Synthesis and Properties of Random and Alternating Fluorene/Carbazole Copolymers for Use in Blue Light-Emitting Devices

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Random and alternating fluorene/carbazole (**F/Cz**) copolymers with various carbazole contents (20−50 mol %) have been designed and synthesized for use as the hole-transporting as well as light-emitting layer in blue light-emitting diodes (LEDs). DSC analysis has indicated the complete suppression of the crystallizability of these polymers by the introduction of 3,6-carbazole linkages into the polymer backbone, which also results in changes in their optical properties. The absorption maximum has been blue-shifted with an increase in the carbazole content due to the interruption in the main chain conjugation. Meanwhile, the photoluminescent properties have been influenced by the sequence distribution of the fluorene segments as well as the carbazole content. The emission maxima and vibronic features of the alternating copolymers have changed with carbazole content, reflecting the differences in the electronic structures of the repeat units. However, in the case of the random copolymers, the emission spectra remain almost unchanged and are similar to poly(9,9-dioctylfluorene) (**PF**), despite the fact that the carbazole content increases up to 33 mol %. This feature has been attributed to the existence of longer fluorene segments in the random copolymers, which would be expected to have lower energy gaps, and thus effectively collect excitons from other parts of the polymer backbone. Consequently, the light emitted from these energy traps is similar to that from **PF**. Electrochemical studies indicate that the introduction of carbazole units effectively raises the HOMO energy levels, thereby facilitating hole injection. Controlling the carbazole content between 20 and 33 mol % results in copolymers with stable and reversible p-doping and n-doping processes. A test for a LED device from **P(F3-*alt*-Cz)** indicates that the **F/Cz** copolymers could be a good candidate for blue light-emitting and hole-transporting materials.

Introduction

Blue light-emitting diodes (LEDs) fabricated with polyfluorenes have shown poor stability with a drastic loss in quantum yield and the appearance of an undesired green emission after a short period of operation.[1] Although the causes for these phenomena are still the subject of intensive investigation, chemically this instability is believed to attribute to the formation of excimer aggregates of polymer chains[1d,2] or the presence of quenching defects such as keto groups formed by oxidation.[3] In addition, polyfluorene-based LEDs usually require higher driving voltages since these polymers have intrinsically larger optical band gaps compared with other conjugated polymers that emit longer wavelength light.[4] Under high electrical fields strength, chemical or physical degradation of the polymer is likely to occur, leading to a more rapid failure of the devices.[5] On the other hand, the high-energy barrier between the emissive layer and the electrodes and the imbalance between the hole and electron transporting in the emissive layer are also possible causes for the poor performance of a device. In this regard, it is well-recognized that the charge injection and transport can

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be facilitated by sandwiching the emissive layer between a hole-injecting/transporting layer (HTL) above the anode (often ITO) and an electron-injecting/transporting layer (ETL) under the cathode. The use of such a multilayer structure consisting of the appropriate HTL and ETL can not only lower the turn-on voltages but also balance the hole/electron populations within the emissive layer, thereby extending the lifetime of the device and enhancing the quantum yield.[6,7d] An alternative approach addressing these issues is to vary the chemical structure of polyfluorenes. For example, the incorporation of electron-withdrawing or -donating groups into the polyfluorene main chains or side chains can influence the electron- or hole-injecting/-transporting capabilities of the polymers.[7] However, it is unclear whether the poor efficiency of polyfluorene-based LEDs is caused by the limitation of hole injection or electron injection or both.[8] The purpose of this study was to incorporate electron donor and acceptor groups into the polyfluorene main chain to raise the HOMO level and to reduce the LUMO level, respectively, and at the same time to maintain their emission color in the blue region. The use of these energetically modified polyfluorenes in LEDs devices can give a better understanding of the role of the injecting/transporting of both hole and electron on device performance such as quantum yields and color stability. We have first synthesized a series of fluorene-based copolymers containing oxadiazole units.[9a] The strongly electron-withdrawing oxadiazole groups lower the LUMO energy levels of polymers (values as low as 2.93 eV have been recorded), which effectively improves the electron injection/transport from the low work function metal anodes such as Mg/Ag and Al.[9b] Consequently, these polymers have been shown to be suitable for the electron-transporting layer, while at the same time being capable of emitting pure blue light with high efficiency.

It is well-known that carbazole-containing polymers or small molecules are good hole-transporting materials due to the electron-donating capabilities associated with the nitrogen in the carbazole.[10] It is also demonstrated by Xia et al., that the incorporation of 3,6-carbazole units into the fluorene polymer chain will improve the luminescent stability by interrupting the linear conjugate structures of the polymers.[10b] In this study, we copolymerized 9-octylcarbazole with 9,9-dioctylfluorene to produce random and alternating copolymers with raised HOMO energy levels. The influences of the carbozole content and its distribution pattern in the polymer chain on the thermal, photophysical, and electrochemical properties are examined. The results indicate that the incorporation of varying the amount of carbazole units in the polymers produces materials with improved hole-transporting capabilities and higher blue light-emitting stabilities.

Results and Discussion

Polymer Synthesis. The synthetic procedures used to prepare the monomers and polymers are outlined in Schemes 1 and 2. 9,9-Diocylfluorene-2,7-bis(diethylene boronate), **2**, was synthesized from 2,7-dibromofluorene using a modified literature procedure.[11] 9-Octylcarbazole-3,6-bis(diethylene boronate), **4**, was synthesized starting from carbazole as follows. First, carbazole was brominated with *N*-bromosuccimide (NBS) in DMF at room temperature to afford 3,6-dibromocarbazole. The resulting dibromocarbazole was then alkylated with 1-bromooctane in the presence of 50% NaOH in DMSO. The obtained dibromo compound **3** was then further reacted with *n*-BuLi in THF at −78 °C, followed by the addition of triisopropylboronate and then hydrolysis with 2 N HCl. The resulting carbazole diboronic acid was then esterified with ethylene glycol (EG) to give the diboronate **4**. Alternating and random 9,9-dioctylfluorene/9-octylcarbazole (**F/Cz**) copolymers were synthesized using the Suzuki coupling reaction of the appropriate diboronates and dibromo compounds in refluxing toluene for 48 h in the presence of $Pd(PPh_3)_4$ (0.005 equiv), 2 M $NaCO_3$ (3.3 equiv), and a phase-transfer catalyst, tricaprylylmethylammonium chloride (Aliquat 336). The random copolymers **P(F2-*co*-Cz)**, **P(F3-*co*-Cz)**, and **P(F4-*co*-Cz)** were synthesized by the copolymerization of the fluorene diboronate **2** (1 equiv) with a mixture of 2,7-dibromo-9,9-dioctylfluorene, **1**, and 3,6-dibromo-9-octylcarbazole, **3**, with the appropriate molar ratios (i.e., [**1**]/[**3**] = 0.5, 1, and 1.5, respectively; [**1**] + [**3**] = 1 equiv). The alternating copolymers **P(F-*alt*-Cz)**, **P(F2-*alt*-Cz)**, **P(F3-*alt*-Cz)**, and **P(F4-*alt*-Cz)** were prepared by reacting 1 equiv of carbazole diboronate **4** with 1 equiv of the appropriate dibromo compound **1**, **8**, **10**, and **12**, respectively. Poly(9,9-dioctylfluorene) (**PF**) was synthesized in a similar manner and used for comparison purposes. The number average molecular weights (M_n) of these polymers were determined by gel-permeation chromatography (GPC) against polystyrene standards, ranging from 13.1 to 47.2 kDa (Table 1).

The structures of the polymers were verified by NMR and FT-IR. ^{1}H NMR spectra of the alternating **F/Cz** polymers were shown in Figure 1. Among them, the spectrum of **P(F-*alt*-Cz)** displays the simplest resonance pattern for the aromatic protons. The peaks at 8.49 (singlet), 7.75 (doublet), and 7.51 ppm (doublet) can be assigned to the protons d, e, and f of the carbazole unit, while peaks at 7.83 (protons a and b) and 7.72 (proton c) are attributed to the protons of the fluorene unit. The peaks at 4.38 and 1.94 ppm are due to the resonance of the protons 1′ and 2′ of the octyl group on the carbazole unit. The peak at 2.12 ppm is attributable to proton 1 of the octyl group adjacent to the 9-position

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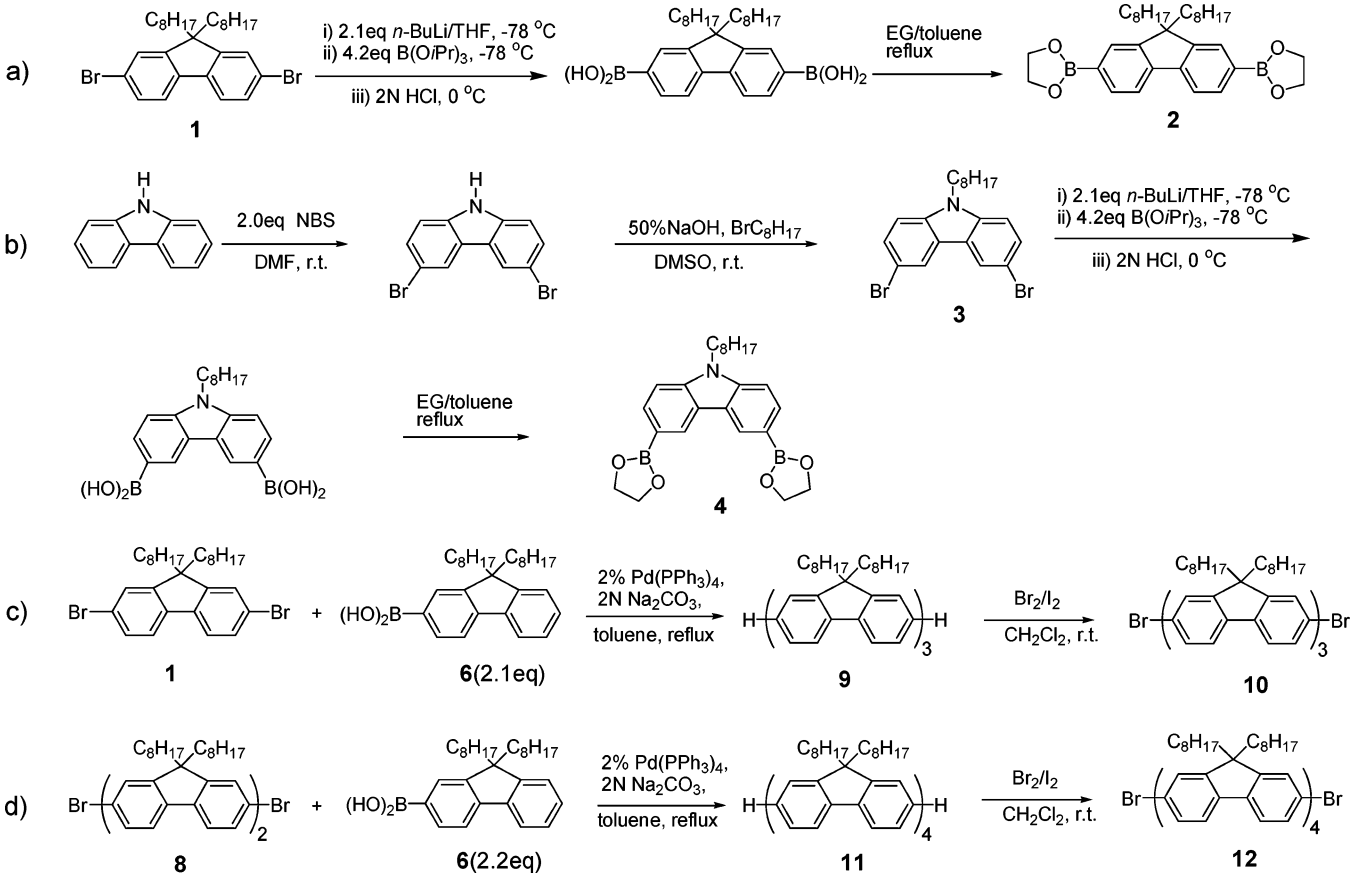
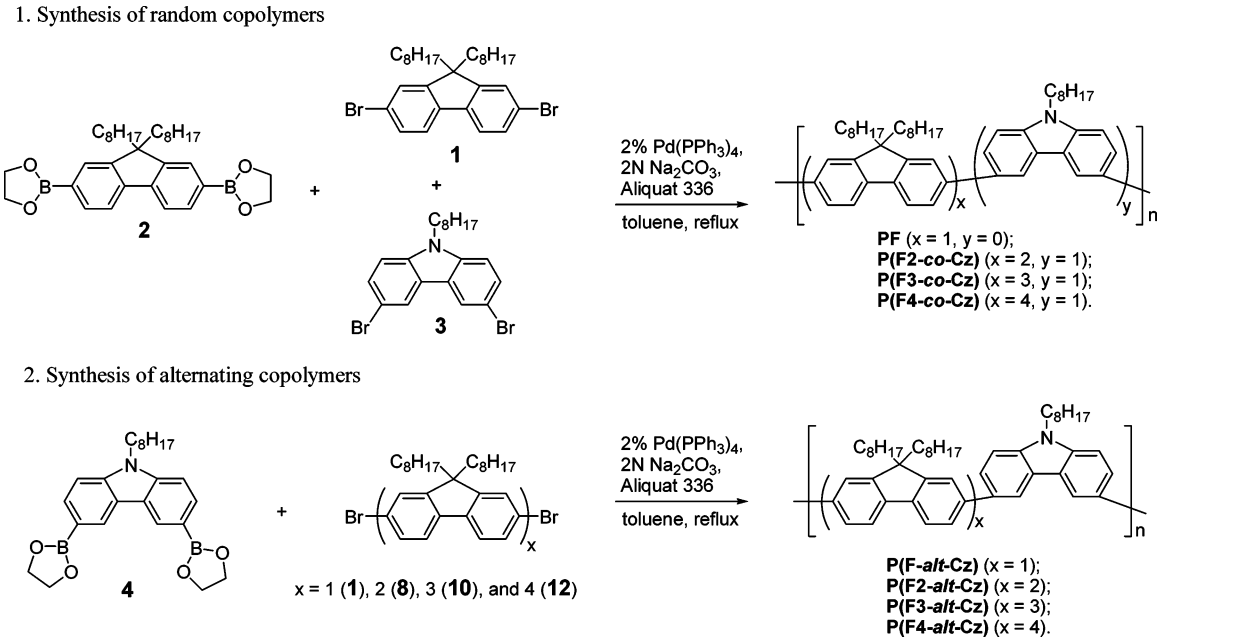
Scheme 1. Synthetic Routes for the Preparation of the Diboronate and Dibromo Monomers



Scheme 2. Synthesis and Structures of Random and Alternating F/Cz Copolymers



of the fluorene unit. The spectra of the other alternating polymers showed a very similar pattern, but the peaks of protons a and c display a complicated mode due to two different chemical structural environments associated with them, that is, adjacent to a fluorene unit and to a carbazole unit. As the content of the carbazole units in the copolymers decreases, the ^{1}H NMR spectra display a corresponding reduction in the intensity of the peaks associated with them. It was also noted that the NMR and IR spectra of the random (not shown) and alternating copolymers with the same **F/Cz** ratios were very similar.

Thermal Properties. All the polymers were characterized by both differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) and the results are summarized in Table 1. **PF** had a crystallization temperature of 113 °C and a melting point of 159 °C, indicating the crystalline nature of this polymer

Table 1. GPC and Thermal Analysis Results of F/Cz Copolymers

polymers	yield,[a] %	M_n[b] (kDa)	M_w[b] (kDa)	M_w/M_n[b]	T_g, °C	$T_{d,5\%}$, °C
PF	90	47.2	162.8	3.45	n.d.[c]	418
P(F-*alt*-Cz)	84	26.0	59.4	2.29	113	422
P(F2-*alt*-Cz)	77	35.9	90.0	2.51	108	421
P(F3-*alt*-Cz)	89	31.0	82.1	2.65	98	420
P(F4-*alt*-Cz)	86	13.1	25.7	1.97	86	422
P(F2-*co*-Cz)	84	28.1	62.2	2.21	108	422
P(F3-*co*-Cz)	81	36.3	146.1	4.02	101	421
P(F4-*co*-Cz)	83	18.5	42.6	2.30	88	421

[a] Isolated yield. [b] Values determined against polystyrene standards. [c] No noticeable T_g was observed; instead a peak crystallization temperature of 113 °C and a peak melting temperature of 159 °C were noted.

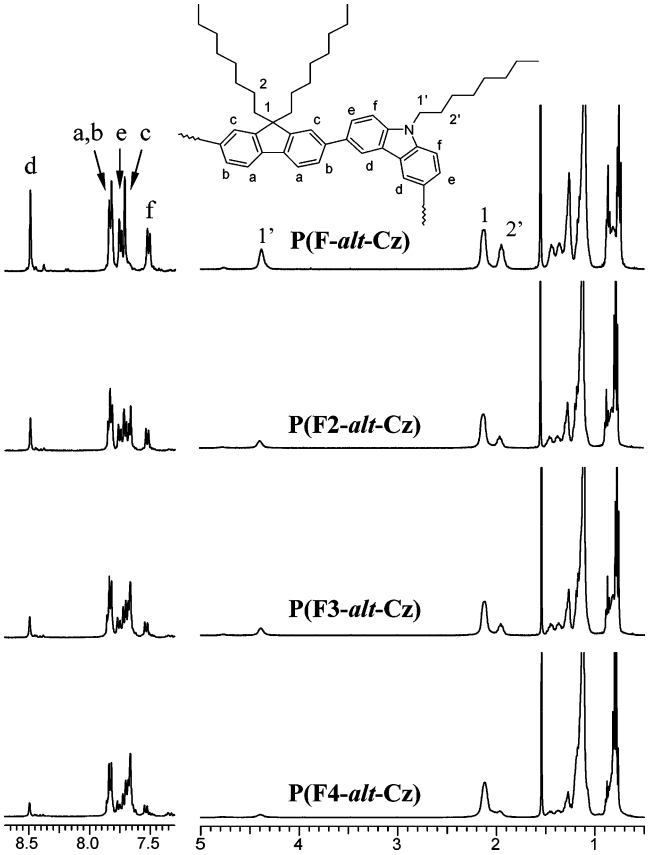


Figure 1. ^{1}H NMR spectrum of the alternating **F/Cz** copolymers in $CDCl_3$.

as reported previously.[12] The incorporation of carbazole units (**F/Cz** = 4/1 to 1/1) into both the random and alternating copolymers resulted in DSC traces that show no crystallizing and melting peaks but only glass transition temperatures. This clearly indicates that the presence of the carbazole units in these copolymers effectively suppresses the crystallizability (or chain aggregation) of the polymer chains. The glass transition temperatures (T_g's) of these polymers ranged from 86 to 113 °C, increasing with the amount of carbazole in the copolymer. The T_g's of all of these copolymers were above room temperature and higher than the operation temperatures required for the LED devices. TGA analysis showed that all polymers were thermally stable with

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Table 2. Optical Properties of F/Cz Copolymers

	solution			films			
	UV	PL		UV, λ_{max}		PL, λ_{em}	
polymers	λ_{max}	λ_{em}	Φ_{fl}[a]	As-sp[b]	Ann[d]	As-sp[b]	Ann[d]
PF	392	414, 439	0.84	393(387[c])	388	420	430, 455
						442	485, 512
P(F-*alt*-Cz)	350	397	0.68	351(346)	346	407	408
P(F2-*alt*-Cz)	367	409, 431	0.76	367(362)	363	414, 438	415, 437
P(F3-*alt*-Cz)	372	412, 435	0.76	371(368)	368	416, 440	418, 442
P(F4-*alt*-Cz)	375	414, 438	0.80	376(371)	373	419, 443	419, 443
P(F2-*co*-Cz)	370	413, 436	0.72	369(365)	365	419, 442	419, 443
P(F3-*co*-Cz)	375	413, 436	0.74	374(370)	371	419, 443	420, 444
P(F4-*co*-Cz)	380	414, 438	0.74	378(375)	375	419, 443	420, 445

[a] 9,10-Diphenylanthrecene standard (Φ_{fl} = 90% in cyclohexane). [b] Obtained from the as-prepared films with an absorbance of ~0.3. [c] Values in brackets were obtained for films with an absorbance of ~0.6. [d] Films annealed at 150 °C under vacuum for 24 h.

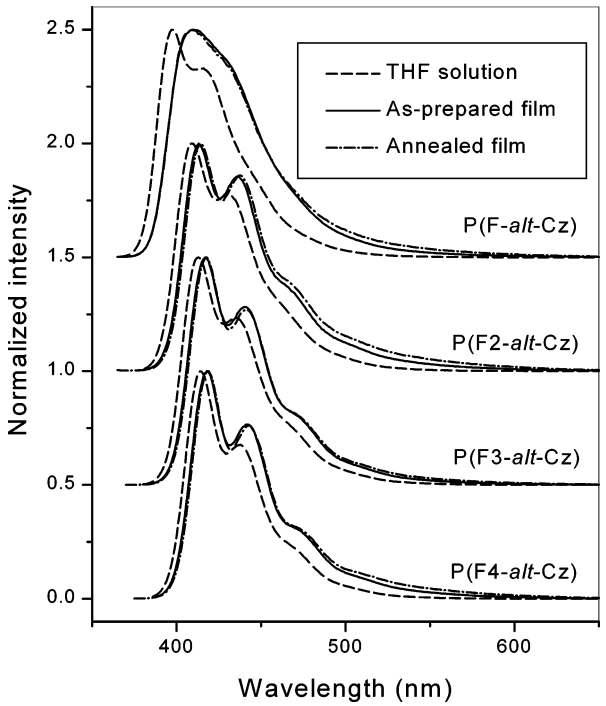


Figure 2. PL spectra of the alternating **F/Cz** copolymers in THF solutions (dashed lines), in as-prepared films (solid lines), and in films annealed at 150 °C under vacuum for 24 h (dash−dot lines).

5% weight loss temperatures being around 420 °C (Table 1).

Optical Properties. UV−vis absorption and photoluminescence (PL) data of the polymers are shown in Table 2 and Figures 2 and 3. **P(F-*alt*-Cz)** displayed an absorption maximum (λ_{max}) at 350 nm in THF solution, resulting in a 42-nm blue shift compared with that of **PF** (λ_{max} = 392 nm). This behavior is similar to the analogous polymer with hexyl side chains, which shows a 31-nm blue shift.[10a] This is due to the interruption of the delocalization of the π-electrons along the polymer backbone by the 3,6-carbazole linkages.[10b] This effect also manifests itself in the solution PL spectrum, where the emission peak is blue-shifted to 397 nm as compared with **PF** (414 nm). With the decrease in the amount of the carbazole units, the alternating copolymers show their absorption and emission peaks getting close to those of **PF** with the values of $\lambda_{max,abs}$ = 367 nm/$\lambda_{max,em}$ = 409 nm for **P(F2-*alt*-Cz)**, $\lambda_{max,abs}$ = 372 nm/$\lambda_{max,em}$ = 412 nm for **P(F3-*alt*-Cz)**, and $\lambda_{max,abs}$ = 375 nm/$\lambda_{max,em}$

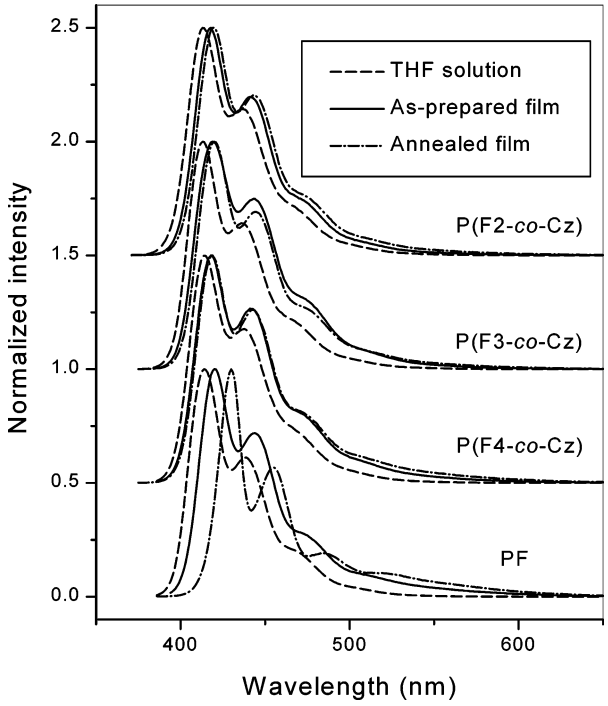
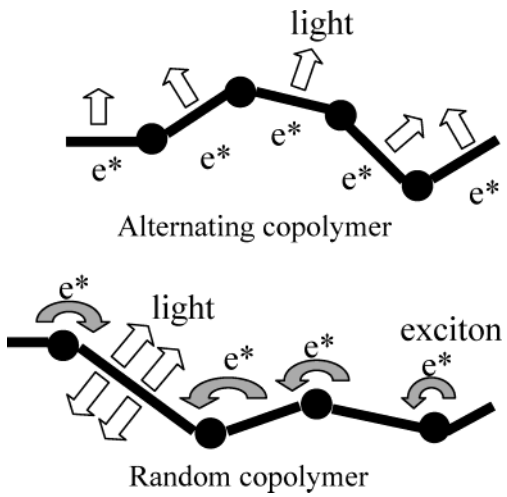


Figure 3. PL spectra of **PF**, **P(F2-*co*-Cz)**, **P(F3-*co*-Cz)**, and **P(F4-*co*-Cz)** in THF solutions (dashed lines), and in as-prepared films (solid lines), and films annealed at 150 °C under vacuum for 24 h (dash−dot lines).

= 414 nm for **P(F4-*alt*-Cz)**. It was also noted that, in contrast with **PF**, which exhibits distinct 0−0, 0−1, and 0−2 intrachain singlet transitions (see Figure 3), **P(F-*alt*-Cz)** has a less resolved PL spectrum, reflecting its different electronic structures. The vibronic structures became progressively resolved and more resembling of the intrachain singlet transition of the **PF** as the amount of carbazole units decreased.

In the case of random copolymers, the absorption peaks appeared at 370 nm for **P(F2-*co*-Cz)**, 375 nm for **P(F3-*co*-Cz)**, and 380 nm for **P(F4-*co*-Cz)**, only a few nanometers red-shifted compared with those observed for the corresponding alternating copolymers. However, their PL spectra showed obviously results different with those of the alternating copolymers. Interestingly, all the PL spectra are strikingly similar to that of the homopolymer **PF** in the vibronic structures and peak positions. A similar phenomenon is also reported for the random copolymers with lower carbazole contents (10 and 12.5 mol %).[10b] These distinct differences in the emission features between the alternating and random copolymers are most likely due to the differences in their chain sequence distributions. In the case of alternating copolymers, the sequence lengths of the fluorene units are exactly defined at 2 for **P(F2-*alt*-Cz)**, 3 for **P(F3-*alt*-Cz)**, and 4 for **P(F4-*alt*-Cz)**. The main-chain conjugation of these polymers is interrupted by the presence of the 3,6-carbazole units. Consequently, the absorption and emission features of the alternating copolymers are governed by the electronic nature of the repeating units; that is, the longer the fluorene sequence, the longer the absorption and emission wavelengths. However, in the case of the random copolymers, the sequence distribution is statistically controlled by the nature of the polymerization. Since the copolymerizations using mixed dibromo monomers do not seemingly favor the formation of uniform sequences, fluorene segments having unit numbers larger than the feed ratio of **F/Cz** can be expected. These longer fluorene sequences apparently can give rise to longer effective conjugation lengths and lower energy gaps. Therefore, in the emission process, once the excitons are formed in the polymer chain, they tend to migrate to energetically favored sites[13] (longer fluorene segments) and emit longer wavelength lights (Chart 1). It has been reported that as the number of fluorene units is larger than five, the emission wavelength of the oligofluorenes approaches that of the high molecular weight polyfluorenes.[14] The strikingly similar emissions observed for these random copolymers in comparison with that of **PF** might suggest that the 3,6-carbazole units in the polymer backbone do not prevent efficient energy transfer in these copolymers so that most of the excitons migrate to the lower energy fluorene segments, despite the carbazole units efficiently interrupting the conjugation of the polymer chain as discussed above.

Chart 1. Difference in Light-Emitting and Exciton Migrations between Alternating and Random Copolymers



The PL efficiencies (Φ_{fl}) of polymers were measured in dilute THF solution using 9,10-diphenylanthrecene (Φ_{fl} = 0.90 in cyclohexane) as a reference. In general, these copolymers showed slightly decreased PL efficiencies (Φ_{fl} = 0.68−0.80) compared with **PF** (Φ_{fl} = 0.84). It was also noticed that the PL efficiencies of the alternating copolymers are marginally higher than their corresponding random copolymers. This might imply that the excitons are confined to the repeat units in the alternating copolymers, thereby giving higher fluorescence yields, whereas in the case of random copolymers some energy loss might happen during the exciton migration.

Polymer thin films were fabricated by spin-coating the polymer solutions in THF (10−15 mg/mL). These films were subjected to both UV and PL measurements. It was found that the absorption λ_{max} was somewhat dependent upon the thickness of the film. The absorption λ_{max} of thin films with an absorbance below 0.3 were almost identical to the values measured in solution,

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whereas thicker films (with higher absorbance) showed lower absorption λ_{max} (see Table 2). This suggests that the thinner films have slightly more ordered morphologies, probably due to surface energy effects or different affinities of the polymer backbone and the side chains for the (glass) substrates.[5,15] The PL spectra of all polymer films showed bathochromic shifts of a few nanometers and some broadening of the emission bands in comparison to their solution spectra. However, their vibronic features remained unchanged. To investigate the luminescent stability, the polymer thin films were heated at 150 °C, a temperature well above their glass transition temperatures. The experiments were conducted in a vacuum oven to completely eliminate oxygen since traces of defects formed via oxidation could also cause drastic spectral changes.[3] As indicated in Table 2 as well as Figures 2 and 3, annealing **PF** film results in a significant red shift of ~10 nm and a pronounced emission at 485 nm, in addition a featureless broad peak centered around 520 nm in its emission spectrum. These spectral changes have been observed previously for fluorene homopolymers and are believed to be due to the formation of low-energy excimer aggregates at high temperatures.[1] Since the incorporation of Cz units into polyfluorene suppressed crystallizability of the polymer as indicated by the DSC measurements, it could be expected that these copolymers would be less prone to chain aggregation and thus possess improved fluorescent stabilities. In fact, annealing of all copolymer films at 150 °C for 24 h resulted in no obvious changes in the absorption and emission spectra as compared with those of as-prepared films. This clearly suggests that in these copolymers the formation of excimer aggregates is effectively suppressed even at temperatures much higher than their T_g's. This result is very similar to those reported by Xia and Advincula for the **F/Cz** random copolymers prepared by Yamamoto coupling reaction.[10b] And as explained in this literature, this effect is probably due to the interruption of the linearity of the polymer backbones by the 3,6-carbazole units that hampers the close packing of the aromatic units.

Electrochemical Study. Cyclic voltammetry (CV) was used to assess the ionization potentials (hole-injecting ability) and the electrochemical stability of these copolymers. The measurement was performed in a 0.1 M *n*-Bu_4NPF_6 solution in acetonitrile at room temperature. The CV curves were referenced to an Ag quasi-reference electrode, which was calibrated using an internal standard, ferrocene/ferrocenium redox couple (0.35 V vs Ag/AgCl). According to Leeuw et al,[16] the ionization potential (E_{HOMO}) and electron affinity (E_{LUMO}) of a conjugated polymer are approximately equal to the onset oxidation potential (vs SCE) and the onset reduction potential (vs SCE) plus 4.4 eV (the SCE energy level below the vacuum level), respectively. The potential of the Ag quasi-reference electrode used in this experiment was determined to be −0.02 V vs SCE. Therefore, the HOMO and LUMO energy levels of the polymers can be estimated using the equations $E_{HOMO} = E_p' + 4.38$ eV and $E_{LUMO} = E_n' + 4.38$ eV, respectively, where E_p' and E_n' are the onset potentials for oxidation and reduction relative to the Ag quasi-reference electrode.

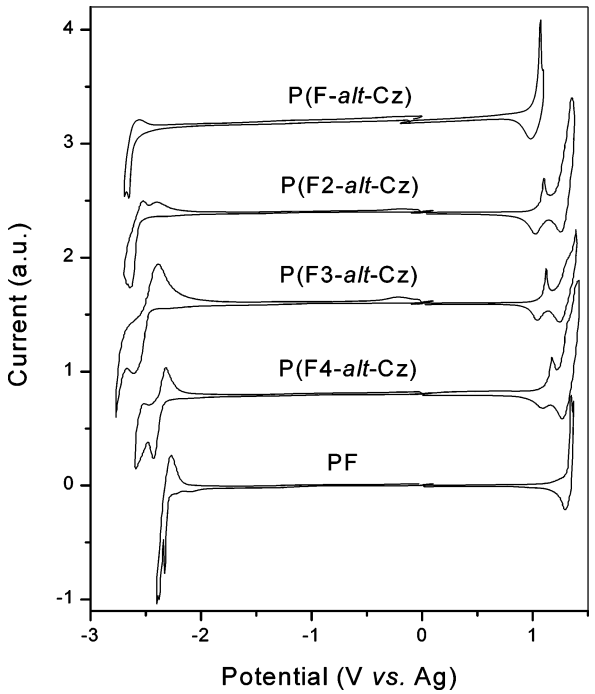

Figure 4. CV curves of the thin films of **PF**, **P(F-*alt*-Cz)**, **P(F2-*alt*-Cz)**, **P(F3-*alt*-Cz)**, and **P(F4-*alt*-Cz)** measured in 0.1 M Bu_4NPF_6 acetonitrile solution at a scan rate of 50 mV s^{-1} at room temperature (versus an Ag quasi-reference electrode).

Table 3. Electrochemical Properties of F/Cz Copolymers Films

polymers	E_p', V[a]	E_n', V[a]	E_{HOMO}, eV[b]	E_{LUMO}, eV[b]	E_g, eV[c]
PF	1.25	−2.00	5.63	2.38	3.25
P(F-*alt*-Cz)	0.95	−2.36	5.33	2.02	3.31
P(F2-*alt*-Cz)	0.96	−2.34	5.34	2.04	3.30
P(F3-*alt*-Cz)	1.01	−2.21	5.39	2.17	3.22
P(F4-*alt*-Cz)	1.03	−2.17	5.42	2.21	3.21
P(F2-*co*-Cz)	0.99	−2.31	5.37	2.07	3.30
P(F3-*co*-Cz)	1.05	−2.26	5.43	2.12	3.31
P(F4-*co*-Cz)	1.06	−2.25	5.44	2.13	3.31

[a] Onset oxidation (p-doping) and reduction (n-doping) potentials versus an Ag quasi-reference. [b] Estimated from the onset oxidation and reduction potential by using $E_{HOMO} = E_p' + 4.38$ eV and $E_{LUMO} = E_n' + 4.38$ eV. [c] Electrochemical band gaps determined using $E_g = E_{HOMO} - E_{LUMO}$.

The **PF** thin films showed typical reversible n-doping and p-doping patterns similar to those reported previously for polyfluorene[17] (Figure 4 and Table 3). However, the gap between the n-doping and the p-doing peaks in this work is slightly narrower than that reported in ref 17. This difference is believed to be due to the difference in the barrier for the charge injection, which appears to be affected by the thickness of the polymer films. In this work, reproducible CV curves were obtained from thin films and showed an onset oxidation potential (E_p') of 1.25 V and an onset reduction potential (E_n') of − 2.00 V. These values correspond to an E_{LUMO} of 2.38 eV and an E_{HOMO} of 5.63 eV. Consequently, the hole injection

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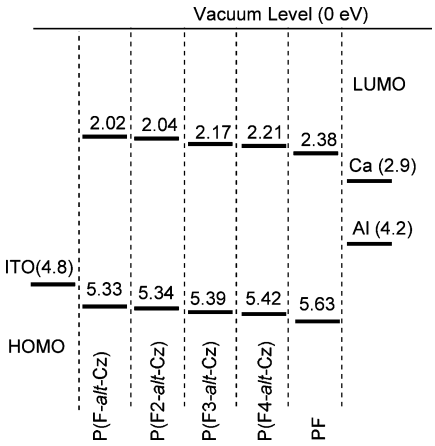
Chart 2. Fine-tuning of the Energy Levels of Alternating F/Cz Copolymers by the Incorporation of Carbazole Units



from the ITO anode (W_a = 4.8 eV) to **PF** has a large energy barrier of ca. 0.83 eV. When 50% of the fluorene units was replaced by carbazole units, the E_{HOMO} of the resulting alternating copolymer, **P(F-*alt*-Cz)**, was noticeably raised to 5.33 eV, indicating a much lower barrier for hole injection from ITO (0.53 eV). However, it should be noted that this copolymer had an irreversible n-doping process. This implies that the electron-charged (n-doped) state of this polymer is rather unstable. It is noteworthy that similar behavior has been reported for the polymer with the same backbone structure as **P(F-*alt*-Cz)** but the hexyl group as the side chain,[10a] from which the E_{HOMO} was found to be 0.22 V higher than that of **PF**. When the carbazole content was decreased to 33 mol %, the copolymer **P(F2-*alt*-Cz)** gives rise to two separate peaks during the p-doping process. Its E_{HOMO} value (5.34 eV) from the onset potential of the p-doping is almost identical to that observed for the **P(F-*alt*-Cz)** copolymer. It showed a partially reversible n-doping process, suggesting an improved stability to n-doping. Meanwhile, when the carbazole contents further decrease to 25 and 20 mol %, the copolymers display a slightly lower HOMO level with values of 5.39 eV for **P(F3-*alt*-Cz)** and 5.42 eV for **P(F4-*alt*-Cz)**, but still much higher than the value of **PF** (5.63 eV). This result indicates a smaller barrier for hole injection to the copolymers from ITO. Similar trends were also observed in their redox processes for the random copolymers, which were observed to be stable in both the p-doping and n-doping processes. This effect was reported to remain even when only ca. 10 mol % carbazole was incorporated into the polymers,[10b] where the copolymers were found ca. 0.2 V higher in E_{HOMO} compared with **PF**. As a result in whole, while the LUMO level of polyfluorenes can be reduced through the incorporation of oxadiazole units to facilitate the electron injection from a metal cathode such as Mg/Ag,[9] this study showed that their HOMO energy level can be raised from 5.63 to 5.33 eV by the introduction of the carbazole units to enhance the hole injection from the ITO anode (see Chart 2).

Electroluminescence Properties (EL) of LED Devices. To evaluate the improvement in the hole-transporting property of the **F/Cz** copolymers, a device of **P(F3-*alt*-Cz)** has been fabricated and its electroluminescence (EL) behavior was compared with the

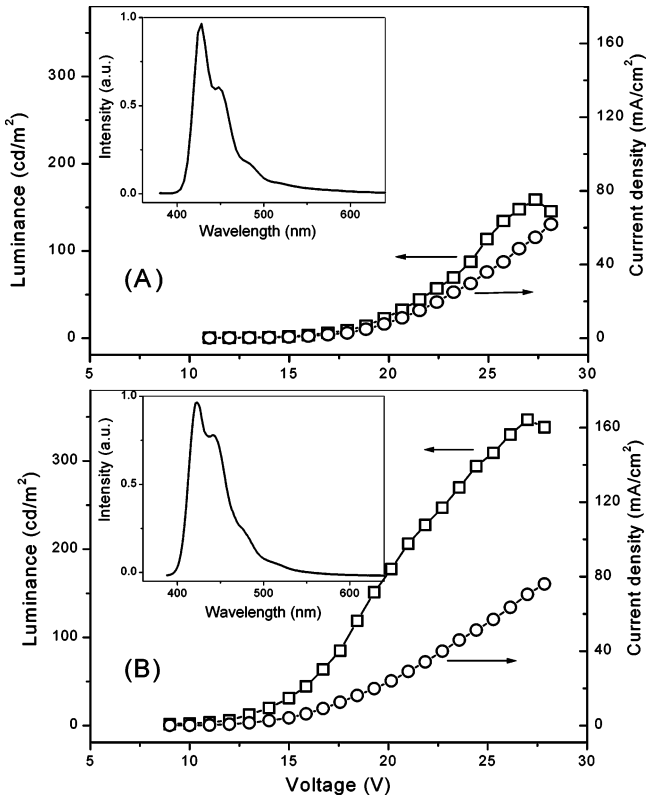


Figure 5. EL spectrum and L−V as well as I−V characteristics of the devices of (A) ITO/**PF**/**F-TBB**/Alq_3/LiF/Al and (B) ITO/**P(F3-*alt*-Cz)**/**F-TBB**/Alq_3/LiF/Al.

device of **PF**. Therefore, multiple layer devices have been designed and fabricated with the configuration of ITO/**polymer**/**F-TBB**/Alq_3/LiF/Al, where **polymer** represents **P(F3-*alt*-Cz)** or **PF**. In these devices, a hole-blocking layer, **F-TBB**,[18] has been inserted between the polymer and Alq_3 layers so that the holes can be confined in the polymer layer to ensure that the recombination of the holes and electrons only occurs in the polymer emissive layer. The EL spectra and luminance/current curves from both devices are shown in Figure 5. Both polymers exhibited a similar behavior in EL spectra by comparing with the PL spectra of the corresponding films. The first emission peak from the **P(F3-*alt*-Cz)** device appears at 423 nm, about 7-nm red shift compared with its PL value of the film (416 nm), while the second peak is at 443 nm, showing 3-nm red shift. Meanwhile, the **PF** device gives 7-nm red shift for both the first and the second peaks. No obvious emission peaks are noted from the **P(F3-*alt*-Cz)** device in the region of 500−600 nm with the intensity somewhat lower than that in the same region of the spectrum from the **PF** device.

The maximum luminance of the **P(F3-*alt*-Cz)** device is 350 cd/m^2 at 27 V, and its luminance efficiency is 0.72 cd/A at a practical brightness of 100 cd/m^2. In contrast, the maximum luminance of the **PF** device is only 160 cd/m^2 at 27 V with the luminance efficiency less than half of the **P(F3-*alt*-Cz)** device (0.30 cd/A at a brightness of 100 cd/m^2). The higher luminance and luminance efficiency of the **P(F3-*alt*-Cz)** device can be explained by a more efficient hole injection into the polymer

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emitting layer in this device. This result indicates that **F/Cz** copolymers could be good candidates for hole-transporting and blue light-emitting materials.

Conclusion

Random and alternating copolymers with **F/Cz** ratios varied from 1/1 to 4/1 have been designed and synthesized using Suzuki coupling reactions. These copolymers are amorphous with T_g's ranging from 86 to 113 °C, satisfying the requirements for LED applications. While the random and alternating copolymers exhibited similar UV absorption spectra, their emission spectra both in solution and in film are very different. The emission λ_{max} and the vibronic features of the alternating copolymers reflect the properties of the individual repeat units. However, all the random copolymers show almost identical emission spectra, which are similar to that of the homopolymer **PF**. This observation has been attributed to the existence of longer fluorene sequences (more than five fluorene units) in the random copolymers. In these cases the excitons formed in the polymer chains can migrate to these longer fluorene segments and emit light with similar features as those from **PF**. Annealing of these **F/Cz** copolymers at 150 °C for 24 h caused almost no changes in their emission spectra, unlike what has been observed with **PF**. The electrochemical studies have shown that the incorporation of carbazole units into polyfluorene backbones with carbazole contents in a range from 33% to 20% possess raised HOMO energy levels and stable electrochemical properties. The incorporation of **P(F3-*alt*-Cz)** as a hole-transporting and emissive layer into a multiple layered device together with Alq_3 as an electron-transporting layer demonstrated good performance. The maximum luminance is 350 cd/m^2 at 27 V and the luminance efficiency is 0.72 cd/A at a practical brightness of 100 cd/m^2, which is 1-fold higher than that of the **PF** device. This result indicates the **F/Cz** copolymers lead to better hole-transporting characteristics and improved device performance.

Experimental Section

Measurements. ^{1}H NMR spectra were obtained in $CDCl_3$ on a 400-MHz Varian Unity Inova spectrometer. Molecular weights were determined using gel permeation chromatography (GPC) on a Waters Model 515 HPLC equipped with μ-Styragel columns (10^3, 10^4, and 10^5) using THF as an eluant with polystyrene standards. IR spectra were recorded on a Midac M1200-SP3 spectrophotometer. UV−vis absorption spectra were obtained on a Hewlett-Packard 8453 spectrophotometer. Fluorescence measurements were carried out on a Spex Fluorolog 3 spectrometer. The absorption λ_{max} of polymers were used as the excitation wavelengths (λ_{exc}) for the measurement. THF solutions of copolymers with absorbance in the range 0.03−0.05 were deoxygenated prior to conducting their fluorescence measurement and the percentage fluorescence quantum yield Φ_{fl} (≤10% error) were determined at room temperature using 9,10-diphenylanthracene in cyclohexane (Φ_{fl} = 90%) as a reference.[19] Polymer films with absorbance in the range 0.2−0.6 were prepared on a glass substrate by spin-coating polymer solutions in THF (10−15 mg/mL). These films were subjected to UV−vis and fluorescence measurements. The differential scanning calorimetry (DSC) analysis and the thermogravimetric analysis (TGA) were performed under a nitrogen atmosphere (50 mL/min) on a TA Instruments DSC 2920 and a TGA 2950 Thermogravimetric Analyzer at heating rates of 10 °C/min (DSC) and 20 °C/min (TGA), respectively. Cyclic voltammetry (CV) measurements were conducted in a 0.1 M Bu_4NPF_6 acetonitrile solution at room temperature using a Solartron SI 1287 potentiostat at a scan rate of 50 mV s^{-1}. A silver wire (ϕ 1.5 mm), a platinum wire (ϕ 0.5 mm), and a platinum disk (ϕ 1 mm) sealed in a soft glass rod were used as the quasi-reference electrode, counter electrode, and working electrode, respectively. The working platinum electrode was coated with the polymer film by using a toluene solution and heated in an oven at 80 °C for 1 h. After the cell was evacuated and filled with argon three times, the 0.1 M Bu_4NPF_6 solution in anhydrous acetonitrile was loaded. The Ag quasi-reference electrode was calibrated using a ferrocene/ferrocenium redox couple (0.35 V versus Ag/AgCl) as an internal standard prior to measurements.

Electroluminescence Device Fabrication and Testing. Patterned ITO-glass substrates (15 Ω/□) were ultrasonicated sequentially in detergent, acetone, and 2-propanol and then dried under nitrogen. A thin layer of **P(F3-*alt*-Cz)** or **PF** was spin-coated onto the ITO substrate from its chloroform solution (ca. 12 mg/mL) at a spin rate of 2000 rpm. The thickness of the resulting films was measured on a Dekta-3 surface profilometer and found to be about 950 Å for both polymers. A hole-blocking layer of **F-TBB**[18] (20 nm) was then vacuum-deposited on top of the polymer film at below 1×10^{-6} Torr, followed by the deposition of Alq_3 thin film (10 nm). The device fabrication was completed by the evaporation of LiF and aluminum. EL emission spectra and device luminance were recorded with a Photo Research PR-650 SpectraScan. Current−voltage and brightness−voltage analysis was performed using a Keithley 238 Source meter.

Materials. Triisopropyl borate and tetrakis(triphenylphosphine) palladium(0) ($Pd(PPh_3)_4$) were prepared according to the literature methods.[20,21] Other starting materials were purchased from Aldrich and used without further purification. Tetrahydrofuran (THF) and diethyl ether were dried over a Na/K alloy and distilled prior to use. Acetonitrile used in the electrochemical measurements was refluxed in the presence of calcium hydride under argon and distilled prior to use. 9,9-Dioctylfluorene,[21] 2-bromo-9,9-dioctylfluorene (**5**),[22] 2-dihydroxyboranyl-9,9-dioctylfluorene (**6**),[9a,23] 2,2′-bis(9,9-dioctylfluorenyl) (**7**),[9a,23] 2,2′-bis(7-bromo-9,9-dioctylfluorenyl) (**8**),[9a] and 2,7-dibromo-9,9-dioctylfluorene (**1**)[24] were prepared according to the procedures outlined in the literature.

3,6-Dibromocarbazole. Carbazole (35.65 g, 0.213 mol) was dissolved in dimethylformamide (DMF) (400 mL) in a 1-L three-necked flask. After the solution was cooled to 0 °C, *N*-bromosuccinimide (NBS) (75.89 g, 0.426 mol) in DMF (100 mL) was added dropwise through a dropping funnel. The mixture was allowed to warm to room temperature and stirred for an additional 2 h. The mixture was then poured into water (2 L). The white precipitates collected by filtration were recrystallized from ethanol to give colorless crystals. Yield: 52.0 g (75.0%). ^{1}H NMR ($CDCl_3$): δ 8.13 (d, J 2.0 Hz, 2H), 8.09 (b, 1H), 7.52 (dd, J_1 8.4 Hz, J_2 2.0 Hz, 2H), 7.31 (d, J 8.4 Hz, 2H). IR (KBr): 3405, 1561, 1472, 1459, 1430, 1285, 1126, 1050, 1018, 901, 869, 809, 805, 686, 640 cm^{-1}. mp: 215−216 °C.

3,6-Dibromo-9-octylcarbazole (3). To a 250-mL three-necked flask containing 3,6-dibromocarbazole (16.25 g, 50

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mmol) in DMSO (100 mL) were added 1-bromooctane (14.48 g, 75 mmol) and 50% NaOH solution (50 mL). The mixture was stirred at room temperature for 4 h, after which ether (100 mL) and deionized water (100 mL) were added. The organic layer was washed with brine and water and dried over $MgSO_4$. After filtration and evaporation of the solvent, the resulting solid was dissolved in hexane and purified by passing through a silica gel column. Recrystallization from heptane produced white crystals. Yield: 18.35 g (84%). ^{1}H NMR: δ 8.14 (d, J 1.6 Hz, 2H), 7.55 (dd, J_1 8.8 Hz, J_2 1.6 Hz, 2H), 7.26 (d, J 8.8 Hz, 2H), 4.24 (t, J 7.4 Hz, 2H), 1.82 (m, 2H), 1.20−1.30 (m, 10H), 0.85 (t, J 6.8 Hz, 3H). IR (KBr): 3058, 2953, 2926, 2853, 1472, 1437, 1347, 1287, 1226, 1147, 1053, 1018, 866, 830, 797 cm^{-1}. mp 86−87 °C.

9-Octylcarbazole-3,6-bis(ethyleneboronate) (4). To a solution of **3** (4.37 g, 10 mmol) in THF (50 mL) at −78 °C was added dropwise 2.5 M *n*-BuLi in hexane (8.4 mL, 21 mmol) over 15 min. The resulting mixture was stirred for 1 h while maintaining the temperature at −78 °C, after which triisopropylboronate (7.9 g, 42 mmol) was added and the mixture was stirred at −78 °C for an additional hour. The reaction mixture was then allowed to warm to room temperature and stirred for 15 h. The mixture was then cooled to 0 °C and 2 N HCl (40 mL) added. After the mixture was stirred for 30 min, the organic layer was separated using ether, washed with brine three times, and finally dried over $MgSO_4$. After filtration and evaporation of the solvents, a light yellow viscous liquid was obtained. Dissolving this liquid in THF followed by precipitation to hexane gave a white solid. The solid was filtered, washed with hexane three times, and dried briefly (30 min) under vacuum at room temperature. The resulting compound (3,6-bis(dihydroxyboranyl)-9-octylcarbazole) was mixed with toluene (100 mL) and ethylene glycol (**EG**, 1.86 g, 30 mmol). The mixture was heated to reflux for 3 h; meanwhile, the water produced was removed using a Dean−Stark trap. The mixture was cooled and the solvent was removed. Excess ethylene glycol was removed by heating (130 °C) under vacuum. Recrystallization from hexane gave the product as colorless crystals. Yield: 4.19 g (80.2%). ^{1}H NMR: δ 8.64 (s, 2H), 7.91 (dd, J_1 8.0 Hz, J_2 1.4 Hz, 2H), 7.41 (d, J 8.0 Hz, 2H), 4.42 (s, 4H), 4.30 (t, J 7.4 Hz, 2H), 1.86 (m, 2H), 1.20−1.40 (m, 10H), 0.85 (t, J 7.0 Hz, 3H). IR (KBr): 2957, 2906, 2853, 1625, 1595, 1467, 1383, 1364, 1331, 1290, 1206, 1086, 990, 941, 818, 747 cm^{-1}. mp: 162−163 °C.

2,2′:7′,2″-Ter(9,9-dioctylfluorene) (9). To a 250-mL flask equipped with a condenser was added 2,7-dibromo-9,9-dicotylfluorene, **1** (5.48 g, 10 mmol), 2-dihydroxyboranyl-9,9-dioctylfluorene, **6** (9.13 g, 21 mmol), toluene (120 mL), and 2 M Na_2CO_3 solution (80 mL). The flask was then evacuated and filled with argon three times to remove air from the system. The flask was then transferred to a glovebox under nitrogen where $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol) was added. The flask was again briefly evacuated and filled with argon three times. The mixture was heated to reflux and maintained for 48 h under an argon atmosphere. The resulting mixture was poured into a separation funnel and the organic layer was separated and dried over $MgSO_4$. Removal of the solvents by evaporation produced a brown viscous liquid. This liquid was dissolved in hexane and passed through a short silica gel column to remove the catalyst residue. The resultant solid, upon removal of solvents, was dissolved in CH_2Cl_2 and precipitated from methanol three times. A pale-yellow solid was obtained after drying under vacuum (8.72 g, 75%). ^{1}H NMR (in $CDCl_3$): δ 7.60−7.84 (m, 14H), 7.30−7.40 (m, 6H), 2.00−2.14 (m, 12 H), 1.02−1.24 (m, 60H), 0.64−0.86 (m, 30H). IR (KBr): 3059, 2954, 2926, 2854, 1610, 1465, 1451, 1377, 1254, 1101, 885, 817, 740 cm^{-1}. mp: 63−65 °C. UV−vis (in CH_2Cl_2): λ_{max} 352 nm.

7,7″-Dibromo-2,2′:7′,2″-ter(9,9-dioctylfluorene) (10). To a solution containing **9** (8.0 g, 6.85 mmol), iodine (5 mg, 0.02 mmol), and CH_2Cl_2 (100 mL) at 0 °C was added dropwise a bromine solution (2.19 g, 13.7 mmol in 10 mL of CH_2Cl_2) over 15 min. The mixture was then allowed to warm to room temperature and stirred for 20 h in the absence of light. 15% $NaHSO_3$ solution (50 mL) was then added and the mixture vigorously stirred for 30 min until the brown color disappeared. The organic layer was separated, washed with water three times, and dried over $MgSO_4$. Evaporation of the solvent produced a light yellow viscous liquid. The crude product was dissolved in acetone (900 mL) and recrystallized at −40 °C three times to give a white solid (7.82 g, 86%). ^{1}H NMR ($CDCl_3$): δ 7.80 (d, J 8.0 Hz, 2H), 7.74 (d, J 8.0 Hz, 2H), 7.57−7.67 (m, 10H), 7.48 (s, 2H), 7.45 (dd, J_1 8.0 Hz, J_2 2.0 Hz, 2H), 2.10 (m, 8H), 2.03 (m, 8H), 1.04−1.24 (m, 60H), 0.62−0.88 (m, 30H). IR (KBr): 2953, 2926, 2853, 1455, 1405, 1377, 1256, 1062, 1001, 884, 811, 755, 722 cm^{-1}. mp: 77−78 °C. UV−vis (in CH_2Cl_2): λ_{max} 355 nm.

2,2′:7′,2″:7″,2‴-Quater(9,9-dioctylfluorene) (11). This compound was prepared using **8** (4.69 g, 5 mmol) and **6** (4.78 g, 11 mmol) under conditions similar to those used to prepare **9**. The final reaction mixture was poured into a separation funnel and the organic layer was separated and dried over $MgSO_4$. Removal of the solvents gave a brown viscous liquid, which was dissolved in hexane and passed through a short silica gel column to remove catalyst residues. The viscous liquid (∼6.0 g) was then dissolved in hot acetone (200 mL) and the solution cooled to room temperature and then to −40 °C. A greenish solid was obtained upon recrystallization for four times (5.08 g, 65.3%). ^{1}H NMR ($CDCl_3$): 7.28−7.38 (m, aromatic protons, 6H), 7.58−7.85 (m, aromatic protons, 20H), 1.96−2.14 (m, α-methylene, 16H), 1.02−1.24 (m, 80H), 0.60−0.86 (m, 40H). IR (KBr): 3058, 3017, 2954, 2928, 2854, 1610, 1463, 1452, 1403, 1376, 1254, 1000, 885, 815, 740 cm^{-1}. UV−vis (in CH_2Cl_2): λ_{max} 363 nm.

7,7‴-Dibromo-2,2′:7′,2″:7″,2‴-quater(9,9-dioctylfluorene) (12). This compound was prepared using **11** (4.0 g, 2.57 mmol) and bromine (0.82 g, 5.14 mmol) following the procedure used in the preparation of **10**. Recrystallization three times using acetone (400 mL) at − 40 °C gave a greenish solid (3.34 g, 76%). ^{1}H NMR ($CDCl_3$): δ 7.45−7.85 (m, 24H), 1.92−2.16 (m, 16H), 1.02−1.26 (m, 80H), 0.62−0.88 (m, 40H). IR (KBr): 2953, 2926, 2853,1455, 1404, 1376, 1255, 1062, 1000, 885, 811, 756, 722 cm^{-1}. mp: 59−60 °C. UV−vis (in CH_2Cl_2): λ_{max} 366 nm.

Polymerization. The following generalized procedure was used for the preparation of all the copolymers. To a 50-mL one-necked flask was added tricaprylylmethylammonium chloride (Aliquat 336) (∼20 wt % based on monomers),[11] the appropriate diboronate (1 equiv), the appropriate dibromide (1 equiv), and toluene. Once all the monomers were dissolved, 2 M Na_2CO_3 aqueous solution (3.3 equiv) was added. The flask equipped with a condenser was then evacuated and filled with argon three times to remove traces of air. $Pd(PPh_4)_3$ (0.005 equiv) was then added under an argon atmosphere. The flask was again evacuated and filled with argon three times. The mixture was then heated to reflux and maintained for 48 h under argon. The reaction mixture was then cooled to room temperature and the organic layer was separated, concentrated, and precipitated into methanol. The resultant polymer was collected, dried, and further purified by the following procedure. It was redissolved in dichloromethane. 6 N HCl was added to the solution and the mixture was vigorously stirred for 1 h. The organic layer was once again separated, dried over $MgSO_4$, and passed through a short silica gel column to remove the catalyst residues. The resulting copolymer solution was collected, concentrated, and precipitated into methanol. The white solid obtained was dried overnight under vacuum at 50 °C.

Data for **P(F-*alt*-Cz)** follows. ^{1}H NMR: δ 8.49 (s, Cz-4,5, 2H), 7.72−7.84 (m, 8H), 7.52 (d, J 8.0 Hz, Cz-1,8, 2H), 4.38 (s, −N−CH_2−, 2H), 2.12 (b, 4H), 1.95 (b, −N−CH$_2$CH_2−, 2H), (d, J 8.0 Hz, 2H), 7.55 (d, J 8.0 Hz, 2H), 7.26 (d, J 8.8 Hz, 2H), 4.24 (t, J 7.4 Hz, 1.10−1.45 (m, 30H), 0.74−0.88 (m, 13H). IR (KBr): 3058, 2953, 2925, 2853, 1603, 1496, 1462, 1411, 1378, 1351, 1293, 1268, 1228, 1154, 1133, 879, 824, 802 cm^{-1}.

Other copolymers showed similar NMR and IR spectra to those of **P(F-*alt*-Cz)** except that the relative intensities of signals are different due to the different fluorene/carbazole ratios.

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