Green Emission from End-Group-Enhanced Aggregation in Polydioctylfluorene

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Received: May 15, 2005; In Final Form: June 29, 2005

Green emission in polyfluorenes (PFs) has been attributed to aggregation or excimer emission, but recently it was reassigned as an on-chain fluorenone defect. We show here that, in dialkyl-substituted PFs that is hydrogen-free at the 9′-position of the fluorene, blue emission with very weak green emission is observed from end-capped polydioctylfluorene (PFO) for both photoluminescence and electroluminescence spectra, while the low-energy green emission at 507 nm is very pronounced only in uncapped PFO (PFOun). The facts that there is no detectable infrared absorption at around 1721 cm^{-1} due to >C=O stretching vibration in PFOun and no charge-trapping occurring in the light-emitting device from PFOun are in contrast with those found in the literature-reported copolymers with fluorenone units, which have detectable infrared absorption at 1721 cm^{-1} and charge-trapping in devices. We found that this green emission at around 507 nm originates from the end-group-enhanced aggregation by use of UV−vis absorption, photoexcitation spectra, and steady-state photoluminescent and electroluminescent spectra. The end-group-enhanced aggregation is much weaker in other PFs with less-ordered structures.

Introduction

Blue electroluminescent (EL) polymers are very important for fabrication of full color display, because they not only emit blue light but also are essential for white light emission[1] or other visible light emissions.[2,3] Polyfluorenes (PFs)[4−11] are one of the best blue-light-emitting polymers due to their high photoluminescence (PL) and EL quantum efficiencies and thermal, chemical, and electrochemical stabilities, as well as their facile modifications at the 9,9-position of the fluorene unit and the copolymerization capability of the monomers with many other monomers. However, the broad green emission is a big problem for blue color purity and lifetime stability, though a green emission may be helpful for white light emission.[12] The origin of the green emission is being increasingly debated. It was assigned to aggregates[13] or an excimer,[4b,14] but recently it was reassigned to a fluorenone defect.[14a,15−20] The fluorenone defect[14a,21] was first found from oxidation of an unsubstituted fluorene end-capper (2-bromofluorene). It was then introduced by oxidation of monosubstituted 9-alkyl fluorene or fluorenone monomers directly. Thus, this green emission can be suppressed by using stable end-cappers instead, such as a cross-linkable styryl unit, anthracene, dihexylfluorene, or silsesquioxane.[21,22] End-capping with hole transport moieties can also suppress the green emission.[23] Blending with low-molecular-weight hole transport materials or other polymers can also suppress the green emission.[5c,24] Further, it was found that this green emission comes from fluorenone-based excimer emission instead of localized fluorenone defects,[19] and this excimer emission can be suppressed by a high-molecular-weight polystyrene block in a terfluorene-*b*-styrene copolymer.[20] There are only a few reports[25,26] that address the uncapped-end-group effect on the green emissions, but a systemic study on this topic is needed. In fact, the green emissions in the energy position in the literature are not clear. In most cases, one could find only a shoulder at around 510−520 nm for PL spectra in pristine films,[7c,13b,14d] a broad peak at around 510 nm,[5b] or two broad peaks at 510 and 530 nm[18] in EL spectra. Very recently, Sim et al.[19] defined the green emission at 535 nm as *g*-band, which comes from fluorenone excimer emission. In the present article, we found that the existence and characterization of green emissions depend on the preparation method of the polyfluorenes and their side-chain structures. We show that the green emission at around 507 nm in PFO originates from the uncapped-end-group enhanced aggregation by use of UV−vis absorption, photoexcitation spectra (PLE), and PL and EL spectra. This end-group-enhanced aggregation is found to be much weaker in other PFs with less-ordered structures.

Experimental Section

1. Synthesis of Monomers and Polymers. 9,9-Di-(*n*-octyl)-2,7-dibromofluorene and 9,9-dioctylfluorene-2,7-bis(trimethylene boronate) were prepared as described in the previous work.[11]

9,9-Bis(2′-ethylhexyl)-2,7-dibromofluorene. To a solution of 2,7-dibromofluorene (28.5 g, 88 mmol) in THF (800 mL), sodium hydride (60%) (8.8 g, 0.22 mmol) was added successively in several portions at room temperature. The mixture was heated at 60 °C, and 2-ethylhexyl bromide (43 g, 0.22 mmol) in THF (200 mL) was added dropwise into the mixture, and the resulting mixture was refluxed overnight. The mixture was concentrated and diluted with water slowly, and then extracted with diethyl ether. After washing with brine, the ether solution was dried over anhydrous MgSO$_4$, and the ether was then removed by evaporation. This crude solid was purified by a silica chromatography with hexane to give a viscous colorless liquid (39 g, 81%). ^{1}H NMR (500 MHz, CDCl$_3$), δ(ppm): 7.50 (4H, m), 7.43 (2H, d), 1.89 (4H, d), 0.52−0.81 (36 H, m); GC-MS: M$^+$ 548.

9,9-Bis(N-carbazolyl-hexyl)-2,7-dibromofluorene. Preparation was followed by the literature method.[21] ^{1}H NMR (500 MHz,

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SCHEME 1: Suzuki Polymerizations of PFO and PFOEH with Two-Step End-Capping.

PFO, R= n-octyl-;
PFOEH, R= 2-ethylhexyl-
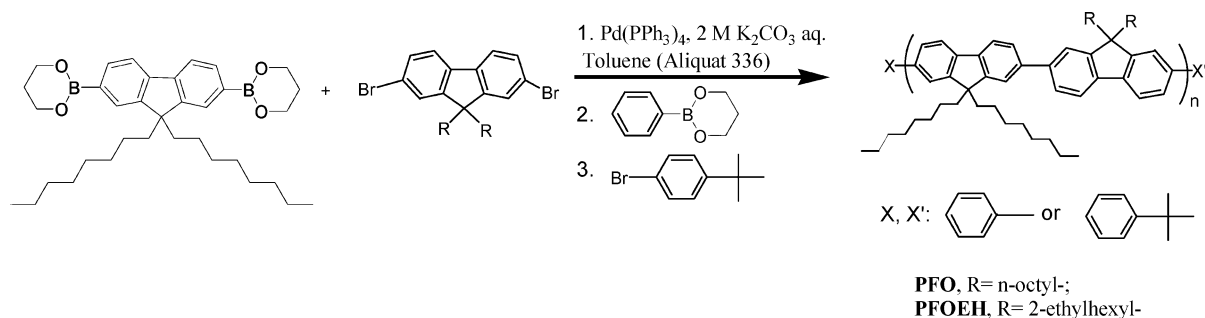
SCHEME 2: Suzuki Polymerization of PFOun and PFOEHun without End-Capping.

PFOun, R= n-octyl-;
PFOEHun, R= 2-ethylhexyl-
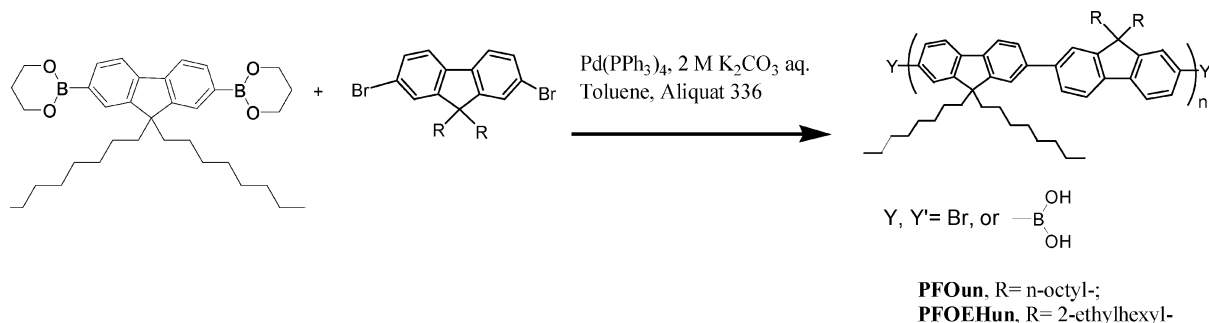
CDCl₃), δ(ppm): 8.09 (d, 4 H), 7.20−7.49 (m, 18 H), 4.17 (m, 4 H), 2.04 (B, 4 H), 0.52−1.82 (m, 20 H).

Preparation of the PFs. The preparation procedure of PFO by Suzuki coupling was reported previously.[11] The same method was also applied to PFOEH. For preparation of PFOun and PFOEHun, a similar method was applied, except no end-capping agents were used.

Another polyfluorene copolymer, poly[(bis(*N*-carbazolyl-hexyl)fluorene)$_{0.25}$-*co*-(dioctylfluorene)$_{0.75}$] (PFO6Cz25), was prepared according to the reported method[11] by Yamamoto coupling polymerization. *tert*-Butyl benzyl bromide as an end-capping agent was used for comparison with two similar copolymers without end-capping in the literature.[27] ¹H NMR (500 MHz, CDCl₃), δ(ppm): 8.02 (m, 1 H), 7.83 (m, 2 H), 7.66 (m, 4 H), 7.36 (m, 1 H), 7.26 (m, 1 H), 7.21 (m, 1 H), 4.12 (m, 1 H), 2.04 (B, 4 H), 0.74−1.70 (m, 36 H). Anal. Calcd for (C₂₉H₄₀)$_{0.75}$(C₄₉H₄₆N₂)$_{0.25}$: C, 89.32; H, 9.15; N, 1.53. Found: C, 88.75; H, 9.10; N, 1.23.

PFOun. ¹H NMR (500 MHz, CDCl₃), δ(ppm): 7.83 (d), 7.66 (m), 2.11 (m), 0.78−1.23 (m). Anal. Calcd for C₂₉H₄₀: C, 89.62; H, 10.38. Found: C, 89.22; H, 10.52.

PFOEH. ¹H NMR (500 MHz, CDCl₃), δ(ppm): 7.81 (d), 7.65 (m), 2.12 (m), 0.61−1.23 (m). Anal. Calcd for C₂₉H₄₀: C, 89.62; H, 10.38. Found: C, 89.05; H, 9.57.

PFOEHun. ¹H NMR (500 MHz, CDCl₃), δ(ppm): 7.81 (d), 7.61−7.67 (m), 2.08 (m), 0.58−1.23 (m). Anal. Calcd for C₂₉H₄₀: C, 89.62; H, 10.38. Found: C, 87.90; H, 10.23.

2. Instrumentation. ¹H NMR spectra were recorded with Varian Unityinova 500 NMR. GC-MS was recorded with HP (5890 gas chromatograph and 5972 mass selective Dector). Elemental analyses were performed using Heraeus CHN-O Rapid, Heraeus VarioEL, or Perkin-Elmer CHN-2400. Ultraviolet−visible (UV−vis), photoluminescent (PL), photoexcitation (PLE), and electroluminescent (EL) spectra were measured by an UV−vis−near-IR spectrometer (Perkin-Elmer, Lambda 19) and a fluorescence spectrometer (AB2 from AMINCO), respectively. Polymer films were made by spin-casting from THF solutions. For concentrated solutions and thin solid films,

PL spectra were collected on the front-face geometry to avoid reabsorption. Annealing of the films was carried out in a glovebox with argon (∼0.1 ppm oxygen or moisture). Gel permeation chromatography from Waters with a UV detector and three columns in series (Styragel HR2 ∼ 4 from Waters) was used to measure molecular weight distributions relative to polystyrene standards at 40 °C. The calibration curve was determined by use of 10 specified standards from 1360 to 1.29 × 10⁶. THF was used as the carrier solvent at the flow rate of 1.0 mL/min. The electric characteristics and luminance of the device were measured by a Keithley power supply (model 238) and luminance meter (BM8 from TOPCON), respectively, controlled with a Labview program. Thickness of the polymer film was measured by a Tencor P-10 Surface Profiler.

3. Device Fabrication and Characterization. An indium−tin oxide (ITO) glass plate was exposed to oxygen plasma at a power of 30 W and a pressure of 200 mTorr for 5 min. A thin-hole injection layer (40 nm) of poly(ethylenedioxythiophene) (PEDOT/PSS, designated as PEDOT for simplicity) (Baytron P CH 8000 from Bayer Co.) was spin-coated on the treated ITO. On top of it, a thin layer (80−120 nm) of PF was spin-cast from its solution in THF (7−10 mg/mL). In some cases, the polymer film was then annealed at 100 °C in a glovebox. Finally, a thin layer of calcium (about 5 nm) covered with a layer of aluminum as the cathode was deposited in a vacuum thermal evaporator through a shadow mask at a pressure of less than 10⁻⁶ Torr. The active area of the diode was about 10 mm².

4. Time-of-Flight (TOF) Measurements. The samples were prepared by spin-casting polymer films (1−3-μm thick) from toluene solutions on the pretreated ITO-coated glass substrates in the glovebox. Aluminum as the charge collection electrode was then deposited by thermal evaporation (at 10⁻⁶ Torr) through a shadow mask. All measurements were performed at room temperature at a vacuum of less than 10⁻⁶ Torr. The photocurrent was generated by a nitrogen-laser-pumped dye laser at 390 nm with a pulse width of 500 ps through the transparent ITO electrode. The transient current was measured across the load resistor using a 500-MHz digital storage oscilloscope. The
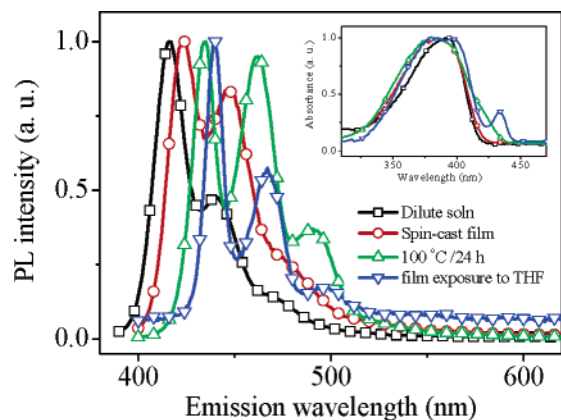
Figure 1. PL spectra of PFO in dilute solution, spin-cast film, film after annealing at 100 °C for 24 h, and film exposed to THF vapor. The inset is their corresponding absorption spectra.

TABLE 1: Polyfluorenes and Their Molecular Weights and Polydispersities (PDI)

polymer	Mw (10^3)	PDI
PFO	160	3.21
PFOun	304	3.75
PFOEH	80	2.37
PFOEHun	45	1.97
PFO6Cz25	84	2.30

carrier mobility μ is related to the transit time t_{tr} by the relation $\mu = d/t_{tr}E$, where d is the film thickness and E is the external electric field.

Results and Discussion

The Monomers and Polymers. Preparations of PFO and PFOun are depicted in Schemes 1 and 2. The monomers, 2,7-dibromodioctylfluorenes, were purified by column chromatography first and then recrystallized from ethanol. It appeared as white needlelike crystals and had no detectable yellowish impurity (fluorenone) by GC-MS and NMR. From this pure monomer, we obtained the corresponding diboronic esters through a Grignard reaction followed by reaction with boronic ester and then reaction with 1,3-propylenediol. This monomer, in the form of white crystals, is obtained by recrystallization from hexane after column chromatography purification, and no detectable yellowish 2,7-dibromofluorenone was observed. The Suzuki coupling reaction was used for preparing both PFO and PFOun. The difference between PFO and PFOun is only that the former is end-capped and the latter is not capped. Similarly, PFs with linear and branch side-chain PFOEH and PFOEHun were obtained. Although the exact contents of the uncapped end group in our polymers are not detectable by elemental analysis and NMR, the uncapped bromine end group in other polyfluorene copolymers has been detected by X-ray fluorescence spectra, while no bromine was detected in the corresponding end-capped copolymers recently.[28] Those copolymers were also prepared by the Suzuki coupling polymerization in exactly the same way as our PFOs, and thus our polymers could have similar end groups as depicted in Schemes 1 and 2. The average molecular weights and polydispersities of the polymers are shown in Table 1.

Absorption, Photoluminescent, and Photoexcitation Spectroscopy Studies on PFO and PFOun. For PFO, Figure 1 shows the PL spectra of its solution in THF (5 mg/L), as a spin-cast film, both after annealing at 100 °C (the glass transition temperature of PFO is around 75 °C[4c]) for 24 h in a glovebox and after further exposure to THF vapor. We did annealing in
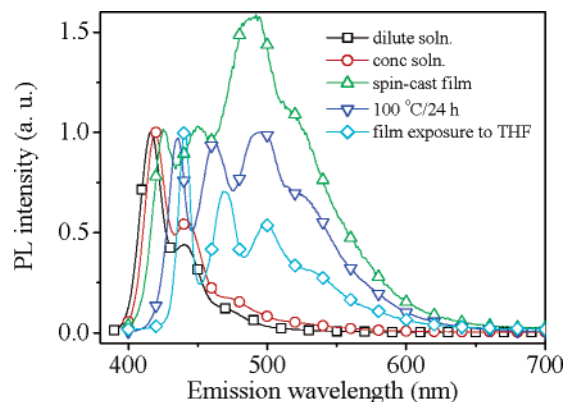

Figure 2. PL spectra of PFOun in dilute solution, concentrated solution, spin-cast film, film after annealing at 100 °C for 24 h, and film exposed to THF vapor.
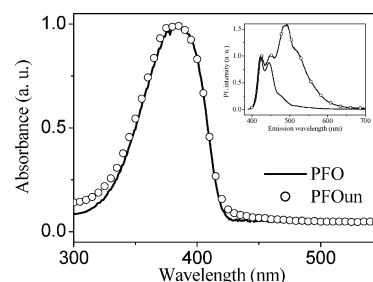

Figure 3. UV−vis absorption spectra of spin-cast films of PFO and PFOun. Inset is their corresponding PL spectra.
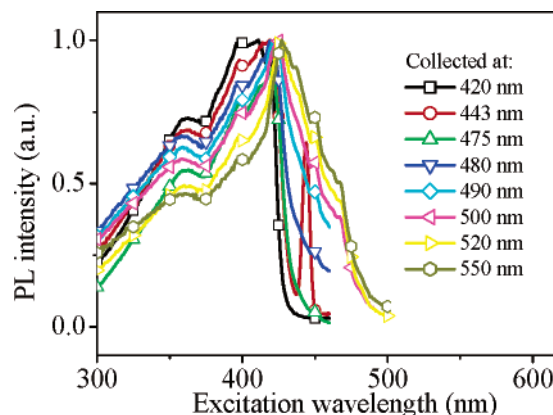

Figure 4. PLE spectra of PFOun in concentrated THF solution (10 mg/mL), collected at indicated wavelengths. The sharp peak at 443 nm is from Rayleigh scatter of the excitation light.

a glovebox in order to avoid fluorenone formation, and thus any long-wavelength emissions should originate from something else. These PL spectra exhibit red-shift in their main peaks from the dilute solutions at 416 nm to the spin-cast film at 423 nm and to the film after exposure to THF vapor at 438 nm, and their corresponding vibronic peaks (for example, for pristine PFO film, peaks at 423, 446, and 477 nm are from 0 to 0, 0 to 1, and 0 to 2 vibronic transitions, respectively[29]) also red-shift accordingly. The corresponding UV−vis spectra in the inset of the figure have maxima at around 390 nm, and the red absorption edge red-shifts successively from the dilute solution to the spin-cast film, and then to that with thermal annealing, and finally becomes an additional peak with the maximum at 431 nm after exposure to THF vapor. A similar phenomenon was found originally for PFO by others[30a] and attributed to the intrachain ordering[30] (extension of conjugation length) induced by annealing and more strongly by solvent-vapor-induced

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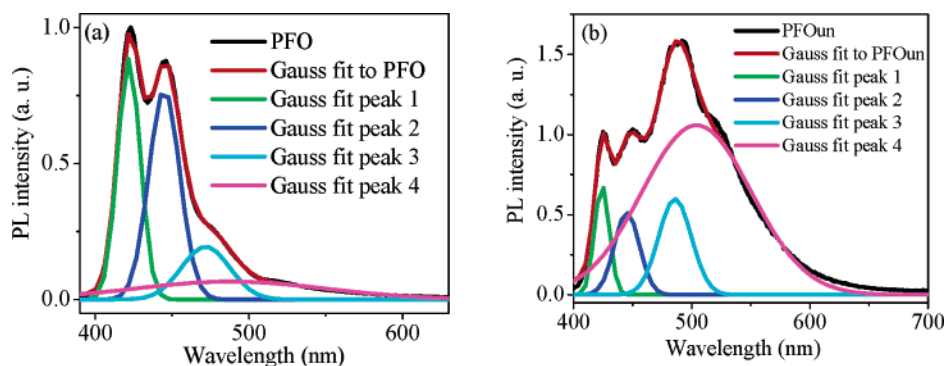*J. Phys. Chem. B, Vol. 109, No. 37, 2005* **17499**

Figure 5. Gauss fits to PL spectra of PFO (a) and PFOun (b) pristine spin-cast films. Gauss-fit peaks 1−3 are typical emissions for PFs due to 0−0, 0−1, and 0−2 vibronic transitions; Gauss-fit peaks 4 are broad green emission at around 510 nm.

swelling stress, which has been found due to β-phase formation. Different from that reported in the literature,[30a] we found no obvious emissions at long wavelengths over 500 nm, which are usually attributed to aggregate/excimer emission and recently attributed to a fluorenone defect.

For PFOun, in addition to the typical blue emissions, however, we do find a very strong and broad green emission in the uncapped PF with a linear side chain, PFOun, as shown in Figure 2 for a spin-cast pristine film, both after thermal annealing and after exposure to THF vapor. Successive red-shifts of the main peak along with the corresponding vibronic transitions are also found from the dilute solution to concentrated solution (10 mg/mL in THF), to spin-cast film, to that after thermal annealing, and then to that after exposure to THF vapor. The typical blue emissions are due to the β-phase formation, while the green emission is new and appears at quite similar positions. As the only difference between PFO and PFOun is the end groups, we can correlate the enhanced green emission to the end-group effect.

The absorption spectrum of PFOun film is quite similar to that of PFO film, but there is still a slight difference in that PFOun has a slightly larger absorption at the red edge, as shown in Figure 3, possibly due to the presence of aggregates. Such a slight difference is usually neglected; however, in distyrylbenzene polymers[31] the presence of small amounts of aggregates can give a pronounced effect on their emission spectra. Photoluminescence excitation (PLE) spectroscopy is a powerful tool for detecting the presence of trace aggregates and thus is also used here. Figure 4 shows the PLE spectra of the concentrated solution of PFOun in THF (10 mg/mL). The emissions at long wavelengths over about 480 nm have relative red-shifted PLE intensity. The red-shifted PLE intensity indicates that at longer excitation wavelength over 430 nm some species can be excited directly to give emission at longer wavelength. This is direct evidence that there is aggregation or some red-shifted emissive species such as fluorenone, but not from the excimer. Since there is no detectable FTIR absorption from fluorenone at 1721 and 1606 cm^{-1}, the longer-wavelength emission most probably comes from a trace amount of aggregates. For the solid films, as the green emission is more pronounced than for the concentrated solution, the aggregates are easier to detect, and the energy transfer from monomeric blue emission to the aggregate emission is more efficient where both intermolecularly and intramolecularly energy transfer can occur.

To define the exact position and shape of the green emission, the PL spectra of PFO and PFOun pristine films are deconvoluted with Gaussian fit shown in Figure 5. Both PL spectra can be deconvoluted to fit into four peaks: the first three Gaussian
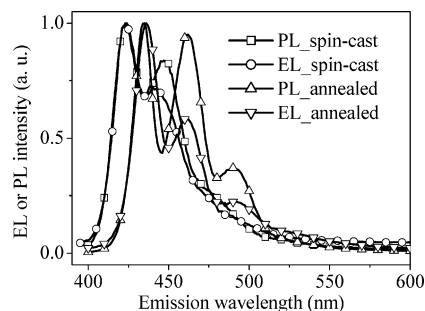

Figure 6. Comparison of EL and PL spectra from PFO as spin-cast films and films annealed at 100 °C for 24 h.
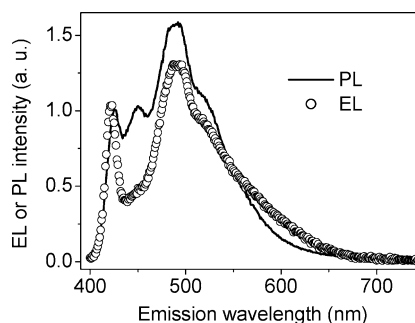

Figure 7. Comparison of EL and PL spectra from PFOun as spin-cast films.

fit peaks are from the 0−0, 0−1, and 0−2 transitions which are very typical for PFs; the fourth Gaussian fit peak is very broad, located at a maximum of around 507 nm. This broad green peak is very weak for PFO, but it is very pronounced for PFOun. For those PL spectra of PFOun after annealing or exposure to THF vapor shown in Figure 2, deconvolution can also give four Gaussian peaks along with the three red-shift vibronic transitions from the β-phase, and there are also green emissions at around 507 nm. Thus, both in the presence and absence of β-phase formation, the green emissions appear at around 507 nm. The position of this green emission is different from the 535-nm *g*-band found in PFs with a fluorenone excimer, and thus the origin of this broad and featureless green emission at 507 nm may have another source, as will be described later.

Electroluminescent Spectroscopy Study. The EL and PL spectra of PFO films from spin-casting and after annealing at 100 °C for 24 h in a glovebox are shown in Figure 6. The annealing process results in red-shifts of both the PL and EL spectra in a similar way. That is, the main emission peaks together with their vibronic peaks red-shift to almost the same locations. Only very weak green emissions were found for these devices, similar to the corresponding PL spectra. For the EL
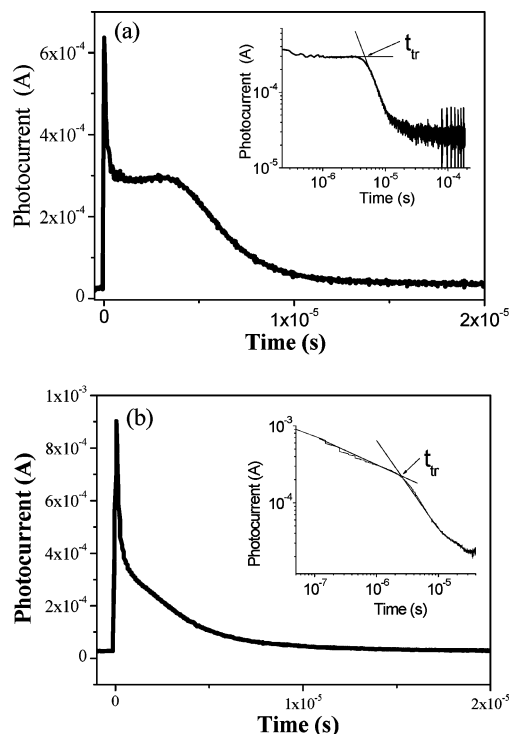
Figure 8. The photocurrent transients for an ITO/polymer/Al device with (a) PFO, (b) PFOun. The insets show the data replotted on log−log axes. The transit time t_{tr} is determined from the intersection of the asymptotes to the plateau and the declining slope of the current transient.
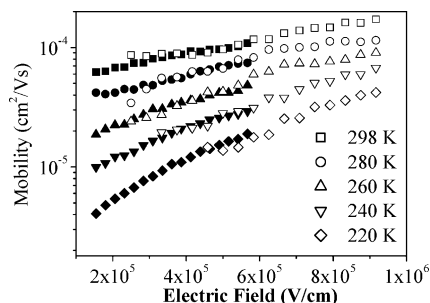

Figure 9. Field-dependent hole mobilities for PFO (solid symbol) and PFOun (empty symbol) at indicated temperatures.

spectrum based on PFOun, we do find strong green emission along with the typical blue emission, as shown in Figure 7. In comparison with the corresponding PL spectrum, however, no big difference is observed, indicating no apparent charge-trapping in the aggregates, in contrast to that of fluorenone-containing copolyfluorenes, in which charge-trapping occurs.[15]

TOF study. To get more information on the end group effect, we measured the hole mobilities by the TOF technique. The photocurrent due to the hole transit in PFO is shown in Figure 8a as we reported before.[32] It exhibits a clear plateau, indicating a well-defined transit and nondispersive nature of the charge transport. The observed nondispersive hole transport is an indication of its excellent purity and chemical regularity. The transient time is determined from the intersection point of the asymptotes in the double-logarithmic current versus time plot (see the inset). In comparison with that for PFO, Figure 8b shows dispersive hole transport in PFOun. Although PFO and PFOun have different transport behaviors, their field depend-ences of the mobilities are very similar, as shown in Figure 9. In our previous study,[32] hole transients in a conjugated polymer would appear to be nondispersive or dispersive transport, depending on the morphology of films cast from solution in
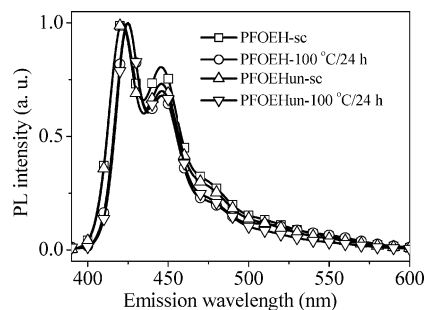

Figure 10. The PL spectra of PFOEH and PFOEun as spin-cast films and after annealing.

different solvents, but the field-dependent mobilities are similar. For both PFOun and PFO, we use the same solvent to cast films, and thus the morphological variation as well as the resultant dispersive hole transient in PFOun are caused by the uncapped end groups, which may probably form aggregates as traps.

End-Group Effects on Other PFs. For other PFs with alternating linear and branch side chains (PFOEH and PFOE-Hun), end groups have only little effect on the PL spectra (Figure 10). Their spin-cast films show almost no green emission, as shown in Figure 10; upon annealing, their PL maxima show only 3-nm red-shift and weak green emission at wavelengths over 500 nm relative to those without annealing. For PFs with only branch side chain such as PFEH, only a little difference in the PL spectra can be found after annealing, which is in agreement with a similar observation reported by the others,[7c] that is, no β-phase is found.[7c,33] Xia et al.[27] found green emissions in two copolyfluorenes containing dioctylfluorene units and fluorene units with Cz-capped hexyl at 9,9-positions (20 and 30% by mole) and attributed them to the incorporation of Cz groups. As we have found no green emission by photoexcitation on a similar polyfluorene with Cz-capped decyl,[11] one might ask if the difference in spacer length could cause such a difference in emission. Thus, to clarify this point, we also prepared a similar PF by the same Yamamoto polymerization method from the same comonomers with a Cz content (25% by mole) between their two PFs and used 4-(*tert*-butyl)bromobenzene for end-capping. This polymer emits only blue emission but without green emission, similar to the present end-capped PFO, indicating that the green emissions from their two copolymers may originate from the uncapped end groups or other defects such as fluorenone due to the possible impurity or oxidation. The dramatic difference in the end-group effects for PFs with a linear side chain such as PFO versus PFs with a branch side chain such as PFEH might be related to their difference of microscopic structures[34] (i.e., the difference in packing).

Mechanism Proposed for the Green Emission from PFs. Our results show some major differences for the origins of the green emissions from the fluorenone emissions: (1) PFOun shows no detectable FTIR absorption from fluorenone at 1721 and 1606 cm^{-1}. In contrast, the reported copolymers[15c] with 0.1−1.0% of fluorenone unit all have detectable IR absorption. Since the PL intensity of the green emission relative to the blue emission for PFOun is very pronounced and between those of the two copolyfluorenes with fluorenone unit of 0.5% and 1.0%, the green emission from PFOun must not come from a fluorenone defect. (2) No charge-trapping on green emission species occurs in the device with our PFOun, while the literature reported devices from the copolymers with fluorenone have pronounced charge-trapping on green emission species.[15] (3) The green emission in PFOun is located at around 507 nm, while

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the green emission from fluorenone is located at 535 nm. As we found aggregation from PLE and UV−vis spectra, this green emission at 507 nm in PFOun can be ascribed to the end-group-enhanced emission from aggregates.

From the molecular weight of PFOun, it can be estimated that the end-group molar concentration is around 1%. As the presence of the polar end groups such as bromo- or boronic acid (converted from boronic ester in base aqueous solution during reaction) might be the main reason for the green emission other than a fluorenone defect in the PFOun, the possible explanation is the following: in PFOun the polar end groups may interact intermolecularly with each other or with fluorene segments to form aggregates and contribute to the green emission via efficient energy transfer, while the polar end groups in PFOEHun with less-ordered structure are more-or-less randomly distributed and weakly interact with less-ordered main-chain segments; thus, no significant aggregation can be formed. The aggregates induced by the polar end groups in PFOun can makes it significant in the PL spectra by efficient energy transfer, similar to those in aggregates[31] or doped systems.[11,12,35] Yang et al.[25] and Woudenbergh et al.[26] both reported that end-capping of one possible end group boronic acid or the bromide after the Suzuki polymerization can suppress the green emission in PFO-based PLED, though there are still some green emissions, which could be contributed from the another uncapped bromide or boronic acid chain ends.

Aggregation emission is well-known for other conjugated polymers such as MEH−PPV,[36] and it is also reported in polyfluorene.[37] It is solvent-[38] and process-dependent, and it may be a general phenomenon in conjugated polymers.

Conclusion

In addition to the green emission at 535 nm from fluorenone, polar end group-enhanced aggregation emission at 507 nm is another source of green emission found in PFs. The latter is more pronounced in PFs with order structures such as PFO. The large difference of the end-group effect on different PFs with different structures of side chain can be used for designing new materials with various optical properties by modification of ends of the main chain or the side chain.

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