Supporting Information

A Facile Strategy for Intrinsic Low-k Dielectric Polymers: Molecular Design Based on Secondary Relaxation Behavior

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Synthesis and characterization of monomers and polyimides

Scheme S1. The chemical structure and schematic of synthesis of TPAHF via thermal imidization.

N-TPA

As shown in Scheme S1, aniline (4.660 g, 50 mmol), CsF (15.900 g, 100 mmol), 1-fluoro-4-nitrobenzene (17.638 g, 125 mmol) and DMSO (200 ml) were added into a 500 ml 3-neck round-bottom flask and reacted for 24 h at 150 °C under nitrogen. After pouring into 500 ml of cold saturated salt water, yellow precipitates were collected and purified by chromatography on silica gel with dichloromethane/hexane as an eluent. The purified product was light yellow needle type crystals with a yield of 68%. $^1$H NMR (400 MHz, DMSO, $\delta$) 8.15 (d, $J = 8.2$ Hz, 4H), 7.46 (t, $J = 7.2$ Hz, 2H), 7.33 (t, $J = 7.2$ Hz, 1H), 7.16 (d, $J = 7.2$ Hz, 6H).$^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$): 151.85, 144.87, 142.79, 130.55, 127.22, 126.27, 125.54, 122.36. HRMS (ESI) m/z: 335 [M+H]$^+$ calcd for C$_{18}$H$_{13}$N$_3$O$_4$, 335.0906. Anal. calcd for C$_{18}$H$_{13}$N$_3$O$_4$: C 64.48, H 3.91, N 12.53; found: C 63.75, H 3.81, N 12.21.

A-TPA

The N-TPA (6.706 g, 20 mmol), one spoonful of 10% Pd/C catalyst (~0.05 g) and ethanol (100 ml) were charged into a 500 ml 3-neck round-bottom flask and then hydrazine hydrate (6 ml) was added dropwise. The reaction was followed by refluxing under nitrogen for 24 h. After removing the ethanol by rotary evaporation, the white precipitates were collected and then purified by chromatography on silica gel with
dichloromethane/hexane as an eluent. The purified product was grey crystals with a yield of 80%. $^1$H NMR (400 MHz, DMSO, $\delta$): 7.02 (t, $J = 7.8$ Hz, 2H), 6.77 (d, $J = 8.5$ Hz, 4H), 6.61 (t, $J = 7.2$ Hz, 1H), 6.56 (d, $J = 8.0$ Hz, 2H), 6.50 (d, $J = 8.5$ Hz, 4H), 4.97 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$): 142.32, 139.52, 128.76, 126.84, 123.42, 122.16, 119.84, 119.55, 116.11. HRMS (ESI) m/z: 275 [M+H]$^+$ calcd for C$_{18}$H$_{17}$N$_3$, 275.1422. Anal. calcd for C$_{18}$H$_{17}$N$_3$: C 78.52, H 6.22, N 15.26; found: C 77.90, H 6.18, N 15.33.

TPAHF

The A-TPA (0.275 g, 1 mmol), 6FDA (0.444 g, 1 mmol) and purified DMF (4.8 ml) were added in a 50 ml flask, achieving a solid content of approximately 15 wt %. The mixture was stirred at room temperature under argon for about 4 h to form a viscous poly(amic acid) (PAA) solution. The PAA solution was subsequently coated uniformly on a clean and dry glass plate with a controlled film thickness, and then thermally imidized in a vacuum oven with the temperature program of 100 °C (1 h)/200 °C (1 h)/350 °C (1 h) to produce the TPAHF film. The TPAHF film was removed from the glass substrate after the oven cooled to room temperature. The characterization of the TPAHF film is shown in Figure S1.

Scheme S2. The chemical structure and schematic of synthesis of the TpBPHF via thermal imidization.
N-TpBr

As shown in Scheme S2, 4-bromoaniline (5.160 g, 30 mmol), CsF (9.120 g, 60 mmol), 1-fluoro-4-nitrobenzene (10.582 g, 75 mmol) and DMSO (150 ml) were added into a 500 ml 3-neck round-bottom flask and reacted for 24 h at 150 °C under nitrogen. After pouring into 500 ml of cold saturated salt water, yellow precipitates were collected and purified by chromatography on silica gel with dichloromethane/hexane as an eluent. The purified product was light yellow needle type crystals with a yield of 69%. 1H NMR (400 MHz, DMSO, δ): 8.17 (d, J = 9.1 Hz, 4H), 7.66 (d, J = 8.7 Hz, 2H), 7.21 (d, J = 9.0 Hz, 6H). 13C NMR (100 MHz, CDCl3, δ): 152.22, 144.99, 142.31, 136.14, 132.53, 126.52, 124.83, 121.17. HRMS (ESI) m/z: 413 [M+H]+ calcd for C18H12BrN3O4, 413.0011. Anal. calcd for C18H12BrN3O4: C 52.19, H 2.92, N 10.14; found: C 52.11, H 2.89, N 10.01.

N-TpBP

The N-TpBr (4.142 g, 10 mmol) and 4-biphenylboronic acid (2.178 g, 11 mmol) were added into a 500 ml 3-neck round-bottom flask and then moderate Aliquat-336 was added. Next, tetrakis(triphenylphosphine)palladium (Pd(PPh3)4) (0.207 g, 0.18 mmol), aqueous K2CO3 solution (2 N) (35 ml) and THF (200 ml) were also charged, followed by refluxing under nitrogen for 24 h. After removing the aqueous layer, the yellow precipitates were collected by rotary evaporation and purified by chromatography on silica gel with dichloromethane/hexane as an eluent. The purified product was light yellow needle type crystals with a yield of 86%. 1H NMR (400 MHz, DMSO, δ): 8.19 (d, J = 8.8 Hz, 4H), 7.85 (d, J = 7.9 Hz, 2H), 7.76 (d, J = 7.4 Hz, 4H), 7.72 (d, J = 8.4Hz, 2H), 7.47 (t, J = 7.9 Hz, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.7 Hz, 2H), 7.26 (d, J = 8.8 Hz, 4H). 13C NMR (100 MHz, CDCl3, δ): 151.76, 144.02, 142.90, 140.70, 140.40, 139.40, 138.50, 128.90, 127.69, 127.57, 127.32, 127.03, 125.60, 122.55. HRMS (ESI) m/z: 487 [M+H]+ calcd for C30H21N3O4, 487.1532. Anal. calcd for C30H21N3O4: C 73.91, H 4.34, N 8.62; found: C 73.42, H 4.28, N 8.43.
A-TpBP

The N-TpBP (4.875 g, 10 mmol), one spoonful of 10% Pd/C catalyst (~0.05 g) and ethanol (100 ml) were charged into a 500 ml 3-neck round-bottom flask and then hydrazine hydrate (3 ml) was added dropwise. The reaction was followed by refluxing under nitrogen for 24 h. After removing the ethanol by rotary evaporation, the grey precipitates were collected and then purified by chromatography on silica gel with dichloromethane/hexane as an eluent. The purified product was grey crystals with a yield of 69%. $^1$H NMR (400 MHz, DMSO, δ): 7.66 (d, J = 8.7 Hz, 6H), 7.43 (d, J = 7.1 Hz, 4H), 7.32 (t, J = 8.2 Hz, 1H), 6.84 (d, J = 7.4 Hz, 4H), 6.65 (d, J = 6.8 Hz, 2H), 6.54 (d, J = 6.4 Hz, 4H), 5.00 (s, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$, δ): 144.20, 142.83, 140.80, 139.73, 138.24, 135.90, 134.85, 129.27, 128.81, 127.91, 127.61, 127.23, 123.20, 117.25. HRMS (ESI) m/z: 427 [M+H]$^+$ calcld for C$_{30}$H$_{25}$N$_3$, 427.2048. Anal. calcld for C$_{30}$H$_{25}$N$_3$: C 84.28, H 5.89, N 9.83; found: C 83.37, H 5.82, N 9.61.

TpBPHF

The A-TpBP (0.427 g, 1 mmol), 6FDA (0.444 g, 1 mmol) and purified DMF (5.8 ml) were added in a 50 ml flask, achieving a solid content of approximately 15 wt %. The mixture was stirred at room temperature under argon for about 4h to form a viscous poly(amic acid) (PAA) solution. The PAA solution was subsequently coated uniformly on a clean and dry glass plate with a controlled film thickness, and then thermally imidized in a vacuum oven with the temperature program of 100 °C(1h)/200 °C (1h)/350 °C (1h) to produce the TpBPHF film. The TpBPHF film was removed from the glass substrate after the oven cooled to room temperature. The characterization of the TpBPHF film is shown in Figure S1

<table>
<thead>
<tr>
<th>Polyimide</th>
<th>[η]$^a$</th>
<th>Solvent$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dL/g</td>
<td>NMP</td>
</tr>
<tr>
<td>TmBPHF</td>
<td>0.52</td>
<td>++</td>
</tr>
</tbody>
</table>

$^a$The diameter of capillary tubes is about 0.46 mm, and the bathing temperature is 30 °C.

Table S1. The intrinsic viscosity and solubility of polyimide TmBPHF
Legend: (+++) soluble at room temperature; (+) partially soluble at room temperature, soluble on heating (80 °C). The solubility was determined using 10 mg of the TmBPHF film in 1 mL of solvent.

Table S2. The thermal properties of polyimide TmBPHF

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
<th>CTE$^a$ (ppm/K)</th>
<th>$T_{d5%}$ (°C)</th>
<th>Char yield$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TmBPHF</td>
<td>302</td>
<td>38.4</td>
<td>549</td>
<td>70</td>
</tr>
</tbody>
</table>

$^a$The temperature range was 50 °C to 250 °C.

$^b$The corresponding temperature was 800 °C.

Table S3. The mechanical properties of the polyimide TmBPHF film

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (GPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TmBPHF</td>
<td>85.8 ± 3.5</td>
<td>2.02 ± 0.11</td>
<td>5.87 ± 0.18</td>
</tr>
</tbody>
</table>

Table S4. 2θ and interlayer distance of the polyimide films

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ (°)</th>
<th>$d^a$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kapton</td>
<td>18.68</td>
<td>4.74</td>
</tr>
<tr>
<td>TPAHF</td>
<td>15.76</td>
<td>5.61</td>
</tr>
<tr>
<td>TpBPHF</td>
<td>15.64</td>
<td>5.67</td>
</tr>
<tr>
<td>TmBPHF</td>
<td>14.92</td>
<td>5.93</td>
</tr>
</tbody>
</table>

$^a$Calculated by Bragg equation.
Figure S1. The FT-IR spectrum of the diamine molecules and polymer films.

Figure S2. The DMA curves of the polyimide films.
Figure S3. Experimental setup of the dielectric constant measurement.

Figure S4. The storage modulus and loss modulus curves of the TmBPHF film.