Supporting Information

Fused Thieno[3,2-b]thiophene-dithiophene Based Donor Molecule for Organic Photovoltaics: Structural Comparative Study with Indacenodithiophene

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SYNTHESIS

4-Bromo-7-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo[c][2,1,3]thiadiazole, Compound 1

To a 100 ml 3 neck flask was added 4,7-dibromo-2,1,3-benzothiadiazole (1.5 g, 5.1 mmol), 5tributylstannyl-5'-hexyl-2,2'-bithiophene (2.3 g, 4.3 mmol) and degassed Toluene 20 ml, followed by adding Pd(PPh3)4 (450 mg, 0.39 mmol), and purged with nitrogen gas. The reaction was refluxed for overnight. The cooled mixture was poured into water and extracted with DCM. The organic layer was collected, dried over anhydrous MgSO4. The filtrate was evaporated and the residue was purified by flash column chromatography on silica gel using Hexane:Chloroform = 4:1 (v/v) as eluent to yield compound 1as red solid (990 mg, 50%).

¹H NMR (400 MHz, CDCl₃): δ 8.15 (d, *J*=4 Hz, 1H), 7.843 (d, *J*=7.5 Hz, 1H), 7.685 (d, *J*=7.5 Hz, 1H), 7.180 (d, *J*=4 Hz, 1H), 7.107 (d, *J*=4 Hz, 1H), 6.726 (d, *J*=4 Hz, 1H), 2.817 (t, 2H), 1.702 (m, 2H), 1.5-1.2 (m, 6H), 1.0-0.8 (m, 3H); MS (MALDI-TOF) m/z: 461 (M+); calcd 462.0

4-Boronic acid pinacol ester-7-(5'-hexyl-[2, 2'-bithiophen]-5-yl)benzo[c][2,1,3]thiadiazole, Compound 2

To a 50 ml 2 neck flask was added compound 1(880 mg, 1.9 mmol), B2pin2 (1.45 g, 5.7 mmol), KOAc (560 mg, 5.8 mmol) and thoroughly degassed Toluene 15 ml, followed by adding Pd(dppf)Cl2 (78 mg, 0.1 mmol), and purged with nitrogen gas. The reaction was heated up to 80 °C and stirred for 9 hrs. The cooled mixture was poured into water and extracted with DCM. The organic layer was dried over anhydrous MgSO4, filtrate, and dried by rotary evaporator. The crude product was purified by short column chromatography on silica gel using Hexane:THF =2:1 (v/v) as eluent to yield slight crude compound as red viscous oil (440 mg, 45 %). The product was used immediately to following reaction as was found to be unstable.

di(HTh2BT)IDT

diBr-IDT (135 mg, 0.11 mmol), compound 2 (170 mg, 0.33 mmol), Pd(PPh3)4 (20 mg, 0.017 mmol) were added to round-bottom flask purged with nitrogen gas, followed by THF (freeze pump thaw x3) 20 ml. The reaction was started by injecting K2CO3 aq (2M, 1 ml) and heating to 80 °C for reflux. The

reaction was completed in 2 hrs and quenched by adding water, followed by extraction with DCM. The organic layer was dried by anhydrous MgSO4, filtrate, and dried by rotary evaporator. The crude product was purified by column chromatography on silica gel using Hexane:chloroform =4:1 (v/v) as eluent (twice), followed by recrystallization with (Acetone/chloroform) to yield dark purple powder (110 mg, 52 %).

¹H NMR (400 MHz, CDCl₃): δ 8.07 (s, 2H), 8.02 (d, 2H, *J*=4Hz), 7.80 (m, 4H), 7.54 (s, 2H), 7.28–7.26 (m, 8H), 7.18 (d, 2H, *J*=4Hz), 7.12–7.09 (m, 10H), 6.72 (d, 2H, *J*=4Hz), 2.82 (t, 4H, *J*=7.6Hz), 2.58 (t, 8H, *J*=8.0 Hz), 1.73–1.55 (m, 8H), 1.40–1.28 (m, 40H), 0.90–0.84 (m, 18H); ¹³C NMR (100 MHz, CDCl₃): δ 156.8, 153.8, 152.5, 152.4, 146.1, 143.3, 142.1, 141.8, 141.6, 139.3, 137.5, 135.5, 134.6, 128.4, 128.2, 128.0, 126.3, 125.3, 125.1, 125.0, 124.7, 123.8, 123.8, 123.2, 117.7, 63.2, 35.6, 31.7, 31.6, 31.3, 30.2, 29.2, 28.8, 22.6, 14.1; MS (MALDI-TOF) m/z: 1671 (M+); calcd 1670.6; Elemental analysis calcd (%) for C104H110N4S8: C, 74.68; H, 6.63; N, 3.35; found: C, 74.87; H, 6.49; N, 3.33

Precursor 3

To a 250 ml 3 neck flask was added 2,5-Bis(trimethylstannyl)thieno[3,2-b]thiophene (2.51 g, 5.4 mmol), 2-Bromo-3-thiophene carboxylic acid ethyl ester (2.67 g, 11.4 mmol) and degassed Toluene 20 ml, followed by adding Pd(PPh3)4 (600 mg, 0.52 mmol), and purged with nitrogen gas. The reaction was refluxed for overnight. After the reaction, the solvent was removed by rotary evaporator and the residue was purified by flash column chromatography on silica gel using Hexane:DCM = 1:2 (v/v) as eluent. The compound was further purified by recrystallization from hot THF to yield compound as red powder (1.65 g, 68 %).

¹H NMR (400 MHz, CDCl₃): δ 7.67 (s, 2H), 7.51 (d, 2H, *J*=5.2 Hz), 7.23 (d, 2H, *J*=5.2 Hz), 4.31 (q, 4H, *J*=7.2 Hz), 1.33 (t, 6H, *J*=7.2) MS (MALDI-TOF) m/z: 447 (M+); calcd 448.0

Precursor 4

The 100 ml round-flask was equipped with activated magnesium turning (1.08 g, 44.4 mmol), a small portion of iodine and anhydrous THF 5ml under nitrogen atmosphere in ice bath. 4-n-octyl-bromobenzene (7.0 ml, 32.5 mmol) dissolved in THF 25 ml was dropwised into the system so that inside temperature should not exceed 40 °C and stirred for 1 hr. To a precursor 3 (1.67 g, 3.7 mmol) in a round-flask under nitrogen atmosphere was added the prepared Grignard reagent at room temperature. The resulting mixture was heated up to reflux for 2 hrs. After cooling down to room temprature, the reaction mixture was quenched by HCl aq. and was extracted DCM/0.1 M HClaq, and washed with brine. The combined organic layer was dried in anhydrous MgSO4, filtrated, and dried by rotary evaporator. The residue was purified by short column chromatography on silica gel using Hexane:DCM = 1:2 as eluent to yield a compound as orange powder (3.3 g, 79%)

¹H NMR (400 MHz, CDCl₃): δ 7.15-7.08 (m, 20H), 6.63 (s, 2H), 6.44 (d, 2H, *J* =5.2 Hz), 2.59 (t, 8H, *J* =8.0 Hz), 1.61-1.59 (m, 8H), 1.30–1.26 (m, 40H), 0.87 (t, 12H, *J* =6.4 Hz); MS (MALDI-TOF) m/z: 1099 (M-OH); calcd 1116.6

dibromo-DTCTT, Precursor 5

Precursor 4 (3.3 g, 2.95 mmol), Amberlyst 1.4 g and degassed Toluene 200 ml were added to a roundbottom flask and purged with nitrogen gas. The reaction was refluxed for 3 hrs. After filtration, the solvent was removed by rotary evaporator and the residue was purified by short column chromatography on silica gel using Hexane:DCM = 10:1 (v/v) to yield cyclized compound as yellow oil (2.47 g) and was immediately used to following reaction as was found to be unstable. The cyclized compound (2.47 g) and degassed chloroform 100 ml was added to a round-bottom flask, purged with nitrogen gas, and placed in ice bath. N-bromosuccimide (850 mg, 4.8 mmol) was slowly added into the system. After 1 hr of reaction time, the reaction was quenched by NaOH aq, followed by extraction with DCM/0.1 M NaOH aq., washed with brine. The combined organic layer was dried with anhydrous MgSO4, filtrated, and dried by rotary evaporator. The crude oil was purified by recrystallization (Acetone/DCM) to yield bright yellow powder (1.22 g, 33 % in 2 steps). ¹H NMR (400 MHz, CDCl₃): δ 7.12-7.04 (m, 18H), 2.55 (t, 8H), 1.6-1.1 (m, 44H), 0.867 (t, 12H); Elemental analysis calcd (%) for C72H86S4Br2: C, 69.77; H, 6.99; S, 10.35; found: C, 70.16; H, 6.58; S, 10.16

di(HTh2BT)DTCTT

This compound was synthesized with the same method of Th2BT-IDT from precursor 5 (150 mg, 0.12 mmol) to yield as dark green powder (110 mg, 50 %). ¹H NMR (400 MHz, CDCl₃): δ 8.14 (s, 2H), 8.02 (d, 2H, *J*=4 Hz), 7.79 (s, 4H), 7.25 (m, 8H), 7.18 (d, 2H *J*=4 Hz), 7.13-7.10 (m, 10H), 6.72 (d, 2H, *J*=4 Hz), 2.82 (t, 4H, *J*=7.6 Hz), 2.56 (t, 8H, *J*=7.6 Hz), 1.73-1.50 (m, 12H), 1.40-1.24 (m, 52H), 0.92-0.86 (m, 18H); ¹³C NMR (100 MHz, CDCl₃): δ 158.2, 152.5, 152.2, 149.3, 146.0, 142.0, 140.3, 139.5, 139.3, 139.2, 137.7, 137.6, 136.0, 134.7, 128.6, 128.1, 127.9, 126.2, 125.1, 125.0, 124.9, 124.1, 123.8, 123.7, 123.4, 62.4, 35.6, 31.9, 31.6, 31.3, 30.3, 29.5, 29.4, 29.2, 28.8, 22.6, 22.6, 14.1; MS (MALDI-TOF) m/z: 1844 (M+); calcd 1844.7; Elemental analysis calcd (%) for C112H124N4S10: C, 72.84; H, 6.77; N, 3.03; S, 17.36; found: C, 73.21; H, 6.50; N, 2.95



Fig. S1 Electronic cloud distribution of LUMO and HOMO levels for di(HTh2BT)DTCTT and di(HTh2BT)IDT calculated by B3LYP/6-31g(d,p) method.

The density functional theory (DFT) were performed to optimize the geometries of molecules by exchange-correlation functional B3LYP together with basis sets 6-31G(d, p). The resulting electronic cloud densities of LUMO and HOMO levels were plotted with an isovalue of 0.02 e/Å^3 . All the calculations were done with Gaussian09 program (Revision B.01)¹).



Fig. S2 Thermal gravimetric analysis graph of di(HTh2BT)DTCTT.

Thermal gravimetric analysis (TGA) was performed using TGA Q500 (TA Instruments) under nitrogen flow (heating rate of 10 °C/min).



Fig. S3 Polarized optical microscope image of di(HTh2BT)DTCTT on 2nd heating cycle; images were collected from samples on glass slide. Inset shows the same image without cross polarization filter. The yellow scale bar is 10 µm.

Polarized optical microscopy (POM) images were obtained with a Nikon Eclipse E600 POL equipped with a linkam THMS600 heating and cooling stage connected to a TMS92 temperature controller, recorded with Lumenera Inifinity-1 microscope camera.



Fig. S4 Dark *J-V* curves of hole-only devices composed of di(HTh2BT)DTCTT with thickness of 200 nm (blue square) and di(HTh2BT)IDT with thickness of 100 nm (red square) pristine film, respectively. The solid lines are fit to the experimental data according to the equation 1.

The hole mobilities of the DTCTT and IDT pristine film were estimated by fitting the dark current to space charge limited current (SCLC) model using hole-only devices with the configuration of ITO/PEDOT:PSS/pristine film/Au, where Vbi =0.1 (Work function of PEDOT:PSS is -5.2 V and that of Au is -5.1 V). ITO/PEDOT:PSS substrates were prepared with the same procedure with the OPV device fabrication. Both pristine film was made by spincoating solution of 15 mg/ml chloroform:oDCB = 9:1 mixed solution onto substrates, resulting in the film thickness of 200 nm and 100 nm, respectively. Au was thermally deposited on the film with the rate of 0.1 Å/s so as to minimize the penetration into pristine films and finally, 10 devices were made for each.

The SCLC mobility was estimated from the Equation 1.

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 exp^{[m]} \left(0.89\beta \sqrt{\frac{V - V_{bi}}{L}} \frac{(V - V_{bi})^2}{L^3} \right)$$
(1)

where *J* is dark current density, ε_0 is the vacuum permittivity, ε_r is the relative permittivity of material (ca. 3 for organic material), μ_0 is the hole mobility at zero field, β is the field activation factor, *L* is thickness of thin film. The internal potential is obtained by subtracting the built-in potential V_{bi} from the applied voltage *V*. Fitting to the model, the extracted hole mobility of the DTCTT and the IDT are 1.6 x 10⁻³ and 7.3 x 10⁻⁵ cm²/V·s, respectively.



Fig. S5 Out-of-plane XRD pattern for thin film of the DTCTT pristine film (square), the annealed film at 200 °C for 3 min (circle), the IDT pristine film (filled square), and the DTCTT/PC71BM blend film with the ratio of 1 to 1 (triangle). All film was prepared by spincoating solution from chloroform:oDCB=9:1 mixed solvent.



Fig. S6 UV-vis absorption spectra of the DTCTT (square) and PC71BM (filled square) pristine film and the blend film with the ratio of 1 to1 (triangle) and 1 to 3 (circle).

Reference

(1) Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.