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ARTICLE TYPE

Bipolar π–Conjugation Interrupted Host Polymers by Metal-Free Superacid-catalyzed Polymerization for Single-layer Electrophosphorescent Diodes

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Novel aromatic bipolar host polymers (**P1** and **P2**) containing pyridine as electron transporting unit and carbazole and fluorene as hole transporting units in the π–conjugation interrupted polymer backbone have been synthesized by metal-free superacid-catalyzed polyhydroxyalkylation. The present polymers show good thermal stability with high glass transition temperatures and decomposition temperatures. The conjugation lengths of polymers are effectively confined into the repeating units due to the δ–C bond interrupted polymer backbone giving rise to quite high triplet energy (2.79 eV for **P1**) and wide band gap around 3.33 eV, which make them promising hosts for phosphorescent OLEDs. The results suggest that the strategy of incorporating bipolar blocks into the π–conjugation interrupted polymer backbone can be a promising approach to obtain host polymer with high triplet level for green and even blue phosphorescent polymer light-emitting diodes upon simple device structure and solution-processed technique.

1 Introduction

Organic Light-emitting diodes (OLEDs) based on polymer materials have attracted considerable attention in fabricating flexible and large area flat-panel displays and lighting devices due to low-cost spin-coating or ink-jet printing technology.[1-2] To effectively utilize radiative recombination of both singlet and triplet excitons, OLEDs usually dope phosphorescent emitter into polymer matrix forming host-guest system to achieve nearly quantitative internal quantum efficiency (IQE).[3-4]

Typical host polymers such as polyfluorenes have relatively low triplet energy (E_T) (< 2.4 eV) due to the π-electron delocalizations along the polymer backbone and can only host green and red phosphorescent emitters.[5-9] For hosting blue phosphorescent emitter, the object host polymer should possess an appropriate E_T (> 2.65 eV) higher than that of phosphorescent emitter to prevent energy transfer back.[10-13] One of the representative host polymers suitable for phosphorescent blue emitters is Poly (*N*-vinylcarbazole) (PVK) which possess comparatively high E_T level of 3.0 eV nearly identical to that of the single carbazole unit due to non-conjugated polymer backbone.[14] However, the PVK-based devices usually suffer from high driving voltage because of the imbalanced carrier injection/transportation, since the hole mobility of PVK is about three orders higher than that of electron.[15-17]

Blending electron transported small molecule with PVK is a good approach to balance carrier transportation. For example, the electrophilic small molecule PBD (2-tertbutylphenyl-5-biphenyl-1,3,4-oxadiazole) is usually blended into PVK to improve electron transportation.[17-20] The added small molecule has quite lower glass transition temperature (T_g) than PVK possibly leading to phase separation under operation and decreasing device performances. Covalent attachment of the electron-transport small molecule into host polymer could be a good solution to suppress phase separation.

Giving consideration to the E_T level and charge transport properties, non-conjugated bipolar polymer hosts by simultaneously incorporating electron-rich and electron-deficient moieties have been studied recently.[21-22] Yan et al. reported a polysiloxane-typed host PCzMSi containing silicon-oxygen linkage in the backbone and carbazole moieties in the side chain with high E_T of 3.0 eV.[23] Ding et al. reported bipolar poly(aryl ether) host containing phosphine oxide in main chain and carbazole in side chain with E_T of 2.96 eV.[24] Ogino et al. reported a series of random and block copolymers containing triphenylamine and oxadiazole moieties as charge transportation layer via nitroxide mediated radical polymerization.[25] Scherf et al. reported host copolymer containing conjugated fluorenetetrafluorobenzene building blocks in non-conjugated backbone with E_T of 2.40 eV in solid state.[26]

We previously reported an aromatic host polymer PICzFB containing carbazole–tetrafluorinebeneze–carbazole repeating units in the π–conjugation interrupted backbone with considerable high E_T level of 2.73 eV and have successfully been applied in the green and even the blue PLEDs.[27] However, the π-electron delocalization in repeating units of PICzFB has not been interrupted and it would be extended along the elongated molecular axis (carbazole–tetrafluorinebeneze–carbazole) due to the para linkages of tetrafluorinebeneze with carbazole, that would lead to E_T level lowering.[28] To further interrupt π-electron delocalization, in this work, we use meta linkage carbazole–

pyridine–carbazole and fluorene–pyridine–fluorene as repeating units, respectively, in δ–C connection polymer backbone to prepare two new bipolar host polymers (**P1** and **P2**) via superacid-catalyzed metal-free polyhydroxyalkylation. Such metal-free copolymerization is essentially quite favorable for avoiding exciton quenching resulting from heavy metal catalyst residue in traditional cross-coupling copolymerization reaction.[29] The presented polymer **P1** shows quite high triplet energy of 2.79 eV due to the further all meta linkage in repeating units (carbazole–pyridine–carbazole) allowing the conjugation between the carbazole and pyridyl units interrupted. Furthermore, the simultaneous introduction of both electron-deficient pyridine and electron-rich carbazole in each repeat unit is supposed to exhibit bipolar carrier transportation characteristics.

2 Experimental part

2.1. Materials and Measurements

Tetrakis(triphenylphosphine)palladium (0), trifluoromethanesulfonic acid (TFSA), and N-methylisatin were purchased from Sigma-Aldrich Chemical Industry. Toluene and dichloromethane were distilled and dried overnight over 4A molecular sieves prior to use. Other commercially available reagents were used without further purification.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer in deuterated chloroform solution with tetramethylsilane as internal reference. UV–visible absorption spectra were recorded on a HP 8453 spectrophotometer. PL spectra were measured with a cooled charge coupled device (CCD) coupled to a monochromator using the 325-nm line of the He-Cd laser as the excitation. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). Thermogravimetric analyses (TGA) were performed on a Netzsch TG 209 at a heating rate of 20 ˚C min^{-1}. DSC measurements were performed on a Netzsch DSC 204 under N_2 flow at the heating rate of 10 ˚C min^{-1}. All samples were typically subjected to a heating scan to about 250 °C, a cooling scan to room temperature and a re-heating scan. Liquid chromatograph-mass (LC-MS) was recorded on a LCQ DECA XP spectrometer. The molecular weights of the polymers were estimated by Waters GPC 2410 with tetrahydrofuran (THF) as eluent. Cyclic voltammetry (CV) data were measured on CHI660A electrochemical workstation using tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M in acetonitrile) as electrolyte with scan rate of 50 mV s^{-1} at room temperature under the protection of argon. A platinum electrode coated with a thin polymer film was used as the working electrode, Pt wire as counter electrode and Ag wire as reference electrode. At the end of measurement, the ferrocene/ferrocium potential was measured and used as reference.

2.2. Fabrication of PLEDs

The devices with structure ITO/PEDOT:PSS/LEL/CsF/Al (ITO: iridium tin oxide, PEDOT:PSS: poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid), LEL: light-emitting layer) were fabricated followed a well-established process: PEDOT:PSS was spin-coated onto the cleaned ITO-coated glass substrate from aqueous solution and then heated at 120 ˚C for 20 min to remove the residual water solvent. Polymer doped with phosphorescent emitters was used as light-emitting layer, which was spin-coated in chlorobenzene to form a uniform 80 nm thickness film on the top of PEDOT:PSS layer. All films were then annealed at 100 ˚C on a hotplate for 20 min. A Tencor Alpha-step 500 Surface Profilometer was used to evaluate the thicknesses of polymer films. Finally, 1.5 nm CsF followed by 120 nm aluminum were thermally evaporated through a shadow mask at a base pressure of 3.0×10^{-4} Pa to form the cathode. The current density-luminance-voltage (J –L –V) characteristics were measured in the nitrogen dry-box using a keithley 236 source-measurement unit with a calibrated silicon photodiode. The electroluminescence spectra and CIE coordinates were recorded on a PR-705 SpectraScan spectrophotometer (Photo Research).

2.3. Syntheses of Monomers and Polymers

9-Decyl-3-bromo-9*H*-carbazole (2)

40 mL dried THF in a 100-mL three-neck flask was purged with nitrogen and stirred, then 1.2 g (0.05 mol) NaH was added carefully. 9.88 g (0.04 mol) 3-bromocarbazole (1) was added slowly into the mixture. 11.05 g (0.05 mol) 1-bromodecane diluted by 10 mL THF was added dropwise into the flask and refluxed for 12 h. The reactant was cooled to room temperature and then the solvent was removed by evaporation. The residue was mixed with 60 mL H_2O and extracted with methylene chloride. The extracted solution was dried with anhydrous $MgSO_4$ and then filtrated. Compound (**2**) was isolated by silica gel column chromatography with petroleum ether and ethyl acetic (20/1, v/v) as the eluent (yield 80%). ^{1}H NMR (300 MHz, DMSO, δ, ppm): 8.39 (s, 1H, ArH), 8.20 (d, 1H, *J* = 6.0 Hz, ArH), 7.56–7.62 (m, 3H, ArH), 7.48 (d, 1H, *J* = 7.20 Hz, ArH), 7.21 (t, 1H, *J* = 7.92 Hz, ArH), 4.38 (t, 2H, *J* = 7.02 Hz), 1.72–1.78 (m, 2H), 1.17–1.25 (m, 14H), 0.81 (t, 3H, *J* = 7.02 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.09, 22.64, 26.84, 27.31, 29.07, 29.24, 29.42, 29.49, 29.53, 31.83, 108.58, 109.11, 118.17, 118.78, 120.36, 122.87, 122.99, 125.61, 127.50, 133.71, 139.79, 149.68; Anal. Calcd (%) for $C_{22}H_{28}BrN$: C, 68.39; H, 7.30; N, 3.63. Found: C, 68.82; H, 7.41; N, 3.69; EIMS: *m*/*z* 386 $(M + 1)^+$.

9-Decyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9*H*-carbazole (3)

Compound (**2**) was dissolved in dry tetrahydrofuran (THF, 150 mL) and cooled to –78 °C and 1.6 M *n*-BuLi solution in hexane(1.2 eq) was slowly dropped into it under argon. The resulting solution was allowed to stir for 2 hours at –78 °C and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3 eq) was added. The mixture was warmed to RT and stirred for 24 h, then was poured into water and extracted with ethyl ether. The organic layer was dried by anhydrous magnesium sulfate. Silica gel column chromatography with petroleum ether and ethyl acetic (15/1, v/v) as the eluent to isolated compound **3** as colorless oil (yield 63%).^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.62 (s, 1H, ArH), 8.15 (d, 1H, *J* = 7.74 Hz, ArH), 7.93 (d, 1H, *J* = 8.25 Hz, ArH), 7.40–7.48 (m, 3H, ArH), 7.24 (s, 1H, ArH), 4.32 (t, 2H, *J* = 7.08 Hz), 1.85–1.90 (m, 2H), 1.25–1.42 (m, 26H), 0.87 (t, 3H, *J* = 6.27 Hz).

2,6-bis(9-decylcarbazole-3-yl)pyridine (M1)

2, 6-dibromopyridine (2.7 g, 6.23 mmol), 9-decyl- 3-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolane-2-yl)-9H-carbazole (3) (0.68g, 2.83mmol), 2M Na_2CO_3 (6 mL), toluene (20 mL) and ethanol (8 mL) were added in a 100-mL three-neck flask, and degassed for 10 minutes, then tetrakis(triphenylphosphino)Pd(0) (0.23 g, 0.1 mmol) was added to the mixture stirred and refluxed for 24 h under argon. The reaction was quenched by adding 10 ml water and extracted by chloroform (100 mL). The organic layer was subsequently washed with brine and water, and dried over by anhydrous Na_2SO_4. The solvents removed by rotary evaporation, and the residue was purified by column chromatography over silica gel using a mixture of petroleum ether and ethyl acetic (10/1, v/v) to give a white solid 1.17 g (yield, 70 %). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.94 (s, 2H, ArH), 8.41 (d, 2H, *J*=7.08 Hz, ArH), 8.26 (d, 2H, *J*=7.77 Hz, ArH), 7.80–7.88 (m, 3H, ArH), 7.44–7.57 (m, 6H, ArH), 7.30–7.32 (m, 2H, ArH), 4.38 (t, 4H, *J*=7.02 Hz), 1.89–1.96 (m, 4H), 1.27–1.43 (m, 28H), 0.89 (t, 6H, *J*=6.18 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.08, 22.64, 27.32, 29.01, 29.07, 29.25, 29.42, 29.50, 29.52, 31.84, 108.77, 108.86, 117.47, 119.02, 119.18, 120.60, 123.24, 123.34, 125.17, 125.72, 130.89, 137.30, 141.01, 141.17, 157.72; Anal. Calcd (%) for $C_{49}H_{59}N_3$: C, 85.34; H, 8.56; N, 6.09. Found: C, 85.30; H, 8.34; N, 6.08; EIMS: *m/z* 690 $(M + 1)^+$.

2-bromo-9,9-dioctylfluorene (5)

The synthesis of compound 5 was similar to that of compound 2 except that the 3-bromocarbazole (1) was replaced with 2-bromofluorene (4). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.66–7.70 (m, 1H, ArH), 7.58 (d, 1H, *J* = 6.0 Hz, ArH), 7.47 (s, 1H, ArH), 7.45 (s, 1H, ArH), 7.33–7.36 (m, 3H, ArH), 1.98 (t, 4H, *J* = 9.18Hz), 1.06–1.30 (m, 20H), 0.88(t, 6H, *J* = 6.99Hz), 0.59–0.63 (m, 4H).

9,9-dioctylfluorene-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6)

The synthesis of compound 6 was similar to that of compound 3 except that the 9-Decyl-3-bromo-9*H*-carbazole (2) was replaced with 2-bromo-9,9-dioctylfluorene (5).

2,6-bis(9,9-dioctylfluorene-2-yl)pyridine(M2)

The synthesis of **M2** was similar to that of **M1** except that the 9-decylcarbazole boronic ester (3) was replaced with 9,9-dioctylfluoren boronic ester (6) to give a white solid 0.5 g (yield, 70%). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.20 (d, 4H, *J*=9.48 Hz, ArH), 7.78–7.91 (m, 7H, ArH), 7.36–7.41 (m, 6H, ArH), 2.06 (d, 8H, *J*=8.76 Hz), 1.08–1.40 (m, 48H), 0.73–0.87 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.00, 22.56, 23.83, 29.23, 30.10, 31.77, 40.45, 55.18, 118.38, 119.80, 119.96, 121.40, 122.93, 125.93, 126.78, 127.23, 137.35, 138.38, 140.73, 142.12, 151.22, 151.35, 151.17; Anal. Calcd (%) for $C_{63}H_{85}N$: C, 88.36; H, 10.00; N, 1.64. Found: C, 87.30; H, 11.10; N, 1.56; EIMS: *m/z* 857 $(M + 1)^+$.

Syntheses of Polymers

The polymers were prepared according to the literature method[26] as follows: Trifluoromethanesulfonic acid (0.5 ml) was added to a mixture of dichloromethane (3 mL), N-methylisatin (0.5 mmol), and **M1/M2** (0.5 mmol). The reaction mixture was stirred for 12 h at room temperature under argon before poured slowly into methanol. The resulting mixture was neutralized with 2M NaOH aqueous solution and extracted with chloroform. The organic layer was subsequently washed with brine and water, and dried over by anhydrous Na_2SO_4. The solution was concentrated by rotary evaporation, and poured slowly into methanol. The white polymers were filled off, and washed with hot methanol and acetone, and subsequently washed using Soxhlet extraction with methanol and acetone to remove oligomers and catalyst residues and dried under vacuum to give white polymer fibers.

Poly{[2,6-bis(9-decylcarbazole-3-yl)pyridine-6,6′-diyl]-alt-[N-methylisatin-2-one-3, 3-diyl]} (P1). 260 mg, yield: 90 %. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.64 (s, 2H, ArH), 8.46 (d, 2H, *J*=9 Hz, ArH), 8.13 (s, 2H, ArH), 7.73 (s, 3H, ArH), 7.47–7.54 (m, 5H, ArH), 7.34–7.38 (m, 3H, ArH), 7.17 (t, 1H, *J*=7.32 Hz, ArH), 7.02 (d, 1H *J*=7.62 Hz, ArH), 4.3 (s, 4H), 3.41 (s, 3H), 1.87 (s, 4H), 1.23–1.34 (m, 28H), 0.85 (t, 6H, *J*=6.06 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.10, 22.64, 26.84, 27.31, 29.07, 29.24, 29.42, 29.49, 29.53, 31.83, 62.69, 108.91, 120.17, 123.04, 126.87, 134.34, 140.11, 141.47, 157.56, 178.86.

Poly{[2,6-bis((9,9-dioctylfluoren-2-yl)pyridine-7,7′-diyl]-alt-[N-methylisatin-2-one-3, 3-diyl]} (P2). 290 mg, yield: 89 %. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.20 (d, 2H, *J*=8.76 Hz, ArH), 8.12 (s, 2H, ArH), 7.74–7.87 (m, 6H, ArH), 7.66 (d, 2H, *J*=8.43 Hz, ArH), 7.28–7.39 (m, 5H, ArH), 7.11 (t, 1H, *J*=7.47 Hz, ArH), 6.99 (d, 1H, *J*=7.8 Hz, ArH), 3.39 (s, 3H), 1.87–1.98 (m, 8H), 1.06–1.45 (m, 48H), 0.72–0.85 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.10, 22.61, 22.62, 24.00, 26.76, 29.28, 29.35, 30.10, 31.83, 40.12, 55.24, 62.94, 118.41, 119.93, 121.32, 123.06, 126.05, 127.27, 128.23, 138.35, 139.83, 141.33, 141.69, 143.18, 151.41, 151.52, 157.14, 177.61.

3 Results and discussion

3.1. Synthesis of Monomers and Polymers

The **M1/M2** was synthesized by Suzuki-type aryl-aryl cross-coupling between the boronic ester (3 or 6) and the aryl halides. The polymers were prepared by metal-free, superacid-catalyzed polyhydroxyalkylation (**Scheme 1**). N-methylisatin was used as hydroxymethylation component coupling with bifunctional aromatic monomers at the electron-rich positions (3,6 positions for carbazole (M1), 2,7 positions for fluorene (M2)), in the presence of TFSA, to give linear, high molecular weight polymers. The number average molecular weights (M_n) of P1 and P2 are estimated by gel permeation chromatography using tetrahydrofuran as eluent (Table 1). The evidence of polymerization includes the emergence of a new signal with δ = 3.40 ppm in ^1H NMR spectrum of P1/P2, as can be ascribed to the methyl group in the *N*-methylisatin unit, indicating the connection of *N*-methylisatin unit with M1/M2 unit (**Fig. S3-S6**).

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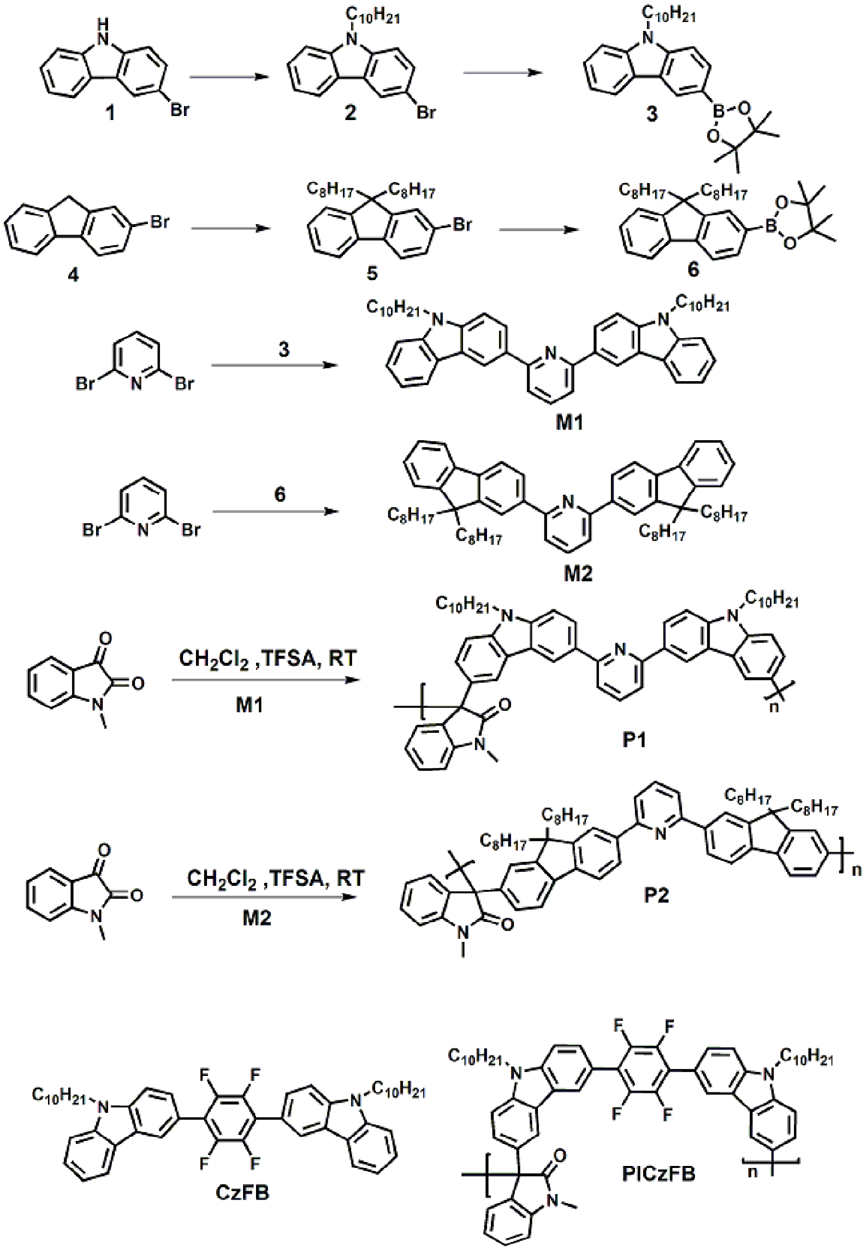

Scheme 1 Synthetic routes of the monomers and polymers

3.2. Thermal Properties

Thermal properties were investigated by thermogravimetric analyses (**TGA**) (**Fig. 1)** and differential scan calorimetry (**DSC**) and the data are shown in Table 1. The polymers exhibit good thermal stabilities, with comparatively high glass transition temperatures (T_g) (185˚C for P1, 110˚C for P2) and decomposition temperatures (T_d corresponding to 5 wt % loss) (414˚C for P1, 405˚C for P2). The high T_g and T_d are important for the practical PLED of polymer materials, and it would be expected to prevent device degradation during the long-term operation.

3.3. Electrochemical Properties

Electrochemical properties of the polymers were investigated by cyclic voltammetry (**Fig. 2**) and summarized in Table 1. The onset of oxidation potentials of **P1** and **P2** are 0.92 and 1.11 V versus ferrocene/ferrocenium (Fc/Fc^+). The reduction processes of the polymers cannot be observed, and the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are calculated according to the equation: $E_{\mathrm{HOMO}} = -\mathrm{e}(E_{\mathrm{ox,onset}} + 4.80)$ eV, $E_{\mathrm{LUMO}} = E_{\mathrm{g}} - E_{\mathrm{HOMO}}$, with regard to the energy level of ferrocene 4.8 eV below vacuum. The calculated HOMO/LUMO of **P1** and **P2** are -5.72/-2.39 eV and -5.91/-2.57 eV, respectively. The higher HOMO of **P1** can be attributed to the electron-rich nature of carbazole units which increase the electron density of the polymer.

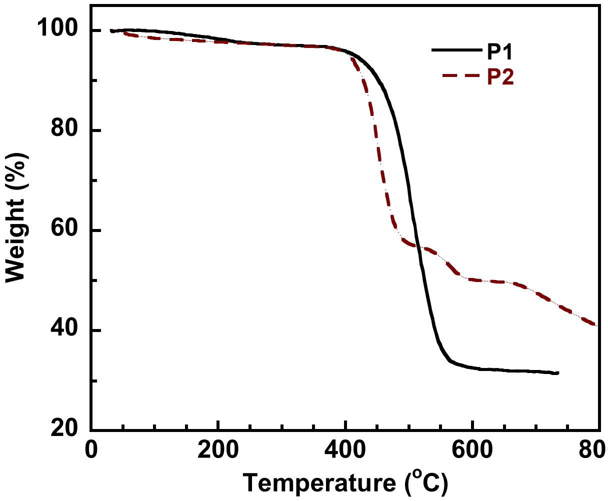

Fig. 1 TGA curves of P1 and P2.

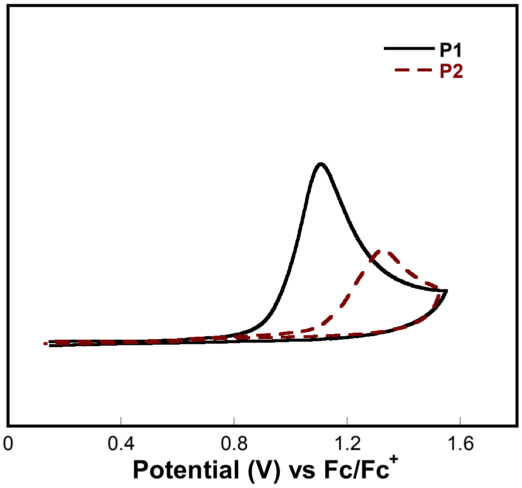

Fig. 2 Cyclic voltammograms of P1 and P2 in acetonitrile solution.

3.4. Photophysical Properties

The absorption spectra of **P1** and **P2** were measured in dilute CH_2Cl_2 solution and in film state (**Fig. 3**). In solution, **P1** show absorption peaks at 252 and 299 nm possibly corresponding to the n-π* and π-π* transition, respectively, with a weak absorption at *ca*. 330 nm corresponding to the intramolecular charge transfer (ICT) with regard to the interaction between the electron-donor carbazole and the electron-withdrawing pyridine. In the case of **P2,** it show a π-π* transition absorption band centred at 340 nm and no obvious ICT transition can be observed due to the weaker electron-donor nature of fluorene. Compared to solution absorption, **P1** and **P2** films show similar profile but broader absorption bands ascribing to the molecular aggregation in solid state. The optical gaps of **P1** and **P2** are 3.33 and 3.34 eV, respectively (Table 1), as estimated from the onset of the absorption in film.

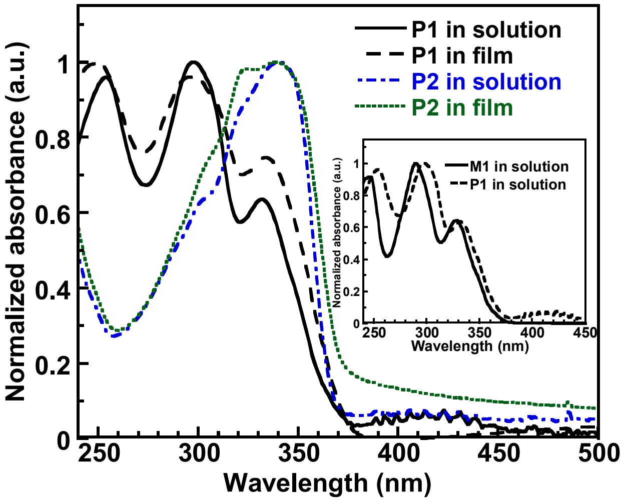

Fig. 3 Absorption spectra of P1 and P2 in solution and film state (inset: absorption spectra of M1 and P1 in dilute solution).

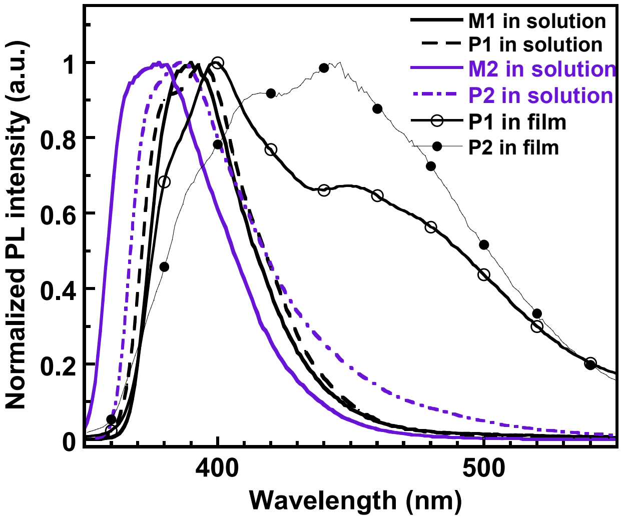

Fig. 4 PL spectra of the monomers and polymers in film and diluted solution (10^{-5} M).

To further study the effectiveness of the conjugation breaking in the polymer backbone, both photoluminescence (PL) spectra and absorption spectra of **M1/P1** and **M2/P2** were measured in CH_2Cl_2 solutions (10^{-5} M) (**Fig. 4 and Fig. S2**). The PL spectra of **P1/P2** in solution show slight red-shift (only about 5 nm) compared with that of **M1/M2**, as well as their absorption spectra (**Fig. S2** and inset of **Fig. 3**), indicating that the conjugation lengths of the polymers are successfully confined into the repeating units because of the non-conjugated δ–C bond connection in polymer backbone. However, the polymers in film show broader and red-shifted emission than in solution probably due to the severe molecular aggregation in solid state.

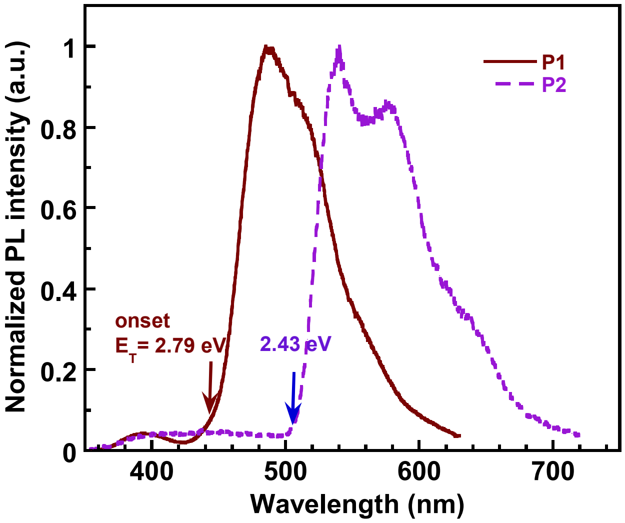

Fig.5 Phosphorescence spectra of P1 and P2 in 77 K in film state.

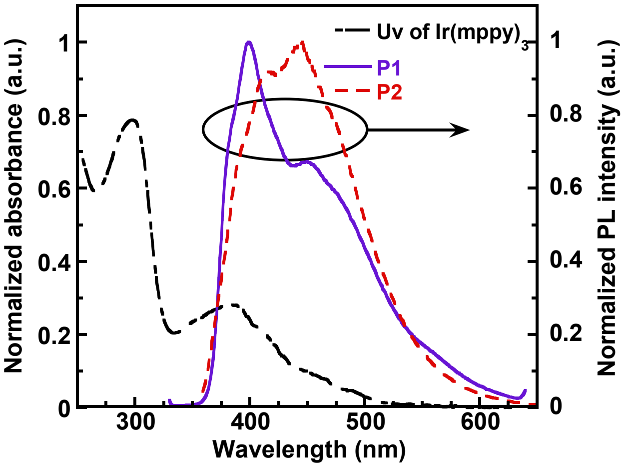

Fig. 6 PL spectra of P1 and P2 and absorption of Ir(mppy)$_3$.

The phosphorescence spectra of **P1/P2** were measured at 77 K in film according to the literature method[30] (**Fig. 5**). The triplet energy levels (E_T) of **P1** and **P2** are located at 2.79 and 2.43 eV respectively, relative to the onset of the phosphorescence spectra. The Lower E_T of **P2** can be ascribed to the fluorene unit which itself has lower triplet energy levels than carbazole unit. In addition, the para linkages of fluorene with pyridine in **P2** extend the π-electron delocalizations along fluorene–pyridine ring allowing a lower E_T. Compared to PICzFB (E_T =2.73 eV) we published earlier[27], the slightly higher E_T of **P1** (2.79 eV) could be ascribed to the all meta linkages between carbazole and pyridine units which possibly further interrupt the molecular conjugation along the repeating units and increase the triplet energy levels. It is worth mentioning that the E_T of **P1** is also higher than some copolymers published in literature such as poly(9,9-dialkyl-3,6-dibenzosilole) (2.55 eV),[31-32] poly(9,9-dioctylfluorene-2,7-diyl-co-2,8-dihexyldibenzo-thiophene-S,S-dioxide-3,7-diyl) (2.46 eV)[33] and also higher than that of the widely used green-emitting phosphorescent dopant tris(2-(4-tolyl)phenylpyridine)iridium (Ir(mppy)3) (2.38 eV)[34] as well as the blue-emitting iridium(III) [bis(4,6-difluorophenyl)pyridinato-N,C2']-picolinate (FIrpic) (2.65 eV).[35-37]

When considering that the high E_T is an important prerequisite for host materials to effectively prevent energy back transfer from phosphorescent complex to polymer host, it is thus expected that the present high-E_T copolymer have great potential for application as host for both blue and green phosphorescent emitters.

To evaluate the potential of the polymers as host for green phosphorescent PLEDs, the absorption of Ir(mppy)$_3$ (tris(2-(4-tolyl)phenylpyridine)iridium) and emission of polymers were investigated to confirm energy transfer between **P1**/**P2** and Ir(mppy)$_3$ (**Fig. 6**). As seen from Fig. 6, Ir(mppy)$_3$ exhibits a strong absorption band centred at 370 nm which overlaps well with the emission of polymers **P1** and **P2**, implying the possibly effective energy transfer from the polymers to Ir(mppy)$_3$.

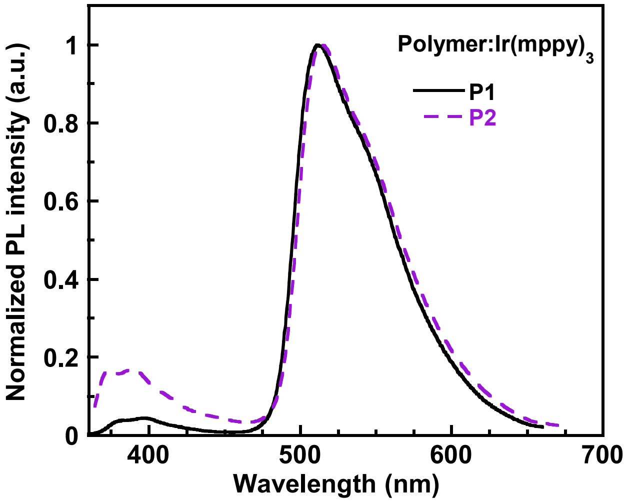

Fig. 7 PL spectra of P1 and P2 films doped with Ir(mppy)$_3$ (5 wt%).

PL spectra of **P1** and **P2** doped with Ir(mppy)$_3$ were investigated (**Fig. 7**). The blended films exhibit strong emission at 516 nm arising from Ir(mppy)$_3$, together with a minor contribution at 380 nm from the polymer. This indicates that efficient energy transfer occurs from the polymers to Ir(mppy)$_3$ and the back energy-transfers do not occur in a substantial degree. These results suggest that the polymers can be used as host for green phosphorescent PLEDs.

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Table 1 Physical and Electrochemical Properties of the Polymers.

Polymer	M_n(×10^3)	PDI	T_d^a(°C)	T_g(°C)	HOMO(eV)/E_{ox}	LUMO(eV)^b	E_g^c(eV)	E_T^c(eV)
P1	49.9	1.65	414	185	-5.72 (0.92V)	-2.39	3.33	2.79
P2	76.5	1.86	405	110	-5.91 (1.11V)	-2.57	3.34	2.43

^{a} Corresponding to 5 wt % loss. ^{b} Estimated from HOMO levels and the optical gaps. ^{c} Calculated from the onset of the spectra.

3.5. Electroluminescence Properties

Single-layer PLEDs based on **P1/P2** as host and Ir(mppy)$_3$ as guest with devices configuration ITO/PEDOT:PSS/LEL/CsF/Al were fabricated (LEL denotes **P1/P2** films doped with 5 wt % Ir(mppy)$_3$). In contrast with PL spectra, the EL (Electroluminescence) spectra of both **P1** and **P2** exhibit only green emission peaked at 515 nm deriving from Ir(mppy)$_3$ and no emission can be observed from polymers (**Fig. 8**) suggesting that both energy transfer and direct charge trapping/recombination at Ir(mppy)$_3$ were responsible for the EL mechanism.

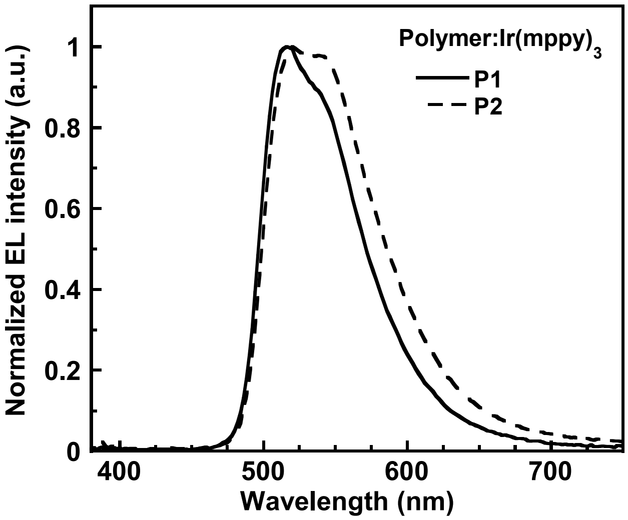

Fig. 8 EL spectra of the device ITO/PEDOT/ polymer: Ir(mppy)$_3$ (5 wt %)/CsF/Al.

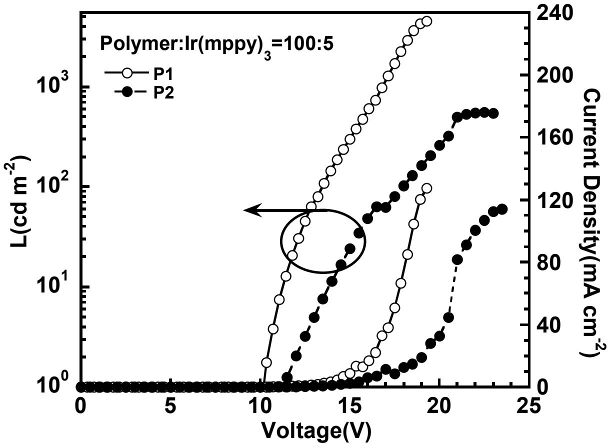

Fig. 9 Luminance-current density-voltage properties of the devices structure of ITO/PEDOT/polymer: Ir(mppy)$_3$ (5 wt %)/CsF/Al.

Luminance-current density-voltage characteristics are shown in **Figure 9** and the results summarized in Table 2. The **P1**-based device shows best EL properties with maximum external quantum efficiency of 1.26%, luminance efficiency of 4.4 cd A^{-1} and brightness of 4493 cd m^{-2} in such a preliminary device configuration, compared to the **P2**-based device and our previously reported PICzFB-based device. The higher efficiency for **P1**-device could be ascribed to higher triplet energy as well as the balanced charge transportation/injection due to the excellent hole-transport carbazole and electron-transport pyridine units incorporated in the polymer backbone. According to the energy levels, **P1** has a higher HOMO (-5.72 eV) than PICzFB (-5.82 eV) and **P2** (-5.91 eV). The high HOMO facilitates the holes injection from PEDOT to the LEL and leads to lower turn on voltage (Table 2).

Table 2 Device performance with P1/P2 as Host and Ir(mppy)$_3$ as guest (device structure: ITO/PEDOT/ polymer: Ir(mppy)$_3$ (5 wt %) /CsF/Al).

Polymer^a	V_{on}^b (V)	L_{max} (cd/m^2)	LE_{max} (cd/A)	EQE$_{max}$(%)	Brightness = 100 cd/m^2				
					V(V)	J(mA/cm^2)	LE(cd/A)	EQE (%)	CIE^c
P1	10	4493	4.4	1.26	13	2.6	4.16	1.2	(0.31, 0.61)
P2	11	552	0.98	0.39	18	12	0.81	0.32	(0.34, 0.59)
PICzFB	15	1242	4.2	1.18	22	3.2	3.7	1.1	(0.32, 0.61)

^{a} Doped with 5 wt % Ir(mppy)$_3$. ^{b} Corresponding to luminance of 1 cd m^{-2}. ^{c} Measured at 12 mA m^{-2}.

Although the efficiencies of P1-based devices are lower than those of multilayer devices reported in previous literature[38-39], the results here are obtained in a very simple device structure: single-layer device without blending additional electron/hole-transporting materials into the host which would be advantageous in the future market. The presented results suggest that **P1** actually have high triplet energy as well as balanced carrier transportation and could be a promising host polymer for green-emitting PLEDs. The relevant work of P1-host for blue-emitting PLEDs is also in progress.

4 Conclusions

In summary, two novel bipolar host polymers based on carbazole-pyridine-carbazole and fluorene-pyridine-fluorene repeating units are prepared, respectively, by metal-free superacid-catalyzed polyhydroxyalkylation. The polymers show good thermal stability with high glass transition temperatures (185 ˚C for **P1** and 110 ˚C for **P2**), wide band gap about 3.33 eV and considerable high triplet energy (2.79 eV for **P1**). Efficient single-layer green phosphorescent PLEDs are realized using **P1** as host and $Ir(mppy)_3$ as guest without blending any electron/hole-transporting materials. The superior results can be ascribed to the all meta linkages in repeating units as well as the conjugation-confined main chain by the δ–C bond interrupted polymer backbone.

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Notes and references

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