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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.1–12 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 (ET) (< 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 ET (> 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 possesses comparatively high ET 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 (Tg) 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 ET 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-type host PCzMSi containing silicon-oxygen linkage in the backbone and carbazole moieties in the side chain with high ET 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 ET 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 fluorenethetafluorobenzene building blocks in non-conjugated backbone with ET 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 ET 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 ET level lowering.28 To further interrupt π-electron delocalization, in this work, we use meta linkage carbazole–.
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.

1H NMR and 13C 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 N₂ 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 using tetrahydrofuran (THF) as eluent. Cyclic voltammetry (CV) data were measured on CHI660A electrochemical workstation using tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, 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 thin 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-9H-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-bromodecanol 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 H₂O and extracted with methylene chloride. The extracted solution was dried with anhydrous MgSO₄ and then filtrated. Compound (2) was isolated by silica gel column chromatography with petroleum ether and ethyl acetate (20/1, v/v) as the eluent (yield 80%). 1H 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). 13C NMR (75 MHz, CDCl₃, δ, ppm): 14.09, 22.64, 26.84, 27.31, 29.07, 29.24, 29.49, 29.53, 31.83, 108.58, 109.11, 118.17, 118.78, 120.12, 122.87, 129.24, 129.49, 129.53, 131.78, 131.91, 149.68; Anal. Calcd (%) for C₂₃H₂₆BrN: 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-dioxaborolan-2-yl)-9H-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-dioxaborolan (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 acetate (15/1, v/v) as the eluent to isolated compound (3) as colorless oil (yield 63%). 1H NMR (300 MHz, CDCl₃, 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-decylocbazole-3-yl)pyridine (M1)

2, 6-dibromopyridine (2.7 g, 6.23 mmol), 9-decyl-3-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl)-9H-carbazole (3) (0.68g,
2.83 mmol), 2M Na₂CO₃ (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(triphenylphosphine)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 anhydrous Na₂SO₄. 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 acetate (10/1, v/v) to give a white solid 1.17 g (yield, 70%). ¹H NMR (300 MHz, CDCl₃, 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, J=6.06 Hz). ¹³C NMR (75 MHz, CDCl₃, δ ppm): 140.18, 22.64, 23.83, 29.23, 123.04, 126.87, 134.34, 140.11, 141.47, 157.56, 178.86.

The synthesis of 2-bromo-9,9-dioctylfluorene (5) was similar to that of compound 2 except that the 3-bromocarbazole (1) was replaced with 2-bromo(4).

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The synthesis of compound 6 was similar to that of compound 3 except that the 2,6Obis(9,9OdioctylfluoreneO2Oyl)pyridine (M2) was replaced with 2-bromo-9,9-dioctylfluorene (5).

The synthesis of compound 6 was similar to that of compound 3 except that the 2,6Obis(9,9OdioctylfluoreneO2Oyl)pyridine (M2) was replaced with 2-bromo-9,9-dioctylfluorene (5).

The synthesis of compound 6 was similar to that of compound 3 except that the 2,6Obis(9,9OdioctylfluoreneO2Oyl)pyridine (M2) was replaced with 2-bromo-9,9-dioctylfluorene (5).

The synthesis of compound 6 was similar to that of compound 3 except that the 2,6Obis(9,9OdioctylfluoreneO2Oyl)pyridine (M2) was replaced with 2-bromo-9,9-dioctylfluorene (5).

Poly[[2,6-bis(9-decylcarbazole-3-yl)pyridine-6,6’-diyl]alt-[N-methylanisate-2-one-3, 3-diyl]] (P1) 260 mg, yield: 90 %.

Poly[[2,6-bis(9-decylcarbazole-3-yl)pyridine-6,6’-diyl]alt-[N-methylanisate-2-one-3, 3-diyl]] (P2) 290 mg, yield: 89 %.

The synthesis of Monomers and Polymers

The M1/M2 was synthesized by Suzuki-type ary-aryl cross-coupling between the boronic ester (3 or 6) and the aryl halides. The polymers were prepared by metal-free, superacid-catalyzed polyhydroxylation (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 (Mₐ) 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).
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

Scheme 1 Synthetic routes of the monomers and polymers
molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are calculated according to the equation: $E_{\text{HOMO}} = -e(E_{\text{ox,onset}} + 4.80)$ eV, $E_{\text{LUMO}} = E_g - E_{\text{HOMO}}$, with regard to the energy level of ferrocene 4.8 eV below vacuum. The calculated HOMO/LUMO of $P_1$ and $P_2$ are -5.72/-2.39 eV and -5.91/-2.57 eV, respectively. The higher HOMO of $P_1$ can be attributed to the electron-rich nature of carbazole units which increase the electron density of the polymer.

3.4. Photophysical Properties

The absorption spectra of $P_1$ and $P_2$ were measured in dilute CHCl$_3$ solution and in film state (Fig. 3). In solution, $P_1$ show absorption peaks at 252 and 299 nm possibly corresponding to the n-$\pi^*$ and $\pi$-$\pi^*$ 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 $P_2$, it show a $\pi$-$\pi^*$ 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, $P_1$ and $P_2$ films show similar profile but broader absorption bands ascribing to the molecular aggregation in solid state. The optical gaps of $P_1$ and $P_2$ are 3.33 and 3.34 eV, respectively (Table 1), as estimated from the onset of the absorption in film.

To further study the effectiveness of the conjugation breaking in the polymer backbone, both photoluminescence (PL) spectra and absorption spectra of $M_1/P_1$ and $M_2/P_2$ were measured in CHCl$_3$ solutions ($10^{-5}$ M) (Fig. 4 and Fig. S2). The PL spectra of $P_1/P_2$ in solution show slight red-shift (only about 5 nm) compared with that of $M_1/M_2$, 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 $\delta$–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.
The phosphorescence spectra of P1/P2 were measured at 77 K in film according to the literature method\(^\text{30}\) (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 \(\pi\)-electron delocalizations along fluorene–pyridine ring allowing a lower \(E_T\). Compared to PICzFB (\(E_T = 2.73\) eV) we published earlier\(^\text{27}\), 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-dibenzoisilole) (2.55 eV),\(^\text{31-32}\) poly(9,9-dioctyfluorene-2,7-diyl-co-2,8-dihexyldibenzo-thiophene-S,S-dioxide-3,7-diyl) (2.46 eV)\(^\text{33}\) and also higher than that of the widely used green-emitting phosphorescent dopant tris(2-(4-tolyl)phenyl)pyridine)iridium (Ir(mppy))\(^\text{3}\) (2.38 eV)\(^\text{34}\) as well as the blue-emitting iridium(III) [bis(4,6-difluorophenyl)pyridinato-N,C2']-picolinate (FIrpic) (2.65 eV).\(^\text{35-37}\)

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)\(^\text{3}\) (tris(2-(4-tolyl)phenyl)pyridine)iridium) and emission of polymers were investigated to confirm energy transfer between P1/P2 and Ir(mppy)\(^\text{3}\) (Fig. 6). As seen from Fig. 6, Ir(mppy)\(^\text{3}\) 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)\(^\text{3}\).

PL spectra of P1 and P2 doped with Ir(mppy)\(^\text{3}\) (5 wt%) were investigated (Fig. 7). The blended films exhibit strong emission at 516 nm arising from Ir(mppy)\(^\text{3}\), together with a minor contribution at 380 nm from the polymer. This indicates that efficient energy transfer occurs from the polymers to Ir(mppy)\(^\text{3}\) 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.
Table 1 Physical and Electrochemical Properties of the Polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$($\times10^3$)</th>
<th>PDI</th>
<th>$T_d$($^\circ$C)</th>
<th>$T_g$($^\circ$C)</th>
<th>HOMO(eV)/E$\text{en}_\text{m}$</th>
<th>LUMO(eV)$^b$</th>
<th>$E_p$(eV)</th>
<th>$E_t$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>49.9</td>
<td>1.65</td>
<td>414</td>
<td>185</td>
<td>-5.72 (0.92V)</td>
<td>-2.39</td>
<td>3.33</td>
<td>2.79</td>
</tr>
<tr>
<td>P2</td>
<td>76.5</td>
<td>1.86</td>
<td>405</td>
<td>110</td>
<td>-5.91 (1.11V)</td>
<td>-2.57</td>
<td>3.34</td>
<td>2.43</td>
</tr>
</tbody>
</table>

$^a$ 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:PPS/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.

![Normalized EL intensity vs. wavelength](image)

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

![Luminance vs. current density and voltage](image)

**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).

<table>
<thead>
<tr>
<th>Polymer$^a$</th>
<th>$V_{\text{on}}$(V)</th>
<th>$L_{\text{max}}$(cd/m$^2$)</th>
<th>$LE_{\text{max}}$(cd/A)</th>
<th>EQE$\text{max}$%</th>
<th>$I$(mA/cm$^2$)</th>
<th>$J$(mA/cm$^2$)</th>
<th>$LE$(cd/A)</th>
<th>EQE (%)</th>
<th>CIE$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>10</td>
<td>4493</td>
<td>4.4</td>
<td>1.26</td>
<td>13</td>
<td>2.6</td>
<td>4.16</td>
<td>1.2</td>
<td>(0.31, 0.61)</td>
</tr>
<tr>
<td>P2</td>
<td>11</td>
<td>552</td>
<td>0.98</td>
<td>0.39</td>
<td>18</td>
<td>12</td>
<td>0.81</td>
<td>0.32</td>
<td>(0.34, 0.59)</td>
</tr>
<tr>
<td>PICzFB</td>
<td>15</td>
<td>1242</td>
<td>4.2</td>
<td>1.18</td>
<td>22</td>
<td>3.2</td>
<td>3.7</td>
<td>1.1</td>
<td>(0.32, 0.61)</td>
</tr>
</tbody>
</table>

$^a$ 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