Electronic Supplementary Information

Effect of polymer chain conformation on field-effect transistor performance: synthesis and properties of two arylene imide based D-A copolymers

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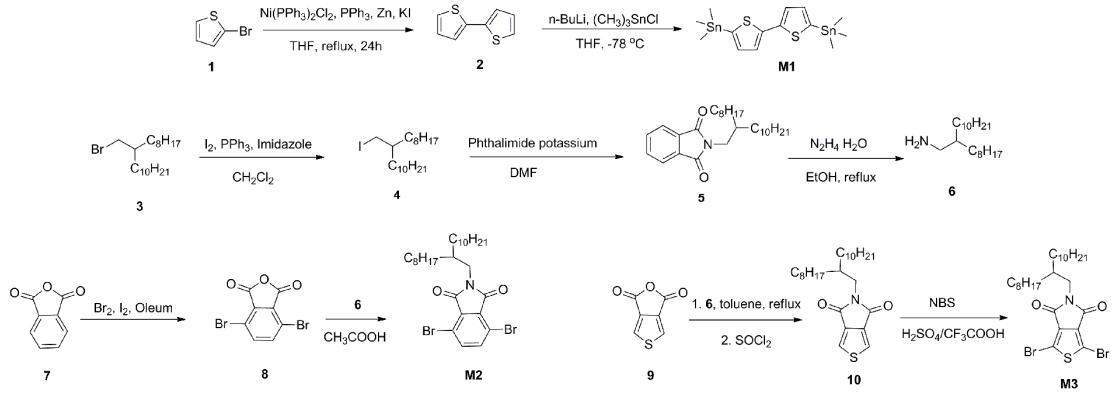
Materials

Toluene and THF was dried over and distilled from K-Na alloy under an atmosphere of argon. Compound **3** and **9** was purchased from J&K Scientific Ltd. and used without further purification. Compound **M1**[1], **6**[2], **8**[3]and **M3**[4] were synthesized according to literature procedures or with some modifications. Other reagents were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). The synthetic routes of intermediates and monomers are shown in Scheme S1.



Scheme S1 The synthetic routes of intermediates and monomers

*2,2'-bithiophene (**2**)*: Zinc powder (1.95 g, 30 mmol) was slowly added to a solution of 2-bromothiophene (**1**, 4.89 g, 30 mmol), triphenylphosphine (1.57 g, 6 mmol), potassium iodide (0.2 g, 1.2 mmol) and $Ni(PPh_3)_2Cl_2$ (1.96 g, 3 mmol) in THF, then the mixture was refluxed under argon for 24 h. After cooling to room temperature, the solution was filtered and the filtrate was collected. The solvent was evaporated and the solid residue was purified by column chromatography on silica gel with petroleum ether as eluent to give greenish solid. Yield: 2.1 g, 84%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 7.20 (d, J = 4.8 Hz, 2H), 7.17 (d, J = 3.6 Hz, 2H), 7.02-7.00 (m, 2H).

*5,5'-bis(trimethylstannyl)-2,2'-bithiophene (**M1**)*: Compound **2** (1.00 g, 6.02 mmol) was dissolved in 60 mL of THF under argon, then the solution was cooled to −78 °C. 2.2 M of n-BuLi (6.0 mL, 13.2 mmol) was slowly added to the solution by syringe in 15 min. The reaction was maintained at −78 °C for 30 min, and warmed up to 20 °C for another 30 min. Then the solution was cooled to −78 °C again, and trimethyltin chloride (1 M, 14 mL, 14 mmol) was added to the mixture at once. After 1h, the reaction was moved to room temperature and stirred overnight. The solvent THF was evaporated, and the solid residue was redissolved in diethyl ether and washed with water. The organics were collected and dried over anhydrous Na_2SO_4. After the solvent was removed via rotary evaporation, the crude product was purified by recrystallization from ethanol to give white solid. Yield: 2.1 g, 70%. ^{1}H NMR (*d*-DMSO, 300 MHz) δ [ppm]: 7.33 (d, J = 2.4 Hz, 2H), 7.14 (d, J = 2.1 Hz, 2H), 0.35 (s, 18H).

*1-Iodo-2-octyldodecane (**4**)*: Iodine (6.06 g, 23.9 mmol) was added to a solution of 2-octyl-1-dodecanol (6.20 g, 20.8 mmol), triphenylphosphine (6.53 g, 24.9 mmol), and imidazole (1.69 g, 24.9 mmol) in 40 mL of dichloromethane at 0 °C. After stirring for

15 min, the reaction mixture was allowed to warm to room temperature for 12 h before 5 mL of sat. Na_2SO_3 (aq) was added. The solution were washed two times with 100 mL of water, and dried over Na_2SO_4. The organics were concentrated by evaporation and purified by column chromatography on silica gel with petroleum ether as eluent to give light yellow oil. Yield: 3.00 g, 35%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 3.27 (d, J = 3.9 Hz, 2H), 1.87 (b, 1H), 1.30-1.20 (b, 32H), 0.88 (t, J = 5.7 Hz, 6H).

*2-(2-octyldodecyl)isoindoline-1,3-dione (**5**)*: Compound **4** (2.60 g, 6.37 mmol) and potassium phthalimide (2.00 g, 10.8 mmol) were taken up in 25 mL of DMF and vigorously stirred for 72 h at 25 °C. The reaction mixture was then taken up in 200 mL of hexane, washed three times with 100 mL of water, dried over Na_2SO_4, and concentrated to give light yellow oil. The crude product was further purified by column chromatography on silica gel with petroleum ether as eluent to give colorless oil. Yield: 1.50 g, 56%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 7.84 (d, J = 2.4 Hz, 2H), 7.72 (d, J = 2.7 Hz, 2H), 3.57 (d, J = 7.2 Hz, 2H), 1.87 (b, 1H), 1.30-1.20 (b, 32 H), 0.87 (b, 6H).

*2-octyldodecan-1-amine (**6**)*: Compound **5** (1.50 g, 3.51 mmol) was taken up in 50 mL of ethanol, 2 mL of hydrazine hydrate was added, and the mixture was refluxed overnight. After the reaction, ethanol was removed via rotary evaporation. The resulting solid was dissolved in 100 mL of water, and the solution was made alkaline by addition of 6 M NaOH (aq). The mixture was then taken up in 100 mL of chloroform, washed three times with water, and concentrated. The crude product was further purified by column chromatography on silica gel with chloroform/methanol (10/1) as eluent to give colorless oil. Yield: 0.82 g, 79%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 2.62 (d, J = 5.1 Hz, 2H), 2.25 (b, 1H), 1.30-1.20 (b, 32H), 0.89 (t, J = 6 Hz, 6H).

*4,7-dibromoisobenzofuran-1,3-dione (**8**)*: A mixture of phthalic anhydride (**7**, 8 g, 54 mmol), oleum (50% free SO_3, 15 mL), bromine (10.4 g, 65 mmol), and iodine (51 mg, 0.2 mmol) was stirred at 60 °C for 24 hours. After cooling to room temperature, the solution was poured into ice water carefully before 20 mL of saturated Na_2SO_3 (aq) was added. The solid was collected by filtration and purified by recrystallization from acetic acid. White needle shape crystals were obtained. Yield: 5.05 g, 31%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 7.86 (s, 2H).

*4,7-dibromo-2-(2-octyldodecyl)isoindoline-1,3-dione (**M2**)*: Compound **8** (0.54 g, 1.8 mmol), **6** (0.58 g, 1.9 mmol) and glacial acetic acid (20 ml) were combined and refluxed under argon for 4 hours. After the acetic acid was removed under reduced pressure, the target **M2** was separated by column chromatography on silica gel with chloroform/petroleum ether (1/2) as eluent. Yield: 0.40 g, 38%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 7.66 (s, 2H), 3.57 (d, J = 6.9 Hz, 2H), 1.86 (b, 1H), 1.24 (b, 32H), 0.88-0.87 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ [ppm]: 165.08, 139.49, 131.19, 117.49, 42.88, 36.92, 31.92, 31.47, 29.94, 29.64, 29.38, 29.32, 26.30, 22.71, 14.18. Anal. Calcd for $C_{28}H_{43}Br_2NO_2$ (%): C, 57.44; H, 7.40; N, 2.39. Found: C, 57.32; H, 7.51; N, 2.28.

*5-(2-octyldodecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (**10**)*: Compound **9** (0.43g, 2.79 mmol), **6** (0.98 g, 3.30 mmol) and 20 mL of toluene were combined and refluxed under argon overnight. After the toluene was removed under reduced pressure, the residue was mixed with 15 mL of $SOCl_2$ and stirred at 80 °C for 4 hours. After the reaction was completed, the solvent was evaporated and the residue mixture was purified by column chromatography on silica gel with chloroform/petroleum ether (1/1) as eluent to give light yellow oil. Yield: 1.10 g, 91 %. ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 7.81 (s, 2H), 3.50 (d, J = 7.5Hz, 2H), 1.84 (s, 1H), 1.25 (b, 32H), 0.88-0.86 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ [ppm]: 163.16, 136.82, 125.64, 42.95, 37.07, 32.12, 31.62, 30.19, 29.85, 29.57, 26.46, 22.91, 14.35.

*1,3-dibromo-5-(2-octyldodecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (**M3**)*: Compound **10** (1.10 g, 2.53 mmol) and NBS (1.35 g, 7.59 mmol) were dissolved in a mixed solvent of sulfuric acid (5 mL) and trifluoroacetic acid (15 mL). The solution was stirred at room temperature overnight. Then the mixture was poured into ice water carefully, and extracted with chloroform. The organics were collected and dried over anhydrous Na_2SO_4. The solvent was removed via rotary evaporation and the residue solid was purified by column chromatography on silica gel with chloroform/petroleum ether (1/3) as eluent to give white solid. Yield: 1.21 g, 80%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 3.48 (d, J = 3.6 Hz, 2H), 1.81 (b, 1H), 1.34-1.25 (m, 32H), 0.89-0.87 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ [ppm]: 160.88, 134.93, 113.13, 43.30, 37.06, 32.13, 31.65, 30.34, 29.86, 29.57, 29.53, 26.50, 22.91, 14.30. Anal. Calcd for $C_{26}H_{41}Br_2NO_2S$ (%): C, 52.8; H, 6.99; N, 2.37. Found: C, 52.4; H, 7.30; N, 2.18.

Theoretical calculations:

The Gibbs free energies of all possible conformers were calculated at wb97xd/6-311g(d,p) level, and the one with the lowest energy was considered to be the stable conformer.

As shown in Table S1 and S2, the stable conformation of the repeating unit is *O-O* for **P1** and is *S-O* for **P2**. When the repeating unit is joined together to form polymer, there exist two conformations for the bithiophene unit (*cis*-form and *trans*-form) as shown in Table S3 and S4. Results revealed that both **P1** and **P2** dimers showed lower Gibbs free energies when the bithiophene units adopt *trans*-conformation with two sulfur atoms on the opposite side.

Table S1 The calculated Gibbs free energy at wb97xd/6-311g(d,p) level of three possible conformers of the repeating unit in **P1**.

conformation	the repeating unit in **P1**	Gibbs free	Relative Gibbs

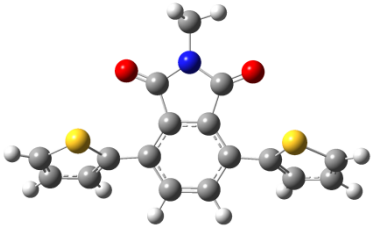
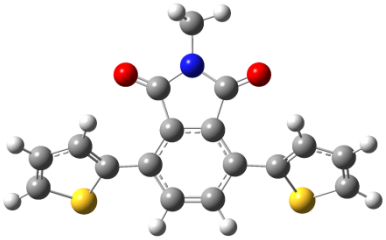
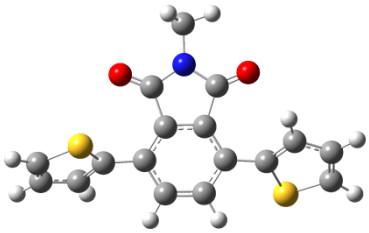
		energy (A.U.)	free energy (Kcal/mol)
S-S		-1655.758499	1.50
O-O		-1655.760889	0
S-O		-1655.759857	0.65

Table S2 The calculated Gibbs free energy at wb97xd/6-311g(d,p) level of three possible conformers of the repeating unit in **P2**

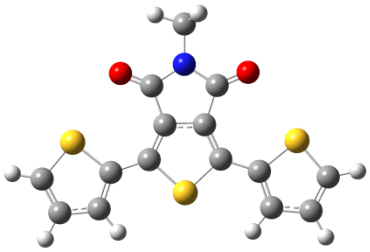
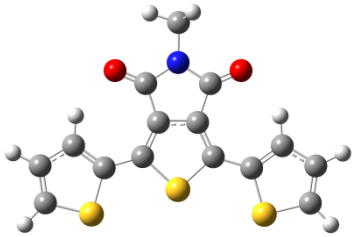
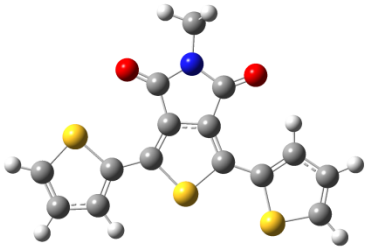
conformation	the repeating unit in **P2**	Gibbs free energy (A.U.)	Relative Gibbs free energy (Kcal/mol)
S-S		-1976.565831	3.72
O-O		-1976.568192	2.24
S-O		-1976.571762	0

Table S3 The calculated Gibbs free energy at wb97xd/6-311g(d,p) level of two possible conformers of the dimer in **P1.**

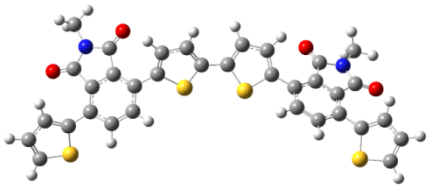
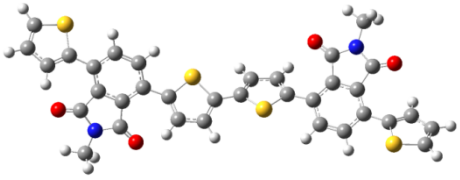
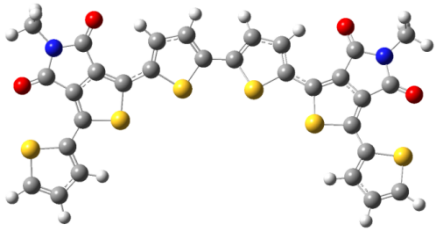
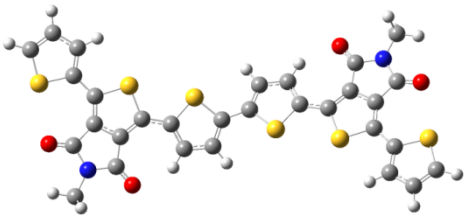
conformation of bithiophene	**P1** dimer	Gibb's free energy (A.U.)	Relative Gibb's free energy (Kcal/mol)
Cis		-3310.330090	0.84
Trans		-3310.331429	0

Table S4 The calculated Gibbs free energy at wb97xd/6-311g(d,p) level of two possible conformers of the dimer in **P2.**

Conformation of bithiophene	**P2** dimer	Gibb's free energy (A.U.)	Relative Gibb's free energy (Kcal/mol)
Cis		-3951.942773	1.16
Trans		-3951.944620	0

Reference:

1 S. Kotani, K. Shiina and K. Sonogashira, *J. Organomet. Chem.*, 1992, **429**, 403.

2 J. A. Letizia, M. R. Salata, C. M. Tribout, A. Facchetti, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 2008, **130**, 9679.

3 X. Guo, M. D. Watson, F. S. Kim and S. A. Jenekhe, *J. Am. Chem. Soc.*, 2009, **131**, 7206.

4 C. Piliego, C. H. Woo, P. M. Beaujuge, J. M. J. Frechet, T. W. Holcombe and J. D. Douglas, *J. Am. Chem. Soc.*, 2010, **132**, 7595.