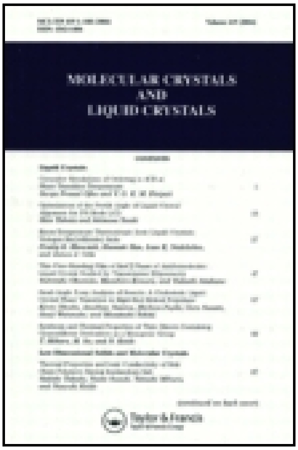

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Alternating Copolymers of N-(2-Ethylhexyl)-Carbazole Derivatives with Aniline Units: Synthesis and Properties

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Alternating copolymers such as P(3,6-EHCZ-alt-Al), P(Bis-EHCZ-alt-Al) and P(2,7-EHCZ-alt-Al), based on blue-emitting carbazole and hole-transporting triarylamine units in the polymer backbone, were successfully synthesized by using palladium-catalyzed polycondensation reaction. P(Bis-EHCZ-alt-Al) exhibited blue shift both in UV-Vis absorption and PL emission, while P(2,7-EHCZ-alt-Al) showed red shift in UV-Vis absorption and blue shift in PL emission, compared to P(3,6-EHCZ-alt-Al). It was observed from the optical and electrochemical characterization that band gap energy (2.91 $\sim$ 3.07 eV) and HOMO ($-5.25 \sim -5.11$ eV) levels of the copolymers could be fine-tuned by the carbazole content in the repeating unit and different reaction linkage on the carbazole ring.

Keywords: alternating copolymer; carbazole; palladium-catalyzed polycondensation; triarylamine

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INTRODUCTION

Organic light-emitting diode (OLED) and polymeric light-emitting diode (PLED) have been considered as potential candidates for large screen flat-panel color-display in future [1]. In PLEDs, π-conjugated polymers are an important class of materials because of their electrical and optical properties. Since the first report of PLED, this field has been attracted worldwide attention by both academic and industrial laboratories [2–4]. These electroactive and photoactive polymers are normally based on organic moieties such as fluorene, phenylene, thiophene and their derivatives [5–7], and their conjugated backbone can be obtained mainly by the utilization of a variety of synthetic tools such as Suzuki coupling, Yamamoto, Kumada Still and so on [5,8]. These synthesized polymers show great advantages of high purity, emitting different colors across the entire visible spectrum and spin-coating of the polymers to yield thin film.

Multiplayer structures in OLEDs were generally constructed with hole-transporting, emitting, electron-transporting and hole-block materials sandwiched between anode and cathode diodes, which resulted in a good charge balance of electrons and holes [9]. Common classes of materials used for hole transporting layers were low molecular weight arylamines such as *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diaimine (TPD) and *N*,*N*′-diphenyl-*N*,*N*′-bis (α-naphthyl)benzidine (NPB) [11,12]. While, TPD had a low T_g of around 60°C that caused crystallization and thermal breakdown during the operation of OLEDs. To avoid this defect, triarylamine-based hole-transporting polymers were usually synthesized by Ullmann coupling [10] or Pd-catalyzed amination reaction [11], and fluorene-based copolymers were prepared by Suzuki coupling reaction [12,13].

Stable blue PLEDs have been still a challenge for polymer scientists. Because of the large band gap between HOMO and LUMO energy levels, it is difficult to achieve a balanced charge injection [14,15]. In this regard, the design and synthesis of blue emitting polymers have been extensively investigated. Recently, increasing interest has been paid to carbazole-based polymers. Huang *et al*. [16] reported wide band gap energy (3.2 eV) of polycarbazoles and synthesized an entirely new class of polycarbazole-based main chain copolymers with varieties of aromatic rings and heterocycles as a comonomer by Suzuki coupling reaction. Leclerc's research group first reported a series of homopolymers and copolymers derived from *N*-alkyl-2,7-carbazoles [8]. Conjugated poly(*N*-alkyl-3,6-carbazole) derivatives were available by Xia and his coworkers [15]. Besides wide band gap energy and hole-transporting property, the carbazole-based polymers exhibited excellent chemical and physical stability in air.

In present study, we prepared a new series of thermally stable alternating copolymers with dual functions consisting of a blue-emitting carbazole moiety and hole-transporting triarylamine group by Pd-catalyzed polycondensation reaction. The effect of content and reaction positions (2,7- or 3,6-linkage) of carbazole group in the repeating unit was discussed.

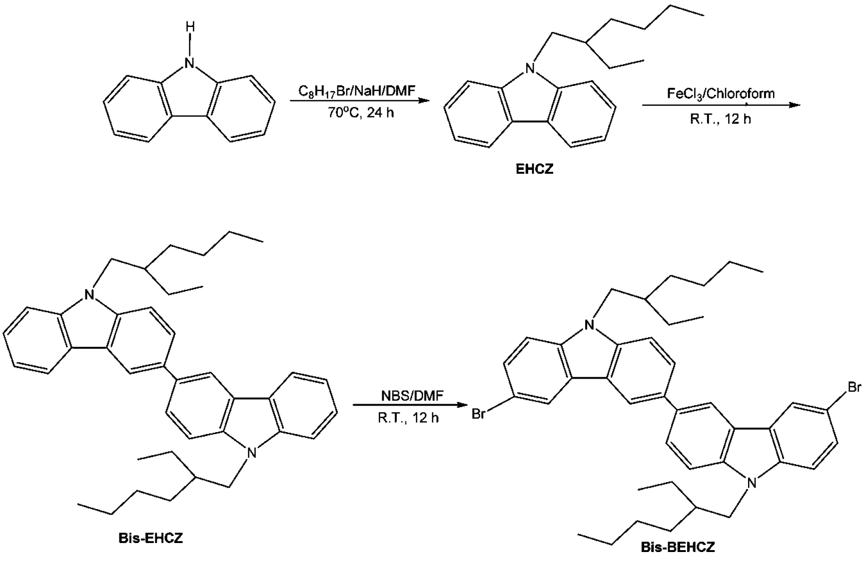
EXPERIMENTAL

Synthesis of Monomers

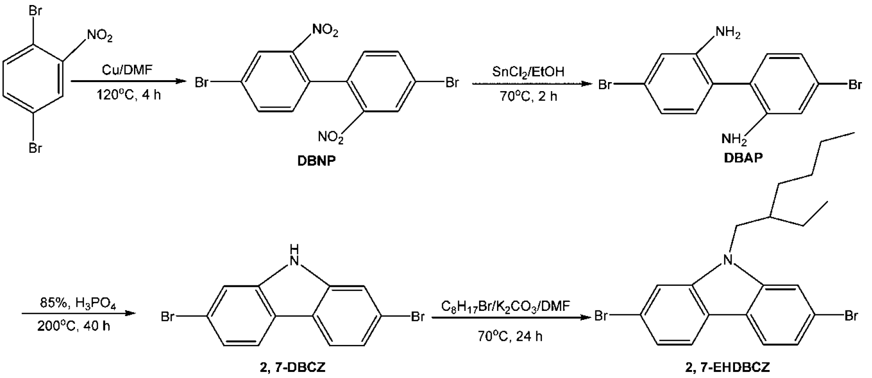
N-(2-Ethyhexyl)-3,6-dibromocarbazole (3,6-DBEHCZ) was synthesized according to the Ref. [17]. Bis[6-bromo-*N*-(2-ethylhexyl)-carbazole-3-yl] (Bis-BEHCZ) was synthesized [18], as shown in Scheme 1.

N-(2-Ethylhexyl)-2,7-dibromocarbazole (2,7-EHDBCZ)

The synthetic procedure was shown in Scheme 2. A mixture of 2,5-dibromonitrobenzene (21.4 mmol), Cu powder (50 mmol) and 40 ml of DMF was heated at 120°C with stirring 4 h. After the reaction, the mixture was cooled to room temperature and dissolved in benzene. Insoluble materials were filtered out, and the benzene solution was washed with water, dried with $MgSO_4$, and evaporated. The residue



SCHEME 1 Synthetic route to Bis-BEHCZ.



SCHEME 2 Synthetic route to 2,7-EHDBCZ.

was recrystallized from ethanol and pale yellow 4,4′-dibromo-2,2′-dinitrobiphenyl (DBNP) was obtained with the yield of 60%. ^{1}H-NMR (300 MHz in $CDCl_3$): δ 8.44 (2H, Ar-H), 8.09 (2H, Ar-H), 7.50 (2H, Ar-H); ^{13}C-NMR (300 MHz in $CDCl_3$): δ 147.4, 136.9, 133.0, 131.4, 127.3, 122.1.

A mixture of DBNP (10 mmol), $SnCl_2$ (60.7 mmol) and ethanol (30 ml) was heated at 70°C for 2 h. After the mixture was cooled to room temperature, 1 M NaOH solution was added until the mixture became alkaline. After extraction with ethyl acetate, the combined organic layers were washed with brine, dried with $MgSO_4$ and evaporated. The residue was recrystallized from ethanol and pale brown 4,4-dibromo-2,2′-diaminobiphenyl (DBAP) was obtained with the yield of 90%. ^{1}H-NMR (300 MHz in $CDCl_3$): δ 6.86 (2H, Ar-H), 6.95 (2H, Ar-H), 7.25 (2H, Ar-H), 3.56 (4H,-NH); ^{13}C-NMR (300 MHz in $CDCl_3$): δ 145.3, 132.2, 122.7, 122.0, 121.7, 118.1.

A solution of DBAP (26.3 mmol) in 85% H_3PO_4 (45 ml) was stirred at 200°C for 40 h. After reaction, the mixture was cooled to temperature and dissolved in toluene. Insoluble materials were filtered out, and the concentrated filtrate was diluted with hexane to give beige crystal 2,7-dibromocarbazole (2,7-DBCZ) with the yield of 80%. ^{1}H-NMR (300 MHz in $CDCl_3$): δ 8.08 (2H, Ar-H), 7.73 (2H, Ar-H), 7.35 (2H, Ar-H); ^{13}C-NMR (300 MHz in $CDCl_3$): δ 123.2, 122.6, 114.8.

2,7-DBCZ (1.8 mmol) and K_2CO_3 (3.7 mmol) in DMF (20 ml) were refluxed. After 30 min. 2-ethylhexylbromide was added dropwise. After reflux for 24 h, the mixture was cooled to room temperature and isolated by extraction with diethylether/water. The organic layer was dried by $MgSO_4$, then filtered and evaporated. After column chromatography, white solid 2,7-EHDBCZ was obtained with the yield of

58%. ^{1}H-NMR (300 MHz in $CDCl_3$): δ 7.85 (2H, Ar-H), 7.48 (2H, Ar-H), 7.33 (2H, Ar-H), 4.04 (2H, $-N-CH_2-$), 2.00 (1H, $-CH-$), 1.55–1.26 (8H, $-CH_2-$), 0.89 (6H, $-CH_3$); ^{13}C-NMR (300 MHz in $CDCl_3$): δ 141.8, 122.5, 121.4, 121.2, 119.6, 112.2, 47.6, 39.1, 30.7, 28.5, 24.3, 23.0, 14.0, 10.9.

Polymerization

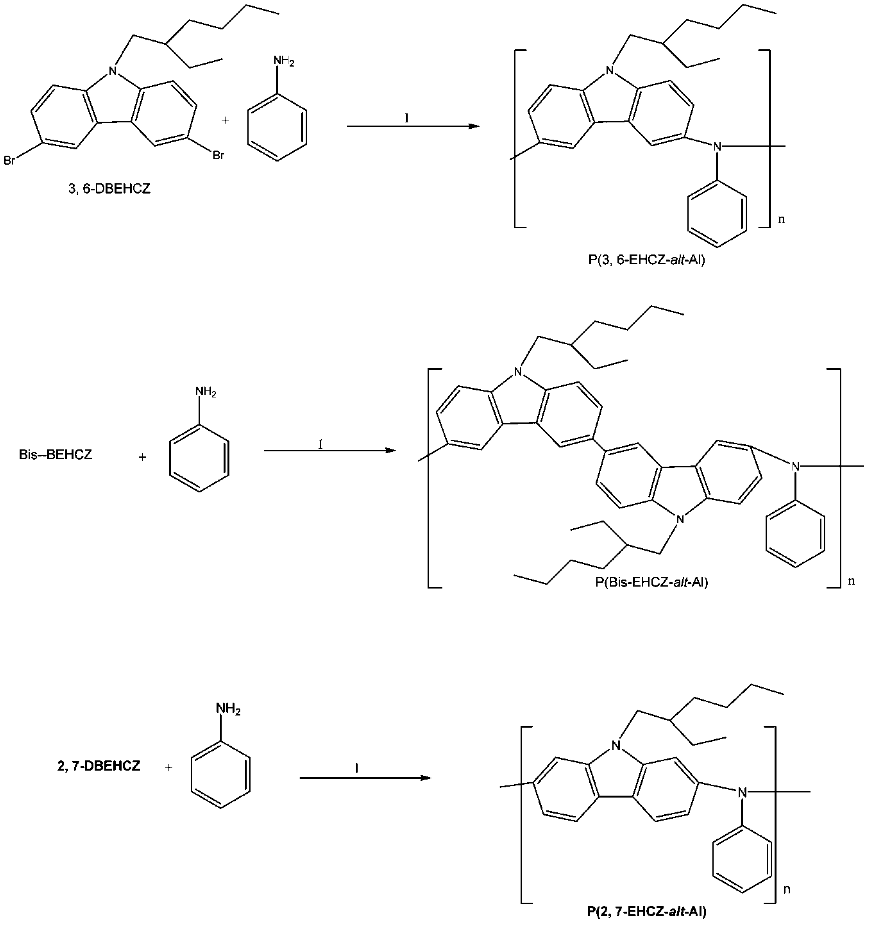
A mixture of monomer 3,6-EHDBCZ (2.58 mmol) (2,7-EHDBCZ or Bis-BEHCZ) and aniline (2.58 mmol) was dissolved in toluene (25 ml). NaO-*t*-Bu (7.74 mmol), $Pd_2(dba)_3$ (0.065 mmol) and $P(t\text{-}Bu)_3$ (0.39 mmol) were added to the solution at room temperature. The reaction mixture was stirred at 100°C for 48 h. After cooling to room temperature, the mixture was quenched by adding aqueous ammonia (50 ml) and the product was extracted with $CHCl_3$. The organic fraction was concentrated and reprecipitated from $CHCl_3$/methonal several times. Then, the products were filtered and dried in vacuum.

Characterization

NMR spectra were recorded on a Varian Unity Plus 300 with solvent of $CDCl_3$. Molecular weight were measured by Water gel permeation chromatograph (GPC) equipped with Styragel HR 5E column using THF as eluent against polystyrene standards at room temperature. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating of 20°C/min for thermogravimetry analyzer (TGA) and at a heating of 10°C/min for differential scanning calorimetry (DSC). UV-visible absorption spectra were taken by Shimadzu UV-2100. The photoluminescence (PL) spectra excited by He-Cd laser at 325 nm were monitored by Optical Multichannel Analyzer (Laser Photonics, OMA system). The ionization potential (IP) was measured by a photoelectron spectroscopy (Riken Keiki AC-2).

RESULTS AND DISCUSSION

The procedures for preparing the alternating copolymers are outlined in Scheme 3. These alternating copolymers were synthesized by using Pd-catalyzed polycondensation of carbazole-based derivatives such as *N*-(2-ethyhexyl)-3,6-dibromocarbazole, bis[6-bromo-*N*-(2-ethylhexyl)-carbazole-3-yl]and *N*-(2-ethyhexyl)-2,7-dibromocarbazole with aniline. The polymerization resulted in alternating copolymers with a blue-emitting carbazole moiety and hole-transporting triarylamine group in the main chain. In this study, the effect of increased carbazole



SCHEME 3 Polymerization via palladium-catalyzed polycondensation; Polymerization condition (I): Toluene, NaO-*t*-Bu, $Pd_2(dba)_3$, $P(t\text{-}Bu)_3$, 100°C.

content in P(Bis-EHCZ-*alt*-Al) was compared with P(3,6-EHCZ-*alt*-Al). P(2,7-EHCZ-*alt*-Al) was also synthesized to compare the effect of reaction positions between 2,7- and 3,6-linkages on the carbazole ring.

All copolymers were found to be soluble in common organic solvents such as toluene, benzene, chloroform and tetrahydrofuran, due to the 2-ethylhexyl group substituents in the *N*-position of carbazole. In addition, the copolymers showed good film forming quality. Molecular weights and molecular weight distributions were determined by GPC and summarized in Table 1. The molecular weights (M_n) of the copolymers were in the range of 3,500–7,800 g/mole with polydispersity

TABLE 1 Physical Properties of Polymers

Polymers	M_n (g/mol)	M_w/M_n	T_g (°C)	T_d (°C)[a]
P(3,6-EHCZ-*alt*-Al)	5,600	1.3	—	442
P(Bis-EHCZ-*alt*-Al)	2,900	1.2	—	467
P(2,7-EHCZ-*alt*-Al)	3,500	1.6	95	416

[a] Temperature resulting in 5% weight loss based on initial weight.

indices of 1.2–1.6. Thermal properties of the polymers were determined by TGA and DSC. All the polymers showed good thermal stability with onset decomposition temperatures of 416–467°C at 5 wt% loss under a nitrogen atmosphere. Compared with the reported decomposition temperature ($T_d = 400°C$) of fluorene-based poly(iminoarylene)s, the synthesized copolymers were more stable. Over the decomposition temperature, the weight loss curves fell rapidly, as shown in Figure 1, indicating the decomposition of the backbone of the polymers. In the DSC measurement, P(2,7-EHCZ-*alt*-Al) showed higher T_g at 95°C than that of TPD, well-known low molecular weight hole-transporting material, while T_g of P(3,6-EHCZ-*alt*-Al) and P(Bis-EHCZ-*alt*-Al) could not be measured.

UV-Vis absorption and PL emission spectra of the polymers in the dilute THF solution are presented in Figures 2 and 3, respectively. The maximum absorption peaks of P(3,6-EHCZ-*alt*-Al) and P(Bis-EHCZ-*alt*-Al) appeared at 309 nm and 305 nm with absorption edges at 452 nm and 439 nm. The maximum absorption peak for P(2,7-EHCZ-*alt*-Al) moved to higher wavelength at 374 nm with the

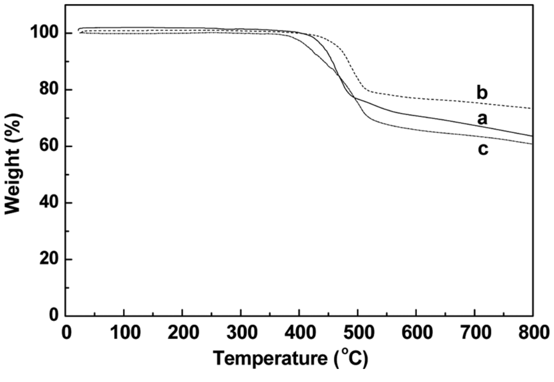


FIGURE 1 TGA curves of polymers: (a) P(3,6-EHCZ-*alt*-Al), (b) P(Bis-EHCZ-*alt*-Al), (c) P(2,7-EHCZ-*alt*-Al).

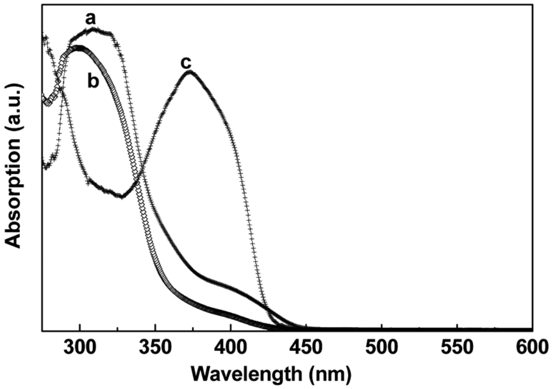


FIGURE 2 UV-Vis absorption spectra of polymers: (a) P(3,6-EHCZ-*alt*-Al), (b) P(Bis-EHCZ-*alt*-Al), (c) P(2,7-EHCZ-*alt*-Al).

absorption edge at 429 nm. With excited at their $\lambda_{\mathrm{max,UV}}$, P(3,6-EHCZ-*alt*-Al), P(Bis-EHCZ-*alt*-Al) and P(2,7-EHCZ-*alt*-Al) showed the maximum peaks of PL in the blue emission range with the maximum peaks at 452, 442 and 423 nm, respectively. The PL emission of P(Bis-EHCZ-*alt*-Al) was slightly blue-shift with respect to P(3,6-EHCZ-*alt*-Al). The weak blue shift was partially due to more steric hindrance induced by two 2-ethylhexyl groups in P(Bis-EHCZ-*alt*-Al), resulting in more twisted backbone. In comparison with P(3,6-EHCZ-*alt*-Al), maximum PL peak of P(2,7-EHCZ-*alt*-Al) shifted to shorter wavelength. It was worth noting from the previous studies that poly

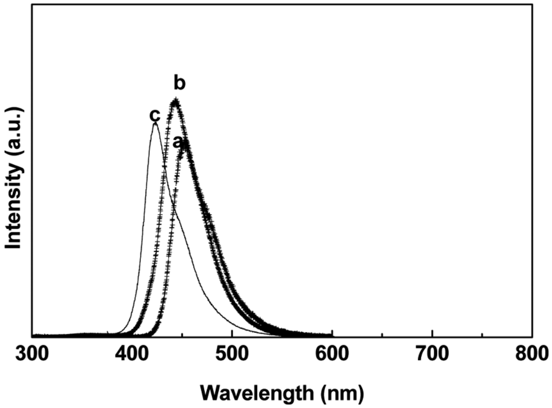


FIGURE 3 Photoluminescence spectra of polymers: (a) P(3,6-EHCZ-*alt*-Al), (b) P(Bis-EHCZ-*alt*-Al), (c) P(2,7-EHCZ-*alt*-Al).

TABLE 2 Electronic Properties of the Polymers

Polymers	$\lambda_{\text{max,UV}}$ (nm)	$\lambda_{\text{max,PL}}$ (nm)	Band gap (eV)[a]	HOMO (eV)[b]	LUMO (eV)[c]
P(3,6-EHCZ-*alt*-Al)	309	452	2.91	–5.19	–2.28
P(Bis-EHCZ-*alt*-Al)	304	442	3.06	–5.25	–2.19
P(2,7-EHCZ-*alt*-Al)	374	423	3.07	–5.11	–2.04

[a] Calculated from the crosspoint of UV-Vis and PL spectrum.
[b] Measured by a RIKEN Keiki AC-2.
[c] Estimated from the HOMO and band gap.

(*N*-alkyl-2,7-carbazole) exhibited two PL emission peaks at 417 and 450 nm [8], while PL emission peaks of poly(*N*-alkyl-3,6-carbazole) showed red-shift to 420 and 520 nm [16]. The similar trends of optical properties were also observed between P(3,6-EHCZ-*alt*-Al) and P(2,7-EHCZ-*alt*-Al).

It has been known that structural characteristics of materials used in light-emitting diodes play a crucial role in fine-tuning energy levels of HOMO and band gap. It appeared in Table 2 that three copolymers had wide band gap energy (2.91 $\sim$ 3.07 eV), calculated from the junction of UV-Vis absorption and PL emission spectra. The wide band gap can afford polymers with qualification as good host material in emitting layer, particularly for P(2,7-EHCZ-*alt*-Al) with higher band gap (3.07 eV) than those of other two polymers. HOMO levels of alternating polymers were measured to be in the range of $-5.11 \sim -5.25$ eV. Such energy levels may provide a closer match to the function of ITO anode when the copolymers are used as hole-transporting materials in the PLEDs. For monomers such as 3,6-EHDBCZ, 2,7-EHDBCZ and Bis-BEHCZ, they showed HOMO energy at -6.09, -6.19 and -5.60 eV, respectively [18]. Decrease in the HOMO energy levels demonstrated the increased hole-transporting ability of the copolymers. Especially, P(2,7-EHCZ-*alt*-Al) could be expected to have better hole injection capability from ITO anode (work function of -4.7 eV).

CONCLUSIONS

We have succeeded in synthesizing three different types of alternating copolymers such as poly(3,6-EHCZ-*alt*-Al), P(2,7-EHCZ-*alt*-Al) and P(Bis-EHCZ-*alt*-Al) by Pd-catalyst polycondensation reaction. Common structural characteristics of these copolymers were alternating structure of a blue-emitting carbazole and a hole-transporting triarylamine unit in the polymer backbone. The synthesized copolymers were soluble in common organic solvents, and showed good film forming and good thermal stability. From the optical and electrochemical characterization, these copolymers exhibited blue PL emission with wide band gap energy and HOMO levels, well matched with the function of ITO anode. It revealed that P(2,7-EHCZ-*alt*-Al) copolymer with 2,7-linkage on the carbazole ring had wider band gap and higher HOMO energy levels, implying that it could be used as a good blue host material or hole-injection material with low energy barrier.

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