

Novel Hyperbranched Polymers as Host Materials for Green Thermally Activated Delayed Fluorescence OLEDs*

Ling-yun Zhao^{a†}, Ya-nan Liu^{a†}, Shi-fan Wang^{a,b}, You-tian Tao^{a,**}, Fang-fang Wang^a,
Xin-wen Zhang^{c,**} and Wei Huang^{a,c,**}

^a Key Laboratory for Flexible Electronics & Institute of Advanced Materials (IAM), Jiangsu National Synergistic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing 211816, China

^b School of Chemistry and Chemical Engineering, Xuzhou Institute of Technology, Xuzhou 221111, China

^c Key Laboratory for Organic Electronics and Information Displays and Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing 210046, China

Abstract A series of novel hyperbranched polymers (HBPs) consisting of a 2,7-substituted 9-(heptadecan-9-yl)-9H-carbazole unit (A₂+A₂') and a tetra-substituted green thermally activated delayed fluorescence (TADF) dye of 2,3,5,6-tetra(9H-carbazol-9-yl)-4-pyridinecarbonitrile (4CzCNPy, B₄) have been synthesized *via* Suzuki cross-coupling reaction following an "A₂+A₂' + B₄" method. The polymers are named according to the polymerization ratio of 4CzCNPy monomer (5 mol%, 10 mol% and 15 mol% for HBPs of P2–P4 respectively, and 0 mol% for the control linear polymer P1). Their thermal, optoelectronic and electrochemical properties have been characterized by a combination of techniques. All the polymers exhibit high thermal stability with the decomposition temperatures (*T*_d) above 400 °C and glass transition temperatures (*T*_g) up to 98 °C. Unfortunately, the incorporation of TADF moiety into these HBP materials induced non-TADF characteristics. However, when the HBPs functionalized as the host for our previously developed 4CzCNPy TADF dopant in solution processed devices, maximum external quantum efficiency of 5.7% and current efficiency of 17.9 cd/A have been achieved in P3-based device, which is significantly higher than those of 1.5% and 4.2 cd/A for the linear polymer P1.

Keywords Hyperbranched polymers; Host; Dopant; Polymer lighting-emitting diodes; Thermally activated delayed fluorescence

INTRODUCTION

Organic light-emitting diodes (OLEDs) have attracted tremendous efforts for their great potential application in the full-color flat-panel displays and solid state lightings^[1]. Compared with most small molecular organic materials based on high-vacuum thermal deposition for device fabrication, the electroluminescence of conjugated polymers could employ a relatively simple solution process^[2, 3]. Thus, solution-processed polymer light-emitting diodes (PLEDs) have attracted much attention in both scientific and industrial communities for their advantages of good thermal stability, low-cost processing, flexibility, large area mass production, *etc*^[4–9].

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** Corresponding authors: You-tian Tao (陶友田), E-mail: iamyttao@njtech.edu.cn
Xin-wen Zhang (张新稳), E-mail: iamxwzhang@njupt.edu.cn
Wei Huang (黄维), E-mail: iamwhuang@njtech.edu.cn

† These authors contributed equally to this work.

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PLEDs based on traditional fluorescent materials are usually limited to external quantum efficiency (EQE) around 5% by spin statistic rules, which greatly restricts its comprehensive application. Additionally, the PLED devices incorporating organometallic phosphors can achieve almost 100% internal quantum efficiency (IQE) by harvesting both singlet and triplet excitons simultaneously through intersystem crossing (ISC)^[10, 11]. However, the phosphorescent materials based on heavy metal complexes generally contain noble metal such as Ir or Pt. These metals are rather expensive and dependent on limited global resources, which induced the high cost of the devices^[12]. On the other hand, very recently, thermally activated delayed fluorescence (TADF) OLEDs have attracted broad interest due to the theoretical IQE of 100%, which can harvest both singlet and triplet excitons through reverse intersystem crossing (RISC) by using relatively low-cost pure organic materials^[13]. Similar to the phosphorescent OLEDs, TADF emitters also need to be dispersed into suitable organic host materials to reduce concentration quenching and triplet-triplet annihilation to form host-dopant systems^[14]. Up until now, little progress has been made for solution processable TADF OLEDs^[15–18]; especially, the introduction of conjugated polymer materials either as the host for TADF emitters or as the single polymers with TADF characteristics^[19–24] has been rarely reported.

In comparison to the linear polymers, the electroluminescent hyperbranched polymers (HBPs) have been far less reported^[25–28]. To the best of our knowledge, the involvement of HBPs for the TADF devices has never been documented. It is generally accepted that the HBPs exhibit unique molecular shape, branching pattern, lower intrinsic viscosity, higher solubility, better processability, more stable luminescent spectrum and tunable emission colors because of their three-dimensional (3D) structures^[29, 30]. In addition, the highly branched and globular 3D structure of HBP materials has made them attractive in reducing or eliminating strong intermolecular interactions and aggregations of the polymer chains, and in some cases, improving the emission efficiency and thermal stability^[27, 31]. The HBPs can also improve the morphologies of the thin films and prevent crystallization so as to improve the stability and the efficiency of PLEDs^[32, 33]. Moreover, the HBPs have attracted considerable interest because of their convenient synthetic accessibility, typically by a one-pot synthesis, which allows for the production in an industrial scale.

Based on the concepts mentioned above, we introduced different concentrations of a green TADF dye of 4CzCNPY (according to monomer ratio for polymerization, 0 mol%, 5 mol%, 10 mol%, and 15 mol% for P1–P4 respectively)^[11], with tetra-substituted active sites to the 2,7-carbazole-based polymer backbones. The polymers have been commonly used in PLED for their favourable optical properties and outstanding hole-transporting ability^[34]. A series of polymers (P1–P4) have been synthesized *via* Suzuki coupling reaction following an “A₂+A₂’+B₄” method. The devices by using HBPs as light-emitting materials have been initially developed. Similar to the control sample of linear poly(2,7-carbazole) of P1, all the HBPs of P2–P4 only exhibited nano-scale emission lifetime. And no TADF characteristics were observed due to the quadruple conjugated linkage between 4CzCNPY-TADF moiety and the electron-donating 2-carbazole which dramatically influenced the specific donor-acceptor properties of the TADF dye. However, by using HBPs as the host materials for green 4CzCNPY TADF emitter in the solution processed devices, significantly improved device performance was achieved for the HBPs of P2 and P3 compared to the linear polymer P1.

EXPERIMENTAL

Materials

All the reagents were purchased from Energy Chemical, Suna Tech Inc., Stream, Sigma Aldrich and used without further purification. Reagent grade solvents used in this study were freshly dried using standard distillation methods, except *N,N*-dimethylformamide (DMF) was purchased from Sigma-Aldrich.

Characterization

All the materials have been fully characterized using ¹H-NMR and elemental analysis as described in the experimental section. ¹H-NMR was measured on a MECUYRVX300 spectrometer. Elemental analyses of carbon, hydrogen and nitrogen were performed on a Vario EL III microanalyzer. The transient lifetime was measured in a neat film state using the Edinburgh FLS-920 Instruments with a xenon arc lamp (Xe 900) and a

nanosecond hydrogen flash-lamp (nF920). Number-average (M_n) molecular weight and weight-average (M_w) molecular weight of all the polymers were determined by Agilent Technologies 1200 series gel permeation chromatography (GPC) running in 1,2-dichlorobenzene at 120 °C. UV-Vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. Photoluminescence (PL) spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Thermogravimetric analysis (TGA) was carried out using a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss with a heating rate of 20 K/min from 25 °C to 600 °C. Differential scanning calorimetry (DSC) was measured using a NETZSCH DSC 214 Polyma. Cyclic voltammetry (CV) was measured on a CHI660D electrochemical workstation with a solution of 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile, and the polymer film on a Pt plate as the working electrode, a platinum wire as auxiliary electrode, and an Ag wire as pseudo-reference electrode with ferrocenium-ferrocene (Fc^+/Fc) as the internal standard. The scan rate was 100 mV/s. Atomic force microscopy (AFM) was conducted on SPA300HV in tapping mode using an SPI3800 controller, Seiko Instruments Industry, Co., Ltd.

Device Fabrication and Measurements

The patterned indium tin oxide (ITO) glass substrates were ultrasonically cleaned with detergent, alcohol and acetone, deionized water and then dried at 120 °C in a vacuum oven for over 1 h. After ultraviolet (UV)-ozone treatment for 4 min, a 40 nm poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was spin-coated on the ITO substrate and dried at 120 °C in a vacuum oven for 15 min to remove the residual solvent. Afterwards, the emissive layers (EMLs) were spin-coated on the top of PEDOT:PSS from chlorobenzene and then annealed using a hot plate at 80 °C for 20 min to extract the residual solvent. The thickness of the emissive layer is about 40–45 nm. Following that, the samples were transferred into a thermal evaporator chamber. Then the electron-transport layer (ETLs) of 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBI, 40 nm), LiF (0.8 nm) and Al (100 nm) were deposited by thermal evaporation under a pressure of 5×10^{-4} Pa, respectively. The active area of the device is 13.5 mm². The current density-voltage-luminance characteristics (J - V - L) of the devices were recorded using a combination of a Keithley source-meter (model 2602) and a calibrated luminance meter. Electroluminescence (EL) spectra and Commission International De L'Eclairage (CIE) coordinates were obtained using a spectra-scan PR655 spectrophotometer. The thickness of the organic films was measured using a spectroscopic ellipsometer (α -SE, J.A. Wollam Co., Inc.). All the measurements were carried out at room temperature under ambient conditions.

Synthesis and Characterization

2,3,5,6-Tetra(3-bromo-9H-carbazol-9-yl)-4-pyridinecarbonitrile (Br4CzCNPy)

A mixture of 2,3,5,6-tetrafluoro-4-pyridinecarbonitrile (500 mg, 2.84 mmol), 3-bromo-9H-carbazole (4192 mg, 17.04 mmol) and K_2CO_3 (235 mg, 17.04 mmol) in *N,N*-dimethylformamide (DMF) (15 mL) was stirred at 150 °C for 12 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water, filtered, and then purified by column chromatography over silica gel (eluent: dichloromethane/petroleum ether = 1/4, *V/V*) to afford the title compound as a yellow solid (1.9 g, 62%). ¹H-NMR (300 MHz, CDCl_3 , δ): 7.98–7.97 (m, 2H), 7.91–7.90 (d, J = 3.0 Hz, 2H), 7.82–7.80 (m, 2H), 7.74–7.72 (d, J = 6.0 Hz, 2H), 7.17–7.13 (t, J = 6.0 Hz, 4H), 7.08–7.06 (m, 2H). MS (MALDI-TOF) [m/z], Calcd. for Br4CzCNPy: 1079.91; Found: 1079.93.

Linear polymer P1

A 25 mL schlenk tube was charged with 2,7-dibromo-9-(heptadecan-9-yl)-9H-carbazole (M1, 225.0 mg, 0.40 mmol), 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (M2, 263.0 mg, 0.40 mmol), K_2CO_3 (440.0 mg, 3.20 mmol), two drops of Aliquat 336, and a mixture of toluene/ H_2O (5/1, *V/V*). The reaction vessel was purged with nitrogen for 15 min before $\text{Pd}(\text{PPh}_3)_4$ (8.8 mg, 2 mmol%) was added. After another flushing with nitrogen for 20 min, the reactant was placed into an oil bath and stirred at 100 °C for 72 h. The mixture was cooled down to room temperature and poured into methanol (400 mL), then filtered with Soxhlet thimble, and methanol, acetone and chloroform were subjected to Soxhlet extraction. The

polymer was recovered as a solid from the chloroform fraction by precipitation from methanol. The grey solid was dried under vacuum. Yield: 360 mg (73.8%). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 8.26 (br, 2H), 7.94 (br, 1H), 7.75 (br, 1H), 7.63 (br, 2H), 4.77 (br, 1H), 2.47 (br, 2H), 2.06 (br, 2H), 1.34–1.18 (br, 24H), 0.81 (br, 6H); GPC: $M_n = 25.8$ kg/mol, $M_w = 53.8$ kg/mol, PDI = 2.08. Anal. Calcd. for P1: C, 86.35; H, 10.17; N, 3.47; Found: C, 85.57; H, 10.20; N, 3.50.

P2

A mixture of M1 (202.8 mg, 0.36 mmol), M2 (263.0 mg, 0.40 mmol), Br4CzCNPy (M3, 21.6 mg, 0.02 mmol), K_2CO_3 (440.0 mg, 3.20 mmol), $\text{Pd}(\text{PPh}_3)_4$ (8.8 mg, 2 mmol%), two drops of Aliquat 336, and toluene/ H_2O (5/1, V/V) was used to synthesize P2 according to the procedure described above. 140 mg of yellow solid was obtained. Yield: 28.7%. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 8.24 (br, 2H), 7.93–7.63 (br, 4H), 4.77 (br, 1H), 2.46 (br, 2H), 2.06 (br, 1H), 1.33–1.18 (br, 21H), 0.81 (br, 5H); GPC: $M_n = 9.8$ kg/mol, $M_w = 18.9$ kg/mol, PDI = 1.93. Anal. Calcd. for P2: C, 86.30; H, 9.87; N, 3.83; Found: C, 84.72; H, 10.27; N, 3.49.

P3

A mixture of M1 (180.3 mg, 0.32 mmol), M2 (263.0 mg, 0.40 mmol), M3 (43.2 mg, 0.04 mmol), K_2CO_3 (440.0 mg, 3.20 mmol), $\text{Pd}(\text{PPh}_3)_4$ (8.8 mg, 2 mmol%), two drops of Aliquat 336, and toluene/ H_2O (5/1, V/V) was used to synthesize P3 according to the procedure described above. 100 mg of yellow solid was obtained. Yield: 20.6%. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 8.24 (br, 1H), 7.93–7.62 (br, 3H), 4.77 (br, 1H), 2.46 (br, 1H), 2.06 (br, 1H), 1.33–1.18 (br, 21H), 0.81 (br, 5H); GPC: $M_n = 8.4$ kg/mol, $M_w = 15.6$ kg/mol, PDI = 1.89. Anal. Calcd. for P3: C, 86.00; H, 9.53; N, 4.18; Found: C, 84.43; H, 10.15; N, 3.58.

P4

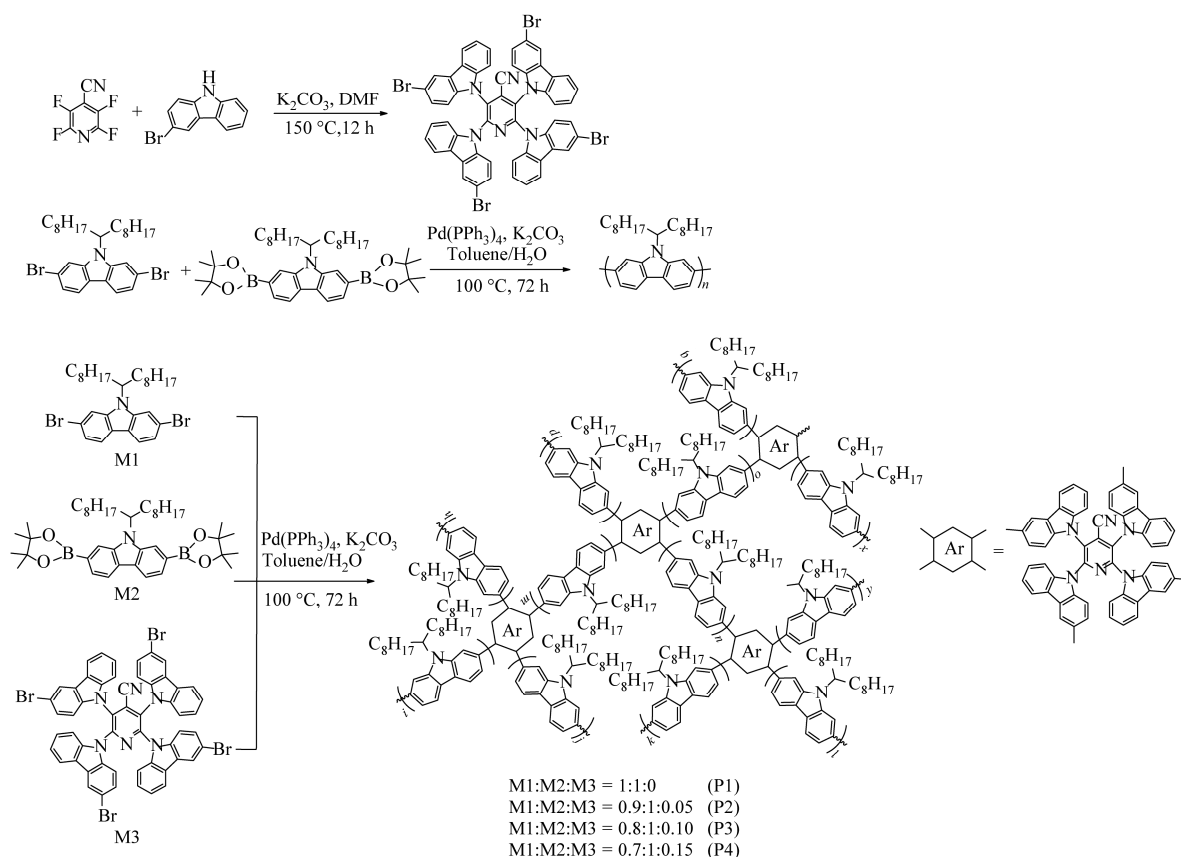
A mixture of M1 (157.8 mg, 0.28 mmol), M2 (263.0 mg, 0.40 mmol), M3 (64.8 mg, 0.06 mmol), K_2CO_3 (440.0 mg, 3.20 mmol), $\text{Pd}(\text{PPh}_3)_4$ (8.8 mg, 2 mmol%), two drops of Aliquat 336, and toluene/ H_2O (5/1, V/V) was used to synthesize P4 according to the procedure described above. 240 mg of yellow solid was obtained. Yield: 49.4%. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 8.25 (br, 1H), 7.93–7.62 (br, 3H), 4.76 (br, 1H), 2.46 (br, 1H), 2.05 (br, 1H), 1.32–1.18 (br, 18H), 0.81 (br, 4H); GPC: $M_n = 13.4$ kg/mol, $M_w = 44.5$ kg/mol, PDI = 3.32. Anal. Calcd. for P4: C, 85.70; H, 9.19; N, 4.53; Found: C, 83.39; H, 9.23; N, 4.37.

RESULTS AND DISCUSSION

The synthetic routes and chemical structures of the polymers P1–P4 are shown in Scheme 1. The monomer Br4CzCNPy was prepared using 2,3,5,6-fluoro-4-cyano-pyridine and 3-Br-carbazole as the starting materials according to our previously developed procedure for 4CzCNPy^[11]. The hyperbranched polymers (HBPs) P2–P4 were synthesized *via* Suzuki coupling polycondensation reaction following an “ $\text{A}_2 + \text{A}_2' + \text{B}_4$ ” method. By adjusting the ratios of 2,7-dibromo-9-(heptadecan-9-yl)-9H-carbazole (M1), 9-(heptadecan-9-yl)-2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (M2) and Br4CzCNPy (M3), four polymers (P1–P4) were obtained. For comparison of the optoelectronic properties with the HBPs, the linear polymer P1 was synthesized by reacting equimolar ratio of M1 and M2. All the polymers were soluble in common organic solvents, such as THF, toluene and chloroform. The molecular structure of the polymers was characterized by $^1\text{H-NMR}$ spectroscopy and elemental analysis. And the M_n and M_w of all the polymers were measured by GPC with 1,2-dichlorobenzene as the eluent and calibrated against polystyrene standards. The M_w of the polymers was in the range of 15.8–53.8 kg/mol and the polydispersity indices (PDI) of 1.89–3.32 (Table 1). It is noted that the molecular weight of the linear polymer was significantly higher than those of HBPs, which is in consistence with other examples^[27].

Table 1 Molecular weights and thermal properties of P1–P4

Polymers	M_n (kg/mol)	M_w (kg/mol)	PDI	T_d (°C)	T_g (°C)
P1	25.8	53.8	2.08	431	92
P2	9.8	18.9	1.93	403	80
P3	8.4	15.8	1.89	405	80
P4	13.4	44.5	3.32	412	98



Scheme 1 Synthetic routes to the linear polymer P1 and the HBPs P2–P4

Thermal Properties

The thermal properties of P1–P4 were measured by TGA. As shown in Fig. 1(a), all of the copolymers exhibited good thermal stability with the decomposition temperatures (T_d , measured at a 5% weight loss) over 400 °C (Table 1). The glass transition temperatures (T_g) measured from DSC were 92, 80, 80 and 98 °C for the polymers P1–P4 (Fig. 1b), respectively. The significantly lower T_g s of the HBPs P2 and P3 could be attributed to their much lower molecular weight. No crystallization and melting signal was detected, indicating the amorphous feature of all the polymers. The favorable thermal stability of these carbazole-containing polymers could be attributed to their rigid structure of the polymer backbones, which qualified the potential application of these polymer materials in PLEDs.

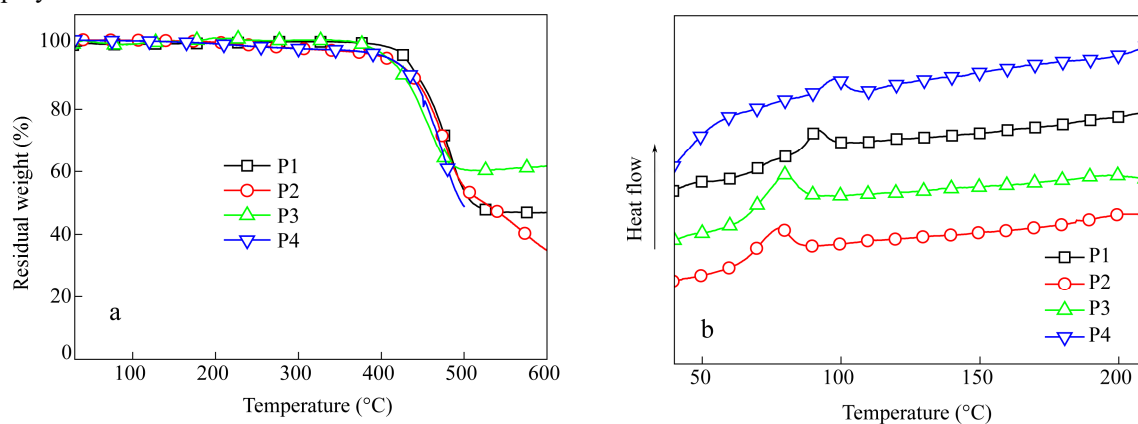


Fig. 1 TGA (a) and DSC (b) curves of the polymers

Photophysical Properties

The UV-Vis absorption and PL spectra of the polymers P1–P4 are shown in Fig. 2. All the polymers were featured by two distinct absorption peaks in both solution and film. The absorption at ~ 270 nm could be attributed to the $n\text{-}\pi^*$ transition of the polymer backbone^[35], while the longer wavelength absorption with the maxima at ~ 390 nm could be assigned to the $\pi\text{-}\pi^*$ transitions of the conjugated polymer backbone^[36]. It is noted that the $\pi\text{-}\pi^*$ transition absorption bands of P4 with the highest branching degree was obviously blue-shift to lower intensity in both solution and film, probably due to the fact that the intrinsic hyperbranched 3D structures reduced the interchain interactions, and the introduction of more 3-positioned carbazole in 4CzCNPY also reduced the conjugation degree of the polymer backbone. The optical band gaps (E_g^{opt}) of P1–P4 estimated from the onset of the absorption spectrum in solid state were similar to 2.92 eV^[37]. The PL spectra in CHCl_3 solution for all the polymers exhibited classic vibronic structures of poly(2,7-carbazoles)^[38]. Compared with the emission spectra of the linear polymer P1 in CHCl_3 , a blue-shift of 8–9 nm was observed for hyperbranched polymers of P2–P4, which is in accordance with blue-shift of $\pi\text{-}\pi^*$ transitions for less conjugation degree of the polymer backbone. However, the PL spectra varied greatly at the film state as compared to the solution. The control linear polymer P1 exhibited the narrowest deep blue emission with photoluminescence peak maxima (λ_{max}) at 423 nm and a shoulder peak at 451 nm. By increasing the 4CzCNPY ratio from 5 mol%, 10 mol% to 15 mol% for P2–P4, they exhibited the red-shifted broader emission with longer wavelength over 500 nm, which might be attributed to the intramolecular charge transfer between the 2,7-carbazoles donor and the 4CzCNPY acceptor. Besides, the relative emission intensity at 420–430 nm of P2–P4 gradually reduced, which nearly disappeared in P4 with the high 4CzCNPY content. Transient PL characteristics of all the polymers were further conducted in the film state, as shown in Fig. 2(d) and Table 2. Only prompt fluorescent emission without any delayed component was

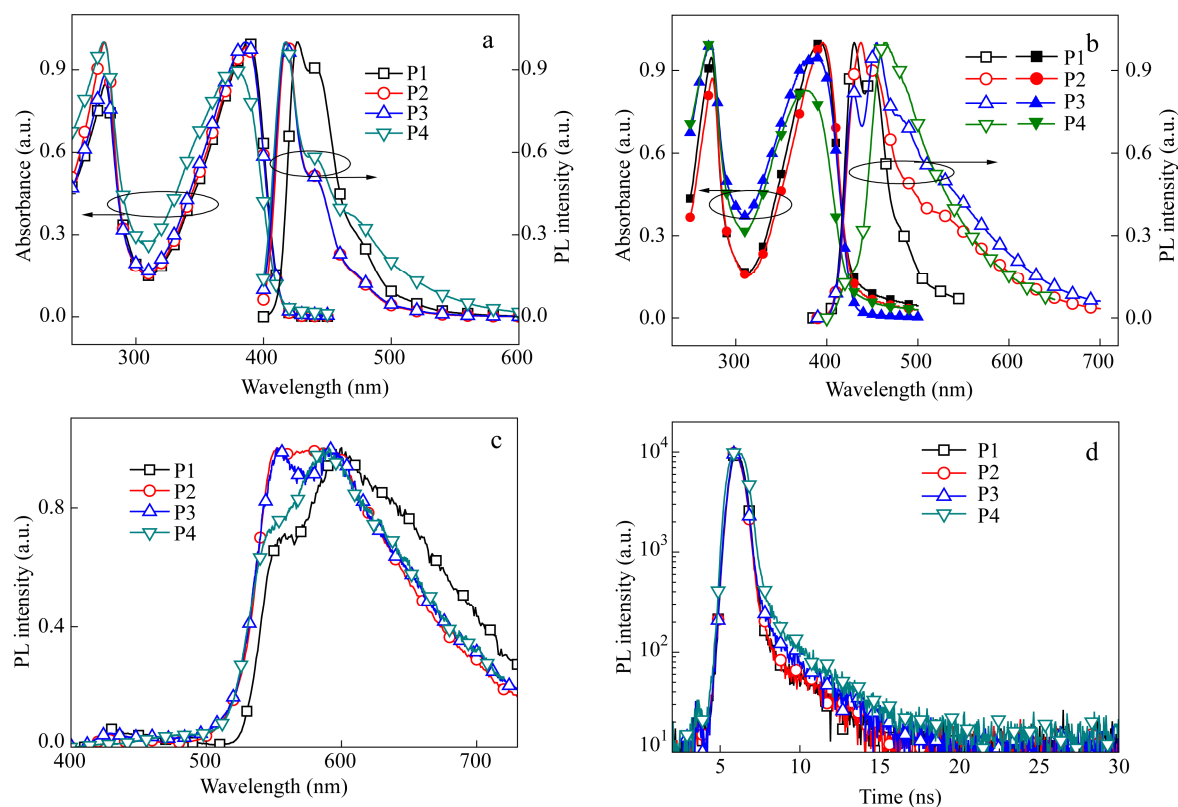


Fig. 2 Normalized UV-Vis absorption and PL spectra of polymers P1–P4 at room temperature in CHCl_3 solution (a) and film state (b), phosphorescence spectra in toluene at 77 K (c) and transient decay curves for P1–P4 in film state (d)

detected for the HBPs P2–P4, despite the introduction of TADF 4CzCNPy moiety. The decayed lifetime was all observed at nanoscale of 0.99, 0.62, 0.73 and 0.83 ns for P1–P4, respectively. It was noted that all the HBPs with TADF unit demonstrated non-TADF performance, possibly due to the extra π -conjugation between 4CzCNPy and 2,7-carbazoles which disturbed the distinct donor-acceptor (D-A) interactions for the 4CzCNPy TADF material. As shown in Fig. 2(c), the triplet energies (E_T) of the copolymers P1–P4 were calculated from the highest-energy vibronic sub-band ($T_1^{v=0} \rightarrow S_1^{v=0}$) of the low-temperature (77 K) phosphorescence spectra. Since the triplet energy for the linear polymer P1 (2.25 eV) was only slightly higher than 2.21 eV of the 4CzCNPy^[11], the corresponding HBPs with different ratio of 4CzCNPy moiety all showed similar triplet energy levels of 2.23–2.25 eV. All the key optical parameters are summarized in Table 2.

Table 2 Optoelectronic properties of P1–P4

Polymers	λ_{abs}^a (nm)	λ_{abs}^b (nm)	λ_{em}^a (nm)	λ_{em}^b (nm)	τ^c (ns)	$E_g^{\text{opt}d}$ (eV)	$E_{\text{HOMO}}/E_{\text{LUMO}}$ (eV) ^e	E_T^f (eV)
P1	388, 276	393, 274	426	423, 451	0.99	2.92	−5.30/−2.38	2.25
P2	387, 276	393, 273	418	437, 452	0.62	2.92	−5.38/−2.46	2.24
P3	386, 276	386, 273	417	429, 455	0.73	2.91	−5.37/−2.46	2.25
P4	377, 275	377, 272	417	—, 464	0.83	2.92	−5.38/−2.46	2.23

^a Absorption peaks (λ_{abs}) and photoluminescence peaks (λ_{em}) measured in dilute CHCl_3 solution at room temperature;

^b Measured in thin film; ^c Transient PL lifetime measured in solid films; ^d E_g^{opt} calculated from the absorption edge of the film UV-Vis spectra; ^e HOMO levels measured by CV, and LUMO calculated by the equation of $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g^{\text{opt}}$;

^f Triplet energy calculated from the low temperature (77 K) phosphorescence spectra in toluene

Electrochemical Properties

The electrochemical behavior of the four polymers was examined through CV by drop-casting the chloroform solution of the polymers into Pt working electrode to form the films in acetonitrile with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte. The HOMO energy levels could be estimated from the onset oxidation potential ($E_{\text{ox,onset}}$) during the anodic scan by using ferrocene (4.8 eV below the vacuum level) as the internal standard. As shown in Fig. 3, all the polymers exhibit quasi-reversible/irreversible oxidation behavior whereas non-detectable reduction processes. The onset of the oxidation potential ($E_{\text{ox,onset}}$) of the polymers (P1–P4) occurred at 0.90, 0.97, 0.98 and 0.98 V, from which the HOMO energy levels were calculated to be −5.30, −5.37, −5.38 and −5.38 eV respectively based on the equation of the $E_{\text{HOMO}} = -(4.4 + E_{\text{ox,onset}})^{[39]}$. It should be noted that the introduction of electron-withdrawing cyanopyridine units lowers the HOMO levels of the HBP P2–P4 compared to the linear poly(2,7-carbazole) of P1. The LUMO levels were calculated by the equation of $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g^{\text{opt}}$, and the E_g^{opt} was calculated from the absorption edge of the film, as listed in Table 2.

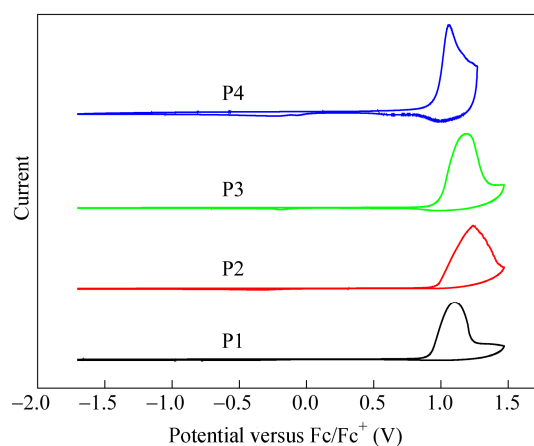


Fig. 3 Cyclic voltammograms of the polymers

Electroluminescent Devices

Using the newly designed polymers as the single-component emitting materials, PLEDs with the configuration of ITO/PEDOT:PSS (40 nm)/polymers (50 nm)/TPBI (40 nm)/LiF (0.8 nm)/Al (100 nm) were initially fabricated. Among them, PEDOT:PSS and LiF were used as the hole- and electron-injecting materials, respectively. TPBI was used to enhance the electron-injection and transport from cathode to the polymer emissive layers and also served as hole-blocking layer due to its relatively deep HOMO level of -6.3 eV^[40]. The current density-voltage-luminance characteristics (J - V - L), current efficiency, external quantum efficiency versus luminance and the electroluminescence (EL) spectra are shown in Fig. 4. The key device data are summarized in Table 3. The linear polymer P1 exhibited light blue emission with CIE coordinates at (0.27, 0.31), and the longer wavelength emission over 500 nm might be attributed to the aggregated state emission of the poly(2,7-carbazoles) and/or the exciplex emission between the donor polymer P1 and the electron-transport TPBI. Peak emission at about 425 and 454 nm of the poly(2,7-carbazole) segment declined gradually with the increase of 4CzCNPy concentration and almost entirely quenched in the HBP P4, indicating that an efficient energy transfer from the 2,7-carbazole oligomeric donor segments to the 2,7-carbazole surrounded 4CzCNPy accepting units. As mentioned in the film state PL emission, due to the non-TADF characteristics, these HPBs-containing polymer fluorescent devices demonstrated poor EL performance. The best results were achieved in the HBP P3-based device, with a maximum current efficiency of 3.9 cd/A, corresponding to the maximum external quantum efficiency of 1.6%, which were much higher than 0.9 cd/A and 0.6% of the linear polymer P1.

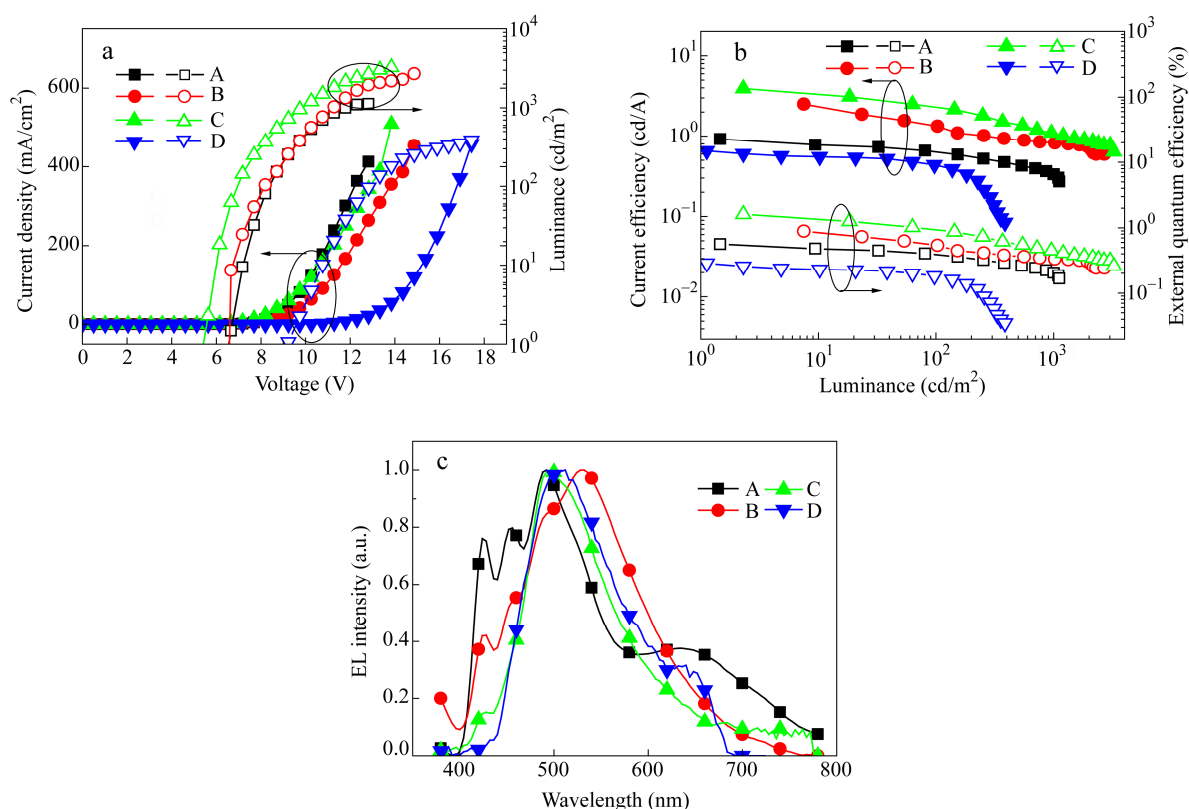


Fig. 4 Current density-voltage-luminance characteristics (a), current efficiency/external quantum efficiency versus luminance curves (b) and normalized electroluminescence spectra at 10 V (c) of devices A–D

Table 3 Electroluminescence properties of devices A–D

Device	EML	V_{on}^a (V)	L_{max}^b (cd/m ²)	$\eta_{\text{e,max}}^c$ (cd/A)	$\eta_{\text{p,max}}^d$ (lm/W)	$\eta_{\text{ext,max}}^e$ (%)	CIE (x, y) ^f
A	P1	6.5	1118	0.9	0.4	0.6	(0.27, 0.31)
B	P2	6.4	2694	2.5	1.0	0.9	(0.30, 0.40)
C	P3	5.4	3248	3.9	2.2	1.6	(0.27, 0.43)
D	P4	9.1	385	0.7	0.2	0.3	(0.29, 0.45)

^a Turn-on voltage at 1 cd/m²; ^b Maximum luminance; ^c Maximum current efficiency; ^d Maximum power efficiency; ^e Maximum external quantum efficiency; ^f Recorded at 10 V

Since polycarbazoles are commonly used as the host materials for the phosphorescent PLEDs^[34], TADF devices E–H with the structure of ITO/PEDOT:PSS (40 nm)/polymers P1–P4:4CzCNPY (8 wt%, 50 nm)/TPBI (40 nm)/LiF (0.8 nm)/Al (100 nm) were then fabricated. Among them, the linear poly(2,7-carbazole) P1 and the HBPs of P2–P4 were used as the host materials for our previously reported highly efficient green 4CzCNPYTADF dopant^[11, 41]. To the best of our knowledge, this is the first report on TADF devices which involve hyperbranched polymer materials. The current density-voltage-luminance characteristics (*J-V-L*), current efficiency, external quantum efficiency versus luminance and the EL spectra of the devices E–H are shown in Figs. 5(a), 5(b), and 5(c), respectively. The key device data are summarized in Table 4. All the devices displayed typical green emission from 4CzCNPY. When the control linear polymer P1 was employed as the host for the TADF dye of 4CzCNPY, the device E demonstrated rather poor device performance, with turn-on voltage at 7.4 V, maximum luminance of 4756 cd/m², maximum current efficiency as low as 4.2 cd/A, corresponding to the external quantum efficiency of 1.5%. However, the performance of device F and G were significantly improved by introducing the hyperbranched P2 and P3 as the host. Device G showed the best performance with a turn-on voltage of 6.0 V, maximum current efficiency, power efficiency and external quantum efficiency of 14.2 cd/A, 6.2 lm/W and 4.4%, respectively. Compared to the linear polymer P1, the introduction of electron-withdrawing cyanopyridine to the HBPs of P2 and P3 (with a certain ratio) lowered their HOMO and LUMO levels (Table 2), thus the hole-injection barrier from PEDOT:PSS to the emissive layer of HBPs increased, which decreased the hole-current in the devices F and G. However, as seen from Fig. 5(a), the current density values of device F and G were higher than that of device E based on P1 host at the same voltages. Therefore, it is deduced that the introduction of cyanopyridine to P2 and P3 significantly enhances the electron-injection and transport properties of the HBPs host, which contribute to the improved EL efficiencies of the devices F and G. On the other hand, the three-dimensional (3D) structures of HBPs could reduce or eliminate the strong intermolecular interactions and aggregation, which might be better to disperse the TADF dopant to reduce the concentration quenching and triplet-triplet annihilation. However, when the ratio of twisted 4CzCNPY moiety was further increased to 15% in the HBP P4, the EL performance of device H greatly reduced with the lowest current density, possibly because the highly branched and globular 3D structure of P4 host hindered the charge transport.

It should be noted that from the EL spectra of Fig. 5(c), the shoulder peak of the polymer host from 400 nm to 500 nm could be observed, especially in the devices E–G, which was contributed to the incomplete energy transfer from the polymer host to the TADF dopant. Therefore, the device performance was allowed to be further improved by the optimization of the doping concentration of 4CzCNPY. Thus, P3 was selected as a candidate of host material for the devices I–L with gradually increased dopant concentration of 12 wt%, 15 wt%, 20 wt% and 25 wt%. As shown from Fig. 6 and Table 4, the best performance was obtained in device I with 12 wt% of the 4CzCNPY dopant, with turn-on voltage of 5.5 V, maximum luminescence of 8887 cd/m², current efficiency of 17.9 cd/A, and power efficiency of 8.9 lm/W, corresponding to the external quantum efficiency of 5.7%. Further increase of the dopant concentration lowered the EL efficiency. Since the triplet energies of the HBPs polymers were 2.23–2.25 eV, only slightly higher or even comparable to 2.21 eV of 4CzCNPYTADF dopant, the reasonable EL efficiency achieved in this work was anticipated to be further improved by enhancing the triplet energy of the HBPs host to prevent reverse triplet energy transfer from the TADF dopant to the HBPs host.

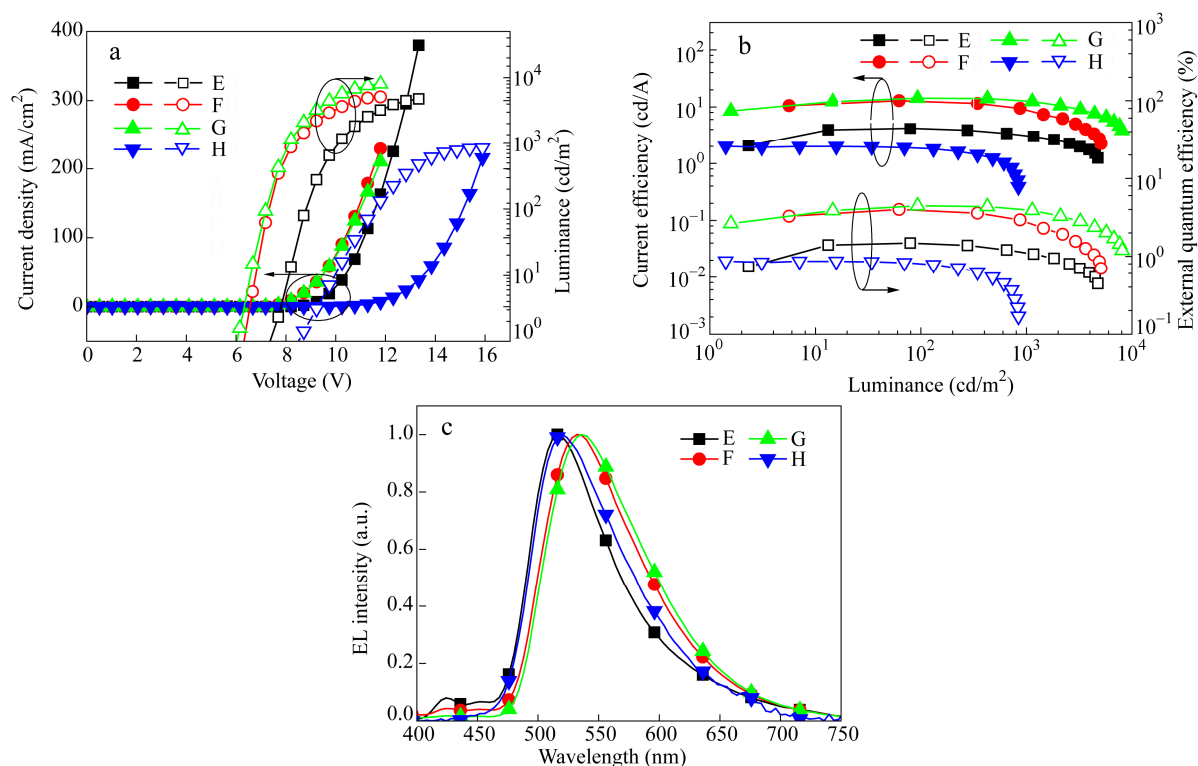


Fig. 5 Current density-voltage-luminance characteristics (a), current efficiency/external quantum efficiency versus luminance curves (b) and the normalized electroluminescence spectra at 10 V (c) of devices E–H

Table 4 Electroluminescence properties of doped devices E–L

Device	EML		V_{on}^b (V)	L_{max}^c (cd/m²)	$\eta_{\text{c, max}}^d$ (cd/A)	$\eta_{\text{L, max}}^e$ (lm/W)	$\eta_{\text{ext, max}}^f$ (%)	CIE (x, y) ^g
	Host	Dopant ^a (%)						
E	P1	8	7.4	4756	4.2	1.5	1.5	(0.31, 0.54)
F	P2	8	6.3	5107	12.8	5.6	4.0	(0.36, 0.56)
G	P3	8	6.0	8086	14.2	6.2	4.4	(0.38, 0.57)
H	P4	8	8.5	840	2.0	0.7	0.9	(0.33, 0.57)
I	P3	12	5.5	8887	17.9	8.9	5.7	(0.38, 0.55)
J	P3	15	6.5	4957	13.7	5.4	4.3	(0.39, 0.57)
K	P3	20	6.6	5123	10.8	3.7	3.3	(0.39, 0.57)
L	P3	25	7.0	4955	10.7	3.9	3.3	(0.39, 0.57)

^a Dopant concentration of 4CzCNPY; ^b Turn-on voltage at 1 cd/m²; ^c Maximum luminance; ^d Maximum current efficiency; ^e Maximum power efficiency; ^f Maximum external quantum efficiency; ^g Recorded at 10 V

Film Morphology

AFM was used to examine the film morphology of the HBPs and HBPs:4CzCNPY blends. HBPs of P3 and P3:4CzCNPY (12%) film were selected as the representatives since the best EL efficiency was achieved either in single-component emissive layer of fluorescent polymer LEDs or doped TADF LEDs. As shown in the AFM images of Fig. 7, both films are smooth and featureless. The root-mean-square (RMS) roughness of the P3 and P3:4CzCNPY blended films, which were spin-coated from chlorobenzene, and treated exactly the same as in the EL devices, were measured to be as low as 0.62 and 0.51 nm, respectively. This indicated that the hyperbranched polymers with three-dimensional-structures could induce a homogeneous morphology, which is favorable for the PLED fabrication^[42].

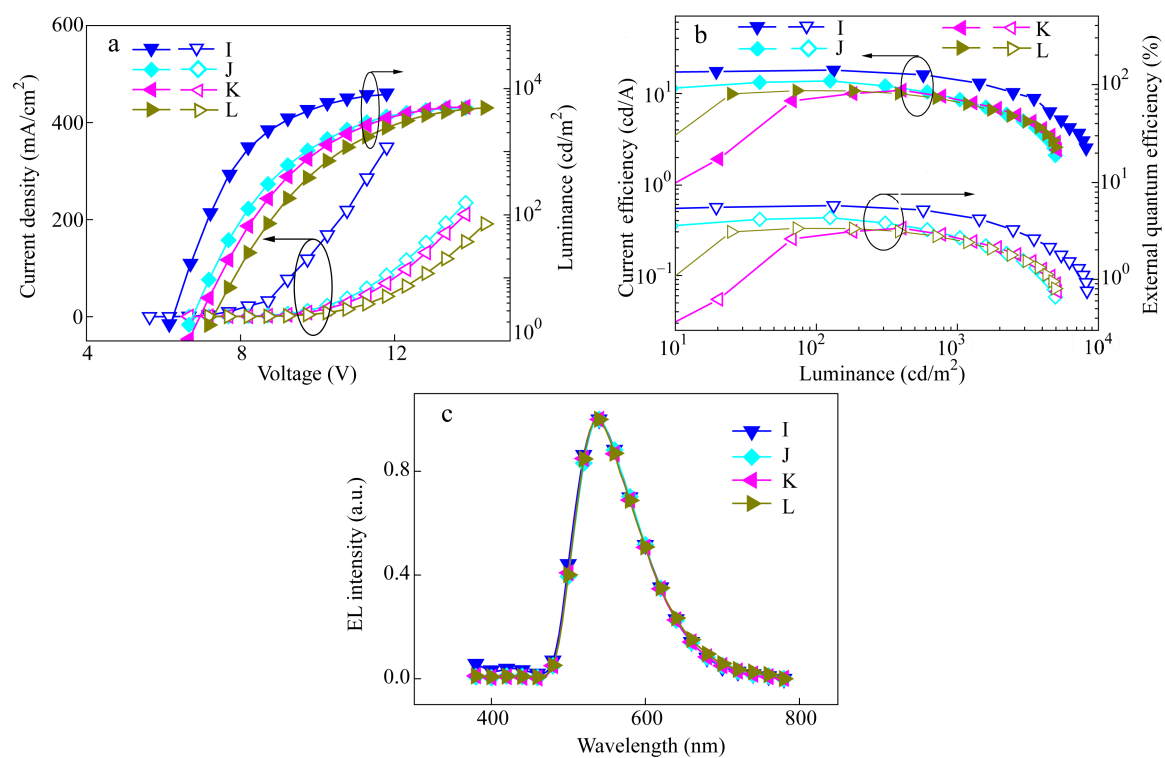


Fig. 6 Current density-voltage-luminance characteristics (a), current efficiency/external quantum efficiency versus luminance curves (b) and normalized electroluminescence spectra at 10 V (c) of devices I–L

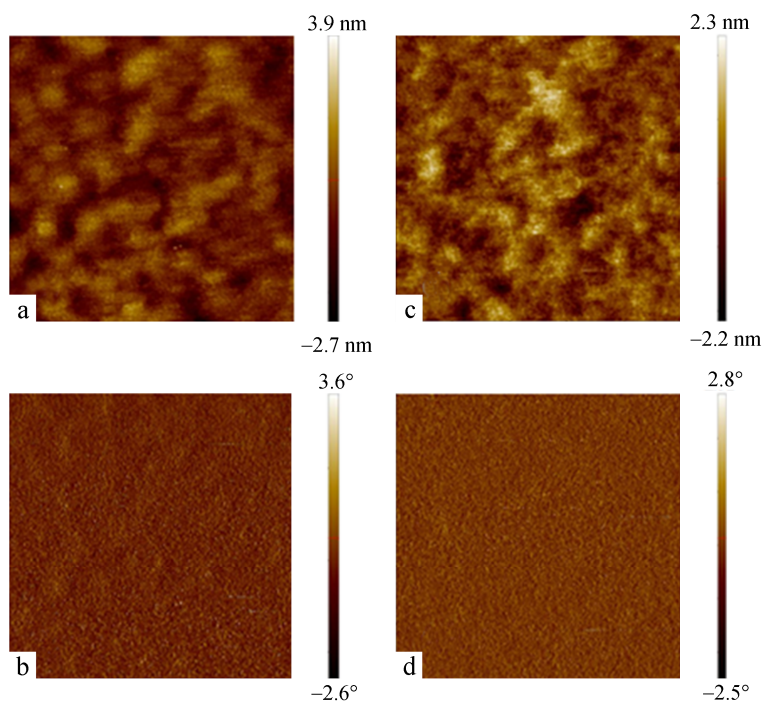


Fig. 7 AFM topographical height (top) and phase (bottom) images of P3 film (a) and (b), and P3:4CzCNPy (12%) blend film (c) and (d) (Size: 5 μm $\times$ 5 μm)

CONCLUSIONS

In conclusion, we have reported the synthesis and the characterization of new HBPs as host materials for TADF OLEDs for the first time. Compared with the linear poly(2,7-carbazole) of P1, the HBP of P3 containing 10 mol% ratio of tetra-substituted 4CzCNPy monomer and 2,7-positioned carbazoles exhibited significantly enhanced device performance when employed as the polymer hosts for the green TADF OLEDs. Maximum current efficiencies of 4.2 and 14.2 cd/A were achieved for the linear P1 and hyperbranched P3 respectively, and the device efficiency was further increased to 17.9 cd/A (corresponding to an external quantum efficiency of 5.7%) by optimizing the dopant concentration. Since the triplet energy of the HBPs host is slightly higher or even comparable to the TADF dopant in this work, it is believed that there is still considerable room for the improvement of the EL efficiency by increasing the triplet energy of HBPs host to prevent triplet energy back transfer from the TADF dopant to the host through rational molecular design. Based on the ease of synthesis and advantages over the traditional linear polymers, the HBPs with 3D-structures are expected to be potential host materials for solution-processible TADF PLEDs. The obviously improved device performance for the HBPs compared with the linear polymer indicates the successful molecular design of hyperbranched structure for the conjugated polymers.

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