Supporting Information for

Synthesis and Photovoltaic Properties of Thiophene–Imide-Fused Thiophene Alternating Copolymers with Different Alkyl Side Chains

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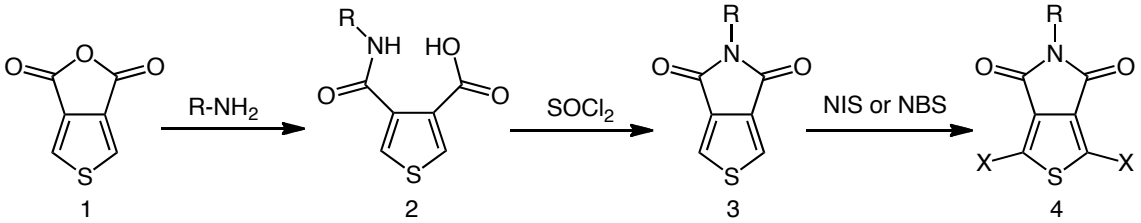
Monomer Synthesis



4-[(1-Octadecylamino)carbonyl]-3-thiophenecarboxylic acid, 2 (n = 18). A solution of thiophene-3,4-dicarboxylic anhydride **1** (468 mg, 3.04 mmol) and *n*-octadecylamine (873 mg, 3.24 mmol) in 50 mL of distilled toluene was refluxed for 24 h. The crude product was collected by filtration of the cold reaction mixture. Another portion of product was precipitated by washing the filtrate with 5 % hydrochloric acid and extracted with $CHCl_3$, and then the solvent was evaporated. Recrystallization from toluene afforded **2 (n = 18)** (1.21 g, 2.86 mmol, 94 %) as white crystals. ^{1}H NMR δ_H (400 MHz, $CDCl_3$): 8.40 (d, 1H), 7.73 (d, 1H), 6.46 (broad s, 1H), 3.41 (t, 2H), 1.58 (quintet, 2H), 1.46 - 0.76 (m, 33H).

4-[[1-(2-Pentylhexyl)amino]carbonyl]-3-thiophenecarboxylic acid, 2 (n = 11). Yield (98%). ^{1}H NMR δ_H (400 MHz, $CDCl_3$): 8.43 (d, 1H), 8.07 (d, 1H), 6.95 (broad s, 1H), 4.11 (m, 1H), 1.56 (m, 4H), 1.30 (m, 12H), 0.87 (t, 6H).

4-[[1-(2-Hexylheptyl)amino]carbonyl]-3-thiophenecarboxylic acid, 2 (n = 13). Yield (94%). ^{1}H NMR δ_H (400 MHz, $CDCl_3$): 8.46 (d, 1H), 7.87 (d, 1H), 6.42 (broad s, 1H), 4.11 (m, 1H), 1.56 (m, 4H), 1.28 (m, 16H), 0.87 (t, 6H).

5-Octadecyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione, 3 (n = 18). A solution of **2 (n = 18)** (1.21 g, 2.86 mmol) in 100 mL of thionyl chloride was refluxed for 3 h. The reaction mixture was concentrated to a light brown oil which was thoroughly dried to pale yellow crystals. Recrystallization from hexanes afforded **3 (n = 18)** (903 mg, 2.23 mmol, 78 %) as white crystals. ^{1}H NMR δ_H (400 MHz, $CDCl_3$): 7.80 (s, 2H), 3.60 (t, 2H), 1.63 (quintet, 2H), 1.54 - 0.86 (m, 33H).

5-(2-Pentylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione, 3 (n = 11). Yield (92%). ^{1}H NMR δ_H (400 MHz, $CDCl_3$): 7.84 (s, 2H), 4.11 (m, 1H), 1.60 (m, 4H), 1.28 (m, 16H), 0.86 (t, 6H).

5-(2-Hexylheptyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione, 3 (n = 13). Yield (85%). ^{1}H NMR δ_H (400 MHz, $CDCl_3$): 7.84 (s, 2H), 4.11 (m, 1H), 1.60 (m, 4H), 1.28 (m, 16H), 0.86 (t, 6H).

1,3-Diiodo-5-dodecyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione, 4 (n = 12, X = I). 3 (n = 12) (0.838 g, 2.70 mmol) was dissolved in 4.2 mL of concentrated sulfuric acid and 14.0 mL of trifluoroacetic acid. *N*-Iodosuccinimide (NIS) (2.44 g, 10.8 mmol) was added in two portions and the reaction mixture was stirred at room temperature for 24 h. The purple solution was then poured into 150 mL of ice water and extracted with dichloromethane. The organic phase was washed with 10 % sodium thiosulfate, dried over anhydrous magnesium sulfate and evaporated to afford the crude product as brown crystals. Purification by column chromatography using silica gel and dichloromethane/hexane (1:1) as eluent followed by recrystallization from aqueous ethanol

gave **4 (n = 12, X = I)** (0.868 g, 1.51 mmol, 56 %) as white crystals. ^{1}H NMR δ_H (400 MHz, $CDCl_3$): 3.59 (dd, 2H), 1.62 (quintet, 2H), 1.25 (m, 18H), 0.88 (t, 3H).

1,3-Dibromo-5-octadecyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione, 4 (n = 18, X = Br). 3 (n = 18) (887 g, 2.19 mmol) was dissolved in 3.4 mL of concentrated sulfuric acid and 11.3 mL of trifluoroacetic acid. *N*-Bromosuccinimide (NBS) (1.56 g, 4.67 mmol) was added in two portions and the reaction mixture was stirred at 55 °C over night. The brown solution was then diluted with 120 mL of water and extracted with 150 mL of dichloromethane. The organic phase was dried over $MgSO_4$ and evaporated to afford the crude product as orange crystals. Purification by column chromatography using silica gel with chloroform as eluent followed by recrystalization from ethanol gave **4 (n = 18, X = Br)** (716 mg, 1.27 mmol, 58 %) as white crystals. ^{1}H NMR δ_H (400 MHz, $CDCl_3$): 3.58 (t, 2H), 1.62 (quintet, 2H), 1.53 - 086 (m, 33H).

1,3-Diiodo-5-(2-Pentylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione, 4 (n = 11, X = I). Yield (61%). ^{1}H NMR δ_H (400 MHz, $CDCl_3$): 4.09 (m, 1H), 1.83 (m, 4H), 1.24 (m, 12H), 0.86 (t, 6H).

1,3-Diiodo-5-(2-Hexylheptyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione, 4 (n = 13, X = I). Yield (58%). ^{1}H NMR δ_H (400 MHz, $CDCl_3$): 4.09 (m, 1H), 1.83 (m, 4H), 1.24 (m, 16H), 0.86 (t, 6H).

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Table S1 Fluorescence Lifetimes (τ) of PnTPDT and P3HT in Chloroform Solutions and Film States

Polymer	τ in $CHCl_3$ (ns)	τ in solid states (ns)[a]
P12TPDT	0.8	0.2 (97%), 0.6 (3%)
P18TPDT	1.1	0.2 (97%), 0.7 (3%)
P11TPDT	1.2	0.3 (89%), 0.6 (11%)
P13TPDT	1.0	0.3 (85%), 0.6 (15%)
P3HT	0.5	< 0.1

[a] The component ratio of each fluorescence lifetime is given in parenthesis.

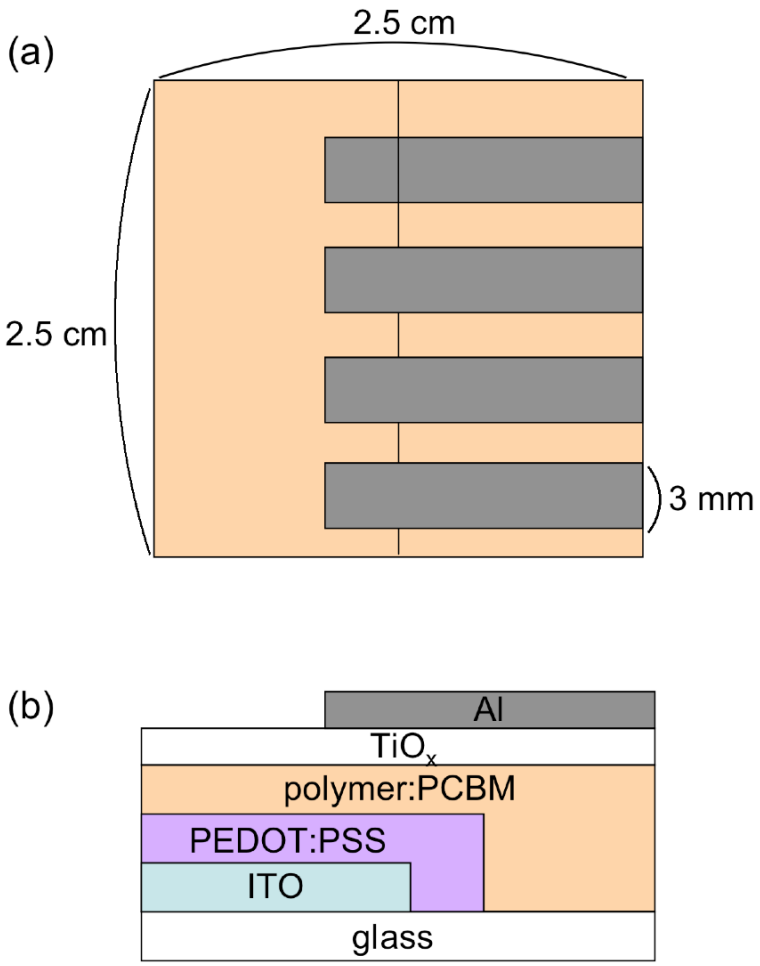


Fig. S1 Schematic illustrations of (a) top and (b) side views of the ITO/PEDOT:PSS/polymer:PCBM/TiO_x/Al device.

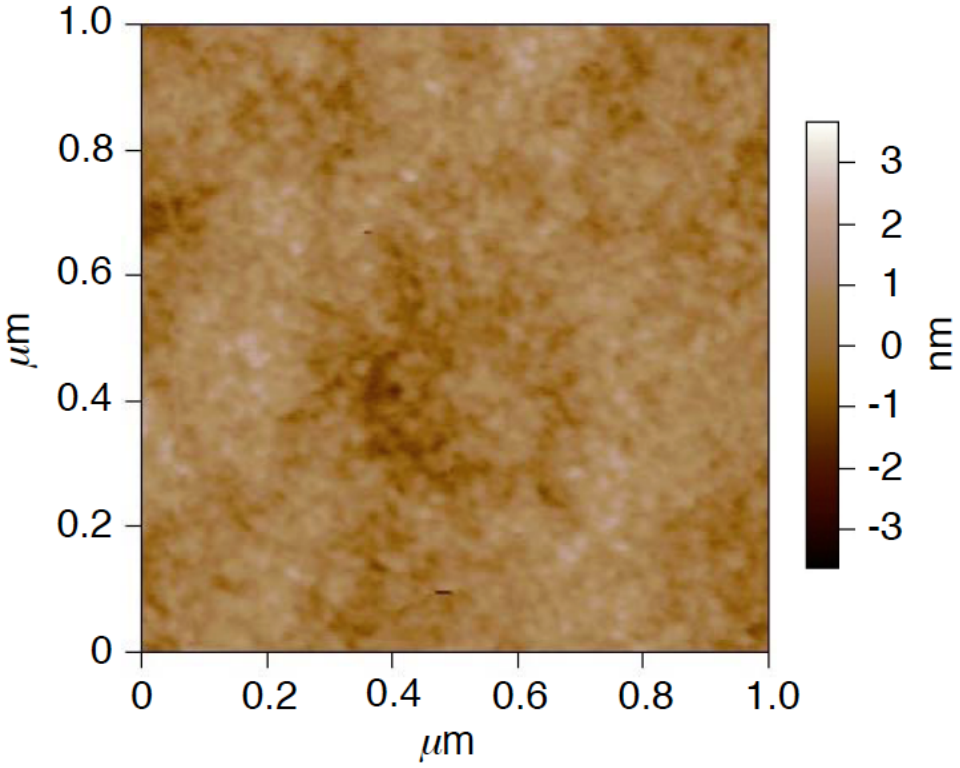


Fig. S2 Tapping-mode atomic force micrograph of P3HT:PCBM film. The color scale represents the height topography, with bright and dark representing the highest and lowest features, respectively.