Supporting Information

Synthesis and Characterization of Large Stokes-shifted Fluorescent Imide and Polyimides Bearing 2-(2'-Hydroxyphenyl)benzothiazole Moieties

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1 Materials

3,5-Dibromo-2-hydroxybenzaldehyde (BIDE, 98%), 2-aminozenenethiol (Energy, 97%), silver nitrate (AgNO₃, Aladdin, 99.8%), dimethyl sulfate (BIDE, 98%), (4-aminophenyl)boronic acid hydrochloride (SUMMEDCHEM, 98%), potassium carbonate (K₂CO₃, Aladdin, 98%), tetakis(triphenylphosphine)palladium (Pd(PPh₃)₄, BIDE, 98%), dimethyl sulfide (DMSO, Macklin, 99.8%), aceton (AC, Macklin, 99.8%), tetrahydrofuran (THF, Macklin, 99.8%) N,N-dimethylformamide (DMF, Macklin, 99.8%), and N-methyl-2-pyrrolidinone (NMP, J&K, 99.5%) were used as received. 2-(2'-Hydroxypyryl)benzothiazole (HTB, Aladdin, 98%) was purified by recrystallization from ethyl alcohol. 4,4'-Oxydianiline (ODA) was purified by vacuum sublimation. 1,2,4,5-Cyclohexanetetracarboxylic dianhydride (HPMDA) and dicyclohexyl tetracarboxylic dianhydride (HBPDA) were purified by recrystallization from acetic anhydride.

2 Synthesis

2.4.1 Synthesis of 2-(benzo[d]thiazol-2-yl)-4,6-dibromophenol (DBrHBT)

3,5-Dibromo-2-hydroxybenzaldehyde (2.78 g, 10 mmol) and 2-aminozenenethiol (1.25 g, 10 mmol) were dissolved in 50 ml anhydrous DMSO. The mixture was stirred at 88 ℃ for h (monitored by TLC). The mixture was diluted by dichloromethane three times and washed with brine. The organic layers were dried over Na₂SO₄, filtered and evaporated in a vacuum. The pure product (2.23 g, 60%) was obtained by silica-gel column chromatography (CH₂Cl₂: hexane = 3: 2). ¹H NMR (400 MHz, Chloroform-d) δ 8.61 (d, J = 2.5 Hz, 1H), 8.13 (dt, J = 8.1, 1.0 Hz, 1H), 7.98 (dd, J = 7.9, 1.3, 0.7 Hz, 1H), 7.82 (d, J = 2.4 Hz, 1H), 7.56 (dd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.46 (d, J = 8.2, 7.2, 1.2 Hz, 1H), 3.99 (s, 3H). HR-MS (APCI, m/z): [M]+ calcd for C₁₇H₁₄Br₂N₃O₅: 385.1. Found: 383.8687.

2.4.2 Synthesis of 2-(3,5-dibromo-2-methoxyphenyl)benzo[d]thiazole (DBrMBT)

DBrHBT (2.68 g, 7.0 mmol) was dispersed into 30 ml dry acetone containing powdered anhydrous K₂CO₃ and dimethyl sulfate. The mixture was stirred at 60 ℃ for 5 h (monitored by TLC). After cooling to room temperature, the mixture was evaporated under reduced pressure. The pure product (2.50 g, 90%) was obtained by recrystallization in ethanol. ¹H NMR (400 MHz, Chloroform-d) δ 8.61 (d, J = 2.5 Hz, 1H), 8.13 (dt, J = 8.1, 1.0 Hz, 1H), 7.98 (ddd, J = 7.9, 1.3, 0.7 Hz, 1H), 7.82 (d, J = 2.4 Hz, 1H), 7.56 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.46 (d, J = 8.2, 7.2, 1.2 Hz, 1H), 3.99 (s, 3H). HR-MS (APCI, m/z): [M]+ calcd for C₁₇H₁₄O₂Br₂N₃: 399.1. Found: 398.3311.

2.4.3 Synthesis of 4,4''-diamino-5'-(benzo[d]thiazol-2-yl)-[1,1':3',1''-terphenyl]-4',4''-ol (HBTN)

DBrHBT (2.68 g, 7 mmol) and (4-aminophenyl)boronic acid hydrochloride (2.18 g, 21 mmol) were dissolved in 100 ml THF, subsequently, 2 M aqueous K₂CO₃ solution (20 ml) was added. Then Pd(PPh₃)₄ (catalytic amount) was added under argon condition. The mixture was stirred at 88 ℃ for 48 h (monitored by TLC). After cooling to room temperature, the mixture was washed with brine, then concentrated. The pure product (2.28 g, 80%) was obtained by silica-gel column chromatography with dichloromethane as an eluent. ¹H NMR (400 MHz, DMSO-d₆) δ 12.57 (s, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 1.9 Hz, 1H), 7.61 (t, J = 7.7 Hz, 1H), 7.57-7.50 (m, 2H), 7.42 (d, J = 8.0 Hz, 4H), 6.67 (td, J = 8.2, 1.7 Hz, 4H), 5.22 (s, 4H). ¹³C NMR (151 MHz, DMSO-d₆) δ 169.85, 153.10, 151.61, 148.62, 148.56, 133.41, 132.98, 131.49, 131.01, 130.47, 127.53, 127.46, 127.13, 126.35, 125.07, 123.25, 122.41, 117.35, 114.82, 113.97. FTIR (KBr): 3334 cm⁻¹ (-NH/stretching vibration). HR-MS (APCI, m/z): [M]+ calcd for C₁₇H₁₄O₂Br₂N₃O₅: 409.5. Found: 410.1320.

2.4.4 Synthesis of 5'-(benzo[d]thiazol-2-yl)-4'-methoxy-[1,1':3',1''-terphenyl]-4',4''-diamine (MBTN)

DBrMBT (2.78 g, 7 mmol) and (4-aminophenyl)boronic acid hydrochloride (2.18 g, 21 mmol) were dissolved in 100 ml THF, subsequently, 2 M aqueous K₂CO₃ solution (20 ml) was added. Then Pd(PPh₃)₄ (catalytic amount) was added under argon condition. The mixture was stirred at 88 ℃ for 48 h (monitored by TLC). After cooling to room temperature, the mixture was washed with brine, then concentrated. The pure product (2.20 g, 82%) was obtained by silica-gel column chromatography with dichloromethane as an eluent. ¹H NMR (400 MHz, DMSO-d₆) δ 8.45 (d, J = 2.5 Hz, 1H), 8.18-8.11 (m, 2H), 7.61-7.53 (m, 2H), 7.50-7.44 (m, 3H), 7.42-7.38 (m, 2H), 6.74-6.67 (m, 4H), 5.29 (d, J = 10.8 Hz, 4H), 3.48 (s, 3H). ¹³C NMR (151 MHz, DMSO-d₆) δ 163.08, 154.16, 152.20, 148.98, 148.94, 137.70, 136.37, 136.17, 130.72, 129.86, 129.26, 127.74, 126.94, 126.81, 126.75, 125.65, 124.88, 123.49, 123.13, 122.37, 114.81, 114.44, 114.42, 60.32. FTIR (KBr): 3334 cm⁻¹ (-N₃/stretching). HR-MS (APCI, m/z): [M]+ calcd for C₂₅H₂₃N₃O₅: 423.5. Found: 424.1479.

2.4.5 Synthesis of 2,2'-(5'-[benzo[d]thiazol-2-yl]-4'-hydroxy-[1,1':3',1''-terphenyl]-4',4''-diyl)bis(hexahydro-1H-isouindole-1,3(2H)-dione) (HTBN-MC)

HTBN (0.50 g, 1.2 mmol) and hydroxydibenzofuran-1,3-dione (0.55 g, 3.6 mmol) were dissolved in 30 ml acetic acid, and sodium acetate trihydrate (0.35 g, 3.6 mmol) was added as catalyst. The mixture was stirred at 150 ℃ for 5 h under argon condition (monitored by TLC). After cooling to room temperature, the mixture was poured into 350 ml cold water. The
yellowish precipitate was collected and the pure product (0.65 g, 80%) was obtained by silica-gel column chromatography with dichloromethane as an eluent. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 13.02 (s, 1H), 8.25 (d, $J = 8.0$ Hz, 1H), 8.15 (dd, $J = 5.1$, 2.8 Hz, 2H), 7.96–7.83 (m, 5H), 7.63 (t, $J = 7.7$ Hz, 1H), 7.55 (t, $J = 7.6$ Hz, 1H), 7.46–7.35 (m, 4H), 3.16 (t, $J = 5.3$ Hz, 4H), 1.82 (d, $J = 20.7$ Hz, 8H), 1.44 (s, 8H). 13C NMR (151 MHz, DMSO-$d_6$) $\delta$ 179.15, 179.11, 169.21, 154.59, 151.40, 139.15, 135.19, 130.41, 130.35, 127.93, 127.67, 127.56, 127.17, 126.61, 126.56, 122.88, 122.55, 118.00, 23.86, 21.97. FTIR (KBr): 3483 cm$^{-1}$ (–OH stretching), 1778 cm$^{-1}$ and 1709 cm$^{-1}$ (C=O stretching). HR-MS (APCI, m/z): [M]+ calcd for C$_{41}$H$_{35}$N$_3$O$_5$S: 681.8. Found: 682.2382.

2.4.6  Synthesis of 2,2'-(5'-benzo[d]thiazol-2-yl)-4'-methoxy-[1,1':3',1''-terphenyl]-4,4''-diyl)bis(hexahydro-1H-isoindole-1,3(2H)-dione (MBTN-MC)

MBTN (0.51 g, 1.2 mmol) and hexahydroisobenzofuran-1,3-dione (0.55 g, 3.6 mmol) were dissolved in 30 mL acetic acid, and sodium acetate trihydrate (0.35 g, 3.6 mmol) was added as catalyst. The mixture was stirred at 150 °C for 5 h under argon condition (monitored by TLC). After cooling to room temperature, the mixture was poured into 350 mL cold water. The white precipitate was collected and the pure product (0.67 g, 80%) was obtained by silica-gel column chromatography with dichloromethane as an eluent. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.78 (d, $J = 2.4$ Hz, 1H), 8.16 (d, $J = 8.1$ Hz, 1H), 7.96 (d, $J = 2.3$ Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.49–7.40 (m, 5H), 3.56 (s, 3H), 3.08 (dt, $J = 6.9$, 4.8 Hz, 4H), 1.96 (d, $J = 12.0$ Hz, 8H), 1.55 (h, $J = 3.2$ Hz, 8H). 13C NMR (151 MHz, DMSO-$d_6$) $\delta$ 179.08, 179.06, 162.31, 155.69, 152.18, 139.05, 137.25, 136.60, 136.20, 135.61, 132.71, 132.66, 129.86, 127.99, 127.83, 127.60, 127.42, 127.00, 126.76, 125.95, 123.32, 122.53, 61.31, 23.86, 21.97. FTIR (KBr): 1793 cm$^{-1}$ and 1704 cm$^{-1}$ (C=O stretching). HR-MS (APCI, m/z): [M]+ calcd for C$_{42}$H$_{37}$N$_3$O$_5$S: 695.8. Found: 696.2527.

2.4.7 Synthesis of the polyimides

All the polyimides were synthesized by one-step method. The HPHBTNms PI polymers were prepared by condensation of two diamines (HBTN and ODA) with commercial dianhydride 1,2,4,5-cyclohexanetetracarboxylic dianhydride (HPMDA) with the feed molar ratios of 6:94:100 (HPHBTN6), 10:90:100 (HPHBTN10). The HBHBTNms PI polymers were prepared by condensation of two diamines (HBTN and ODA) with commercial dianhydride dicyclohexyl-3,4,3',4'-tetracarboxylic dianhydride (HBMDA) with the feed molar ratios of 6:94:100 (HBHBTN6), 10:90:100 (HBHBTN10). HPHBTN6 was used as an example to illustrate the general synthetic procedure. To the solution of ODA (0.9486 g, 4.7 mmol) and HBTN (0.1238 g, 0.3 mmol) in 5 mL anhydrous NMP, HPMDA (1.1297 g, 5.0 mmol) was added in one portion. After stirring at room temperature overnight, benzoic acid (0.0310 g, 0.25 mmol) was added and the reaction system stirred at 80 °C for 2 h. Then the reaction system was stirred at 180 °C for 6 h. After cooling to room temperature, the resulting polymer was precipitated in ethanol, washed with ethanol and dried in a vacuum oven at 70 °C for 24 h. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.28 (d, $J = 8.8$ Hz, 3H), 7.18–7.10 (m, 3H), 4.36 (t, $J = 5.1$ Hz, 1H), 3.45 (qd, $J = 7.0$, 5.0 Hz, 1H), 3.25–3.15 (m, 4H), 2.32–2.22 (m, 2H), 2.00–1.94 (m, 2H), 1.06 (t, $J = 7.0$ Hz, 2H).
3 NMR Spectrum for the Synthesized Compounds

Figure S1. $^1$H NMR spectrum for diamines HBTN (a) and MBTN (b).

Figure S2. $^{13}$C NMR spectrum for diamines HBTN (a) and MBTN (b).
Figure S3. $^1$H NMR spectrum for imides HBTN-MC (a) and MBTN-MC (b).

Figure S4. $^{13}$C NMR spectrum for imides HBTN-MC (a) and MBTN-MC (b).
4 FT-IR Spectrum for diamides and imides

Figure 55. FT-IR spectrum for diamides (HBTN and MBTN) and imides (HBTN-MC and MBTN-MC).

5 Simulated IR for HBT and HBTN-MC

Figure 56. Simulated IR of (a) HBT and (b) HBTN-MC in the O\textsubscript{1}-H\textsubscript{2} stretching band region in the S\textsubscript{0} and S\textsubscript{1} states.

6 Calculated transition wavelength and oscillator strength for HBT and HBTN-MC

Table S1: The calculated transition wavelength and oscillator strength of the keto form of HBT and HBTN-MC in the S\textsubscript{1} state

<table>
<thead>
<tr>
<th>Compound</th>
<th>State</th>
<th>Transition wavelength (nm)</th>
<th>Oscillator strength (f)</th>
<th>Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBT</td>
<td>Keto'-S\textsubscript{2}</td>
<td>517.58</td>
<td>0.3510</td>
<td>HOMO-&gt;LUMO</td>
</tr>
<tr>
<td></td>
<td>Keto'-S\textsubscript{2}</td>
<td>400.83</td>
<td>0.0354</td>
<td>HOMO-1-&gt;LUMO</td>
</tr>
<tr>
<td>HBTN-MC</td>
<td>Keto'-S\textsubscript{2}</td>
<td>573.93</td>
<td>0.4702</td>
<td>HOMO-&gt;LUMO</td>
</tr>
<tr>
<td></td>
<td>Keto'-S\textsubscript{2}</td>
<td>382.14</td>
<td>0.1535</td>
<td>HOMO-1-&gt;LUMO</td>
</tr>
</tbody>
</table>

The vertical excitation energies of S\textsubscript{1}->S\textsubscript{0} for HBT (keto form) and HBTN-MC (keto form) in the dichloromethane solvent environment (with the solvation model density (SMD) implemented in the Gaussian software) were calculated by TD-DFT applying the B3LYP-D3(BJ) functional with 6-311+G (d, p) basis set, and the vertical excitation energy and oscillator strength (f) were obtained under the optimal structure of S\textsubscript{1} state.
7 FT-IR Spectrum for Polyimides

Figure S7. FT-IR spectrum for polyimides.

8. The excitation spectra for the polyimides

Figure S8. The excitation spectra of HBHBTNms in DCM and HBHBTNms and HPHBTNis in film state.
The transient PL decay curves for the polyimides

**Figure S9.** The transient PL decay curves of the polyimides

**Table S2** The chi-square and the residuals and the values for the pre-exponential factors for all the polyimides.

<table>
<thead>
<tr>
<th>Polymides</th>
<th>HBHBTN6</th>
<th>HBHBTN10</th>
<th>HPHBTN6</th>
<th>HPHBTN10</th>
</tr>
</thead>
<tbody>
<tr>
<td>pre-exponential factors</td>
<td>8.908702</td>
<td>7.681269</td>
<td>5.983029</td>
<td>6.33539</td>
</tr>
<tr>
<td>chi-squared Probability</td>
<td>1.9288E-20%</td>
<td>1.9288E-20%</td>
<td>1.9288E-20%</td>
<td>1.9288E-20%</td>
</tr>
<tr>
<td>Negative residuals</td>
<td>36.63775%</td>
<td>36.70089%</td>
<td>34.89715%</td>
<td>36.98243%</td>
</tr>
<tr>
<td>Residuals &lt; 1 s.dev</td>
<td>63.27964%</td>
<td>61.57688%</td>
<td>62.86539%</td>
<td>62.42158%</td>
</tr>
<tr>
<td>Residuals &lt; 2 s.dev</td>
<td>94.05205%</td>
<td>94.43524%</td>
<td>93.90112%</td>
<td>94.82434%</td>
</tr>
<tr>
<td>Residuals &lt; 3 s.dev</td>
<td>98.3891%</td>
<td>99.10567%</td>
<td>98.98953%</td>
<td>98.30614%</td>
</tr>
<tr>
<td>Residuals &lt; 4 s.dev</td>
<td>99.71086%</td>
<td>99.37065%</td>
<td>99.45868%</td>
<td>99.56085%</td>
</tr>
</tbody>
</table>
The spectrum comparison of LED light, sunlight, excitation, and emission of HBHBTN6.

Figure S10. The spectrum comparison of LED light, sunlight, excitation, and emission of HBHBTN6.