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Fine Tuning the Purity of Blue Emission from Polydioctylfluorene by End-Capping with Electron-Deficient Moieties

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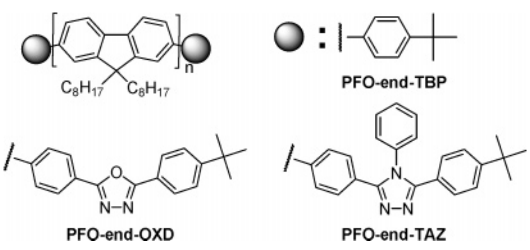
Polyfluorenes (PFs) have been regarded as potential blue-emitting polymers for polymer light emitting diodes (PLED) with high efficiency due to their high photoluminescent quantum yield (PLQY)[1] as well as good thermal, chemical, and electrochemical stabilities. However, PLEDs based on PF homopolymers usually show poor luminance efficiency and additional green emission, which were attributed to an aggregate,[2a] excimer,[2b] or fluorenone defect.[2c] Incorporation of bulky comonomer units, such as anthracene[3a] and spirobifluorene,[3b] or of dendron side chains[3c] on PF backbones or para-*tert*-butyl phenyl as end-cappers[3d] has been attempted to suppress formation of an aggregate or excimer in order to obtain stable blue emission (though their *C.I.E.* color index values are not available), while the device efficiency has not been improved. Another effort using triarylamines as end-cappers[3e] for PFs with branch ethylhexyl side chains (PF2/6)[3f] has led to a suppression of green emission with improved device efficiency, but the blue emission with high purity was obtained only at a voltage higher than 5 V. For prevention from fluorenone defect, it has been reported very recently that replacing a C-9 carbon of PF with silicon gave poly(2,7-dibenzosilole).[3g] Although its blue emission is stable, the improvement in device performance is small and the purity of blue emission is still not saturated (*C.I.E.* color coordinate $x + y > 0.30$ in its electroluminescent (EL) spectrum).[3g] Among PFs, poly(9,9-dioctylfluorene) (PFO) has a simple chemical structure but is rich in morphological features,[4a,b] depending on processing conditions, which can affect device performance and emission color.

Here, we propose a simple way, with PFO as an example, to achieve high stability and improved purity in blue emission as well as improved device efficiency via capping PFO chain ends with electron-deficient moieties (EDMs, such as oxadiazole (OXD) and triazole (TAZ) as shown below), which can induce a minor amount of long conjugating length species (regarded as β phase[4b−e]) to control extents of energy transfer from amorphous matrix to the β phase. It is amazing that the device efficiency of PFO end-capped with TAZ is higher than that with para-*tert*-butyl phenyl (TBP) by a factor of 2 (with CsF/Al as cathode), and its EL spectrum remains stable and with pure blue emission during cyclic operations (*C.I.E.* $x = 0.165$, $y = 0.076$, independent of operating voltage and within the limit for pure blue emission $x + y < 0.30$).



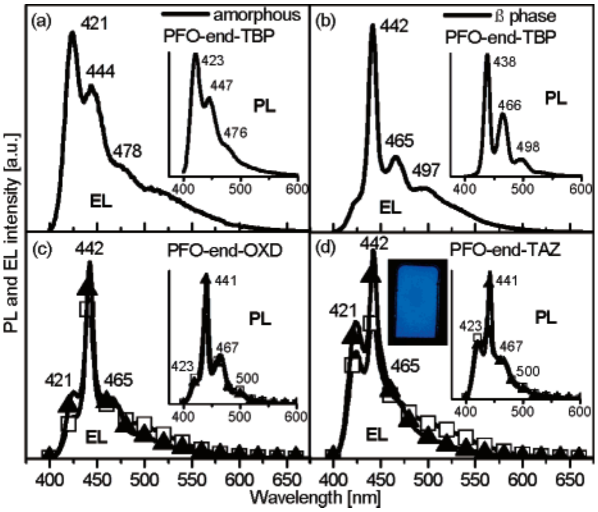


Figure 1. The PL and EL spectra of spin-cast films of PFO-end-TBP, -OXD, and -TAZ: TBP amorphous phase (a) and β phase (b); OXD (c) and TAZ (d), both with their spectral summations from spectra in (a) and (b) (▲: experimental, □: spectral summation). The picture of emission in (d) is from PFO-end-TAZ-based device operated at 4 V.

The photoluminescence (PL) spectrum of spin-cast PFO-end-TBP film is almost totally amorphous (Figures 1a inset, and S1), characterized with $\lambda_{\max}$ at 423 nm (strong peak, 0−0 band), 447 nm (shoulder, 0−1 band), and 470 nm (weak shoulder, 0−2 band).[4b,c] Upon exposure of the polymer film to saturated THF vapor for 15 min and then removing absorbed THF, parts of the chains have extended the conjugating length (regarded as β phase), as evidenced by its PL spectrum with well-resolved vibronic transitions red-shifted by about 0.1 eV at 438 nm (0−0 band), 466 nm (0−1 band), and 498 nm (0−2 band) (Figure 1b inset). For a PFO thin film, generation of the β phase usually requires additional treatments after spin-coating, such as cooling and reheating to room temperature[4c] or exposure to certain solvent vapors,[4b−d] or needs to be processed from its solution in a solvent with low solvent power[4e] or by addition of poor solvent.[2c] These treatments are deleterious to the lifetime of PLEDs due to resulting uneven surface.[4b] Here, we find that end-capping PFO with an electron-deficient moiety, such as OXD and TAZ, can prompt the formation of β phase along chain ends (due to its electron-withdrawing capability) after spin-casting without further treatments, as evidenced by the presence of an absorption peak at 436 nm[4d] in addition to the main absorption peak at 380 nm (Figure 2a and the inset) and an excitation peak at 438 nm in the PL excitation (PLE) spectra, monitored at the emission of 470 nm in Figure 2b. In addition, their PL spectra, excited at the absorption of β phase at 436 nm, show two peaks at 467 and 500 nm, which are very close to those of the β phase (Figure 2b); however, for PFO-end-TBP film prepared from the same condition, no such characteristic peaks were observed. The

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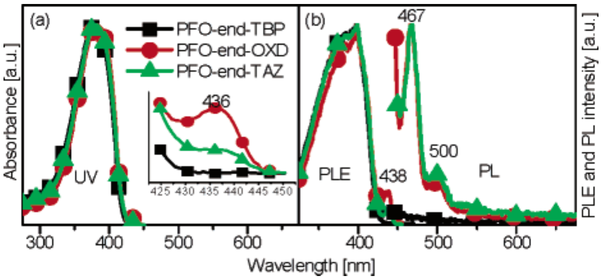

Figure 2. The absorption spectra of PFOs with the enlargement in the inset (a) and the PLE spectra (monitored at 470 nm) and the PL spectra excited at 436 nm (b).

PL spectra of PFO-end-OXD (Figure 1c inset) and -TAZ (Figure 1d inset), excited at the main absorption of PFO chains (380 nm), show the bands from β phase at 441 nm (0−0 band), 467 nm (0−1 band), and 500 nm (0−2 band) and an additional weak 0−0 band from the amorphous matrix at 423 nm. The presence of the additional emission at 423 nm indicates an incomplete energy transfer from the amorphous phase to the end-capper induced β phase, which acts as a self-dopant. Because the energy transfer from the amorphous matrix to the β phase is efficient ($\sim$3 ps),[4d,e] even the amount of energy received is small,[5] the incomplete energy transfer implies that the amount of β phase in PFO-end-OXD and -TAZ is trace, as also supported by the absence of the characteristic peak of β phase in wide-angle X-ray diffraction measurement (Figure S1). The PL spectra of PFO-end-OXD and -TAZ can be reconstructed by spectral summation of the PL spectra from amorphous and β phase PFO-end-TBP at the ratios of 33:67 and 71:29, respectively, as shown in the insets of Figure 1c,d. This is reasonable because the amount of chain-end of the former is 50% more than that of the latter (Table S1).

The PLED devices ITO/PEDOT/PFOs/CsF/Al are fabricated to evaluate the stability of the emission spectrum (Figures 1 and S2) and device efficiency (Table S1). For comparison, the device with an emission from β phase was fabricated by exposing the film of PFO-end-TBP to saturated THF vapor for 15 min. Figure 1a,b shows the EL spectra of PFO-end-TBP from amorphous and β phases, respectively, which are similar to their corresponding PL spectra and have *C.I.E.* color coordinates of (0.176, 0.140) and (0.164, 0.146), respectively. For the EL spectra of PFO-end-OXD (Figure 1c) and -TAZ (Figure 1d), they also resemble their corresponding PL spectra, due to incomplete energy transfer, and their spectral summations of the EL spectra from the amorphous and the β phases at the ratios of 18:82 and 68:32, respectively. Their *C.I.E.* color coordinates are (0.164, 0.088) and (0.165, 0.076), which have $x + y$ values (as 0.252 and 0.241) much smaller than 0.30, and thus are bluer than those of the amorphous phase and β phase both having $x + y > 0.30$. Such high purity in blue emission is due to their stronger intensity of blue components and their weaker long wavelength tail (Figure 1c,d) caused by the bulky electron-deficient end-capper, which leads to less order alignment of long conjugating length species and thus weak 0−1 and 0−2 bands as compared to 0−0 band. Fine tunability by this method is obvious since PFO with TAZ are bluer than that with OXD. Most importantly, the EL spectra of these two capped PFOs are stable under increasing voltages (Figure S2). Excellent blue emission from the PFO-end-TAZ-based device at 4 V taken by a digital camera is inserted in Figure 1d. The device performance is evaluated by the maximum current efficiency and brightness, which are 0.74 cd/A and 2500 cd/m^2 for amorphous PFO-end-TBP, 1.23 cd/A and 8200 cd/m^2 for β phase PFO-end-TBP, 0.56 cd/A and 3400 cd/m^2 for PFO-end-OXD, and 1.67 cd/A and 4000 cd/m^2 for PFO-end-TAZ. The PFO-end-TAZ has the best device performance due to TAZ's larger size and nonplanar structure, which could suppress a possible formation of aggregate at chain ends as supported by the higher PLQY from the film of PFO-end-TAZ (47%) than that of the other two (36 and 38% for PFO-end-TBP and -OXD, respectively), and due to its electron-transporting and hole-blocking characteristics.[6]

For devices with lower molecular weight PFOs ($M_n \sim 20\,000$ or $\sim$50 repeat units versus $M_n \sim 100\,000$ or $\sim$250 repeat units), the performance of devices with OXD- and TAZ-capped PFOs is no better than that of PFO-end-TBP (Table S2), and their EL spectra are characteristic of amorphous phase only and unstable with applied voltage (Figure S3). Since the conjugation length of β phase is about 30 repeat units or more,[4c] it is unfavorable for such low MW PFOs to form β phase after spin-coating.

In conclusion, we report for the first time that a PF homopolymer with end-capping by EDMs can simultaneously provide deep blue emission and improve device efficiency. The deep blue emission is originated from the incomplete energy transfer from the amorphous matrix to the β phase induced by the end-cappers, whereas the improvement of device efficiency is dependent on the structure of EDM, such as size and planarity. Among the three PFOs, simple device architecture using TAZ as the end-capper has the highest efficiency (1.67 cd/A) since TAZ possesses larger size, nonplanar structure, and electron-transporting/hole-blocking characteristics.

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Supporting Information Available: Instrumental, device fabrication details, GPC results, XRD results, and the synthesis details of the monomers and polymers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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