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RESEARCH ARTICLE

Synthesis, optical and electroluminescent properties of novel polyfluorene/carbazole-based conjugated polyelectrolytes and their precursors

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Abstract A series of novel aminoalkyl-substituted fluorene/carbazole-based main chain copolymers with benzothiadiazole (BTDZ) of different contents: poly[3,6-(N-(2-ethylhexyl)carbazole)-(9,9-bis(3′-(N,N-dimethyl-amino)propyl)-2,7-fluorene)-4,7-(2,1,3-benzothiadiazole)] (PCzN-BTDZ) were synthesized by Suzuki coupling reaction. Through a postpolymerization treatment on the precursor polymer, a corresponding quaternized ammonium polyelectrolyte derivatives: poly[3,6-(N-(2-ethylhexyl)carbazole)-(9,9-bis(3′-((N,N-dimethyl)-N-ethylammonium)propyl)-2,7-fluorene)-4,7-(2,1,3-benzothiadiazole)] dibromide (PCzNBr-BTDZ) were obtained. It was found that devices from such polymers with high work-function metal cathode such as Al showed similar device performance to that by using low work-function cathode such as Ba, indicating the excellent electron injection ability of these polymers. The efficient energy transfer from fluorene-carbazole segment to the narrow band gap BTDZ site for both the neutral and the quaternized copolymers was also observed. The addition of BTDZ into the polymer main chain can also improve polymer LED (PLED) device performance. When poly(3,4-ethylenedioxythiophene) (PEDOT)/poly(vinylcarbazole) (PVK) was used as an anode buffer, the external quantum efficiency of the copolymer PCzN-BTDZ1 was 0.99%, which was much higher than the copolymer PCzN without the incorporation of BTDZ in the same device configuration.

Keywords conjugated polyelectrolytes, electroluminescence, carbazole, polyfluorene

1 Introduction

Since the first report on the electroluminescence (EL) for poly(p-phenylenevinylene) (PPV) [1] in 1990, extensive efforts have been made to develop new light-emitting conjugated polymers [2]. With their ionic side groups being attached to the conjugated main chain, conjugated polyelectrolytes (CPs) can offer particular properties when compared with the normal "neutral" conjugated polymers. This has attracted considerable attention in recent years [3]. Most CPs are typically soluble in water or alcohols which are considered as "environmental friendly" solvents and can used as the active layer in light-emitting diodes (LEDs) deposited via layer by layer self-assembling approach [4].

Recently a series of the aminoalkyl-substituted polyfluorene(PF)-based CPs have been synthesized and it is found that this type of polyelectrolytes and their neutral precursors showed excellent electron injection ability from high work-function metals, such as Al, Au and Ag. The insertion of a thin layer of these polyelectrolytes and their neutral precursors between the traditional emitting polymers and the high work function metals greatly enhances the performance of the polymer LEDs (PLEDs) with a high work function metal as cathode [5,6]. It is also reported that by incorporating a narrow-band gap co-monomer into the aminoalkyl polyfluorene CP's main chains, the device performance of PLEDs from such CP copolymers can be greatly improved and the emission color of CPs can turn from green to near-infrared region [7], thereby simultaneously realizing the electroluminescent polymers which bear the high EL efficiency, the electron-injection ability from high work function metals, and the solubility in environment friendly solvents. In order to get alcohol-soluble high-efficiency saturated red emitting polymers, a new series of aminoalkylsubstituted polyfluorene polyelectrolytes and their neutral precursors

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copolymerized with a narrow band gap co-monomer 4,7-di-2-thienyl-2,1,3-benzothiadiazole (DBT), have been synthesized by the palladium-catalyzed Suzuki coupling method [8]. In another research, a series of novel copolymers derived from amino-functionalized fluorene and selenium-containing heterocycles [2,1,3-benzoselenadiazole(BSeD)], synthesized by the palladium-catalyzed Suzuki coupling method, were reported [9].

In this paper we synthesized a series of novel polymers derived from carbazole, aminalkyl substituted fluorene and 2,1,3-benzothiadiazole (BTDZ) by a palladium catalyzed suzuki coupling method. Through a postpolymerization treatment the quaternized salt polyelectrolytes of corresponding composition were obtained. It is well-known that carbazole-containing polymers are good hole-transporting materials due to the electron-donating capabilities associated with the nitrogen in the carbazole [10]. An alternating carbazole and aminoalkyl substituted fluorene copolymer without BTDZ unit was also synthesized for comparative purpose. UV-vis, electrochemical properties, photoluminescence (PL) properties and electroluminescence properties of these copolymers are fully investigated. It was found that the addition narrow band gap comonomers could not only change the polymers' emission color, but also improve their device performance. The efficient energy transfer due to exciton trapping on the narrow band-gap sites has been observed. Light-emitting devices from both neutral precursor and quaternized CPs with high work function metal cathode show similar quantum efficiency as from the low work function metal cathode.

2 Experimental section

2.1 Instrumentations and materials

Waters GPC 2410, HP 8453 UV-Vis spectrophotometer and Instaspec IV CCD spectrophotometer (Oriel Co.) were used for GPC, UV-vis and photoluminescence measurement.

Reagent, carbazole, 2-isopropoxy-4,4,5,5-tetramathyl-1,3,2-dioxaborolane, *n*-BuLi, fluorene, 2-ethylhexylbromide, $Pd(OAc)_2$, 3-Dimethylaminopropylchloride hydrochloride, $(Cy)_3Ph$, $(C_2H_5)_4NOH$ aqueous solution, 2,1,3-benzothiadiazole were obtained from Aldrich, Acros and TCI and used as receiver. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. All the solvents were further purified before use.

2.2 Synthetic route

The Synthetic route of the monomers and the polymers are shown in Fig. 1.

2.3 Synthesis of monomers

The monomers (1)–(6) were prepared according to the published procedures and have been described elsewhere in Refs. [5,11–13].

2.4 Synthesis of copolymers

Copolymer PCzN was prepared via Suzuki coupling with monomers (3), (4) and (6) of different feed ratio. Copolymers with BTDZ molar content of 0.5%, 1%, 5% and 10% were synthesized and named PCzN-BTDZ0.5, PCzN-BTDZ1, PCzN-BTDZ5, and PCzN-BTDZ10, respectively. The neutral polymers were synthesized in a mixture of toluene, THF and aqueous tetraethylammonium hydroxide solution in the presence of palladium acetate and tricyclohexylphosphine by stirring for 72 hours under a nitrogen atmosphere. A few drops of Aliquat 336 were added as the phase transfer catalyst. After the mixture was cooled to room temperature, it was poured into the mixture of methanol and water. The precipitated material was recovered by filtration through a funnel. The resulting solid material was washed for 24 hours by using acetone to remove oligomers and catalyst residues. All polymerization reactions yielded 60%–80%. When the neutral polymers were stirred with bromoethane in THF / DMSO (4:1) at 50°C for 6 days, corresponding polyelectrolytes were obtained and named PCzNBr, PCzNBr-BTDZ0.5, PCzNBr-BTDZ1, PCzNBr-BTDZ5 and PCzNBr-BTDZ10, repectively. Yield: 60%–75%.

3 Results and discussion

The obtained neutral polymers have good solubility in common organic solvents such as toluene, chloroform and THF. The quaternized copolymers are soluble in DMSO and DMF. The number molecular weights (Mn) of neutral polymers are between 5005 and 11521 g/mol with a polydispersity index (Mw/Mn) from 1.34 to 1.59. Since the quaternized polymers tend to aggregate, induced by the ionic groups on the polymer side chain on the column fillers, it is difficult to get the molecular weight of the quaternized polymers by GPC measurement. Since quaternization is conducted in mild conditions, it is reasonably assumed that the polyelectrolyte would have a molecular weight of the same order as that of its neutral precursor.

Figure 2 shows the UV-vis absorption spectra of polymers in solid-state films. All copolymers are dominated by a strong absorption peak at around 350 nm, which can be attributed to the PCzN segment absorption. For polymers PCzN-BTDZ10 and PCzNBr-BTDZ10, it can be clearly observed that the appearance of the absorption bands of BTDZ segments centered at about

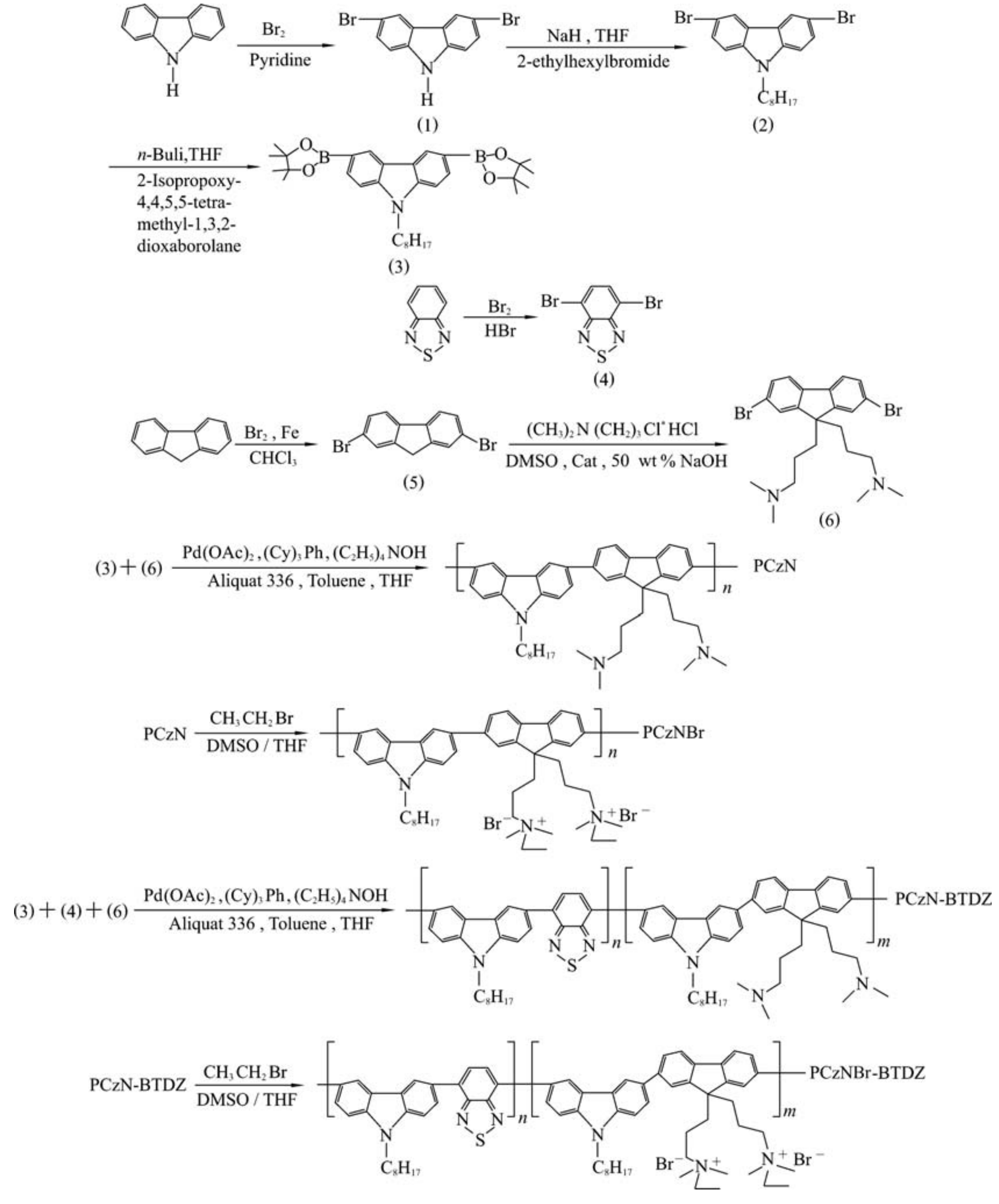
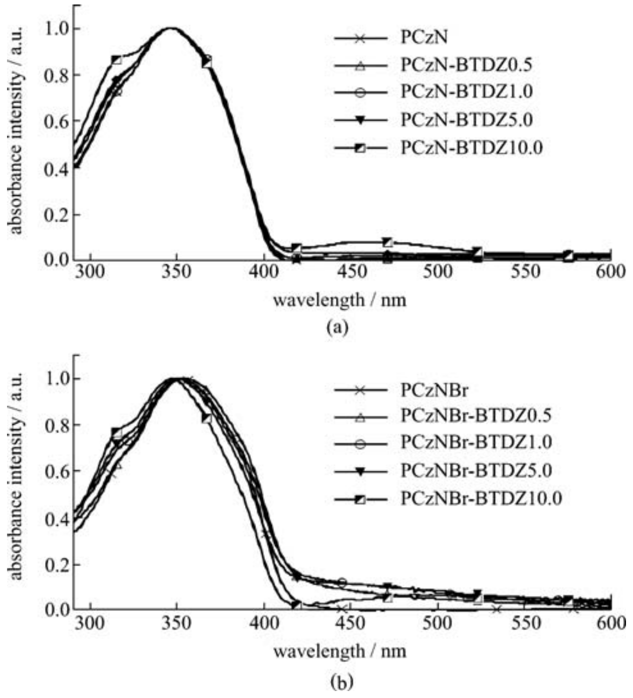


Fig. 1 Synthetic route of monomers and copolymers

470 nm [11]. The UV peak was slightly blue-shifted from 352 nm for PCzNBr to 347 nm for PCzNBr-BTDZ10 with BTDZ incorporation in solid film.

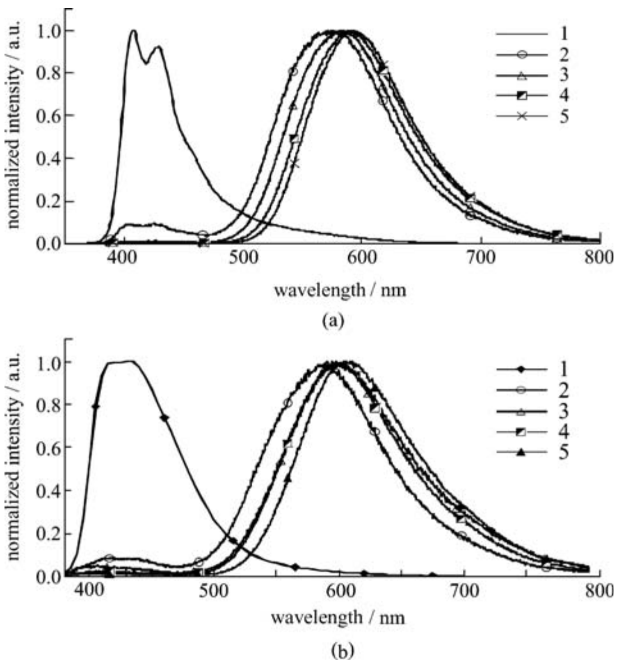
Figure 3 shows the PL emission spectra of the PCzN, PCzN-BTDZ (Fig. 3(a)) and PCzNBr, PCzNBr-BTDZ (Fig. 3(b)) in the thin solid films. The PL quantum yields of the films were determined in an Integrating sphere IS080 (Labsphere) with 325 nm excitation of HeCd laser (Mells Griot). It shows that, by introducing only 1% of BTDZ into the copolymer main chain, the blue emissions of PCzN and PCzNBr homopolymers are almost completely quenched. This fact indicates that the efficient energy transfer from blue-light emitting carbazole and fluorene segment to BTDZ unit occurred. With the increase of BTDZ content in the copolymer, PL peaks of the BTDZ emission were slightly red-shifted. It is found that the PL peak was slightly red-shifted from 574 nm for PCzN-BTDZ0.5 to 590 nm for PCzNBr-BTDZ0.5. It can be explained 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 [5,14].



(a)

(b)

Fig. 2 UV-vis absorption spectra of polymers in solid-state films. (a) PCzN and PCzN-BTDZ; (b) PCzNBr and PCzNBr-BTDZ



(a)

(b)

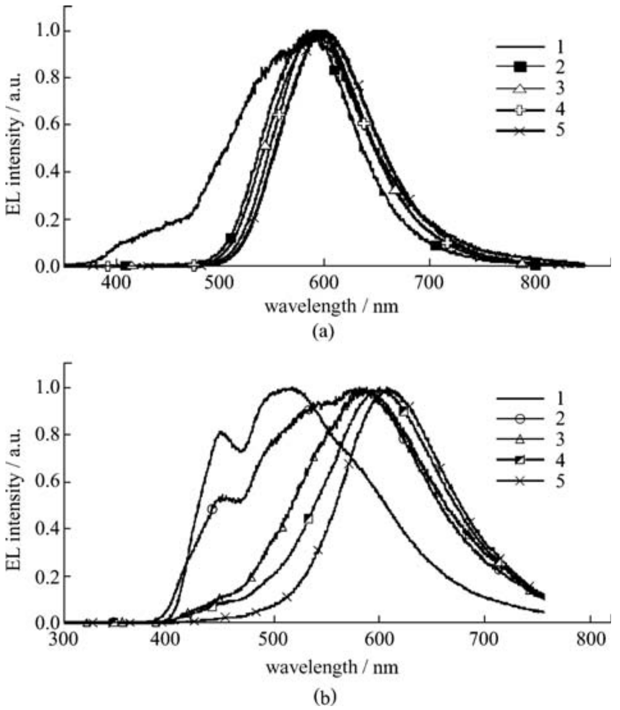
Fig. 3 PL spectra of polymers in solid-state films. (a) PCzN and PCzN-BTDZ; (b) PCzNBr and PCzNBr-BTDZ. (1: PCzN, 2: PCzN-BTDZ0.5, 3: PCzN-BTDZ1.0, 4: PCzN-BTDZ5.0, 5: PCzN-BTDZ10.0 for (a); 1: PCzNBr, 2: PCzNBr-BTDZ0.5, 3: PCzNBr-BTDZ1.0, 4: PCzNBr-BTDZ5.0, 5: PCzNBr-BTDZ10.0 for (b))

The electroluminescence performance of devices from these "neutral" and quaternized polyelectrolytes polymers was examined by using a double layer light-emitting device configuration of ITO/PEDOT/PVK/Polymer/Ba/Al. Table 1 summarizes the device performances from the copolymers of different composition in the device configuration of ITO/PEDOT(or PEDOT/PVK)/EL polymer/Ba/Al (or Al). The devices from such polymers with the high work-function metal cathode, such as Al, show similar device performance to that with the low work-function metal cathode. There has been many studies that reported on high-efficiency organic polymer LEDs with an Al cathode for LiF and other metal fluoride and chloride [15,16] and anionic surfactant [17–19]. It is suggested that the significant enhancement in the external quantum efficiencies for devices from an Al cathode into PCzN-BTDZ and PCzNBr-BTDZ could be based on a similar mechanism where surface dipoles are aligned toward the Al cathode surface [20]. Device from polyelectrolytes after quaternization generally showed lower device efficiencies than that of corresponding neutral precursors. It is also noted that PCzN-BTDZ1 showed much higher quantum efficiency (QE) (0.99%) than that of the device from PCzN (0.14%) without BTDZ incorporation.

Figure 4 shows the EL spectra of devices from these copolymers. It can be seen that the EL spectra of polymers PCzN-BTDZ and PCzNBr-BTDZ show, exclusively, characteristic emission from BTDZ site when BTDZ content is greater or equal 0.5% for neutral precursor which means that the complete quenching of blue emission occurred at lower BTDZ content than that in the PL spectra (> 1%, Fig. 3(a)) for neutral precursor polymer. However, in contrast to the quaternized polyelectrolytes, the EL emission showed notable blue

Table 1 Device performances of some copolymers

polymers	cathode	anode buffer	voltage/V	current/mA·cm^{-2}	lumin/cd·m^{-2}	QE/%
PCzN	Ba/Al	PEDOT/PVK	19.82	8.80	13.29	0.14
	Al	PEDOT/PVK	20.22	22.20	19.47	0.09
PCzN-BTDZ1	Ba/Al	PEDOT/PVK	32.93	18.33	186.39	0.99
	Al	PEDOT/PVK	25.12	31.73	143.44	0.44
PCzNBr	Ba/Al	PEDOT	5.40	85.67	253.24	0.25
	Al	PEDOT	13.44	21.13	28.59	0.19
PCzNBr-BTDZ1	Ba/Al	PEDOT	5.76	319.80	41.90	0.01
	Al	PEDOT	6.00	544.67	35.00	0.01



(a)

(b)

Fig. 4 EL spectra of polymers. (a) PCzN and PCzN-BTDZ; (b) PCzNBr and PCzNBr and PCzNBr-BTDZ. (1: PCzN, 2: PCzN-BTDZ0.5, 3: PCzN-BTDZ1.0, 4: PCzN-BTDZ5.0, 5: PCzN-BTDZ10.0 for (a); 1: PCzNBr, 2: PCzNBr-BTDZ0.5, 3: PCzNBr-BTDZ1.0, 4: PCzNBr-BTDZ5.0, 5: PCzNBr-BTDZ10.0 for (b))

shoulder even for devices from polymers with 5% BTDZ content, which was much higher than that in the PL spectra. Although this is quite uncommon among aminoalkyl-substituted polyfluorene polyelectrolytes [7–9], it is still not clear whether this is related to the incorporation of the carbazole unit into the polymer main chain at this stage of the experiment. Further studies will be targeted on the conformation of polyfluorene and fluorine-carbazole copolymer chains.

4 Conclusions

A series of aminoalkyl-substituted polyfluorene/carbazole-based conjugated polymers and their quaternized polyelectrolytes with various ratios of BTDZ units have been synthesized by Suzuki cross-coupling reaction. The efficient energy transfer from fluorene-carbazole segment to the narrow band-gap BTDZ sites has been observed for the polymers. The use of conjugated polyfluorene/carbazole as a wide band-gap segment provides a new way to combine a good hole-injection property along with the color tuning ability. Furthermore, all the polymers show good electron injection ability from high work-function metal cathode. Devices with Al cathode showed that the device performance was similar to that of the low work-function cathode. The remarkable characteristics of these polymers make them promising candidates for the next generation of light emitting copolymers in flat panel display applications.

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