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# Synthesis and optoelectronic properties of amino-functionalized carbazole-based conjugated polymers<sup>†</sup>

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A series of alcohol soluble amino-functionalized carbazole-based copolymers were synthesized via Suzuki coupling reaction. The pendent amino groups endow them high solubility in polar solvents, as well as efficient electron injection capability from high work-function metals. The relationships between the photophysical and electrochemical properties and the polymer backbone structure were systematically investigated. These alcohol-soluble carbazole-based copolymers were used as cathode interlayers between the high work-function metal Al cathode and P-PPV emissive layer in polymer light-emitting diodes with device structure of ITO/PEDOT:PSS/P-PPV/interlayer/Al. The resulting devices exhibited improved performance due to the better electron injection/transporting ability of the designed copolymers from Al cathode to the light-emitting layer.

polymer light-emitting diodes, amino-functionalized conjugated polymers, electron injection/transporting material, interfacial material, carbazole

### 1 Introduction

Since the demonstration of the first polymer light-emitting diodes (PLEDs) [1], considerable attention has been paid to this area due to their unique characteristics, such as low cost, light weight, and possible flexibility and large-area coverage [2–6]. PLEDs usually adopt a basic architecture composed of an emitting layer (EML) of organic semiconducting material sandwiched between two electrodes. To achieve highly efficient PLEDs, interfacial layers with good hole/electron transporting/injection properties are required to optimize charge injection, transport, and recombination [7–13]. Low work function (WF) metals (such as Ca and Ba) are widely used as a cathode to facilitate electron injection. However, these metals are very sensitive to moisture and oxygen, forming detrimental quenching sites near the inter-

face between the EML and the cathode [14]. In addition, metal ions generated at the metal/organic interface tend to migrate into the EML, thus affecting the long term stability of devices. To circumvent these problems, air-stable high WF metals (such as Al, Ag, and Au) are applied to improve stability. In order to minimize the energy barrier between EML and high WF metals, it is necessary to introduce an interfacial layer between the active layer and the metal electrode, such as LiF [15],  $Cs_2CO_3$  [16],  $TiO_x$ [17], LiN<sub>3</sub>[18], ZnO [19, 20], and organic surfactants [21–26].

Water/alcohol soluble conjugated polymers (WSCPs) have attracted considerable attention in past decade due to their potential application in PLEDs and polymer solar cells (PSCs) as cathode interlayers [13, 27–31]. Their solubility in high polar solvents, which is orthogonal to many commonly used conjugated polymer active materials, allows for fabrication of multilayer devices through solution processing. Most importantly, WSCPs with polar pendant groups can dramatically improve charge injection from me-

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tallic electrodes into organic active layers, resulting in significant enhancement in the device performance [31–39]. Based on these unique characteristics, highly efficient all printable PLEDs were recently realized [40].

Amino-functionalized conjugated polymers (AFCPs) can be dissolved in alcohol in the presence of trace acetic acid because of the weak interaction between the nitrogen atoms in pendent amino groups (PAGs) and acetic acid [41]. By inserting a layer of AFCPs or cross-linked AFCPs between high WF metal cathode and EML in PLEDs, the electron injection from high WF metal cathode could be significantly benefited from the interfacial dipole formation between the PAGs in AFCPs and the metal cathode [33–35, 38–43]. Therefore, AFCP becomes one of the most important WSCPs used as cathode interlayer in PLEDs, PSCs, and so on [44, 45].

Organic material with carbazole skeleton has been widely used in EML and hole transporting layer in PLEDs [46], due to the following advantages: (i) the nitrogen atom can be easily functionalized with a large variety of substituents to modulate the carbazole properties; (ii) carbazole units can be linked at different positions; (iii) excellent luminescent properties and hole transport properties. Polycarbazoles bearing an electron-rich main chain and a large band gap are known as typical p-type semiconductors [46]. Compared with the large family of fluorene-based AFCPs, construction of carbazole-based interlayer polymers for optoelectronic devices receives much less attention [13]. Chen and coworkers reported that the PAGs in polycarbazoles can induce interfacial dipole formation and improve electron injection from high WF metal cathode into EML [47, 48]. Although a large number of AFCPs with different pendent polar groups have been developed, AFCPs with different main chain structures remains very rare [13, 38]. Moreover, the relationship between material structure and properties is of great significance for the development of novel efficient WSCPs interfacial material.

In this work, the amino-functionalized polycarbazoles (PCNs) with branched alkyl were designed, synthesized and used as cathode interlayers in PLEDs (Scheme 1). The tertiary amino groups in branched alkyl substitution not only endows PCNs excellent solubility in polar solvents, but also improves electron injection from high WF metal cathode into EML. The relationships between chemical structure and optoelectronic properties were also systematically investigated. It was found that by using PCNs as an ETL in PLEDs, the device performance was significantly enhanced. The main chain structures not only influence the photophysical properties and electrochemical properties, but also have significant impact on the resulting device performance.

### 2 Experimental section

### 2.1 Measurements and material

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured using a Bruker

AV-300. Molecular weights of the polymers were determined by a Waters GPC 2410 in THF using a calibration curve with polystyrene standards. Thermogravimetric analyses (TGA) were conducted on a NETZSCH TG 209 under a heating rate of 10 °C min<sup>-1</sup> and a nitrogen flow rate of 20 mL min<sup>-1</sup>. Cyclic voltammetry (CV) data were measured on a CHI600D electrochemical workstation by using Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) in acetonitrile as electrolyte, and platinum and saturated calomel electrode (SCE) as the working and reference electrode, respectively. UV-vis spectra were recorded on a HP 8453 spectrophotometer. Photoluminescence (PL) and electroluminescence (EL) spectra were recorded on an Instaspec IV CCD spectrophotometer (Oriel Co.).

All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. All reagents, unless otherwise specified, were obtained from Alfa Aesar or Sigma-Aldrich and used as received. Some of the solvents used were further purified before use (THF from sodium/benzopheone, acetonitrile from CaH<sub>2</sub>, toluene was washed with H<sub>2</sub>SO<sub>4</sub> and then treated with MgSO<sub>4</sub>).

### 2.2 Monomer synthesis

### 1'-((6' -Bromohexyl)oxy)-4-methylbenzene (1)

A mixture of *p*-cresol (28 g, 255 mmol), 1,6-dibromohexane (220 mL, 1426 mmol), tetrabutylammonium bromide (3.8 g, 12 mmol), and potassium carbonate (60 g, 435 mmol) in acetone (150 mL) was refluxed under argon for 48 h. The solid was filtered off and the filtrate was evaporated to dryness. The residue was distilled under reduced pressure to obtain the desired product as a colorless liquid (53.5 g, yield: 76%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.10 (d, 2H, J = 8.7 Hz), 6.80 (d, 2H, J = 8.6 Hz), 3.90 (t, 2H, J = 7.1 Hz), 3.45 (t, 2H, J = 6.9 Hz), 2.28 (s, 3H), 1.85~1.75 (m, 8H).

### 1,13-Bis(p-tolyloxy)tridecan-7-ol (2)

A mixture of **1** (16.1 g, 60 mmol) and magnesium turnings (2.17 g, 90 mmol) in THF (60 mL) was refluxed under argon for 3 h to afford the Grignard reagent, which was cooled to room temperature (rt). In a three neck flame-dried 500 mL round-bottom flask, ethyl formate (1.48 g, 20 mmol) was dissolved in THF (100 mL) and cooled to -78 °C. The freshly prepared Grignard reagent was then added dropwise and the resulting mixture was allowed to stir overnight at rt. The reaction was quenched by methanol and then saturated aqueous NH<sub>4</sub>Cl. The mixture was extracted with dichloromethane (DCM), and the organic phase was washed with brine, and dried over MgSO<sub>4</sub>. The crude product was distilled under reduced pressure to obtain pure product as a white solid (21.07 g, yield: 82%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.10 (d, 4H, J = 8.5 Hz), 6.75 (d, 4H, J = 8.6 Hz), 3.95 (t, 4H, J = 7.3 Hz), 3.67~3.57 (m, 1H), 2.26 (s, 6H), 1.55~1.45 (m, 21H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 157.00, 129.84, 129.66, 114.40, 76.60, 71.91, 68.00, 37.42, 29.44, 29.28, 26.05, 25.57, 20.43.



Scheme 1 Synthetic route of the monomer and target polymers. Reagents and conditions: a) 1,6-dibromohexane, tetrabutylammonium bromide, potassium carbonate, acetone, refluxed, 48 h; b) magnesium turnings, THF, refluxed, 3 h, and then ethyl formate, THF, -78 °C, 2 h; c) *p*-toluenesulfonyl chloride, DCM, Et<sub>3</sub>N, Me<sub>3</sub>N · HCl, 5–10 °C, 90 min; d) fuming nitric acid, glacial acetic acid, 100 °C, 6 h; e) triethyl phosphite, refluxed, 24 h; f) DMSO, KOH, rt, 8 h; g) hydrobromide, glacial acetic acid, refluxed, 48 h; h) DMF, diethylamine, refluxed, 12 h; i) Pd(PPh<sub>3</sub>)<sub>4</sub>, 20% aq. tetraethylammonium hydroxide, toluene, THF, 90 °C, 48 h.

# 1',13-Bis(p-tolyloxy)tridecan-7'-yl-4-methylbenzenesulfonate (3)

*p*-Toluenesulfonyl chloride (4.16 g, 21.8 mmol) in DCM (30 mL) was added to a stirred solution of 2 (6.03 g, 14.55

mmol), Et<sub>3</sub>N (5.1 mL) and Me<sub>3</sub>N·HC1 (1.38 g, 14.55 mmol) in DCM (50 mL) in a 250 mL flask at 0–5 °C. The mixture was stirred for 90 min, then quenched by water. The mixture was extracted three times with DCM. The organic

phase was washed with water, brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (petroleum ether/ethyl acetate as eluent, v/v = 9/1) to obtain pure product as a white solid (6.52 g, yield: 78%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.80 (d, 2H, J = 8.4 Hz), 7.30 (d, 2H, J = 7.9 Hz), 7.10 (d, 4H, J = 8.6 Hz), 6.80 (d, 4H, J = 8.4Hz), 4.61~4.51 (m, 1H), 3.95 (t, 4H, J = 7.5), 2.46 (s, 3H), 2.30 (s, 6H), 1.46~1.36 (m, 20H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 156.93, 144.39, 134.70, 129.87, 129.70, 129.67, 127.72, 144.32, 84.37, 67.85, 34.09, 29.16, 29.04, 25.86, 24.64, 21.60, 20.47.

#### 2,7-Dibromo-carbazole (5)

A mixture of fuming nitric acid (70%, 132 mL) was added dropwise to a stirred solution of 4,4'-dibromobiphenyl (20 g, 64 mmol) in glacial acetic acid (300 mL) at 100 °C. The reaction was allowed to proceed for 6 h followed by cooling to rt. The yellow precipitate was collected by filtration, followed by recrystallization from ethanol to obtain crude product **4** as a white solid. The crude product **4** was used in next step without further purification.

To a 250 mL round bottomed flask equipped with a reflux condenser were added **4** (16.52 g, 46.1 mmol) and triethyl phosphite (60 mL). The resulting mixture was refluxed for 24 h under argon. The excess triethyl phosphite was then distilled off and the residue was purified by silica gel column chromatography using a gradient of solvents ranging from 5–20% ethyl acetate in petroleum ether to yield pure product [49] (9.28 g, yield: 62%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.25~8.15 (br, 1H, NH), 7.90 (d, 2H, J = 8.2 Hz), 7.56 (d, 2H, J = 8.1 Hz), 7.25 (dd, 2H, J = 7.7Hz).

# *N-(1',13'-bis(p-tolyloxy)tridecan-7'-yl)-2,7-dibromo-carbazole*(**6**)

In a flame-dried 250 mL round-bottom flask under argon, a solution of 3 (17.01 g, 30 mmol) in DMSO (50 mL) was added dropwise to a stirred solution of 5 (6.52 g, 20.0 mmol) and KOH (5.61 g, 100 mmol) in DMSO (60 mL). The reaction mixture was stirred at rt for 8 h, then poured into water (200 mL), extracted with DCM ( $3 \times 100$  mL). The combined organic fractions were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by silica gel column chromatography with petroleum ether [49] (11.13 g, yield: 77%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.98 (t, 2H, J = 8.4 Hz), 7.60 (d, 2H, J = 7.9 Hz), 7.35 (dd, 2H, J = 8.1 Hz), 7.08 (d, 4H, J = 7.8 Hz), 6.80 (d, 4H, J = 8.0 Hz), 4.47 (m, 1H, J = 7.4), 3.80 (t, 4H, J = 6.9 Hz), 2.42 (s, 6H), 1.58~1.08 (m, 20H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 156.92, 129.81, 129.65, 122.43, 121.53, 121.29, 119.82, 119.22, 114.36, 112.08, 68.04, 67.81, 56.99, 33.44, 29.11, 29.04, 26.70, 25.77, 20.43.

*N*-(*1'*,13'-dibromotridecan-7'-yl)-2,7-dibromo-carbazole (7) A mixture of **6** (11.0 g, 15.22 mmol), hydrobromide (60 g, wt 50%) in glacial acetic acid (150 mL) was refluxed under argon for 48 h. The reaction mixture was poured into water (300 mL), extracted with DCM (3 × 100 mL), the combined organic fractions were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The white residue was purified by silica gel column chromatography with petroleum ether to yield pure product (7.72 g, yield: 76%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.90 (t, 2H, *J* = 8.0 Hz), 7.65 (d, 2H, *J* = 8.2 Hz), 7.37 (d, 2H, *J* = 7.9 Hz), 4.51~4.38 (m, 1H), 3.35 (t, 4H, *J* = 7.6 Hz), 2.18~2.06 (m, 4H), 1.82~1.68 (m, 4H), 1.30~1.22 (m, 4H), 1.20~0.86 (m, 8H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 122.50, 121.59, 121.34, 119.86, 119.25, 114.42, 112.03, 56.83, 33.79, 33.33, 32.49, 28.37, 27.79, 26.52.

# *N-(1',13'-(N,N-diethylamino)tridecan-7'-yl)-2,7-dibromo-carbazole (M1)*

To a solution of 7 (15 g, 22.6 mmol) in DMF (50 mL) under argon, diethylamine (30 mL) was added in one portion. The mixture was refluxed with vigorously stirring for 12 h under argon atmosphere. After the reaction was cooled to rt, the mixture was poured into ice water, and the aqueous layer was extracted with DCM for several times. The combined organic layers were washed with water and brine, dried over anhydrous MgSO<sub>4</sub>. After removal of the solvent by rotary evaporation, the residue was purified by silica gel column chromatography (petroleum/ethyl acetate/triethylamine, v:v:v = 20:1:0.5) to afford **M1** as pale-yellow viscous liquid [39] (12.52 g, 85%).<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.85 (t, 2H, J = 7.8 Hz), 7.68 (d, 2H, J = 8.2 Hz), 7.35 (d, 2H, J = 8.3 Hz), 4.51~4.32 (m, 1H), 2.50 (q, 8H, J = 6.9Hz), 2.30 (t, 4H, J = 7.4 Hz), 2.10~1.98 (m, 4H), 1.28~1.16 (m, 6H), 1.11~0.68 (m, 22H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 122.10, 121.50, 121.40, 119.45, 114.44, 112.10, 56.98, 52.60, 46.90, 33.55, 29.31, 29.20, 27.30, 26.90, 11.60.

### 2.3 General procedure to prepare PCNs

Polymerization reactions were carried out by palladium(0)catalyzed Suzuki cross-coupling reactions. Diboronic ester/acid monomer (0.5 mmol) and dibromo monomer **M1** (0.5 mmol) were mixed with Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mg) in a mixture of 20% aqueous tetraethylammonium hydroxide (1 mL), toluene (10 mL) and THF (5 mL) under argon. After degassing, the reaction mixture was vigorously stirred at 90 °C for 48 h. The end groups were capped by refluxing 6 h with phenylboronic acid and then bromo-benzene, respectively. After the mixture was cooled to rt, it was poured into methanol (200 mL). The precipitate was collected by filtration through a funnel. The resulting solid material was washed for 24 h using acetone in a Soxhlet apparatus to remove oligomers and catalyst residues. The remaining material was dissolved in 30 mL of toluene, and filtered through a 0.45  $\mu$ m PTFE filter. The filtrate was concentrated, and the solid residue was triturated with methanol, and dried under vacuum to give the anticipated polymers, yield: 65–85%.

# Poly[N-9'-heptadecanyl-2,7-carbazole-alt-N-(1',13'-(N,N-di ethylamino)tridecan-7'-yl)-2,7-carbazole] (PCCN)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.22~7.70 (br, 12H), 4.90~4.45 (m, 2H), 2.60~2.40 (m, 8H), 2.35~2.00 (m, 8H), 1.88~0.62 (br, 60H).  $M_{\rm n}$  = 36500,  $M_{\rm W}/M_{\rm n}$  = 1.62,  $T_{\rm d(5\%)}$  = 425 °C.

## *Poly*[9,9-dioctyl-2,7-fluorene-alt-N-(1',13'-(N,N-diethylami no)tridecan-7'-yl)-2,7-carbazole] (PFCN)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.12~7.24 (br, 12H), 4.56~4.45 (m, 1H), 2.62 (q, 8H, J = 6.8 Hz), 2.36 (t, 4H, J =7.3 Hz), 2.18~1.98 (m, 8H) 1.92~1.80 (m, 8H), 1.82~0.61 (br, 50H).  $M_{\rm n} = 64900$ ,  $M_{\rm W}/M_{\rm n} = 1.69$ ,  $T_{\rm d(5\%)} = 427$  °C.

### *Poly*[1,4-phenylene-alt-N-(1',13'-(N,N-diethylamino)tridecan-7'-yl)-2,7-carbazole] (PPCN)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.12~7.20 (m, 10H), 4.56~4.36 (m, 1H), 2.58~2.41 (m, 8H), 2.38~2.22 (m, 4H), 2.17~1.98 (m, 4H), 1.20~0.60 (m, 28H).  $M_n$  = 29300,  $M_W/M_n$  = 1.53,  $T_{d(5\%)}$  = 419 °C.

#### 2.4 PLEDs fabrication and characterization

For the PLED devices, a thickness of 40 nm PEDOT:PSS (Baytron P4083, BayerAG) layer was spin-coated on a pre-cleaned ITO substrate and dried by baking at 200 °C for 10 min to remove residual water. Then, 90 nm poly[2-(4-(3',7'-dimethyloctyloxy)-phenyl)-p-phenylenevin ylene] (P-PPV) (the structure shown in Scheme 1) layer was spin-casted onto PEDOT:PSS from p-xylene solution. The electron injection materials PCNs were spin-coated onto P-PPV layer from methanol/acetic acid as cathode interlayer. Finally, an 80 nm thick aluminum was thermally deposited as cathode through a shadow mask (defined active area of 0.19 cm<sup>2</sup>) in a chamber with a base pressure of  $<5 \times 10^{-4}$  Pa. The cathode thickness was monitored upon deposition by using a crystal thickness monitor (Sycon). Profilometry (Veeco Dektak150) was used to determine the thickness of the polymer films. Device fabrication was carried out in a N<sub>2</sub> atmosphere dry-box (Vacuum Atmosphere Co.). J-V-L data were collected using a Keithley 236 source meter and a calibrated silicon photodiode in the N2 atmosphere dry-box. After typical encapsulation of the devices with UV epoxy and cover glass, the devices were taken out from dry-box and the external electroluminescence quantum efficiencies (EQEs) were obtained by measuring the total light output in all directions in an integrating sphere (IS-080, Labsphere).

#### **3** Results and discussion

### 3.1 Synthesis and characterization

The chemical structures and synthetic route are shown in Scheme 1. Mono-alkylation of 1,6-dibromohexane with *p*-cresol through Williamson reaction afforded the ether 1. The resulting Grignard reagent from 1 reacted with ethyl formate, leading to the alcohol 2 with a good yield and high purity after distillation under reduced pressure. The tosylate derivative 3 was obtained from alcohol 2 and *p*-toluenesulfonyl chloride in 78% yield. The alkylation reaction of 2,7-dibromo-carbazole 5 with compound 3 was carried out following the procedure described by Marzoni and Garbrecht [49]. The bromide 7 was obtained by treating 6 with aq. HBr and acetic acid, which was further converted to M1 by displacement with excess diethylamine in DMF under argon. Their chemical structures were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

With the key intermediate **M1** in hand, copolymerization with either **M2**, **M3** or **M4** was performed using the standard Pd-catalyzed Suzuki cross-coupling conditions to afford PCNs. All the polymers display excellent solubility not only in common organic solvents (such as THF, chloroform, toluene) due to their long branched alkyl substitutions in the side chains of the polymers, but also in alcohol solvents in the present of trace acetic acid due to the weak interaction between the amino groups in the side chains and acetic acid. In addition, the added acetic acid could be completely removed from the polymers after dried in vacuum, which is beneficial for the fabrication of multilayer PLEDs [41].

The number molecular weight  $(M_n)$  estimated by gel permeation chromatography (GPC) against the polystyrene standard with THF as an eluent ranged from 29300 to 64 900, with a polydispersity index  $(M_w/M_n)$  from 1.53 to 1.69. The thermal properties of the polymers were studied by thermogravimetric analysis (TGA). Figure 1 shows the



Figure 1 Thermogravimetric analysis plots of PCNs.

thermograms of these copolymers, in the temperature range from 25 to 800 °C in the nitrogen atmosphere. The copolymers exhibited excellent thermal stability with 5% weight-loss temperature ( $T_{d(5\%)}$ ) over 400 °C, indicating the polymers can resist the degradation at the operating temperatures of the resulting PLEDs.

### 3.2 Photophysical properties

Figures 2 and 3 show the UV-vis absorption and PL spectra of the polymers in chloroform and in solid film, respectively. Relevant optical parameters are summarized in Table 1. The absorption peak of PPCN in chloroform is observed at 373 nm, while the absorption in film exhibits a little red-shift and peaks at 385 nm. PFCN and PCCN exhibit red-shift of about 15 nm in the absorption spectra as compared with that of PPCN both in chloroform and thin films. This could be attributed to the more effective  $\pi$  electron delocalization in the polymer main chain. The absorption edges of the resulting polymers in thin films were almost identical and located at 423, 426 and 424 nm for PCCN, PFCN and PPCN, respectively, from which the optical band gaps ( $E_g$ ) were calculated to be 2.93 eV for PCCN, 2.91 eV for PFCN, and 2.92 eV for PPCN.

As shown in Figures 2 and 3, all the PCNs copolymers exhibit blue fluorescence under 370 nm excitation from HeCd laser [46–51]. The PL spectra of PFCN and PPCN are red-shifted compared with that of PPFN in chloroform, which are consistent with those observed in the absorption spectra. The PL spectra of all PCNs copolymers show maximum of emission at around 430 nm followed by vibronic sidebands at 450 nm in the solid state. The PFCN and PCCN exhibit broader PL spectra in thin film compared to that of PPCN, suggesting more pronounced aggregation of polymer chains as would be expected on the basis of their more rigid backbone structures.



Figure 2 Absorption and PL spectra of PCNs in CHCl<sub>3</sub>.



Figure 3 Absorption and PL spectra of PCNs in films.

#### 3.3 Electrochemical properties

The electrochemical properties of the polymers were investigated by CV in argon-saturated anhydrous solutions of 0.1 M  $Bu_4NPF_6$  in acetonitrile at a scan rate of 50 mV s<sup>-1</sup> at rt. A platinum electrode coated with a polymer thin film was used as the working electrode. A Pt wire and SCE were used as the counter and reference electrode. The p-doping waves were recorded, but the n-doping process could not be detected in these copolymers. Figure 4 shows C-V curves of the PCNs films measured in 0.1 M  $Bu_4NPF_6$  versus ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) in acetonitrile. Relevant electrochemical and energy level parameters were also summarized in Table 1.

The highest occupied molecular orbital (HOMO) energy levels were calculated according to the empirical formula  $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.80)$  (eV) using ferrocene value of 4.8 eV



Figure 4 CV curves of the PCNs films measured in 0.1 M  $Bu_4NPF_6$  versus Fc/Fc<sup>+</sup> in acetonitrile.

Polymer	$\lambda_{abs}$ (nm)		$\lambda_{\rm em}$ (nm)		$F(\alpha V)$	$E_{(aV)}$	$E_{\rm HOMO}$ <sup>a)</sup>	E <sub>LUMO</sub> <sup>b)</sup>
	CHCl <sub>3</sub>	film	CHCl <sub>3</sub>	film	$L_{g}(eV)$	$L_{\text{ox}}(\mathbf{ev})$	(eV)	(eV)
PCCN	389	398	419	430	2.93	0.48	-5.28	-2.35
PFCN	391	395	421	433	2.91	0.58	-5.38	-2.47
PPCN	373	385	414	428	2.92	0.63	-5.43	-2.52

Table 1 Optical and electrochemical properties of the polymers

a)  $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.80) \text{ eV}$ ; b)  $E_{\text{LUMO}} = (E_{\text{HOMO}} + E_{\text{g}}) \text{ eV}$ 

as the internal standard [52]. With increasing electron density of the main chain, the HOMO energy levels of PCNs increased progressively. The HOMO energy levels of PPCN, PFCN, and PCCN were calculated to be -5.43, -5.38, and -5.28 eV, respectively. The lowest unoccupied molecular orbital (LUMO) levels were estimated from HOMO levels and the  $E_g$ . The LUMO levels of PPCN, PFCN, and PCCN were calculated to be -2.52, -2.47, and -2.35 eV, respectively.

### 3.4 Cathode interlayer function in PLEDs

PCNs with polar pendant amine groups can not only dramatically improve charge injection from high WF metal electrode into EML, but also, due to their excellent solubility in polar solvents, can prevent interfacial mixing between the EML and the adjacent electron transporting layer (ETL). These characteristics suggest that PCNs can be promising new materials for cathode interfacial engineering in PLEDs and improve the overall performance. Herein, PCNs were used as cathode interfacial materials in PLEDs to systematically investigate the relationships between chemical structure and optoelectronic properties.

To evaluate the electron injection properties of PCNs in PLEDs, P-PPV was used as the EML in PLEDs, with device configuration of indium tin oxide (ITO)/poly(3,4-ethyl-enedioxythiophene):poly(styrene sulfonic acid) (PEDOT: PSS)/P-PPV/interlayer/A1. The PCNs were spin-coated from methanol/acetic acid solution onto the P-PPV layer, followed by evaporation of a 100 nm thick A1 cathode. For comparison, the devices using A1 and Ba/A1 as the cathode were also fabricated.

Figure 5 shows the electroluminescence (EL) spectra of the PLEDs. Figure 6 shows the current density (*J*) and luminance (*L*) versus voltage (*V*) characteristics of different devices. Figure 7 shows the luminance efficiency (*LE*) versus *J* characteristics of different devices. Table 2 summarizes device performance at J = 30 mA cm<sup>-2</sup>. As shown in Figure 5, all devices give similar EL spectra, indicating that their exciton recombination zones are all in the P-PPV layer.

Clearly, the bare Al device exhibits very poor device performance due to the high WF of Al (~4.3 eV), with a large barrier for the electron injection from Al cathode into the P-PPV EML. As shown in Figure 7 and Table 2, the bare Al cathode device shows a *LE* of 0.27 cd  $A^{-1}$  with a



Figure 5 EL spectra of the PLEDs.



**Figure 6** J-L-V characteristics of the green devices with different cathodes.

luminance of 97 cd m<sup>-2</sup> at the J = 30 mA cm<sup>-2</sup>, together with maximum *LE* (*LE*<sub>max</sub>) of 0.28 cd A<sup>-1</sup> and maximum *L* (*L*<sub>max</sub>) of 264 cd m<sup>-2</sup>. The device with the low WF metal Ba as the cathode shows much improved device performance due to the greater electron injection from Ba cathode into EML. The turn on voltage (*V*<sub>on</sub>) decreased from 5.4 V for the Al cathode device to 2.8 V for Ba cathode device. The

Cathode	$V_{\rm on}{}^{\rm a)}$	Voltage b)	Brightness b)	LE <sup>b)</sup>	EQE b)	Brightness (max)	LE (max)	EQE (max)
	(V)	(V)	$(cd/m^2)$	(cd/A)	(%)	$(cd/m^2)$	(cd/A)	(%)
Al	5.4	9.2	97	0.27	0.10	264	0.28	0.11
Ba/Al	2.8	5.4	5460	14.32	5.51	26759	16.21	6.23
PCCN/Al	3.4	8.6	3792	11.13	4.43	9805	11.16	4.44
PFCN/Al	3.2	8.6	3900	12.01	4.75	12267	12.07	4.77
PPCN/Al	3.6	8.8	3400	10.04	3.96	13145	10.06	3.97

Table 2 Device performance of PLEDs using different cathodes in device configuration ITO/PEDOT/P-PPV/ETL/Al

a) The driving voltage at a brightness of 1 cd m<sup>-2</sup>; b) device performance at a current density of 30 mA cm<sup>-2</sup>.



Figure 7 *LE-J* characteristics of the green devices with different cathodes.

Ba cathode device shows a *LE* of 14.32 cd  $A^{-1}$  with a luminance of 5460 cd m<sup>-2</sup> at the *J* = 30 mA cm<sup>-2</sup>. The Ba cathode device achieved high efficiency at the expense of sensitivity toward moisture and oxygen which is detrimental to long-term stability of device [14].

The devices with PCNs as ETL also demonstrate significantly improved device performance. By using PPCN as ETL, the device's LE reaches 10.04 cd  $A^{-1}$  with a L of 3400 cd m<sup>-2</sup> at J = 30 mA cm<sup>-2</sup>, and  $V_{on}$  decreases from 5.4 V for the Al device to 3.6 V for PPCN device. The PCCN device's LE reaches 11.13 cd  $A^{-1}$  with a L of 3792 cd  $m^{-2}$  at J = 30 mA cm<sup>-2</sup>, and  $V_{\rm on}$  of 3.4 V. Device with PFCN/A1 cathode exhibits better performance and lower  $V_{on}$ . Further increase was observed for the PFCN device performance, with a *LE* of 12.01 cd  $A^{-1}$  and a *L* of 3900 cd  $m^{-2}$  at *J* = 30 mA cm<sup>-2</sup>. The V<sub>on</sub> decreases from 5.4 V for the Al device to 3.2 V for the PFCN device, the maximum LE (LE<sub>max</sub>) reaches 12.07 cd  $A^{-1}$ , which is more than forty times higher than that of the bare Al device. The improved performance by using PCNs as ETL, indicates that electron injection from Al was facilitated. This may be attributed to the interfacial dipole formation between the pendent amino groups and the high WF metal cathode, which can lower the injection barrier at the interface [13, 33–35].

Although all the above devices with PCNs as ETL show significantly improved device performance, their individual properties are slightly different. Since PCNs have the same pendent amino groups, the differences in device performance are most reasonably attributed to the backbones. Among them, the PPCN device shows slightly lower performance with higher  $V_{on}$  of 3.6 V and lower LE<sub>max</sub> of 10.06 cd A<sup>-1</sup>. One plausible reason for the lower performance of the PPCN device, compared to those of the PFCN and PCCN devices, is that the incorporation of phenylene unit into polymer main chain could induce lesser conjugation length [38].

### 4 Conclusions

In summary, a series of alcohol soluble amino-functionalized carbazole-based copolymers with different backbone were designed and synthesized via Suzuki coupling reaction. Due to the more effective  $\pi$  electron delocalization, PFCN and PCCN exhibit red-shift in the absorption spectra as compared with that of PPCN both in chloroform and thin films. All the PCNs exhibit blue fluorescence under 370 nm excitation. With increasing electron density of the main chain, the HOMO energy levels of PCNs go up progressively. By using PCNs as ETL, the devices show significantly improved device performance attributed to the interfacial dipole formation between the pendent amino groups and the high WF metal cathode. These results support that PCNs are promising candidates as highly efficient electron injection materials for high-efficiency PLEDs.

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