

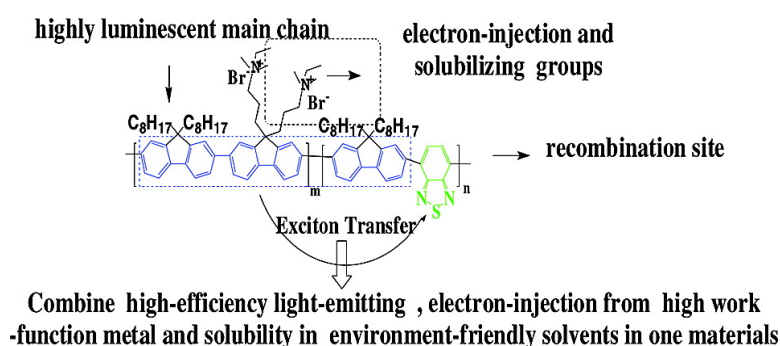
Article

High-Efficiency, Environment-Friendly Electroluminescent Polymers with Stable High Work Function Metal as a Cathode: Green- and Yellow-Emitting Conjugated Polyfluorene Polyelectrolytes and Their Neutral Precursors

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High-Efficiency, Environment-Friendly Electroluminescent Polymers with Stable High Work Function Metal as a Cathode: Green- and Yellow-Emitting Conjugated Polyfluorene Polyelectrolytes and Their Neutral Precursors

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Abstract: A series of aminoalkyl-substituted polyfluorene copolymers with benzothiadiazole (BTDZ) of different content were synthesized by Suzuki coupling reaction, and their quaternized ammonium polyelectrolyte derivatives were obtained through a postpolymerization treatment on the terminal amino groups. Copolymers are soluble in environmentally friendlier solvents, such as alcohols. It was found that the efficient energy transfer occurs by exciton trapping on the narrow band gap BTDZ site under UV illumination. Only 1% of BTDZ content is needed to completely quench a fluorene emission for both the neutral and the quaternized copolymers in the neat film. Absolute PL efficiencies of copolymer films were greatly enhanced as a result of the suppression of excimer formation. Light-emitting devices fabricated from these copolymers show high external quantum efficiencies over 3% and 1% for the neutral precursor and the quaternized copolymers, respectively, with high work function metals such as Al as a cathode. To the best of our knowledge, this is the first report on an electroluminescent polymer which bears the high EL efficiency, the electron-injection ability from high work function metals, and the solubility in environment-friendly solvents at the same time. These features make them a promising candidate for the next generation of light-emitting copolymers in PLED flat panel display application.

Introduction

Conjugated polyelectrolytes (CPs) have attracted considerable attention in recent years, for they offer particular properties compared with the normal "neutral" conjugated polymers due to their ionic side groups attached to the conjugated main chain.¹ These unique properties provide many new opportunities in optoelectronic and biological applications. For example, they can be used as the active layer in light-emitting diodes (LEDs) through layer by layer self-assembling approach.² They are also used as highly sensitive materials in biological³ and chemical sensors.⁴ Most of CPs are typically soluble in water or alcohols which are environment-friendly solvents.

For their versatile applications in optoelectronic and biological research, more and more attention has been paid to the synthesis of new CPs with varieties of conjugated polymer main chain structures, such as the poly (phenylene vinylene) (PPV),⁵ poly (*p*-phenylene) (PPP),⁶ poly (phenylene ethylene) (PPE),⁷ and polyfluorene (PF)⁸ based conjugated polyelectrolytes. Research on the utilization of CPs in polymer LEDs, biosensors, and chemosensors has been widely reported in recent years.

Although water-soluble CPs were used very successfully as biosensors,⁹ in general CPs were not very successful as a light-emitting layer in PLEDs because the device performance

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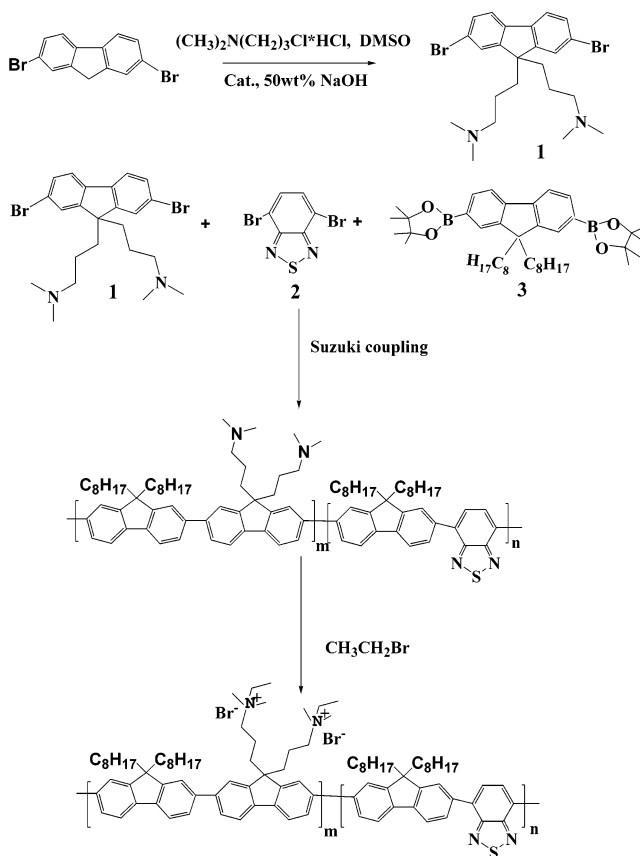
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reported so far was poor. The color purity was disappointing in that the excimer emission is dominant in such rigid polymer systems. Cimrova et al. reported the first LED based on a sulfonated PPP (PPPSO₃Na or PPPSO₃NC₁₄H₂₉(CH₃)₃) as the emission layer in a single-layer device.¹⁰ The external quantum efficiencies of single-layer devices were in the range of 0.5–0.8% with counterions H⁺ or Na⁺. Baur et al.¹¹ reported the fabrication of LEDs with the configuration: ITO/[((-)PPP/polycation)_n]/Al using layer-by-layer self-assembly of cationic and anionic PPP derivatives as the active layer. The highest external quantum efficiency of their devices was 0.01%. Fujii reported yellow emission (540 nm) at an operating voltage of 25 V by using carboxypentoloxo-substituted PPVs.^{5c} Thunemann et al.¹² investigated the influence of cationic counterions on the emission properties in poly(1,4-phenyleneethynylene carboxylate) polyelectrolytes. The peak wavelength of the electroluminescence shifts from 430 to 515 nm for single-layer LEDs when the counterions were changed from tetraethylammonium to sulfonium ions. No data of efficiencies were reported in these reports. More recently we reported the first LEDs based on ammonium functional polyfluorene electrolytes (PF-N⁺R₃).^{8d} We found that these PF-based CPs could be used as the electron injection layer. Insertion of a thin layer of PF-N⁺R₃ between the high work function metals and emitting layers greatly enhances the performance of the LEDs with a high work function metal cathode. However when these PF CPs are used as the active layer in LEDs, the external quantum efficiencies remain very low (from 0.07% to 0.16%). Low efficiency of CP-based PLEDs mainly originates from strong interchain interaction due to the existence of a polar or ionic side group, which is evidenced by a strong excimer emission commonly observed in the LEDs from such polymers.^{5e,8d} On the other hand, a strong excimer emission appearing at the long wavelength side of typical blue emitting polyelectrolyte makes the emission whitish. The color purity of the devices is poor. Therefore, despite numerous efforts, high-efficiency polymer LEDs with good color purity based on conjugated polyelectrolyte remains a great challenge these days.

This paper deals with the synthesis of a series of aminoalkyl-substituted polyfluorene copolymers with different contents of narrow band gap comonomer 2,1,3-benzothiadiazole (BTDZ) by a palladium-catalyzed Suzuki coupling method. The quaternized salt polyelectrolytes of corresponding composition were obtained through a postpolymerization treatment. The BTDZ comonomer unit in the copolymer is isolated from both sides by fluorene host segment functions as a powerful exciton trap which allows efficient energy transfer of the exciton from fluorene segment to BTDZ unit. As a result, the blue and blue-greenish excimer emission for the amino(ammonium)-alkyl-substituted fluorene segment is completely quenched. Devices from such copolymers emit exclusively green or yellow light characteristic of the BTDZ unit. Light-emitting devices from both neutral precursor and quaternized CPs show high quantum efficiency with both low work function metals such as Ba and high work function metals such as Al. The maximal external quantum efficiencies of the polymer light-emitting devices

Scheme 1. Synthetic Route of the Monomer and the Polymers



(PLEDs) exceed 3% and 1% for the neutral polymer and the quaternized polyelectrolyte, respectively, with Al cathode. The solubility of this type of copolymer in environment-friendly solvents (such as alcohol) in combination with the encouraging device performance makes them a promising candidate for the next generation of light-emitting polymers in PLED flat panel display applications.

Results and Discussion

Synthesis and Characterization. The synthesis route is shown in Scheme 1. 2,7-Dibromofluorene,¹³ 4,7-dibromo-2,1,3-benzothiadiazole (2),¹⁴ and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (3)¹⁵ were prepared according to the published procedures and were described elsewhere.¹⁶ The 2,7-dibromo-9,9-bis(3'-(*N,N*-dimethylamino)propyl)fluorene (1) was synthesized by reaction between 2,7-dibromofluorene and 3-dimethylaminopropyl chloride hydrochloride in a two-phase mixture of water and DMSO in the presence of excess NaOH.^{8d} The copolymer of monomer 1 and monomer 3, poly[(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN), and polyelectrolyte derivatives poly[(9,9-bis(3'-(*N,N*-dimethyl)-*N*-

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ethylammonium)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)]dibromide (PFNBr) were synthesized and reported previously.^{8d} Here the small amount of **2** was copolymerized with **1** and **3** by using palladium-catalyzed Suzuki coupling methods. The comonomer feed ratios of **1** to **2** are 99:1, 98:2, 90:10, 70:30 and always keep **1** + **2** = **3**, and the corresponding polymers were named PFN-BTDZ0.5, PFN-BTDZ1, PFN-BTDZ5, and PFN-BTDZ15, respectively. Conversion of the neutral polymers to the polyelectrolytes was achieved by stirring with bromoethane in DMSO/THF (1:4) at 50 °C for 5 days. The obtained polymers were named PFNBr-BTDZ0.5, PFNBr-BTDZ1, PFNBr-BTDZ5, and PFNBr-BTDZ15 corresponding with the neutral precursors. The neutral polymers are readily soluble in common organic solvents such as THF, chloroform, toluene, and xylene but insoluble in DMSO and water. However, the neutral precursor polymer has a good solubility in polar solvents, such as methanol, by adding a trace of weak organic acid, such as acetic acid, due to a weak interaction formed between the nitrogen atoms and the acetic acid.^{8c,d} It was also reported that the added acetic acid could be completely removed from the polymers after dried in a vacuum.^{5d} After quaternization, the resulted polymers are insoluble in THF and chloroform but completely soluble in DMSO, methanol, and DMF. The solubility of these polymers in alcohol offers an opportunity of fabricating multilayer polymer LEDs by spin-coating from such solvents, since most of the electroluminescent polymers and carrier-transporting materials are not soluble in the alcohol. This feature will allow avoiding mixing in the interface between different layers, which is a common and serious problem for the fabrication of multilayer PLEDs by solution processing.

The BTDZ content of the resulted polymers was measured by elemental analysis. The S contents of PFN-BTDZ15 and PFNBr-BTDZ15 were 1.42% and 1.31%, respectively, which indicate that the composition in copolymers is close to the monomer feed ratio of BTDZ/fluorene. For the copolymers with feed ratios 0.5%, 1%, and 5% of BTDZ, their theoretical S content is less than the detection limit of our elemental analysis instrument (0.5%). But from their absorption and PL emission spectra in thin solid films and solutions (Figure 3–5), it can be found that the polymers' BTDZ content show a good correlation with their feed ratio of BTDZ to fluorene.

The number molecular weight (M_n) estimated by gel permeation chromatography (GPC) against the polystyrene standard with THF as an eluent ranged from 10 000 to 27 500 with a polydispersity index (M_w/M_n) from 1.8 to 2.2. It is difficult to get the molecular weight of the quaternized polymers by GPC measurement due to the polymer aggregation on the column fillers induced by the ionic groups on the polymer side chain.^{6c} Since quaternization is conducted in mild conditions, it is safe to assume that the polyelectrolyte would have a molecular weight of the same order as that of its neutral precursor. The thermal properties of the polymers were studied by thermogravimetric analysis (TGA). Figure 1 shows the thermograms of these copolymers, in the temperature range from 25 to 800 °C in the nitrogen atmosphere. The neutral polymers exhibit good thermal stability with an onset of degradation temperature at around 320 °C. In contrast to a single decomposition of neutral precursor, the quaternized copolymers show more a complicated degradation pattern. For the quaternized copolymers, a moderate loss of weight starts from 100 °C which is obviously due to

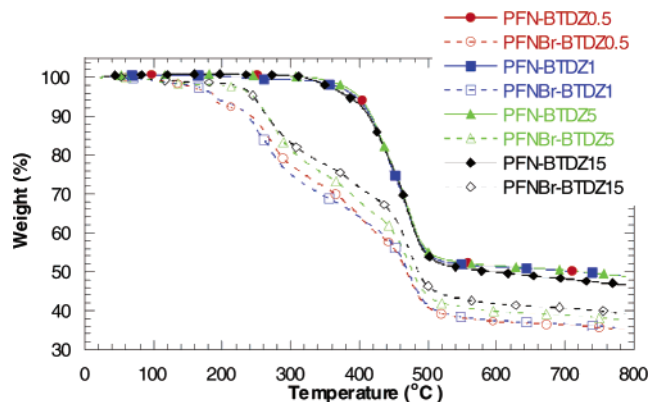


Figure 1. Thermogravimetric analysis of neutral and quaternized polymers in a nitrogen atmosphere.

releasing the associated water, and the amount of water in the polymers was estimated at about 2% to 3% for these quaternized polymers. A major degradation onset can be seen at around 200 °C, corresponding to a decomposition of quaternized ammonium group with releasing the ethyl bromide group. As for the neutral precursor, a significant degradation starts at around 300 °C, which is probably associated with a cleavage of side alkyl chains. These thermal properties were very similar to those of the other conjugated polymer with terminal amino or ammonium side groups.^{6c} It is important to note that introducing a BTDZ unit into copolymers does not change the thermal properties of the aminoalkyl-substituted polyfluorenes and their quaternized polyelectrolytes. Good thermal stability is important for the application of these copolymers in flat panel displays.

Electrochemical Properties. The electrochemical behavior of the polymers was investigated by cyclic voltammetry (CV). As shown in Figure 2a, the neutral polymers have the similar electrochemical properties as PFN, which contains no BTDZ units.^{8d} The neutral polymers show a reversible oxidation wave with onset at around 1.1–1.2 V which can be assigned to the oxidation potential of aminoalkyl-substituted copolymer main chains.^{8c} Two irreversible cathodic waves can be observed with onset at around –1.9 and –2.2 V. A second reduction wave with onset at –2.2 V is very consistent with a reduction wave observed for polyfluorene homopolymer and copolymers,^{16a–c} and it can be assigned to the reduction of polyfluorene main chain. The first reduction wave with onset at around –1.9 V is probably related to reduction of the amino or ammonium groups of the polymers side chains. Similar two reduction waves were reported by Shu et al. for polyfluorenes with a triphenylamine pendant.¹⁷ The quaternized polymers show similar oxidation waves as the neutral precursor (Figure 2b). Unfortunately, we were unable to record their reduction processes after many attempts. Table 1 summarizes the oxidation and reduction potentials corresponding to the polymer main chains. HOMO and LUMO levels of the polymers are calculated according to empirical formulas $E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.4)$ (eV) and $E_{\text{LUMO}} = -e(E_{\text{red}} + 4.4)$ (eV).¹⁸ There are no obvious changes in the HOMO and LUMO levels of the neutral polymers with different BTDZ content. The optical band gaps estimated from absorption onset of the polymers were also listed in Table 1, which are

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Table 1. UV–vis Absorption, Electrochemical, and Photoluminescence Properties of the Polymers (in Solid Films)

polymers	$\lambda_{\text{abs}}/\text{nm}$	optical band gap ^a /eV	E_{ox}/V	E_{red}/V	HOMO/eV	LUMO/eV	E_{gap}/eV	photoluminescence	
								$\lambda_{\text{PL}}/\text{nm}$	$Q_{\text{PL}}/\%$
PFN	390	2.91	1.21	−2.26	−5.61	−2.14	3.47	425	37.3
PFN–BTDZ0.5	384	2.95	1.19	−2.00	−5.59	−2.40	3.19	544	84.7
PFN–BTDZ1	384	2.93	1.21	−2.15, −1.88	−5.61	−2.25	3.36	543	74.6
PFN–BTDZ5	383	2.93, 2.45	1.20	−2.13, −1.94	−5.60	−2.27	3.33	549	77.4
PFN–BTDZ15	375	2.95, 2.45	1.24	−2.09, −1.84	−5.64	−2.31	3.33	550	71.3
PFNBr	400	2.85	1.25	−2.22	−5.65	−2.18	3.47	431	4.7
PFNBr–BTDZ0.5	391	2.87	1.20	−	−5.60	−	−	555	23.3
PFNBr–BTDZ1	390	2.88	1.24	−	−5.64	−	−	558	28.7
PFNBr–BTDZ5	387	2.86, 2.43	1.19	−	−5.59	−	−	564	37.9
PFNBr–BTDZ15	382	2.89, 2.43	1.25	−	−5.65	−	−	580	32.4

^a Estimated from the onset wavelength of optical absorption in solid-state film.

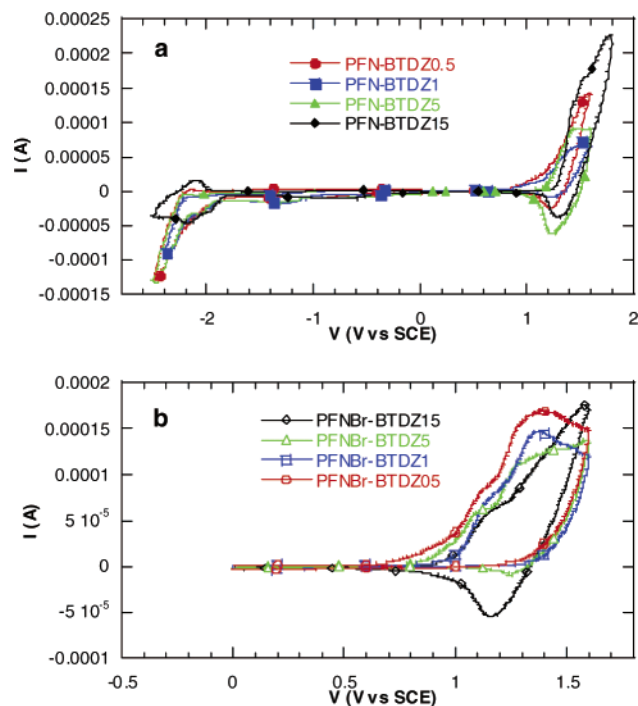


Figure 2. Cyclic voltammograms of the polymers films coated on platinum electrodes (neutral polymers) or on ITO glass (quaternized polymers) in 0.1 mol/L Bu₄NPF₆, CH₃CN solution.

significantly less than those obtained from electrochemical data. The similar phenomenon was observed in poly(9,9-dioctylfluorenes) by Janietz et al.¹⁹ No detailed explanation about the discrepancy between optical and electrochemical gaps was provided in this paper.¹⁹

Photophysical Properties in the Solid-State Films. Transparent and uniform films of the polymers were prepared on quartz substrate by spin-coating from their chloroform solutions (for the neutral copolymers) or from methanol solutions (for the quaternized copolymers). The optical properties of these polymers were investigated (Figure 3). The absorption and PL emission spectra of the PFN (Figure 3a) and PFNBr (Figure 3b) homopolymers without BTZ and the copolymers with different BTZ content in thin solid films are compared. As shown in Figure 3, the absorption spectra of these copolymers are dominated by a strong absorption peak at ca. 380 nm which is attributed to the PFN segment absorption.^{8d} For the copolymer with a BTZ content of 5% and 15%, a clear shoulder can be

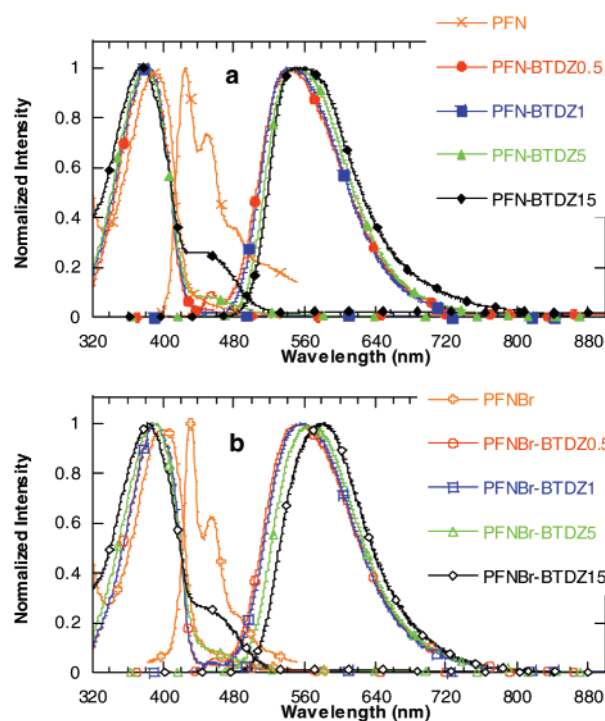


Figure 3. UV–vis absorption and PL emission spectra of polymers in solid-state films: (a) neutral polymers, (b) quaternized polymers.

observed at ca. 450 nm, which is responsible for the BTZ unit in the copolymers. The intensity of the 450 nm shoulder increases with increasing the BTZ content. It is hard to detect 450 nm features for absorption spectra of PFN–BTDZ0.5 and PFN–BTDZ1 copolymers in solid state film, obviously, due to the low sensitivity of the spectrophotometer. However, this feature is clearly observed in solution spectra. We note that the main absorption peak of the polymers shows a slight blue-shift due to the decrease of PFN segments' conjugate length interdicted by the BTZ unit.

Figure 3 shows that, by introducing only 0.5% of BTZ into the copolymer chain, the blue emissions at 425 and 431 nm for PFN and PFNBr homopolymers are almost completely quenched, respectively. The emission is dominated by a green light peaked at 544 and 555 nm for PFN–BTDZ0.5 (Figure 3a) and PFNBr–BTDZ0.5 (Figure 3b), respectively. With further increase in BTZ content to 1% and over, the PFN emission is completely quenched and only a green or yellow emission (550–580 nm) responsible for the BTZ unit can be observed. With the increase in BTZ content in the copolymer, PL peaks were slightly red-shifted from 544 nm for PFN–BTDZ0.5 to 550

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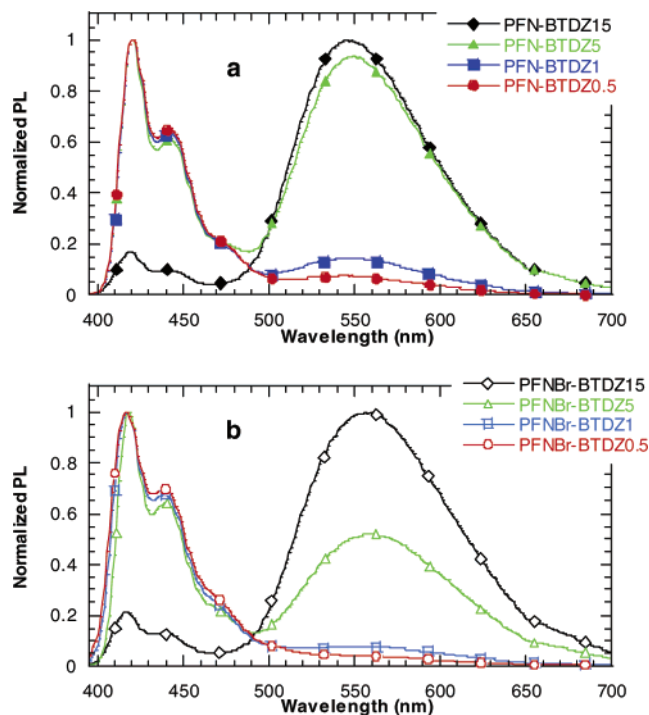


Figure 4. (a) PL spectra of the neutral polymers in chloroform solution (around 2×10^{-2} g/L). (b) PL spectra of the quaternized polymers in methanol solution (around 2×10^{-2} g/L).

nm for PFN-BTDZ15 and from 555 nm for PFNBr-BTDZ0.5 to 580 nm for PFNBr-BTDZ15, respectively (Table 1). The domination of BTZ emission at very low comonomer concentration (as low as 0.5%) in the copolymers suggested that the energy transfer from photogenerated excitons on the PFN segment into BTZ sites is an extremely quick and efficient process.

The PL efficiencies obtained by 325 nm excitation using a HeCd laser were listed in Table 1. It was found that the incorporation of 0.5% of the BTZ unit into the copolymer led also to great increase in the absolute PL efficiencies in comparison with those of the PFN and PFNBr homopolymer. PL efficiencies increased from 37.3% for PFN to 74.6% for PFN-BTDZ0.5 and from 4.7% for PFNBr to 23.3% for PFNBr-BTDZ0.5, respectively. This indicates that the incorporation of a small amount of BTZ comonomer disturbs the strong interchain interaction between amino(ammonium)alkyl-substituted polyfluorene chains. As a result of removing excimer quenching, PL efficiencies increase dramatically. With the further increase in BTZ content of the copolymers, the PL efficiency decreases slightly for PFN-BTDZ copolymers, while it increases for polyelectrolyte salts PFNBr-BTDZ. It can be also found that the absorption and the PL emission spectra for the quaternized polymers are slightly red-shifted (around 10–15 nm) compared with their neutral precursor polymers. PL quantum yields of the quaternized polymers PFNBr-BTDZ are significantly reduced in comparison with the neutral precursors PFN-BTDZ of the same composition. Similar tendency was observed for copolymers PFN and PFNBr.^{3d} Red-shift in absorption, PL spectra, and the reduced PL efficiencies for polyelectrolyte are consistent with the widely accepted concept that a polyelectrolyte has a more rigid chain conformation than that of corresponding neutral precursors due to the strong repulsion between positively charged side groups.²⁰

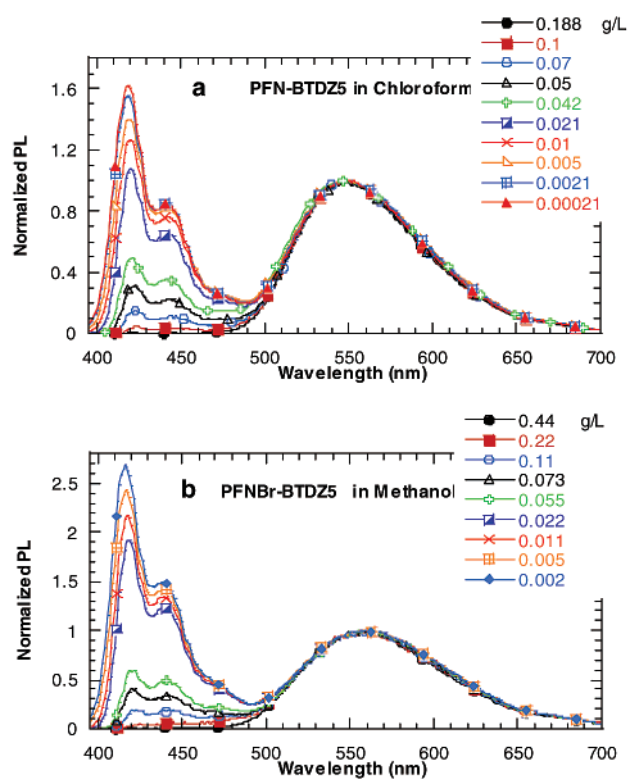


Figure 5. (a) PL spectra of PFN-BTDZ5 polymers in chloroform solution with different concentrations. (b) PL spectra of PFNBr-BTDZ5 polymers in methanol solution with different concentrations.

Photophysical Properties in Solution. In contrast to almost full energy transfer from a fluorene segment to BTZ unit at as low as 1% of BTZ content for PFN-BTDZ and PFNBr-BTDZ copolymer films, PL spectra in solution vary remarkably with BTZ content in copolymer and with solution concentration. Figure 4 shows normalized PL spectra of PFN-BTDZ in chloroform (Figure 4a) and PFNBr-BTDZ in methanol (Figure 4b) solution, respectively, at a solution concentration of 0.02 g/L. It is obvious that at this concentration almost full energy transfer has been observed only for copolymers of high BTZ content (15%) for both neutral copolymers and polyelectrolytes. Figure 5 shows the concentration dependence of PL spectra of PFN-BTDZ5 in chloroform (Figure 5a) and PFNBr-BTDZ5 in methanol (Figure 5b) solutions. Figure 5 indicates that emission at around 420 nm responsible for the PFN or PFNBr segment decreases very quickly with increasing copolymer concentration and that PFN or PFNBr emission can be completely quenched only in highly concentrated solutions. Similar concentration dependence of the PL emission profile is observed for copolymers of other composition. In Figure 6a we plot $I_{\text{BTZ}}/I_{\text{PF}}$ (ratio of the integrated intensities of 550 nm peak to that of 420 nm peak, which can be considered as a measure of energy transfer efficiency from fluorene segment to BTZ unit) versus the concentration of the copolymers with 5% and 15% BTZ for PFN-BTDZ and PFNBr-BTDZ copolymers. Figure 6a indicates that all these polymers show a turning point at which fluorene emission is practically quenched. We define a cross point between the tangent of the $I_{\text{BTZ}}/I_{\text{PF}}$ curve and x -axis as the critical concentration C^* at which BTZ units' emissions

(20) Wang, D. L.; Moses, D.; Bazan, G. C.; Heeger, A. J.; Lal, J. J. *Macromol. Sci. Pure Appl.* **2001**, *38*, 1175.

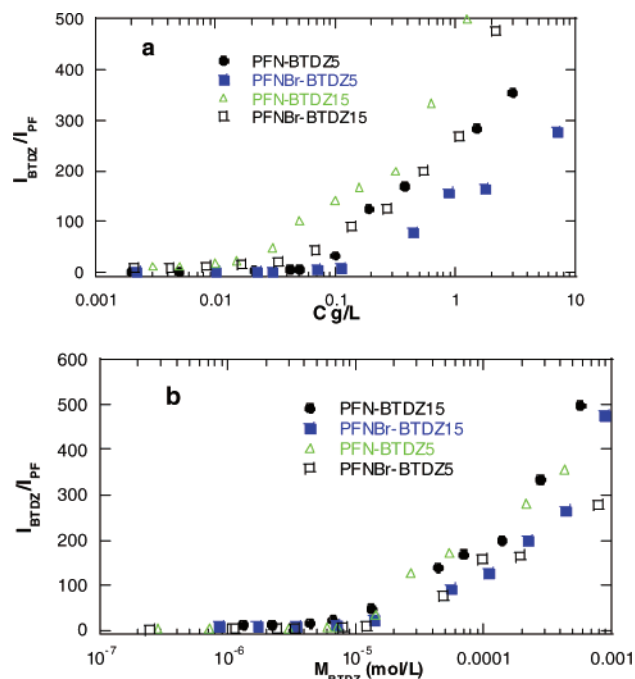


Figure 6. (a) $I_{\text{BTDZ}}/I_{\text{PF}}$ plotted against total polymer concentration C for the polymers. (b) Energy transfer efficiency ($I_{\text{BTDZ}}/I_{\text{PF}}$) per a BTMZ unit in the solution for PFN-BTDZ.

begin to be quickly enhanced, indicating the quickly increasing energy transfer among the polymers. The critical concentration increases with decreasing the BTMZ content in the copolymers. Similar results are observed for a copolymer with 0.5% to 1% of BTMZ content (data of which are not shown in Figure 6 in order to maintain clarity). From Figure 6a and the data from copolymers of other composition, we obtained $C^* = 0.51, 0.38, 0.07,$ and 0.03 g/L for PFN-BTDZ0.5, 1, 5, and 15 and $C^* = 0.47, 0.46, 0.11,$ and 0.06 g/L for PFNBr-BTDZ0.5, 1, 5, and 15, respectively. The existence of critical concentration C^* and the increase of the C^* value with decreasing BTMZ content (from 15 to 0.5%) seem to indicate that both intra- and interchain interaction play an important role in the energy transfer from a wide-gap segment (PFN or PFNBr) to narrow gap unit (BTMZ) in such copolymers. To gain more insight into the relative role of intrachain and interchain interaction, we plot the energy transfer efficiency $I_{\text{BTDZ}}/I_{\text{PF}}$ versus the molar concentration of the BTMZ unit in the solution (M_{BTDZ}), which is equal to the molar concentration of copolymer times BTMZ content in each copolymer in Figure 6b. If the energy transfer efficiency depends only on the total BTMZ content in the solution, all data points of $I_{\text{BTDZ}}/I_{\text{PF}}$ versus M_{BTDZ} (total moles of BTMZ units in a unit volume of copolymer solution (mol/L) must lie in the same curve regardless of copolymer composition. Figure 6b shows that it is indeed the case. All data points are roughly obey the same tendency and lie in the same curve within an experimental error. We interpret this observation as an indication that the interchain molecular energy transfer is a limiting factor in PFN-BTDZ and PFNBr-BTDZ copolymers in the solution. In the case that the intrachain energy transfer is dominant, one would expect that the energy transfer efficiency per unit BTMZ content would be much higher for low-BTMZ-containing copolymers than that for copolymers of high BTMZ content.

Electroluminescence Properties. The electroluminescence properties of these polymers are investigated. Both the neutral

Table 2. Device Performances of PFN-BTDZ0.5 and PFNBr-BTDZ0.5 in Different Device Configurations at Current Density of $\sim 30\text{--}40$ mA/cm²

polymers	anode buffer	cathode	device performances			
			voltage (V)	current intensity (mA/cm ²)	lumin. (cd m ⁻²)	QE (%)
PFN-BTDZ0.5	PEDOT	Ba/Al	20.2	30.7	51	0.14
	PEDOT	Al	16.8	45.3	96	0.18
	PVK	Ba/Al	19.	32.0	451	1.20
	PVK	Al	18.9	29.6	580	2.17
PFNBr-BTDZ0.5	PEDOT	Ba/Al	7.0	40.7	36	0.074
	PEDOT	Al	6.9	37.3	355	0.78
	PVK	Ba/Al	11.9	38.7	200	0.45
	PVK	Al	11.2	34.7	317	0.76

polymers and the quaternized polyelectrolytes were used as the emitting layer in a double layer light-emitting device with the configuration ITO/PEDOT (or PVK)/Polymer/Al (or Ba/Al). All the polymers show similar high external QE regardless of a low work function metal such as Ba or a high work function metal such as Al used as the cathode. Table 2 summarizes the device performances of PFN-BTDZ0.5 and PFNBr-BTDZ0.5 in different device configurations. When PEDOT was used as an anode buffer, the external quantum efficiencies are typically less than 1% regardless of cathode. Since HOMO for this type of copolymer is around 5.6–5.7 eV (Table 1), while the work function of PEDOT is around 5.0–5.2 eV,²¹ it would be possible to expect a much better hole injection once a PVK (work function 5.5–5.6 eV) is used in replacement of PEDOT as an anode buffer. At the current density of around 30–40 mA/cm², the external QEs of PFN-BTDZ0.5 are 2.2% and 1.2% for an Al and a Ba cathode, respectively, as shown in Table 2. Device efficiencies from a quaternized PFNBr-BTDZ0.5 polyelectrolyte are generally lower than that from the corresponding neutral precursor (Table 2). This is consistent with the significantly lower PL efficiency of PFNBr-BTDZ polyelectrolytes due to a more rigid chain conformation. Figure 7 compares I–V and L–V for PFN-BTDZ0.5 (Figure 7a) and PFNBr-BTDZ0.5 (Figure 7b) devices with PVK as anode buffer and Ba and Al as cathode, respectively. The results in Figure 7 clearly indicate that electron injection from an Al cathode is comparable with that from a low work function Ba cathode. Similar I–V characteristics can be observed for devices from copolymers with different BTMZ content (not shown here). We note that the operating voltage of devices from polyelectrolytes (PFNBr) are much lower than that from its neutral precursors regardless of cathode types (Ba or Al) (compare Figure 7b with 7a), although the device efficiencies from the neutral precursors are slightly higher than that from the polyelectrolytes (Table 2). We speculate that more rigid chain conformation, and consequently more dense packing of polyelectrolytes, ensures higher carrier mobility in the emitting layer of polyelectrolyte devices.

Table 3 compares device performances of copolymers of different composition in the device configuration: ITO/PVK/polymer/Al. The device from neutral PFN-BTDZ emits a bright green light with slight red-shift from 520 to 540 nm when BTMZ content increases from 0.5% to 15% (Figure 8a). For comparison, the EL spectrum from PFN homopolymer is also shown in Figure 8a. It is important to note that EL spectra of these

(21) Cao, Y.; Yu, G.; Zhang, C.; Menon, R.; Heeger, A. J. *Synth. Met.* **1997**, *87*, 171.

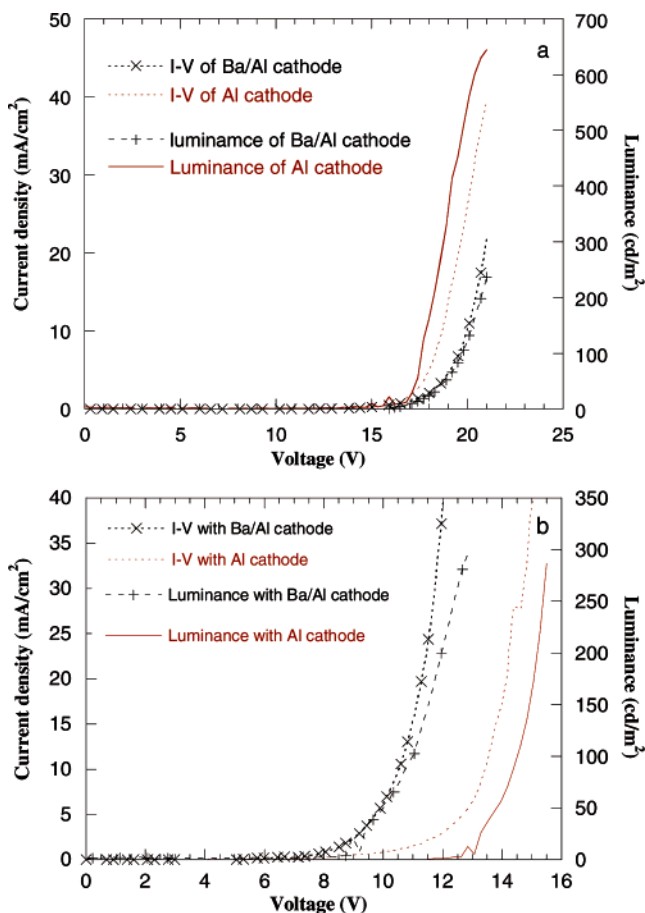


Figure 7. I–V and L–V curves of devices from PFN–BTDZ0.5 (a) and PFNBr–BTDZ0.5 (b) with Al and Ba/Al cathodes (PVK was used as an anode buffer).

Table 3. Device Performances at Maximum External Quantum Efficiency for Copolymers PFN–BTDZ and PFNBr–BTDZ of Different Composition with Al Cathode and PVK as an Anode Buffer (ITO/PVK/copolymer/Al)

polymers	λ_{ELmax}/nm	device performances			
		voltage (V)	current intensity (mA/cm ²)	luminance (cd m ⁻²)	QE (%)
PFN–BTDZ0.5	529	17.9	13	494	3.24
PFN–BTDZ1	546	23.1	2.4	56	1.92
PFN–BTDZ5	547	19.1	1.2	35	2.43
PFN–BTDZ15	543	12.3	8.0	176	1.82
PFNBr–BTDZ0.5	537	10.8	21	235	0.94
PFNBr–BTDZ1	546	10.3	16	200	1.01
PFNBr–BTDZ5	578	11.6	5.0	26	0.44
PFNBr–BTDZ15	581	9.6	8.7	38	0.38

devices show exclusively characteristic emission from the BTDZ site,²² while the 420 nm emission responsible for the PFN segment and excimer emission that peaked at 480 nm observed for the device from the PFN polymer are completely quenched. This fact indicates that intra- (or inter-) molecular energy transfer from the PFN segment to BTDZ sites is a quick and efficient process which suppresses radiative decay from the PF segment and also prevents the excimer emission in PFN interchain aggregates. The highest external QE of 3.24% was obtained for the PFN–BTDZ0.5 copolymer with a luminance of around 500 cd/m² at a current density of 13 mA/cm². With an increase

(22) Millard, I. S. *Synth. Met.* **2000**, *111*, 119.

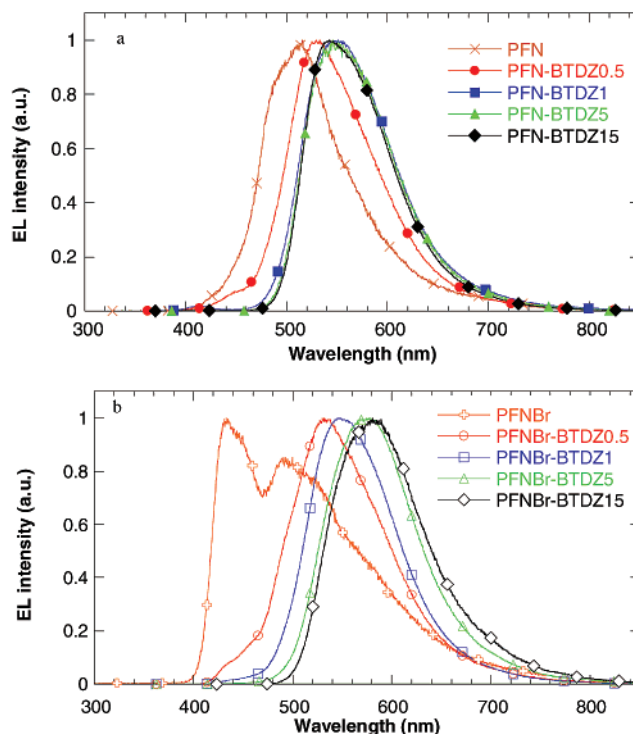


Figure 8. EL spectra of the polymers in device configuration ITO/PVK/polymer/Al: (a) neutral polymers, (b) quaternized polymers.

in the BTDZ content, the device efficiency is slightly reduced to 1.8% for PFN–BTDZ15. For devices from polyelectrolytes, PFNBr–BTDZ0.5 and PFNBr–BTDZ1 show similar device performance with a QE around 1%. Figure 8b shows EL spectra of devices fabricated from PFNBr–BTDZ polyelectrolytes with an Al cathode. Again, the PFN and excimer emission are completely quenched, and the devices emit exclusively BTDZ emission. The EL spectra from polyelectrolytes show much larger red-shift with an increase in the BTDZ content than its neutral precursor. The device with PFNBr–BTDZ15 emits a yellow light peaked at 580 nm which indicates larger aggregation in the polyelectrolyte than that in the neutral precursor.

To the best of our knowledge, this is the first report which provides a device with high efficiency and pure emission color from polyelectrolyte or its precursor which can be processed from environment-friendly solvents. On the other hand, it is important to note that this is also the first time we report high-efficiency devices with an Al cathode without the utilization of an electron injection layer between Al and the emitting layer. There were many reports on fabricating a device with a high work function air stable Al cathode. Strategies of all these efforts were the same in which insulating polar or ionic species such as LiF,²³ Al₂O₃,²⁴ or organic surfactant²⁵ were inserted between Al metal electrode and light-emitting layer. In this study, in one of the materials, conjugated cationic polyelectrolyte and its neutral precursor, we are able to combine a high-efficiency light-emitting function and electron injection from high work function metals without the utilization of an additional electron

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injection layer in one polymer. We speculate that the amino- or ammonium-alkyl groups of the copolymers in this study under the influence of Al nearby produce dipole moments at the polymer/cathode interface. The large dipole moment remarkably decreases the surface potential of the aluminum and also leads to a significant reduction of the effective barrier height between the high work function metal and emitting layer. Studies on injection mechanism for devices from these copolymers from high work function metals are in progress and will be reported in forthcoming papers.

Conclusion

In summary, we have synthesized a series of high-efficiency light-emitting amino- and cationic ammonium-functioned polyfluorenes. The efficient energy transfer due to exciton trapping on narrow band gap BTMZ sites has been observed for both the neutral and the quaternized copolymers. In the solid state PL emission from fluorene segment has been completely quenched at as low as 1% loading of BTMZ comonomer ratio in the copolymer. Copolymers emit green or yellow light specific for narrow band gap BTMZ structure under UV excitation. Absolute PL efficiencies were greatly enhanced as a result of suppression of excimer formation which is common to rigid polyelectrolyte chains. An unexpected feature of this type of copolymer is that light-emitting devices from these copolymers show equally high quantum efficiency with both low work function metals such as Ba and high work function metals such as Al. The maximal external quantum efficiencies of the polymer light-emitting devices (PLEDs) greater than 3% and 1% are realized for the neutral polymers and the quaternized polyelectrolyte, respectively, with an Al cathode. This is the first time that we have been able to prepare a conjugated cationic polyelectrolyte and its neutral precursor which serve as a high-efficiency light-emitting layer and electron injection materials from high work function metals without the utilization of additional electron injection layer. The amino and ammonium ended side chains provide a good solubility of copolymers in alcohol. The solubility in environment-friendly solvents such as alcohol in combination with the encouraging devices performance of these polymers makes them a promising candidate for the next generation of light-emitting copolymers in PLED flat panel display application.

Experimental Section

Measurements The ^1H spectra were collected on a Varian Inova 500 spectrometer in deuterated chloroform solution operating at 500 MHz with tetramethylsilane as reference. Number-average (M_n) and weight-average (M_w) molecular weights were determined by a Waters GPC 2410 in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). UV-visible absorption spectra were recorded on a HP 8453 UV-vis spectrophotometer. The PL quantum yields were determined in an Integrating sphere IS080 (Labsphere) with 325 nm excitation of HeCd laser (Mells Griot). EL efficiency and brightness were carried out with a calibrated silicon photodiode. PL an EL spectra were recorded on Instaspec IV CCD spectrophotometer (Oriel Co.). Cyclic voltammetry was carried out on a CHI660A electrochemical workstation in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) in acetonitrile at a scan rate of 50 mV/s at room temperature under the protection of argon. A platinum electrode (for neutral polymers) or an ITO glass (for

quaternized polymers) was coated with a thin polymer film and was used as the working electrode. A Pt wire was used as the counter electrode, and a calomel electrode was used as the reference electrode. Thermogravimetric analyses (TGA) were conducted on a NETZSCH TG 209 under a heating rate of 10 °C/min and a nitrogen flow rate of 20 mL/min.

LED Fabrication and Characterization. Polymers were dissolved in toluene (for neutral polymers) or methanol (for polyelectrolytes) 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, 150 nm of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) (Batron-P 4083, Bayer AG) or poly(vinylcarbazole) (PVK, Aldrich) from 1,1,2,2-tetrachloroethane solution was spin-coated onto the substrate followed by drying in a vacuum oven at 80 °C for 8 h. A thin film of electroluminescent polymer was coated onto the anode by spin casting inside a drybox. The film thickness of the active layers was around 70 nm, as measured with an Alfa step 500 surface profiler (Tencor). Ba and Al layers were vacuum-evaporated on the top of an EL polymer layer under a vacuum of 1×10^{-4} Pa. Device performances were measured inside a drybox. Copolymers of this study as an active layer was spin-coated on top of a PEDOT layer followed by deposition of 200 nm Al (or 4 nm Ba and 200 nm Al) as a cathode. Current-voltage (I-V) characteristics were recorded with a Keithley 236 source meter. EL spectra were recorded by an Oriel Instaspec IV CCD spectrograph. Luminance and external quantum efficiencies were determined by a calibrated photodiode.

Materials. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. All reagents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Chemical Co. and used as received. All the solvents used were further purified before use.

2,7-Dibromo-9,9-bis(3'-(*N,N*-dimethylamino)propyl)fluorene (1).^{8d} To a stirred mixture of 2,7-dibromofluorene (4 g, 12 mmol) and 60 mL of dimethyl sulfoxide (DMSO) under nitrogen were added tetrabutylammonium bromide (80 mg) and 8 mL of a 50 wt % aqueous solution of sodium hydroxide. A 20 mL aliquot of DMSO solution containing 3-dimethylaminopropylchloride hydrochloride (5 g, 32 mmol) was added dropwise to the mixture. The reaction mixture was stirred at room temperature for 6 h and then was diluted with 50 mL of water, to dissolve all salts. The product was extracted with ether (3 \times 100 mL), and the combined organic layer was washed with 10% NaOH (aq) (2 \times 100 mL), water (3 \times 100 mL), and brine (1 \times 100 mL). The solution was dried over MgSO_4 , filtered, and stripped of solvent by vacuum evaporation to yield a crude solid. The crude solid was recrystallized from MeOH/ H_2O to afford **1** (3.1 g, 51%) as white crystals. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ (ppm): 7.82–7.80 (d, 2H, fluorene ring), 7.69 (s, 2H, fluorene ring), 7.56–7.53 (d, 2H, fluorene ring), 2.04–2.00 (t, 4H, $-\text{CH}_2\text{N}$), 1.92–1.88 (m, 16H, $-\text{NCH}_3$, $-\text{CH}_2-$), 0.60–0.52 (m, 4H, $-\text{CH}_2-$). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 152.37, 139.50, 130.75, 126.51, 122.04, 121.58 (C-fluorene ring), 60.01 ($-\text{CH}_2\text{N}$), 55.70 (C₉-fluorene ring), 45.78 ($-\text{NCH}_3$), 37.96 ($-\text{CH}_2-$), 22.42 ($-\text{CH}_2-$). Element Anal. Calcd for $\text{C}_{23}\text{H}_{30}\text{Br}_2\text{N}_2$: C, 55.89; H, 6.12; N, 5.67. Found: C, 55.76; H, 6.12; N, 5.60.

4,7-Dibromo-2,1,3-benzothiadiazole (**2**)¹⁴ and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**)¹⁵ were prepared according to the published procedures and have been described elsewhere.¹⁶

General Procedure of Polymerization. Carefully purified 2,7-dibromo-9,9-bis(3'-(*N,N*-dimethylamino)propyl)fluorene (**1**), 4,7-dibromo-2,1,3-benzothiazole (**2**), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**), $(\text{PPh}_3)_4\text{Pd}(0)$ (0.5–2.0 mol %), and several drops of Aliquat 336 were dissolved in a mixture of toluene and aqueous 2 M Na_2CO_3 . The mixture was refluxed with vigorous stirring for 3 days under argon atmosphere. After the mixture was cooled

to room temperature, it was poured into methanol. The precipitated material was recovered by filtration through a funnel. The resulting solid material was washed for 24 h using acetone to remove oligomers and catalyst residues. The resulting polymers were soluble in THF, CHCl_3 , and toluene. Yield: 60–80%.

Copolymer PFN–BTDZ0.5. 2,7-Dibromo-9,9-bis(3'-(*N,N*-dimethylamino)propyl)fluorene (**1**) (0.495 equiv), 4,7-dibromo-2,1,3-benzothiazole (**2**) (0.005 equiv), and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**) (0.50 equiv) were used in this polymerization. H NMR (500 MHz, CDCl_3) δ (ppm): 7.83–7.81, 7.69–7.63, 7.47–7.35, 2.20–1.96, 1.67, 1.24–1.12, 0.95, 0.82–0.78. Element Anal. Found: C, 85.66%; H, 9.52%; N, 3.37%; S < 0.5%. $M_n = 11\ 000$, $M_w = 24\ 500$.

Copolymer PFN–BTDZ1. 2,7-Dibromo-9,9-bis(3'-(*N,N*-dimethylamino)propyl)fluorene (**1**) (0.49 equiv), 4,7-dibromo-2,1,3-benzothiazole (**2**) (0.01 equiv), and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**) (0.50 equiv) were used in this polymerization. H NMR (500 MHz, CDCl_3) δ (ppm): 7.83–7.81, 7.69–7.57, 7.47–7.35, 2.20–1.95, 1.61, 1.24–1.12, 0.96, 0.81–0.78. Element Anal. Found: C, 85.39%; H, 9.41%; N, 3.40%; S < 0.5%. $M_n = 10\ 000$, $M_w = 18\ 300$.

Copolymer PFN–BTDZ5. 2,7-Dibromo-9,9-bis(3'-(*N,N*-dimethylamino)propyl)fluorene (**1**) (0.45 equiv), 4,7-dibromo-2,1,3-benzothiazole (**2**) (0.05 equiv), and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**) (0.50 equiv) were used in this polymerization. H NMR (500 MHz, CDCl_3) δ (ppm): 8.06, 7.99, 7.91, 7.82–7.80, 7.69–7.63, 7.50–7.46, 2.33–1.96, 1.58, 1.24–1.12, 0.94, 0.81–0.78. Element Anal. Found: C, 84.80%; H, 9.36%; N, 3.50%; S < 0.5%. $M_n = 16\ 000$, $M_w = 38\ 000$.

Copolymer PFN–BTDZ15. 2,7-Dibromo-9,9-bis(3'-(*N,N*-dimethylamino)propyl)fluorene (**1**) (0.35 equiv), 4,7-dibromo-2,1,3-benzothiazole (**2**) (0.15 equiv), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**) (0.50 equiv) were used in this polymerization. H NMR (500 MHz, CDCl_3) δ (ppm): 8.08, 8.00, 7.93, 7.83–7.81, 7.69–7.64, 7.45–7.35, 2.07–1.96, 1.61, 1.24–1.13, 0.96, 0.80–0.78. Element Anal. Found: C, 83.98%; H, 9.54%; N, 3.64%; S, 1.42%. $M_n = 27\ 500$, $M_w = 46\ 300$.

General Procedure of Quaternization. A 100 mL flask with a magnetic stirring bar was charged the neutral polymer (250 mg)

dissolved in 40 mL of THF. To this was added excess bromoethane and 10 mL of DMSO. The solution was stirred at 50 °C for 5 days. THF and extra bromoethane were evaporated. Polymer was precipitated in about 100 mL of ethyl acetate, collected by centrifugation, washed with chloroform and THF, and dried overnight in a vacuum at 80 °C. Yield: 60–70%.

Copolymer PFNBr–BTDZ0.5. The polymer was derived from PFN–BTDZ0.5 by the above-mentioned way. H NMR (500 MHz, CDCl_3) δ (ppm): 8.24–7.36, 3.41, 3.11, 2.89–2.79, 2.54, 2.30, 1.01, 0.73–0.72. Element Anal. Found: C, 65.69%; H, 8.68%; N, 2.11%; S < 0.5%.

Copolymer PFNBr–BTDZ01. The polymer was derived from PFN–BTDZ01 by the above-mentioned way. H NMR (500 MHz, CDCl_3) δ (ppm): 8.22–7.36, 3.35, 3.12, 2.88–2.78, 2.54, 2.30, 1.02, 0.74–0.70. Element Anal. Found: C, 63.26%; H, 8.59%; N, 2.06%; S < 0.5%.

Copolymer PFNBr–BTDZ5. The polymer was derived from PFN–BTDZ5 by the above-mentioned way. H NMR (500 MHz, CDCl_3) δ (ppm): 8.23–7.36, 3.28, 3.10, 2.84–2.78, 2.54, 2.29, 1.06, 0.75–0.71. Element Anal. Found: C, 67.76%; H, 8.62%; N, 2.46%; S < 0.5%.

Copolymer PFNBr–BTDZ15. The polymer was derived from PFN–BTDZ15 by the above-mentioned way. H NMR (500 MHz, CDCl_3) δ (ppm): 8.23–7.35, 3.28, 3.07, 2.85–2.77, 2.53, 2.28, 1.06, 0.75–0.70. Element Anal. Found: C, 69.02%; H, 8.64%; N, 3.04%; S, 1.31%.

Note: While we finished drafting this paper, we noticed a parallel work on copolymer cationic poly(flourenephenylene) incorporated with 5% of alternating (2,1,3-benzothiadiazole-phenylene) unit for multicolor biosensor in solution published by Liu, B.; et al. In *J. Am. Chem. Soc.* **2004**, *126*, 1942.

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