosphere, and the mixture was refluxed for 10 h. The mixture was cooled to room temperature, poured into stirred methanol, and filtered. The crude product was chromatographed on siliga gel (toluene) and reprecipitated from THF/methanol to give the title copolymers, yield 50−62%.

PFO−PtTPP50: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.77 (4H), 8.62 (2H), 8.14 (8H), 7.74 (4H), 7.72 (8H), 7.50 (4H), 7.31 (2H), 1.96 (4H), 1.11−1.21 (24H), 0.85 (6H).

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