

## Supporting Information

# Polyimide-Based Gate Dielectrics for High-Performance Organic Thin Film Transistors

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### Materials

All materials such as 2-methyl propenoyl chloride, 2-(2,4-diaminophenoxy)ethanol dihydrochloride, di-tert-butyl dicarbonate, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, 4-biphenylmethanol, 4-bromobenzonitrile, dodecanedioic acid, dicyclohexylcarbodiimide, 4-dimethylaminopyridine were used as received. Tetrahydrofuran (THF), methylene chloride (MC) and trimethylamine (TEA) were purified by distillation.

### Synthesis of compound 1, 2, 3 and 4

Compound 1: 2-(2,4-Diaminophenoxy)ethanol dihydrochloride (2.41 g, 10.0 mmol) were dissolved in methanol (50 mL) and TEA (10 mL) at room temperature. And ditertbutyl dicarbonate (8.77 g, 40.0 mmol) was added dropwise, and then stirring reaction in water bath at 50 °C for 24 h. The reaction solution was concentrated and dissolved with ethyl acetate (EA), and washed with saturated sodium chloride solution three times. Column chromatography eluting with EA : hexane (1 : 5 v/v) was performed to purify the solid obtained by removing the solvent under reduced pressure. The target compound was solid of 2.94 g (80%). <sup>1</sup>H NMR (500 MHz, DMSO, δ, ppm): 9.08 (s, 1H), 8.13 (s, 1H), 8.03 (s, 1H), 6.95-7.01 (d, 1H), 6.83-6.87 (d, 1H), 5.07-5.11 (t, 1H), 3.9-3.94 (t, 2H), 3.66-3.71 (q, 2H), 1.44-1.49 (d, 18H).

Compound 2: 2-Methyl propenoyl chloride (4 g, 38 mmol) was added dropwise to a THF solution (40 mL) of compound 1 (7g, 19 mmol) and TEA (5.3mL, 38 mmol). The mixture was stirred at 0 °C for 12 hrs at Ar. The reaction mixture was poured into water and extracted with CHCl<sub>3</sub>. The combined organic extract was washed successively with a saturated aqueous solution of NaHCO<sub>3</sub>, water and brine, and an organic phase separated was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using acetone : hexane (1 : 10 v/v) as eluent to yield 7.2 g (87 %). <sup>1</sup>H NMR (500 MHz, DMSO, δ, ppm): 9.15 (s, 1H), 8.03 (s, 1H), 7.62 (s, 1H), 7.00-7.05 (d, 1H), 6.93-6.95 (d, 1H), 6.05-6.09 (s, 1H), 5.68-5.71 (s, 1H), 4.41-4.45 (t, 2H), 4.18-4.21 (t, 2H), 1.89-1.91 (s, 3H), 1.44-1.47 (d, 18H).

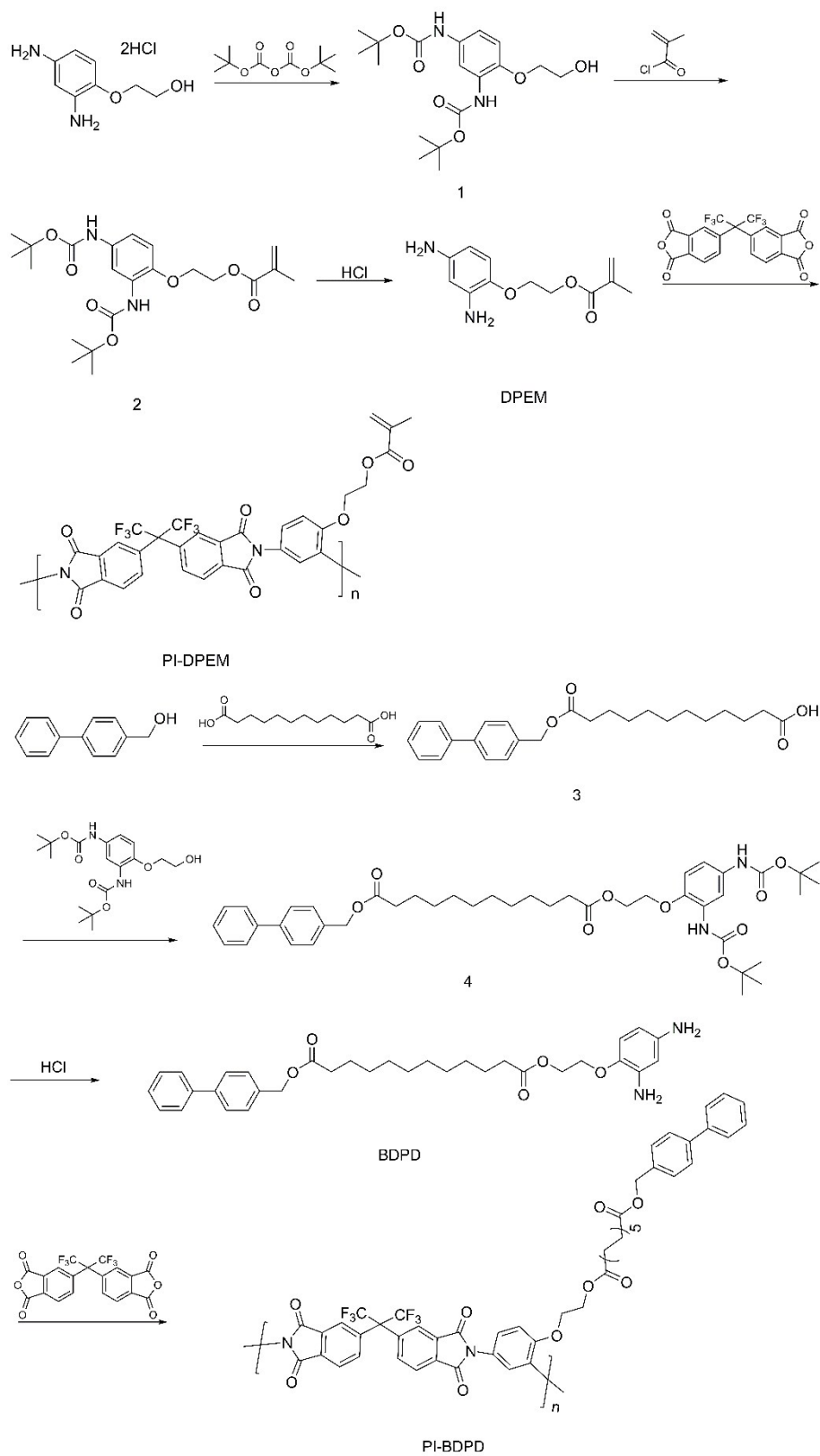
Compound DPem: Under the ice bath, compound 2 (4.36 g, 10 mmol) was added dropwise to a solution of ethyl acetate for hydrogen chloride to stir for 12h. The saturated Na<sub>2</sub>CO<sub>3</sub> solution was slowly added to the reaction mixture until alkaline, and then extracted with ethyl acetate. The combined organic layers were then dried by anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to obtain the target

product. <sup>1</sup>H NMR (500 MHz, DMSO, δ, ppm): 6.5-6.54 (d, 1H), 6.06 (s, 1H), 5.93-5.96 (d, 1H), 5.73-5.77 (dd, 1H), 5.68-5.71 (t, 1H), 4.45 (s, 4H), 4.33-4.37 (t, 2H), 3.98-4.02 (t, 2H), 1.89 (s, 3H).

Compound 3: A THF solution of dicyclohexylcarbodiimide (2.06 g, 10 mmol) was slowly added dropwise to 100 mL THF solution of dodecanedioic acid (11.5 g, 50 mmol). The mixture was stirred at 0 °C for 1 hour. 4-Biphenylmethanol (1.84 g, 10 mmol) and 4-dimethylaminopyridine (0.6 g, 5mmol) were added to the reaction mixture, and the reaction was stirred at 0 °C for 12 hrs at Ar. After the reaction was completed, the resulting solid was filtered-off from the reaction mixture, washed with THF, the organic phase separated was concentrated by a rotary evaporator. The reaction solution was slowly added dropwise to a 2.5 mol/L Na<sub>2</sub>CO<sub>3</sub> aq, and a large amount of white precipitate appeared. After filtration and washing, the solid was acidified and extracted with EA. The organic phase separated was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered to afford product. <sup>1</sup>H-NMR (500MHz, DMSO, δ, ppm): 7.64-7.68 (d, 4H), 7.43-7.49 (q, 4H), 7.35-7.39 (t, 1H), 5.13 (s, 2H), 2.33-2.38 (t, 2H), 2.14-2.20 (t, 2H), 1.90-1.92 (m, 4H), 1.19-1.28 (m, 12H).

Compound 4: Compound 3 (3.97 g, 10 mmol) was dissolved in 30 mL of SOCl<sub>2</sub>. The mixture was heated to reflux and the temperature was maintained for 2 h, and then distilled out the excess SOCl<sub>2</sub> to get a new intermediate. The new intermediate was dissolved in dry MC (15 mL), and it was added dropwise to a dry MC (20 mL) solution of compound 1 (3.68g, 10 mmol), TEA (1.5 mL). The mixture was stirred at 0 °C for 12 hrs at N<sub>2</sub>. A large amount of white precipitate was produced, and the precipitate was filtered. The resulting filtrate was washed with saturated NaCl aqueous solution. The organic phase separated was dried over anhydrous MgSO<sub>4</sub> and concentrated to afford product. <sup>1</sup>H-NMR (500MHz, DMSO, δ, ppm): 9.5-9.15 (d, 1H), 8.13 (s, 1H), 8.03 (s, 1H), 7.63-7.70 (m, 4H), 7.42-7.50 (m, 4H), 7.34-7.40 (m, 1H), 6.95-7.05 (m, 1H), 6.80-6.92 (m, 1H), 5.13 (s, 2H), 4.33-4.37 (t, 2H), 4.12-4.15 (t, 2H), 2.33-2.38 (t, 2H), 2.14-2.19 (t, 2H), 1.90-1.92 (m, 4H), 1.44-1.49 (d, 18H), 1.17-1.28 (m, 12H).

Compound BDPD: The synthesis of compound BDPD follow similar experimental procedures with compound DPEM, except that compound 2 was replaced by compound 4. <sup>1</sup>H-NMR (500MHz, DMSO, δ, ppm): 7.62-7.69 (m, 4H), 7.42-7.51 (m, 4H), 7.35-7.40 (m, 1H), 6.5-6.54 (d, 1H), 5.74-5.76 (m, 1H), 5.67-5.72 (t, 1H), 5.14 (s, 2H), 4.46 (s, 4H), 4.22-4.27 (t, 2H), 3.98-4.02 (t, 2H), 2.32-2.38 (t, 2H), 2.13-2.19 (t, 2H), 1.88-1.92 (m, 4H), 1.16-1.28 (m, 12H).



**Scheme S1.** The synthesis routes of PI-DPEM and PI-BDPD.

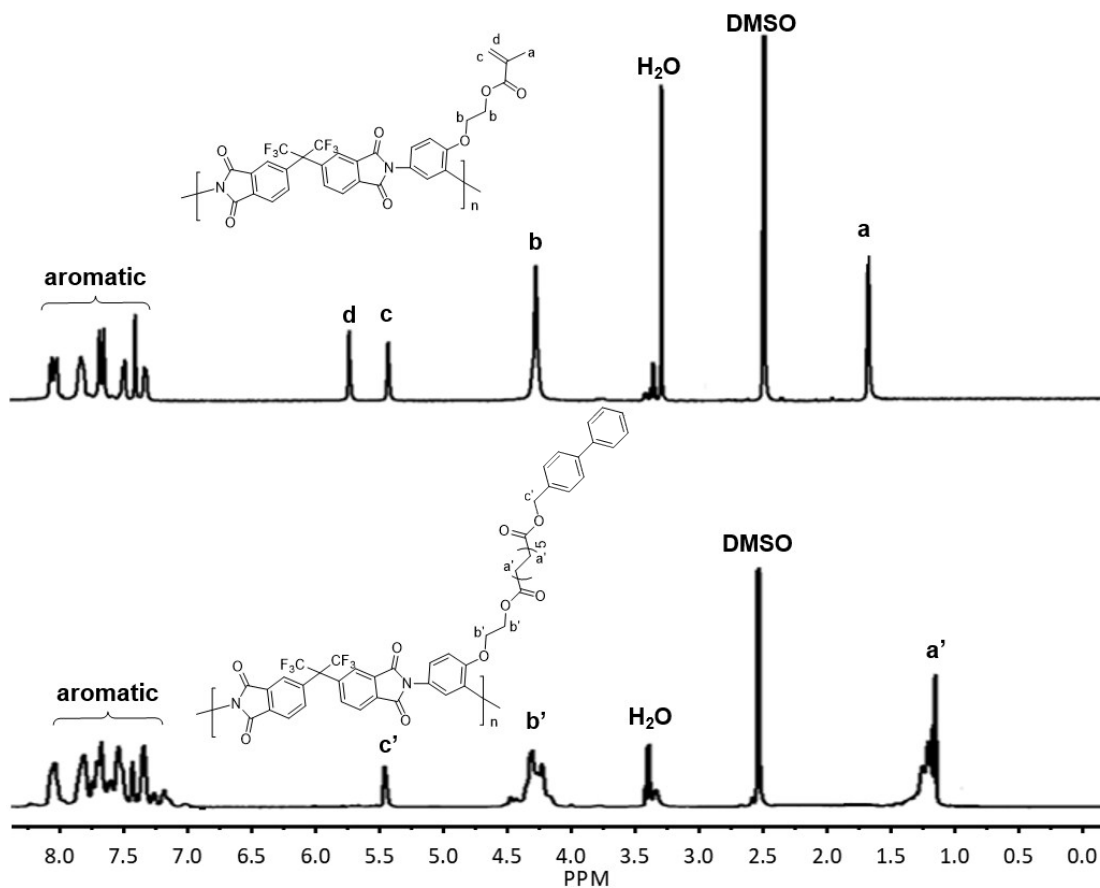


Figure S1. The  $^1\text{H}$  NMR spectra of PI-DPEM and PI-BDPD.