PLED Devices Containing Triphenylamine-Derived Polyurethanes as Hole-Transporting Layers Exhibit High Current Efficiencies

Supplementary Information
Experimental details and NMR, Mass spectral data of compounds 1-6, PU polymers data collected in UV-Vis, PL, IR spectra and thermo property in DSC, TGA. The PLED device fabrication details and measurements for PU polymers. (20 pages)

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**General**

$^1$H NMR spectra were recorded on a Bruker 400 MHz spectrometer. Elemental analyses were performed on an EA Heraeus Vario EL-3 analyzer. FTIR spectra were recorded using a Jasco-480 spectrometer. UV–Vis analyses were performed using a Jasco V-570 UV–Vis spectrophotometer. UV absorbance measurements of solutions were obtained after dissolving the compound (5 mg) in THF (400 mL); for films, samples were prepared by placing a drop of a pertinent THF solution (12 mg/1 mL) onto a quartz slice and spin-coating at 2000 rpm. The UV absorbance spectra of the PU solutions and films were recorded over the range 200–800 nm. The number-average and weight-average molecular weights of the polymers were determined using a Waters GPC-480 system, an AM GPC gel column (10 μm; American Polymer Standard Company), THF as the eluent, and polystyrene standards. TGA and DSC measurements were undertaken using a TGA Perkin–Elmer TGA-7 instrument and a DSC Du Pont 2010 analyzer, operated under a nitrogen atmosphere at a heating rate of 10 °C/min. The thickness of the polymer films was measured using an Alpha step Dektak 3030 profilometer. PL spectra of the polymers were recorded using a Hitachi-4500 spectrofluorometer; solutions: 5 mg/20 mL in THF; films: spin-coating a 15 mg/1 mL THF solution on a quartz slice at 2000 rpm. The excitation wavelength for the fluorescence measurements was 360 nm (Xe lamp). Electroluminescence spectra were recorded using a Minolta CS-1000 instrument. The $I$–$V$ and $L$–$V$ characteristics of the devices were measured by integrating a Keithley 2400 source-meter as the voltage and current source with a Minolta CS1000 instrument as the luminance detector. All measurement and device fabrication processes were performed in air at room temperature under dust-controlled conditions.
Synthesis of Monomers

*N,N*-Bis(4-methoxyphenyl)-*N,N*-diphenylbenzidine (1)

*N,N*-Diphenylbenzidine (20 g, 0.06 mol), 4-iodoanisole (50 g, 0.21 mol), K$_2$CO$_3$ (65.6 g, 0.47 mol), 18-crown-6 (3.1 g, 0.011 mol), and 1,2-dichlorobenzene (400 mL) were charged in a two-neck flask and stirred at 190 °C for 36 h. After the reaction was complete, the excess iodoanisole and solvent in the mixture were removed through distillation under reduced pressure. The mixture was partitioned between CH$_2$Cl$_2$ and H$_2$O and the organic phase separated to remove the inorganic salts. The final product was purified by column chromatography with (CH$_2$Cl$_2$/hexane, 1:1). Evaporation of the solvent yielded 1 (23.35 g, 73%). $^1$H NMR (400 MHz, CD$_3$OD) δ 7.4 (d, $J = 8.4$ Hz, 4H), 7.25–7.21 (m, 4H), 7.11–7.06 (m, 12H), 6.97–6.94 (m, 2H), 6.85 (d, $J = 8.8$ Hz, 4H), 3.81 (s, 6H). $^{13}$C NMR (400 MHz, CD$_3$OD) δ 129.09, 127.09, 122.65, 114.77, 55.47.

*N,N*-Bis(4-hydroxyphenyl)-*N,N*-diphenylbenzidine (2)

*N,N*-Bis(4-methoxyphenyl)-*N,N*-diphenylbenzidine (16.7 g, 0.03 mol) and dichloromethane (45 mL) were charged in a two-neck flask and then a mixture of BBr$_3$ (12 mL) and CH$_2$Cl$_2$ (25 mL) was added and stirred for 2 h at –78 °C. After the reaction was complete, aqueous NaHCO$_3$ (100 mL) was added to the flask dropwise to quench the reaction. The mixture was partitioned between ethyl acetate and H$_2$O and the organic phase separated and evaporated to dryness. The final product was purified by column chromatography (CH$_2$Cl$_2$/EtOAc, 4:1) to yield 2 in 92% yield. $^1$H NMR (400 MHz, CD$_3$OD) δ 7.32 (d, $J = 8.0$ Hz, 4H), 7.19–7.11 (m, 4H), 6.95–6.81 (m, 14H), 6.85 (d, $J = 11.7$ Hz, 4H). $^{13}$C NMR (400 MHz, CD$_3$OD) δ 153.39, 147.58, 146.49, 138.87, 133.17, 128.11, 126.82, 125.98, 121.89, 121.74, 120.84, 115.22.
3,6-Dibromo-9H-carbazole (3)\(^1\)

A two-neck round-bottom flask was equipped with a magnetic stirrer bar, a nitrogen gas inlet and a 250-mL addition funnel. Carbazole (6.5 g, 38.9 mmol) dissolved in toluene (35 mL) was added into the flask and cooled in an ice bath. A solution of N-bromosuccinimide (15 g, 84.2 mmol) in DMF (100 mL) was added into the flask transfer through the addition funnel. After reacting for 30 min, the mixture was poured into cold water to precipitate the product, which was filtered, washed with cold methanol, and then recrystallized (MeOH/hexane, 5:1). The product was obtained as white crystals (11.6 g, 92%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.13 (s, 2H), 8.10 (s, 1H), 7.52 (d, \(J = 6.8\) Hz, 2H), 7.13 (d, \(J = 8.6\) Hz, 2H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\)) \(\delta\) 138.4, 129.3, 124.1, 123.3, 112.7, 112.2.

3,6-Dibromo-9-butylcarbazole (4)\(^2\)

3,6-Dibromo-9H-carbazole (2.63 g, 8.1 mmol), \(\text{C}_4\text{H}_9\text{Br}\) (2.1 mL, 13 mmol), \([(\text{C}_4\text{H}_9)_4\text{N}]\text{HSO}_4\) (0.1 g, 0.03 mmol), and KOH (1 g, 18 mmol) were dissolved in acetone (20 mL) under N\(_2\) in a two-neck round-bottom flask equipped with a stirrer bar and then the mixture was heated under reflux at 90 °C for 5 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane and the organic phase evaporated to dryness. The product (2.3 g, 65%) was obtained after recrystallization (MeOH/hexane, 1:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.11 (s, 2H), 7.54 (d, \(J = 6.8\) Hz, 2H), 7.25 (d, \(J = 10.6\) Hz, 2H), 4.22 (t, \(J = 7.16\) Hz, 2H), 1.84–1.76 (m, 2H), 1.40–1.30 (m, 2H), 0.94 (t, \(J = 7.36\) Hz, 3H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\)) \(\delta\) 139.3, 128.9, 123.4, 114.5, 111.9, 110.3, 43.0, 30.9, 20.4, 13.8.

9-Butyl-3,6-bis(4-methoxyphenyl)carbazole (5)

A two-neck round-bottom flask equipped with a condenser and stirrer bar was placed under vacuum to remove oxygen and then filled with argon. 3,6-Dibromo-9-butylcarbazole (3.97 g, 10 mmol), 4-MeOC\(_6\)H\(_4\)B(OH)\(_2\) (3.19 g, 21
mmol), and Pd(PPh₃)₄ (340 mg, 0.3 mmol) were added to the flask, followed by potassium phosphoric acid solution (2 M, 50 mL), P^t^Bu₃ (0.05 M in toluene, 12 mL, 0.6 mmol), and THF (200 mL). The mixture was heated under reflux for 3 days and then cooled to room temperature and quenched with NaCl solution. Extraction of the mixture with dichloromethane, concentration, and column chromatography (EtOAc/hexane, 1:5) provided the product (3.04 g, 70%). ¹H NMR (400 MHz, CDCl₃) δ 8.30 (s, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.5 Hz, 4H), 7.45 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 12 Hz, 4H), 4.34 (t, J = 8.0 Hz, 2H), 3.88 (s, 6H), 1.92–1.87 (m, 2H), 1.47–1.41 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃) δ 158.5, 140.1, 134.8, 132.0, 128.2, 124.9, 123.4, 118.4, 114.2, 108.9, 55.4, 43.0, 31.2, 20.6, 13.9.

9-Butyl-3,6-bis(4-hydroxyphenyl)carbazole (6)

9-Butyl-3,6-bis(4-methoxyphenyl)carbazole (4.35g, 10 mmol) was dissolved in CH₂Cl₂ (10 mL) in a two-neck round-bottom flask equipped with a stirrer bar, an addition funnel, and a N₂ inlet. BBr₃ (4.9 g, 20 mmol) in CH₂Cl₂ (7.0 mL) was added to the flask at –78 °C. After reacting for 8 h, the mixture was quenched with aqueous Na₂CO₃ at –78 °C. The mixture was partitioned between CH₂Cl₂ and H₂O, the organic phase was separated and evaporated to dryness, and the residue subjected to column chromatography (hexane/CH₂Cl₂, 1:3) to provide 6 (2.84 g, 70%). ¹H NMR (400 MHz, CD₃OD) δ 8.27 (s, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.5 Hz, 4H), 7.47 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 4H), 4.34 (t, J = 8.0 Hz, 2H), 1.88–1.80 (m, 2H), 1.43–1.33 (m, 2H), 0.94 (t, J = 6 Hz, 3H). ¹³C NMR (400 MHz, CD₃OD) δ 155.4, 139.3, 133.0, 131.6, 127.1, 123.8, 122.2, 116.8, 114.6, 108.1, 43.3, 30.3, 19.45, 12.2.
Synthesis of PU Polymers P1–P5

**Typical procedure: (P1).** \(N,N'-\text{Bis}(4\text{-hydroxyphenyl})-N,N'-\text{diphenylbenzidine} \) (0.520 g, 0.001 mol), isophorone diisocyanate (0.265 g, 0.25 mL, 0.001 mol) and dry THF (20 mL) were charged in a two-neck flask and stirred for 24 h at 50 °C under \(N_2\). 4-\text{tert-Butylphenol} (15 mg, 0.1 mmol) was added and the mixture stirred for 2 h. When the reaction was complete, the polymer was precipitated dropwise into methanol and collected. The cycle of dissolution in THF and precipitation in methanol was repeated. The final PU sample (88% yield) was collected and dried under vacuum for 12 h. M.p. 260 °C. Anal. Calcd (based on the calibrated composition listed in Scheme 1): C, 74.1; H, 6.60; N, 9.0%. Found: C, 73.9; H, 6.84; N: 8.8%. \(^1\text{H NMR} \) (400 MHz, DMSO-\text{d}_6) \(\delta \) 7.6–7.4 (m, 4H), 7.3–7.2 (m, 4H), 7.1–6.9 (m, 18H), 3.7–3.6 (m, 4H), 1.2–0.7 (m, 15H). For the syntheses of copolymers P2–P5, the feeding ratios of the reagents are summarized in Scheme 2.

**P2** (92%). M.p. 263 °C. Calcd.: C, 74.0; H, 6.68; N, 8.75%. Found: C, 75.2; H, 7.00; N: 8.8%. \(^1\text{H NMR} \) (400 MHz, DMSO-\text{d}_6) \(\delta \) 7.8–7.4 (m, 8H), 7.3–7.2 (m, 6H), 7.1–6.9 (m, 16H), 3.7–3.6 (m, 4H), 1.2–0.7 (m, 18H).

**P3** (89%). M.p. 265 °C. Calcd.: C, 73.9; H, 6.77; N, 8.51%. Found: C, 74.1; H, 7.00; N, 8.38%. \(^1\text{H NMR} \) (400 MHz, DMSO-\text{d}_6) \(\delta \) 7.7–7.4 (m, 12H), 7.25–7.2 (m, 7H), 7.0–6.7 (m, 15H), 3.65–3.55 (m, 4H), 1.2–0.7 (m, 19H).

**P4** (92%). M.p. 262 °C. Calcd.: C, 73.9; H, 6.85; N, 8.26%. Found: C, 74.64; H, 7.10; N, 8.11%; \(^1\text{H NMR} \) (400 MHz, DMSO-\text{d}_6) \(\delta \) 7.6–7.4 (m, 18H), 7.25–7.2 (m, 10H), 7.0–6.7 (m, 10H), 3.65–3.55 (m, 4H), 1.2–0.7 (m, 20H).

**P5** (90%). M.p. 256 °C. Calcd.: C, 73.8; H, 6.9; N, 8.0%. Found: C, 72.9; H, 7.4; N, 7.4%; \(^1\text{H NMR} \) (400 MHz, DMSO-\text{d}_6) \(\delta \) 8.4–8.6 (m, 2H), 8.0–7.5 (m, 14H), 7.3–7.1 (m, 2H), 1.8–1.3 (m, 17H).
Device Fabrication details and measurements.

The devices were fabricated in two structures: (1) ITO/PU (20 nm)/[Ir(ppy)$_3$+t-PBD+PVK] (50 nm)/Mg (10 nm)/Ag (100 nm) and (2) ITO/PEDOT:PSS (30 nm)/PU (20 nm)/[Ir(ppy)$_3$+t-PBD+PVK] (50 nm)/Mg (10 nm)/Ag (100 nm). The ITO surface was cleaned through sonication and rinsing sequentially in deionized water, aqueous Triton-100 solution, deionized water, acetone, and methanol. For system (1) structures, the hole-injection PEDOT:PSS layer was spin-coated at 5000 rpm for 60 s on top of the ITO glass and then dried on a hot plate at 130 °C for 30 min under vacuum. Each polymer solution for spin coating (concentration: 10 mg/mL in THF) was filtered through a membrane filter having a channel size of 0.45 μm. The PU solution was spin-coated at 4000 rpm for 60 s onto the prepared ITO/PEDOT-PSS anode and then dried under reduced pressure for 30 min at 120 °C. The Ir(PPy)$_3$+PVK+t-PBD solution [Ir(PPy)$_3$, 12.5 mg; PVK, 20 mg; t-PBD, 50 mg] in chloroform (4 mL) was spin-coated at 3000 rpm for 90 s onto the surface of ITO/PEDOT:PSS/PU. The Mg and Ag contacts were deposited on the ITO/PEDOT-PSS/PU at a pressure below 10$^{-6}$ torr. The deposition rates for the Mg and Ag cathodes were 1.5 and 4.5 Å/s, giving an active area of 0.1256 cm$^2$. 
Life-time measurement of devices

Non-linear regression analysis revealed that the decay curves matched well with the equation of $B = B_0(C_1e^{-k_1t} + C_2e^{-k_2t})$, where $k_1$ and $k_2$ are the decay constants for the fast and slow phases of the decay, and $C_1$ and $C_2$ are the contribution of these two processes on the EL. $\tau_1$ and $\tau_2$ are half-lives defined as $\tau_1 = 0.69k_1$, $\tau_2 = 0.69k_2$.

<table>
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<tr>
<th>Device</th>
<th>$B_0$</th>
<th>$C_1$, $k_1$, $\tau_1$ (h)</th>
<th>$C_2$, $k_2$, $\tau_2$ (h)</th>
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<tr>
<td>DP1</td>
<td>1040</td>
<td>0.45, 0.57, 4.02 h</td>
<td>0.26, 0.091, 12.20 h</td>
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<tr>
<td>DP5</td>
<td>1262</td>
<td>0.51, 0.58, 4.17 h</td>
<td>0.24, 0.099, 14.15 h</td>
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<tr>
<td>DDP1</td>
<td>2319</td>
<td>0.48, 0.62, 6.20 h</td>
<td>0.30, 0.035, 43.19 h</td>
</tr>
<tr>
<td>DDP5</td>
<td>2015</td>
<td>0.47, 0.60, 6.23 h</td>
<td>0.34, 0.031, 46.85 h</td>
</tr>
<tr>
<td>S2</td>
<td>1205</td>
<td>0.52, 0.61, 6.13 h</td>
<td>0.31, 0.040, 33.12 h</td>
</tr>
</tbody>
</table>

![Graph showing decay curves and data points for different devices]
UV-vis spectra of P1 to P5 in film

PI spectrum of P1 to P5 in 5mg/20mL in THF solution
FT-IR spectra of PU polymers

DSC of PU polymers
TGA figures of PU polymers and the value of $T_d$ correspond to the 5%-weight-loss temperature.
The $^1$H and $^{13}$C NMR spectrum of the monomers including compound 1 to 6 $^1$H and $^{13}$C NMR of $N,N'$-Bis(4-methoxyphenyl)-$N,N'$-diphenylbenzidine (1)
$^1$H and $^{13}$C NMR of $N,N'$-Bis(4-hydroxyphenyl)-$N,N'$-diphenylbenzidine monomer (2)
$^1$H and $^{13}$C NMR of 3,6-Dibromo-9H-carbazole (3)
$^1$H and $^{13}$C NMR of 3,6-Dibromo-9-butylicarbazole (4)
$^1$H and $^{13}$C NMR of 9-Butyl-3,6-bis(4-methoxyphenyl)carbazole (5)
$^1$H and $^{13}$C NMR of 9-Butyl-3,6-bis(4-hydroxyphenyl)carbazole (6)
The Mass spectrum of monomer 2 and 6
Mass of \(N,N'-\text{Bis}(4\text{-hydroxyphenyl})-N,N'-\text{diphenylbenzidine monomer (2)}\)

C36H28N2O2 Exact Mass: 520.3

Mass of 9-Butyl-3,6-bis(4-hydroxyphenyl)carbazole (6)

C28H25NO2 Exact Mass: 407.2
The H-NMR spectrum of PU polymers from P1 to P5

P1

P2
Reference

