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Diketopyrrolopyrrole-Containing Polyfluorenes: Facile Method To Tune Emission Color and Improve Electron Affinity

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ABSTRACT: A series of novel diketopyrrolopyrrole (DPP)-containing polyfluorenes, coded as PF-DPP01−50, were synthesized through palladium-catalyzed Suzuki polycondensation with different feed ratios between fluorene dibromide and DPP dibromide. Their chemical structures and compositions were verified by ^{1}H NMR and elemental analysis. DSC and TGA results show that they have good to excellent thermal stabilities. Absorption and photoluminescence (PL) properties of PF-DPP01−50, determined in both $CHCl_3$ solutions and thin films, exhibit regular changes with increasing of DPP contents in copolymers, with absolute PL efficiencies being in the range 13.8−26.9%. Electroluminescence (EL) properties of all the copolymers were investigated with device configurations of ITO/PEDOT/copolymer/Ba/Al and ITO/PEDOT/copolymer/Al. A very low content of DPP units (1%) is needed to achieve full energy transfer from fluorene segments to DPP units; hence, exclusive emission of the latter occurs. EL colors of these copolymers vary from orange to red, corresponding to CIE coordinates from (0.52, 0.46) to (0.62, 0.37). The best performance was achieved by orange-emitting PF-DPP01 in device configuration of ITO/PEDOT/copolymer/Ba/Al, with maximum EQE of 0.45% and maximum brightness of 520 cd/m^2. Devices with configuration of ITO/PEDOT/copolymer/Al prove that DPP units can effectively improve the electron affinity of these copolymers. One of these devices (ITO/PEDOT/PF-DPP25/Al) can realize maximum EQE of 0.14% and maximum brightness of 127 cd/m^2. Therefore, color-tuning (red-shift) and improvement of electron affinity can be achieved at the same time through incorporation of DPP units.

Introduction

The initial report[1] in 1990 on electroluminescence (EL) of poly(*p*-phenylenevinylene) (PPV), sandwiched between indium tin oxide (ITO) and aluminum electrodes, opened a totally novel and highly interesting field for polymeric light-emitting diodes (PLED). Compared with traditional inorganic semiconductors and more recently explored organic molecular materials, conjugated polymers combine the advantages of optoelectronic properties of semiconductors and mechanical properties and processability of polymers,[2] which are well-suited for fabrication of flexible large-area flat panel displays.

Enormous efforts have been put and considerable progress has been obtained on electroluminescent conjugated polymers ever since 1990.[3] Polyfluorene derivatives are a promising family of such polymers, as they possess high luminescence efficiency, excellent thermal, oxidative, chemical and photochemical stability, good solubility in common organic solvents, and easy chemical modification of structures.[4] Polyfluorene is typically wide-band-gap and p-type material; hence, it emits blue light, and the injection and transport of holes are more efficient than electrons in PLEDs with polyfluorene as active layer.[5]

Thereby, two main issues still remain or exist: (1) red and green emission are needed for full color display, as sufficient white-emitting polymers are currently lack;[6] (2) electron affinity of polyfluorene should be enhanced to achieve charge carrier balance, which is important for high efficiency and low driving voltage of devices. Generally, there two approaches to these issues: (1) blending and doping system or devices of multilayer structure[7] and (2) attaching functional groups to the ends or side chains of polyfluorene or copolymerization with dedicated comonomers. The first approach is based on the intermolecular interactions, i.e., either energy transfer or charge transfer. To successfully tune emission color to longer wavelength or improve electron injection and transport, proper blending components or dopants should be selected and the concentrations usually need to be strictly controlled.[8] As for multilayer devices, the fabrication is somewhat complicated and difficult.[9] Furthermore, the phase separation or interface contact problems limit the application of this method. The second approach takes the advantage of structural flexibility of polyfluorene and is based on the intramolecular interactions, which is more efficient and quicker than the intermolecular interaction and hence is greatly favored. Many kinds of n-type structures have been utilized to facilitate electron injection and transport,[10] and various narrow-band-gap monomers (or fluorescent dyes and pigments) have been used for color tuning.[11] However, the exploration of novel classes is still needed for further improvements.

We are particularly interested in diketopyrrolopyrrole (DPP) derivatives, which have pyrrolo[3,4-*c*]pyrrole-1,4-dione units as underlying chromophore system[12] and are commercially used as brilliant, strongly fluorescent, so-called high performance[13] for their potentials as building blocks for polyfluorene derivatives to achieve red emission and high electron affinity, based

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on their red fluorescence and electron-withdrawing lactam units. We have previously demonstrated that the different linkage of DPP into main chains obviously affects optoelectronic properties of DPP and fluorene alternating copolymers. Also, we have found that DPP units endow these polymers with reversible reduction processes and greatly lowered LUMO levels.[14] Herein we investigate the structure−property relationships of DPP−fluorene copolymers with different DPP contents to get a full understanding of the role of DPP units in conjugated polyfluorene derivatives.

Experimental Section

Measurement and Characterization. ^{1}H NMR spectra were collected on a Bruker DRX 400 spectrometer in $CDCl_3$ with tetramethylsilane as inner reference. Number-average (M_n) and weight-average (M_w) molecular weights were determined by a Waters GPC 515-410 in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. Thermogravimetric analysis (TGA) was conducted on a Pyris 1 TGA under a heating rate of 10 °C/min and a N_2 flow rate of 20 mL/min. Differential scanning calorimetry (DSC) measurement was performed on a Diamond DSC under N_2 at a heating rate of 10 °C/min. Elemental analysis was performed using a Vario EL III instrument. UV−vis absorption spectra were recorded on a HP 4803 Instrument. PL and EL spectra were recorded on an Instaspec IV CCD spectrophotometer (Oriel Co.). The absolute PL quantum yields were determined in an Integrating sphere IS080 (Labsphere) with 325 nm excitation of He−Cd laser (Mells Griod) or with 405 nm excitation of solid-state laser (Crystal Laser), as the percent of the total output photons in all directions vs the total input photons. The current−luminance−voltage ($I-L-V$) were measured using a Keithley 236 sorce measurement unit and a calibrated silicon photodiode. The luminance was calibrated using a PR-705 SpectraScan spectrophotometer (Photo research). The EL quantum efficiency (QE) was collected by measuring the total light output in all directions in an integrating sphere. It was determined as the percent of the total output photons vs the total input electrons from each electrodes.

Materials. 9,9-Dihexylfluorene-2,7-bis(trimethylene boronate) (**1**) and tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$, were purchased from Lancaster and Aldrich, respectively, and were used without any further purification; other chemicals were obtained from commercially available resources. 2,5-Dioctyl-3,6-bis(4-bromophenyl)yrrolo[3,4-*c*]pyrrole-1,4-diones (**2**) was synthesized through two steps of reactions as we described before.[14] 2-Bromo-9,9-di-*n*-octyl-fluorene and 2,7-dibromo-9,9-di-*n*-octyl-fluorene (**3**) were synthesized from fluorene as a starting material according to the published literature.[15]

General Procedure of Polymerization.[14] 9,9-Dihexylfluorene-2,7-bis(trimethylene boronate) (**1**), 2,5-dioctyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole-1,4-diones (**2**), 2,7-dibromo-9,9-di-*n*-octyl-fluorene (**3**), K_2CO_3 (17 equiv), and $Pd(PPh_3)_4$ (2 mol %) were dissolved in a mixture of THF and water (50/50, v/v) under N_2. Then the mixture was heated to 80 °C and stirred vigorously for 48 h. Additional **1** (6 mol %) was added, and the mixture was refluxed under N_2 for 6 h; subsequently, 2-bromo-9,9-di-*n*-octylfluorene (6 mol %) was added, and the mixture was refluxed for another 6 h. The reaction mixture was cooled, and the solid was precipitated in methanol. The solid was filtered off, washed with dilute HCl, dissolved in chloroform, and precipitated in acetone. After being extracted with acetone in a Soxhlet apparatus for 24 h, polymers were obtained as pale brown to dark red solid with yields of 67−81%.

The purpose of end-capping with additional **1** and 2-bromo-9,9-di-*n*-octyl-fluorene, at the end of polymerization was to avoid possible emission quenching and red-shifting of EL caused by boron and bromides units.[16]

Light-Emitting Devices (LED) Fabrication and Characterization. PF-DPP01−50 were dissolved in toluene−THF (or toluene) and filtered through a 0.45 μm filter. Patterned indium tin oxide (ITO)-coated glass substrates were cleaned with acetone, detergent, distilled water, and 2-propanol, subsequently in an ultrasonic bath. After treatment with oxygen plasma, 50−60 nm of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) (Batron-P 4083, Bayer AG) was spin-coated onto the ITO substrate followed by drying in a vacuum oven. A thin film of PF-DPP01−50 was coated onto the anode by spin-casting inside a drybox. The film thickness of the active layer was 70−80 nm, as measured with an Alfa Step 500 surface profiler (Tencor). For LED with Ba as cathodes, a thin layer of Ba (4−5 nm) and subsequently 150 nm layers of Al were vacuum-evaporated subsequently on the top of an EL polymer layer under a vacuum of 1×10^{-4} Pa; for LED with Al as cathodes, only 150 nm layers of Al were vacuum-evaporated on the top of an EL polymer layer under a vacuum of 1×10^{-4} Pa.

Results and Discussion

Synthesis and Characterizations. Palladium-catalyzed Suzuki polycodensation (SPC) was adopted for the synthesis of copolymers to make sure that DPP units were isolated from both sides by fluorene segments to form more regular arrangements. Moreover, on the basis of the AA−BB approach of SPC,[17] monomers required are conveniently available. These synthetic procedures used to prepare monomer and polymers are outlined in Scheme 1. Synthetic details of monomer **2** were described elsewhere,[14] and the overall yield of the two-step-reaction route was about 32%. The ratio of **1** to **2** and **3** was always kept as (**1**):(**2** + **3**) = 1:1, and comonomer feed ratios of **2** to **3** were 0.2:99.8, 2:98, 10:90, 20:80, 30:70, 50:50, 70:30, and 100:0, respectively. The corresponding copolymers were named PF-DPP01, PF-DPP1, PF-DPP5, PF-DPP10, PF-DPP15, PF-DPP25, PF-DPP35, and PF-DPP50, respectively. Their chemical structures and compositions were verified by ^{1}H NMR and elemental analysis.

In an effort to optimize the conditions of SPC for this specific system, several trials were carried out (Table 1) in the case of PF-DPP50. The effect of inorganic bases was quite obvious as molecular weights of polymers increased according to the tendency of base strength: $NaHCO_3 < K_3PO_4 \cdot 3H_2O \leq Na_2CO_3 < K_2CO_3$. No stronger base was tried for the consideration that the decomposition of monomer **2** may occur under such condition and that the molecular weight achieved (item 6 in Table 1) is quite enough for PLED application. Of course, other factors such as solvent and time were also preliminarily investigated, and a standard Suzuki protocol[18] was also tried (item 7 in Table 1). Other copolymers were prepared applying the optimized condition (item 6 in Table 1) with high yields. All the polymers were obtained as powder, with colors varying from pale brown to orange, pink, red, and dark red as DPP contents increased, and they are readily soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, and THF, but only polymers with low DPP contents such as PF-DPP01 and PF-DPP1 have good solubility in nonpolar solvents like toluene. Molecular weights and polydispersity indices of them are listed in Table 2. M_n of PF-DPP01−35 ranges from 7900 to10 700, without large differences, indicating that reactivities of two dibromides (**2** and **3**) are comparable. Since PF-DPP50 was prepared with $Pd(PPh_3)_4$ freshly purchased, and other polymers were synthesized after $Pd(PPh_3)_4$ had been stored under nitrogen for a period of time, the much higher molecular weight of PF-DPP50 is a direct evidence for decreased activity of $Pd(PPh_3)_4$, which has been reported in the literature.[17,19] However, all of them possess no fewer than 10 repeating units; hence, typical polymeric behavior can be ensured. The polydispersity index (PDI) of PF-DPP35 is somewhat higher with the value of 4.65, while other values are moderate lying in the region of 2.00−

Scheme 1

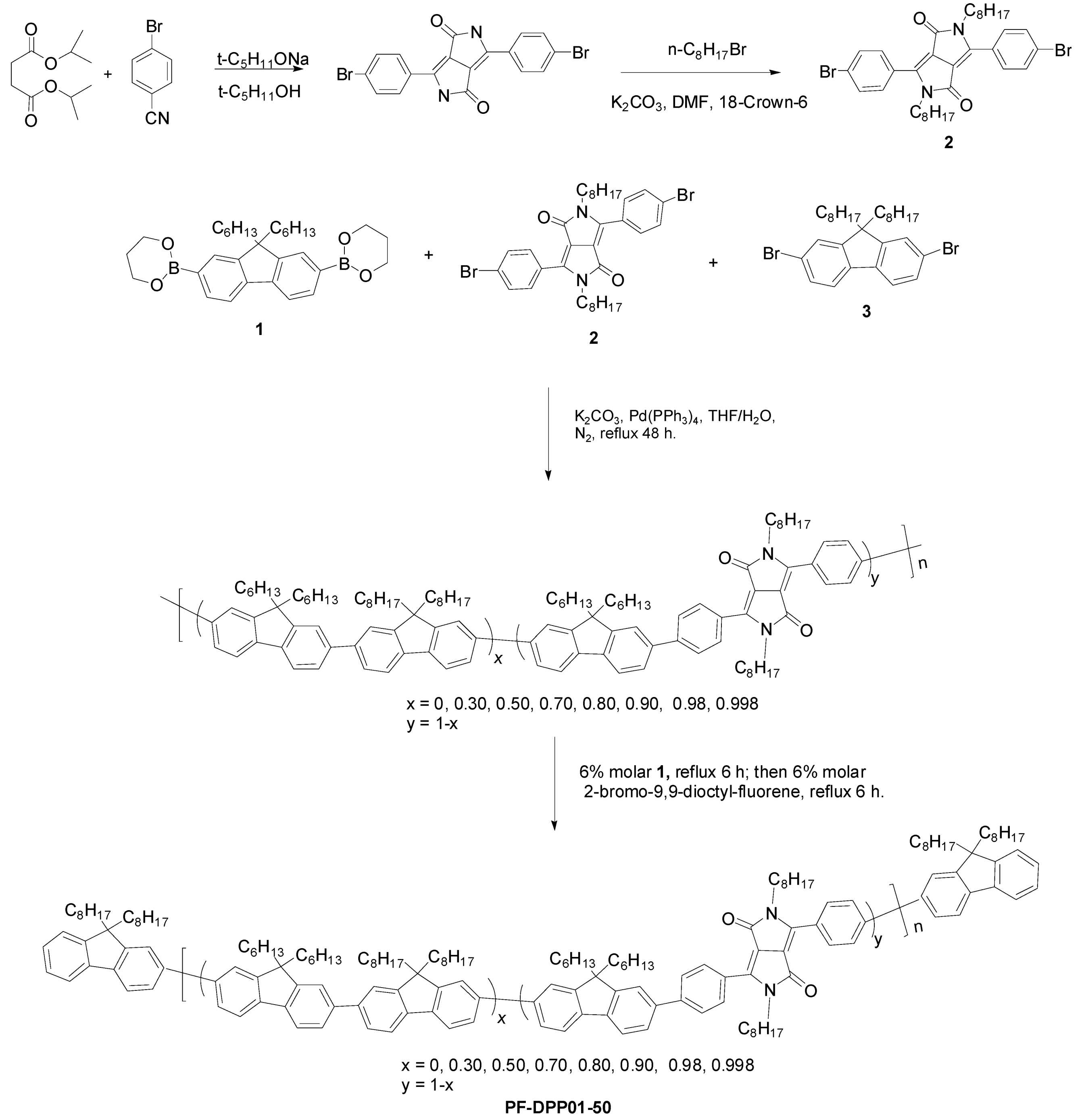

Table 1. Several Trials for the Optimization of Conditions of Polymerization (in the Case of PF-DPP50)

	1	2	3	4	5[a]	6	7[b]
base	$NaHCO_3$	K_3PO_4	K_3PO_4	Na_2CO_3	Na_2CO_3	K_2CO_3	Na_2CO_3
solvent	THF/H_2O	THF	THF	THF/H_2O	THF/H_2O	THF/H_2O	Tol[c]/H_2O
time (h)	48	5	48	48	72	48	48
yield (%)	72	41	79	68	73	69	70
M_n	9700	9900	18000	18100	17500	28700	17600
PDI	2.46	3.48	2.69	2.65	2.38	2.00	2.16

[a] The amount of solvent was doubled. [b] Triethylbenzylamonium chloride was added as phase-transfer catalyst. [c] "Tol" stands for toluene.

3.16. The chemical structures of polymers were confirmed by ^{1}H NMR, as shown in Figure 1. Most signals are broadened and structureless, and only some specific peaks can be clearly assigned; this condition is common in the case for conjugated polymers.[20] As expected, the intensity of signals corresponding to protons of DPP moieties (protons b, g, and h), relative to protons of fluorene moieties (protons f), increase gradually as DPP contents in polymers increase, and only when DPP contents are high enough (310 mol %) can these peaks be observed. The actual compositions of present polymers are calculated from N contents in polymers measured by elemental analysis, and related data are summarized in Table 2. For polymers PF-DPP5−50,

Table 2. Yields, Molecular Weights, N Contents, DPP Contents, and Thermal Properties of Polymers

polymers	yield (%)	M_n	PDI	N (%)[a]	DPP (%)[b]	T_d (°C)[c]	T_g (°C)[d]
PF-DPP01	81	9700	2.17			434	107
PF-DPP1	83	10700	2.50			422	103
PF-DPP5	75	7900	2.64	0.32	4.21	338	104
PF-DPP10	67	9900	2.68	0.68	9.15	256	
PF-DPP15	81	9500	2.96	1.01	13.65	315	
PF-DPP25	73	10300	3.16	1.54	21.51	419	
PF-DPP35	70	10300	4.65	2.16	31.11	399	
PF-DPP50	69	28700	2.00	3.07	46.1	398	

[a] Nitrogen contents in polymers found by elemental analysis. [b] Contents of DPP units calculated according to N%. [c] Based on 5% weight loss. [d] PF-DPP01 exhibits a melting peak at around 175 °C.

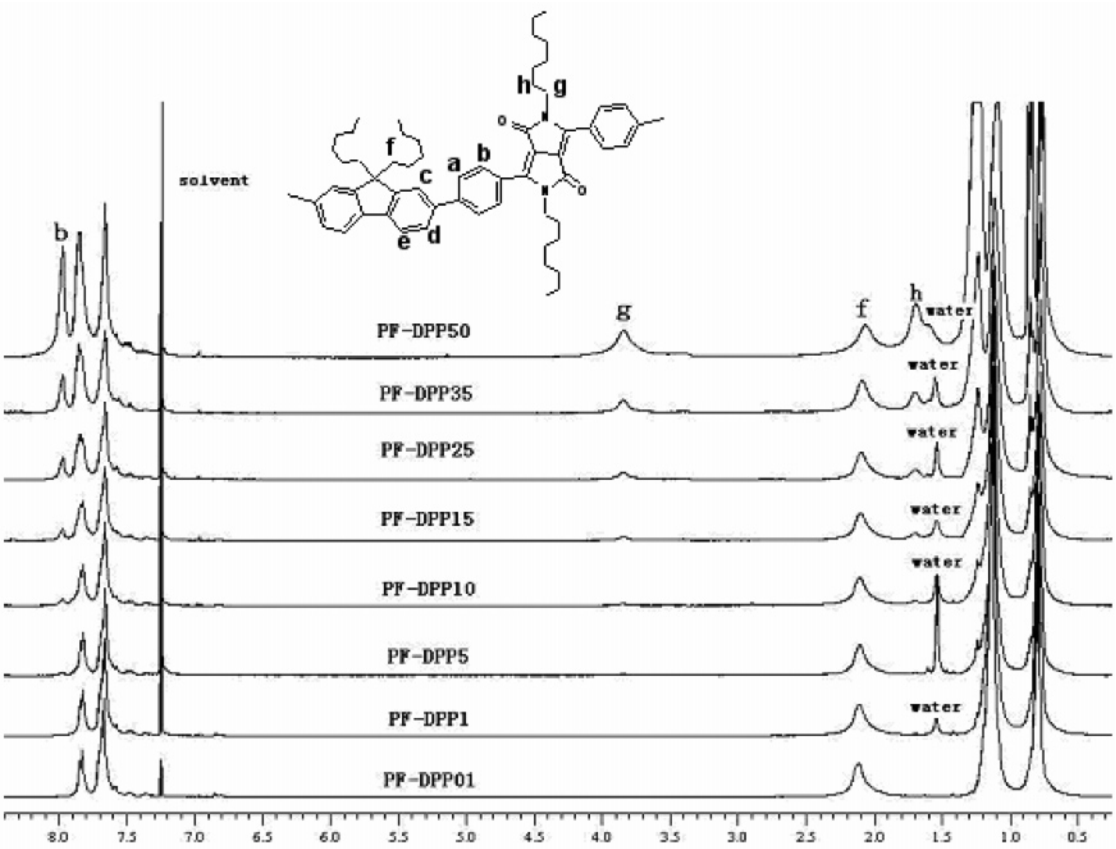

Figure 1. ^{1}H NMR spectra of polymers in $CDCl_3$.

actual DPP contents are a bit lower than the feed ratios of copolymerization. This is reasonable and rational as all the polymers were end-capped with fluorene units (see Experimental Section), which will inevitably add to the contents of fluorene moieties in polymers to an extent that cannot be neglected, especially when molecular weights are not so high for polymers PF-DPP5−35. N contents of PF-DPP01 and PF-DPP1, with theoretical values of 0.0078% and 0.078%, respectively, are too low to be detected. But from their absorption and PL spectra and verified DPP contents of PF-DPP5−50, there are adequate reasons to believe that DPP contents of PF-DPP01 and PF-DPP1 are in good agreement with feed ratios.

Thermal properties of PF-DPP01−50 were evaluated by TGA and DSC, and the results are shown in Table 2. TGA reveals that onset decomposition temperatures (based on 5% weight loss, T_d) are in the range of 256−434 °C, indicative of good to excellent thermal stability. As for DSC results, two thermally induced phase transitions are observed for PF-DPP01: a glass transition ($T_g = 107$ °C) and a melting peak ($T_m = 175$ °C). PF-DPP1 and PF-DPP5 only exhibit glass transitions with T_g of 103 and 104 °C, respectively; no obvious phase transitions are found for other copolymers until 250 °C where slight decompositions begin. This phenomenon represents an apparent enhancement of thermal stability (with respect to thermally induced phase transitions) and demonstrates satisfactorily how the variation of DPP contents will affect the properties of copolymers, as rigid, planar, and polar DPP structure will effectively reduce segmental mobility.

Photophysical Properties. Absorption and photoluminescence properties of copolymers were investigated both in $CHCl_3$ solutions and in spin-coated thin films. All characteristic data of absorption and photoluminescence are summarized in Table 3, and spectra are shown in Figures 2−4.

Figure 2 displays UV−vis absorption spectra and photoluminescence spectra of copolymers in $CHCl_3$, and related spectra of monomer **2** are also included for comparison. For random polymers PF-DPP01−35, the absorption spectra in $CHCl_3$ solutions comprise two distinguished peaks, implying that the electronic states of the two components in random copolymers are not well mixed. Peaks centered at around 380 nm are associated with absorption of fluorene segments,[21] while those located at around 500 nm are caused by DPP segments as their intensity increases almost linearly with the increasing of DPP contents in copolymers and their positions are close to the

Table 3. Photophyscial Properties of Polymers

	solution		thin film			
polymers	λ_{max} (nm)	λ_{pl} (nm)	λ_{max} (nm)	λ_{pl} (nm)	fwhm (nm)[a]	η_{PL} (%)[b]
PF-DPP01	382	419,439,560	384	421, 443, 565	70	14.20
PF-DPP1	380	433, 567(603)	383	421, 443, 571	64	26.90
PF-DPP5	379, 501	432, 568(609)	383, 504	417, 439, 579	64	21.60
PF-DPP10	379, 503	431, 568(608)	378, 505	417, 582	63	20.49
PF-DPP15	376, 503	431, 569(608)	376, 508	584	67	18.00
PF-DPP25	365, 505	426, 569(610)	373, 509	587	68	15.60
PF-DPP35	364, 506	570(611)	362, 511	594	70	14.20
PF-DPP50	330, 382, 512	578(620)	336, 383, 511	609	140	13.80

[a] Fwhm of emission at longer wavelength. [b] η_{PL} value of PF-DPP50 was measured under excitation of 325 nm; others were measured under excitation of 405 nm.

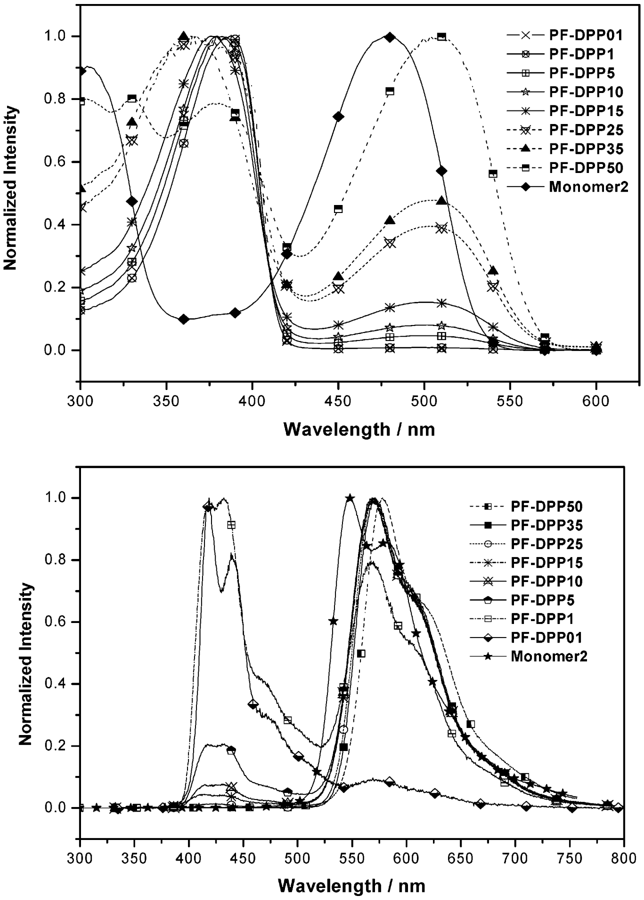

Figure 2. Absorption top and photoluminescent (bottom) spectra of polymers in CHCl$_3$ solutions.

absorption of monomer **2** (475 nm). The alternating copolymer PF-DPP50 is slightly different from others for absorption peaks in the range of 300−400 nm overlap to a continuous band probably due to its unique alternating sequence, which can lead to more efficient conjugation hence more well-mixed electronic states. The gradual blue shift of short wavelength absorption from 382 to 330 nm, together with a small red shift of long-wavelength absorption from 501 to 512 nm, observed in these polymers when DPP contents increase, can be attributed to decrease of conjugation length of fluorene segments and more efficient conjugation between DPP and fluorene as more DPP units are inserted into fluorene units with the increasing of DPP contents.[22]

As illustrated in Figure 2 (bottom), PL spectra of copolymers in CHCl$_3$ solutions (4×10^{-2} g/L) also change regularly with the variation of DPP contents. Photoluminescence of PF-DPP01, similar to polyfluorene homopolymer, exhibits two well-resolved peaks at 419 and 439 nm with the 0−0 transition at 419 nm being the dominant one,[23] while emission at around 560 nm is barely discernible. A distinct growth of 560 nm band to almost the same intensity of 419−439 nm emission appears with PF-DPP1, and the vibronic structures of emission in 419−439 nm region are weakened. When it comes to PF-DPP5, the long-wavelength (560 nm) emission is dominant and the short-wavelength (420−440 nm) emission becomes completely featureless. The relative intensity of the 419−439 nm band to the 560 nm band decreases further when DPP contents reach 10, 15, and 25 mol %. The emission of fluorene segments completely disappears with DPP contents equal to or higher than 35 mol %. Given the low concentration of these solutions, the evolution of PL spectra is considered to be mainly caused by intrachain energy transfer,[24] since narrow-band-gap DPP units, isolated from both sides with wide-band-gap fluorene units, can function as efficient traps for excited states.[25] This mechanism was further studied using CHCl$_3$ solutions of PF-DPP10 at different concentrations of 5×10^{-6}−4×10^{-2} g/L. As shown in Figure 3, even in a very dilute concentration of 5×10^{-6} g/L (low enough to neglect interchain interactions), the PL spectrum of PF-DPP10 is dominated by emission of DPP units. As the concentration decreases, the emission spectrum contains more contribution from fluorene segments. This means interchain interactions play a certain role in energy transfer from flourene segments to DPP units, and energy transfer becomes more incomplete with reduced concentration which leads to less interchain interactions. Through a rather wide range (5×10^{-6}−4×10^{-2} g/L), the relative intensity of emission originated from fluorene to emission originated from DPP units changes very gradually. So it can be concluded that the effect of interchain interactions is quite limited, and energy transfer or charge transfer is largely accomplished via intrachain interactions. Also it should be pointed out that PF-DPP10, with M_n of 9900, has nearly 25 units, so on average there are no fewer than 2 DPP units per chain, which can definitely facilitate very quick and

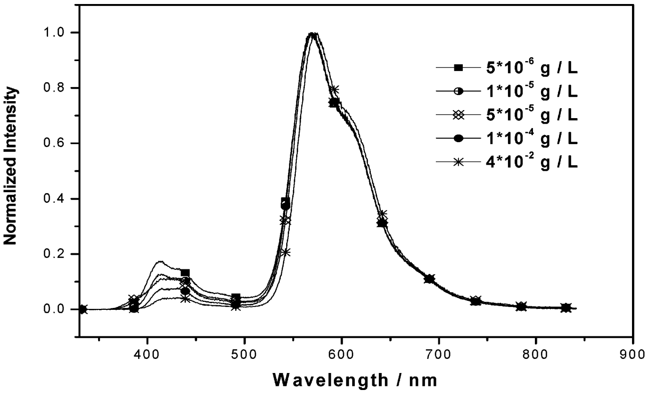

Figure 3. Photoluminescent spectra of PF-DPP10 in CHCl$_3$ solutions with different concentrations.

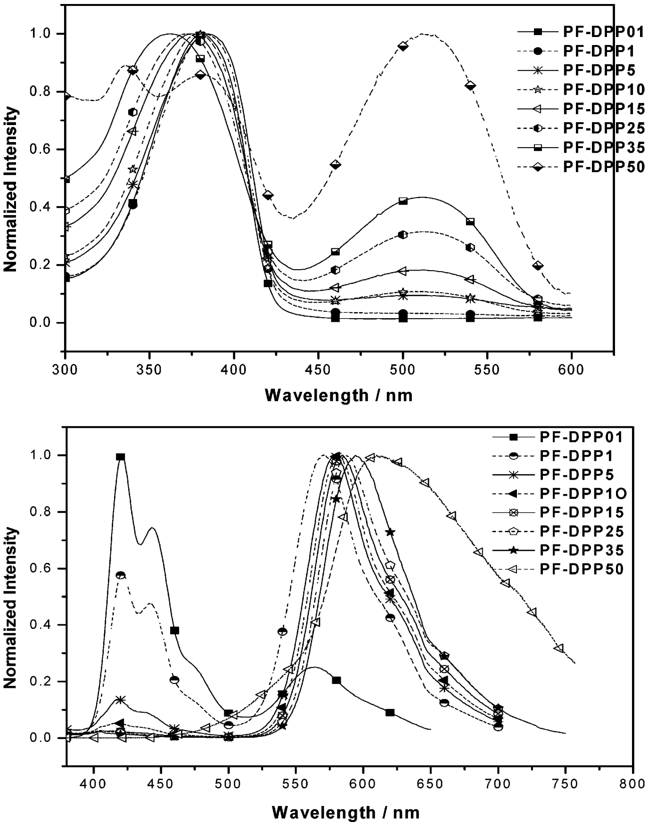

Figure 4. Absorption and photoluminescent spectra of polymers in thin films.

efficient intrachain energy transfer or charge transfer. In copolymers where DPP units are much fewer, maybe intrachain interactions will be more important.

Figure 4 depicts absorption and photoluminescence spectra of copolymers in thin films, which closely resemble spectra in $CHCl_3$ solutions. Some differences should be noticed: first, the maximum emission of photoluminescence is somewhat red-shifted for all copolymers, compared with those in $CHCl_3$ solutions; second, the threshold of DPP contents for complete quenching of emission from fluorene segments is lowered to 15 mol %; third, the PL spectrum of PF-DPP50 is greatly broadened in thin films with full width at half-maximum (fwhm) of 140 nm, in comparison with that in $CHCl_3$ solution or with those of PF-DPP01−35 in thin films. All these phenomena are related to packing or aggregation of main chains in the solid state arising from inherent rigid nature of backbones.[26] The red shift of PL spectra and the more efficient quenching of high-energy emission attributed to this factor were also reported with other systems.[21,24,27] The reason for surprising broadening of PL spectrum of PF-DPP50 in thin films is probably twofold: on one hand, better conjugation and hence well-mixed electronic states are achieved via alternating sequence as mentioned previously; on the other hand, a more regular alternating sequence, along with high polarity of DPP units, is favorable for packing or aggregation of main chains.

Absolute PL efficiencies of all copolymers in thin films were determined under excitation of 405 and 325 nm for random copolymers PF-DPP01−35 and alternating copolymer PF-DPP50, respectively, depending on their relative absorption strength at 405 and 325 nm as revealed by UV−vis absorption spectra in thin films. As listed in Table 3, a tiny incorporation of DPP units 0.1 into polyfluorene main chain can dramatically decrease PL efficiency to 14.8%, compared with PL efficiency of polyfluorene homopolymer.[21] However, when DPP content increases to 1 mol %, PL efficiency achieves a relatively high value of 26.9%. Then, with further increasing of DPP contents, PL efficiencies of copolymers fall gradually. Carbonyl groups which facilitate intersystem crossing of singlet to triplet with their $n-\pi^*$ transition,[28] and possible intramolecular charge transfer similar to those in scientific literature[29] is responsible for the loss of PL efficiency. The obvious enhancement of PL efficiency from 14.2% of PF-DPP01 to 26.9% of PF-DPP1 is probably due to more complete energy transfer originating from bigger amount of DPP units, since the PL spectrum of PF-DPP01 is dominated by blue emission while the PL spectrum of PF-DPP1 is dominated by orange emission, and this variation of degree to which energy transfer is accomplished will lead to less nonradiative decay of excitons. A similar result was obtained with silole−fluorene copolymers though no detailed explanation was available.[30]

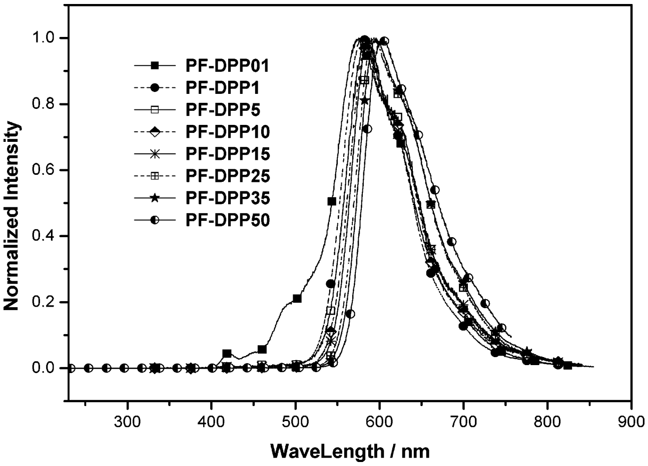

Figure 5. Electroluminescent spectra of polymers in devices with the configuration of ITO/PEDOT/copolymer/Ba/Al.

Electroluminescence. The EL performances of all copolymers were examined in the device configuration of ITO/PEDOT/copolymer/Ba/Al and ITO/PEDOT/copolymer/Al, where PEDOT doped with poly(styrenesulfonic acid) (PSS) functions as a buffer layer and a hole injection/transport layer.

Typical EL spectra of PLEDs constructed from copolymers with the configuration of ITO/PEDOT/copolymer/Ba/Al are presented in Figure 5. In contrast to PL spectra, EL emission consists exclusively of orange or red emission peaked around 575−602 nm originating from DPP units for copolymers containing DPP units equal to or more than 1 mol %. Even for copolymer PF-DPP01, the emission of fluorene segments and excimers[31] or keto defects,[32] responsible for the 400−500 nm band, is much weaker than emission of DPP units at 575 nm. This difference clearly suggests the difference in recombination zone for photoexcitation and electric excitation. Long-wavelength emission in PL spectra arises from energy transfer from fluorene segments to DPP units, while the dominant long-wavelength emission in EL spectra is dominantly produced through charger trapping mechanism as the DPP units serve as efficient electron traps and generated excitons are efficiently confined at them.[33] The trapping process is quick and efficient enough to suppress radiative decay of excitons through other channels; thus, emission from fluorene segments fully disappears even when the DPP content is as low as 1 mol %. This phenomenon has also been reported and discussed before.[21] With increasing DPP contents, EL peaks are gradually red-shifted from 575 nm for PF-DPP01 to 602 nm for PF-DPP50, and this change pattern coincides with the trend of the red shift of PL peaks. All the EL spectra possess a fwhm of about 90 nm.

Table 4. Device Performances with the Configuration of ITO/PEDOT/Copolymer/Ba/Al

polymers	EL emission λ_{max} (nm)	EL fwhm[a] (nm)	CIE coordinate (x,y)	turn-on voltage (V)[b]	max EQE (%)	max brightness (cd/m^2)
PF-DPP01	575	98	(0.52, 0.46)	9.6	0.45	520
PF-DPP1	579	88	(0.54, 0.45)	13	0.10	305
PF-DPP5	580	91	(0.56, 0.44)	7.5	0.24	570
PF-DPP10	584	85	(0.57, 0.43)	20	0.018	18
PF-DPP15	587	84	(0.57, 0.42)	10.5	0.048	50
PF-DPP25	593	91	(0.60, 0.40)	10	0.19	195
PF-DPP35	596	88	(0.61, 0.39)	10	0.13	124
PF-DPP50	602	92	(0.62, 0.37)	8	0.13	153

[a] Full width at half-maximum. [b] Turn-on voltage corresponds to luminance of about 1.5 cd/cm^2.

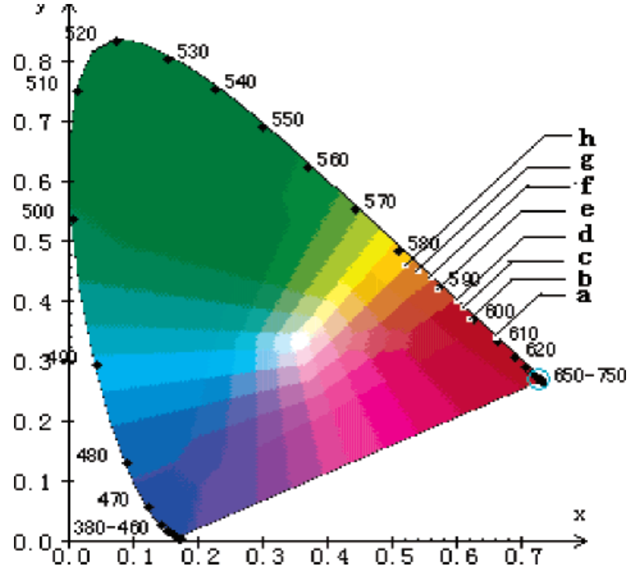

Figure 6. CIE coordinates of standard red demanding by NTSC and emission colors of polymers in devices with the configuration of ITO/PEDOT/copolymer/Ba/Al (from bottom right to top left): a, standard red; b−f, emission colors of polymers PF-DPP50−01.

Commission International de l'Eclairage (CIE) coordinates[34] of all these EL spectra vary from (0.52, 0.46) to (0.62, 0.37), as summarized in Table 4. Figure 6 shows the CIE chromaticity diagram with coordinates corresponding to the emission of all copolymers and Standard Red demanded by National Television System Committee (NTSC).[35] The more DPP contents in copolymers, the more saturated red can be achieved. Maximum external quantum efficiency (EQE), maximum brightness, and turn-on voltages of these devices are also listed in Table 4. The best results were realized using PF-DPP01 as emissive materials, with a maximum EQE of 0.45% and maximum brightness of 520 cd/m^2. The EL performances of these copolymers changes in a different pattern from PL efficiencies, implying a much more complicated mechanism for electroluminescence than photoluminescence.[3c] Copolymers exhibit good EL performances with low DPP contents (PF-DPP01−5) and high DPP contents (PF-DPP25−50), while EL performances of copolymers with medium DPP contents (PF-DPP10−15) are very poor. With respect to main chain structure, copolymers loading few DPP units (PF-DPP01−5) resemble polyfluorene homopolymer to a great degree, while copolymers loading much more DPP units (PF-DPP25−50) are very similar to alternating copolymers. The segments' distribution of these two kinds of copolymers is relatively regular, greatly differing from those most "random" copolymers (PF-DPP10−15); thus, PF-DPP01−5 and PF-DPP25−50 might be superior to PF-DPP10−15 in consideration of conjugation that is responsible for carrier mobility, which is critical for efficient EL.[3c] Moreover, PL efficiencies of these copolymers do not change so dramatically (26.90%−13.80%), which means they will not affect EL performances so obviously. Also, more DPP units will largely improve electron affinity as we have confirmed with the alternating copolymer PF-DPP50.[14] All these factors contribute to the somewhat strange variation of EL performances as a function of copolymer composition.

Table 5. EL Performances of Devices with the Configuration of ITO/PEDOT/Copolymer/Al

polymers	turn-on voltage (V)[a]	max EQE (%)	max brightness (cd/m^2)
PF-DPP01	15	0.045	72
PF-DPP1	15	0.065	159
PF-DPP5	7	0.0095	12
PF-DPP10	21	0.0036	3
PF-DPP15	5.3	0.0015	5
PF-DPP25	12.2	0.14	127
PF-DPP35	14	0.10	75
PF-DPP50	9.6	0.021	18

[a] Turn-on voltage corresponds to luminance of about 1.5 cd/cm^2.

To investigate the expected enhancement of electron injection arising from the lactam structures of DPP units, we fabricated another kind of devices with high work function metal (Al) as cathodes (ITO/PEDOT/copolymer/Al). Responding EL spectra (not shown) are almost identical to those mentioned above. Other parameters are summarized in Table 5. EL properties of copolymers with medium DPP contents are still poor. We find that turn-on voltages are only slightly increased when cathodes have been replaced with Al. Furthermore, in comparison of maximum EQE and maximum brightness with these devices that possess configuration of ITO/PEDOT/copolymer/Ba/Al, performances of devices constructed from PF-DPP01−15 with the configuration of ITO/PEDOT/copolymer/Al are dramatically decreased. However, for PF-DPP25 and PF-DPP35, their performances change little. Figure 7 shows the current intensity−voltage (J−V) and luminance−voltage (L−V) characteristics of devices based on PF-DPP25 and PF-DPP35, with Al (labeled as "Al" on the curves) and Ba (labeled as "Ba" on the curves) as cathodes, respectively. From these results, we can conclude that electron injection from an Al cathode is comparable with that from a low work function Ba cathode, which indicates the improvement of electron affinity by DPP units. It is worthy to note that performances of devices using PF-DPP01 and PF-DPP1 as active layers with Al as cathodes are comparable to devices from polyfluorene homopolymers.[36] Given the much lower PL efficiencies, these values can also be taken as evidence for the improved electron affinity. The reduced LUMO level and reversible reduction process caused by DPP units, as detected in alternating systems,[14] is an important reason for the improvement. But there may also exist Al−N interaction (the formation of complex) on the copolymer−aluminum interface due to the presence of electron-rich nitrogen atoms in DPP units. This mechanism has been extensively studied, and relevant phenomena have been observed with spectroscopy.[37] This kind of interaction can substantially reduce energy barrier for electron

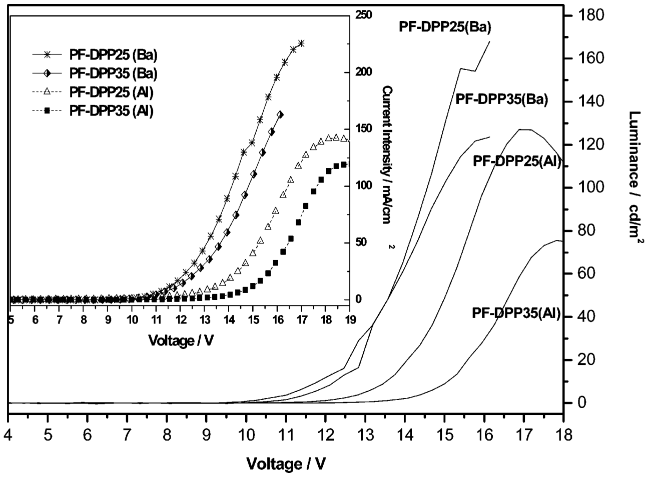

Figure 7. Brightness−voltage and current intensity−voltage curves (inset) of PF-DPP25−35 with device configuration of ITO/PEDOT/copolymer/Al and ITO/PEDOT/copolymer/Ba/Al, respectively.

injection.[38] On the other hand, this kind of interaction can also lead to disruption of conjugation along copolymer backbone, thus resulting in significant falling of efficiency and brightness.[39] Hence, the EL properties of alternating copolymer PF-DPP50, where the most intensive and regular Al−N interactions can occur, with Al as cathode are much inferior to PF-DPP25 and PF-DPP35, while their EL properties in devices with the structure of ITO/PEDOT/copolymer/Ba/Al are of the same order. Also, electroluminescence of PF-DPP5−15, whose conjugation may be already not good due to random segment distribution as speculated from behaviors of ITO/PEDOT/copolymer/Ba/Al devices, is further weakened by this interaction. Similar results that can be attributed to Al−N interactions have been reported previously in scientific literature.[35a]

Conclusion

A series of novel diketopyrrolopyrrole (DPP)-containing polyfluorene derivatives, namely PF-DPP01−50, have been successfully prepared with moderate molecular weights and suitable polydispersity, through Pd-catalyzed Suzuki polycondensation with different feed ratios. ^{1}H NMR and elemental analysis show that these polymers possess well-defined chemical structures and the actual contents of DPP units is close to feed ratios, suggesting almost equal reactivity of fluorene monomer and DPP monomer. DSC and TGA measurements display good to excellent thermal stabilities of these polymers.

Absorption and photoluminescence spectra of these polymers, both in $CHCl_3$ and in thin films, vary regularly with increasing of DPP contents in polymers, and the alternating copolymer PF-DPP50 is different from others due to more well-mixed electronic states. While high DPP contents are needed to completely quench emission from fluorene segments (35 mol % for $CHCl_3$ solutions and 15% for thin films), only very few DPP (1 mol %) units are needed to totally suppress this emission, indicative of different mechanism for photoexcitation and electric excitation. Emission colors of devices with configuration of ITO/PEDOT/copolymer/Ba/Al change from orange to red, corresponding to CIE coordinates from (0.52, 0.46) to (0.62, 0.37), almost linearly with the increasing of DPP contents in copolymers. The best performance of these devices is given by orange-emitting PF-DPP01 with maximum EQE of 0.45% and maximum brightness of 520 cd/m^2. Parameters of devices with structures of ITO/PEDOT/copolymer/Al support the conclusion that incorporation of DPP units into polyfluorene main chain can effectively improve electron affinity.

With all these results, it can be concluded that when incorporating DPP derivatives into polyfluorene, a balance among color purity, efficiency, and brightness should be maintained by cautious selection of DPP contents. Moreover, DPP units can enhance electron injection of copolymers from cathodes and hence can realize efficient PLEDs with air-stable high work function cathodes such as Al to elevate device durability. More efforts will be paid to structure modification of DPP units themselves to get saturated red emission with relatively low contents so that high efficiency and brightness can be ensured at the same time.

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