

Small molecule donors with different conjugated π linking bridges: Synthesis and photovoltaic properties

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Abstract: Three small molecule (SM) donors, namely B-T-CN, B-TT-CN and B-DTT-CN, with different π conjugated bridges were synthesized in this research. Interestingly, with the conjugated fused rings of the π linking bridge increasing, the SM HOMO levels exhibit a decline tendency with -5.27 eV for B-T-CN, -5.31 eV for B-TT-CN and -5.40 eV for B-DTT-CN. After blending the SM donors with the fullerene acceptor PC₇₁BM, the all SM organic solar cells (OSCs) achieved high V_{oc} s of 0.90 to 0.96 V. However, the phase separation morphology and molecule stacking are also unexpectedly changed together with the enhancement of conjugated degree of π bridges, resulting in a lower power conversion efficiency (PCE) for the B-DTT-CN:PC₇₁BM device. Our results demonstrate and provide a useful way to enhance OSC V_{oc} and the morphology needs to be further optimized.

Key words: organic solar cell; small molecule donor; molecule energy levels; morphology

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Supporting Information

Supporting figures

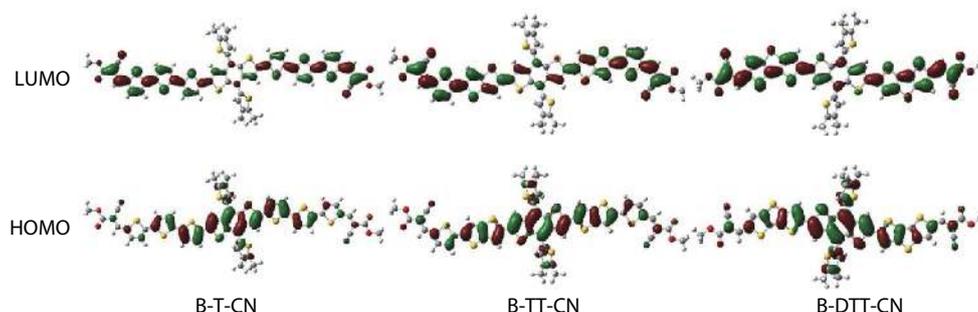


Fig. S1. (Color online) Energy distribution of B-T-CN, B-TT-CN, and B-DTT-CN calculated by DFT.

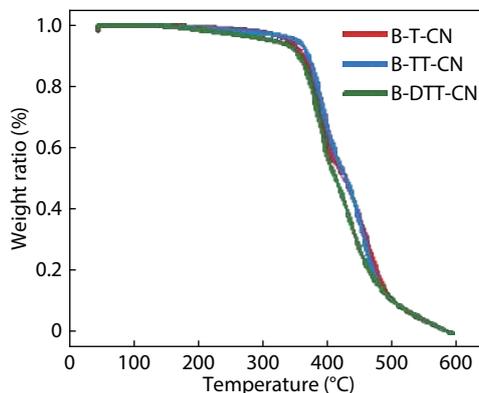


Fig. S2. (Color online) TGA plot for B-T-CN, B-TT-CN, and B-DTT-CN molecules.

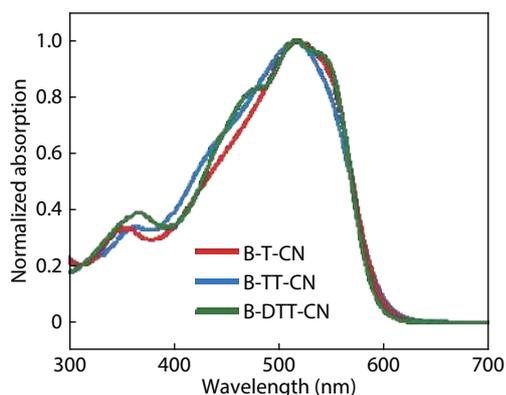


Fig. S3. (Color online) UV-vis in the chloroform solution of B-T-CN, B-TT-CN, and B-DTT-CN.

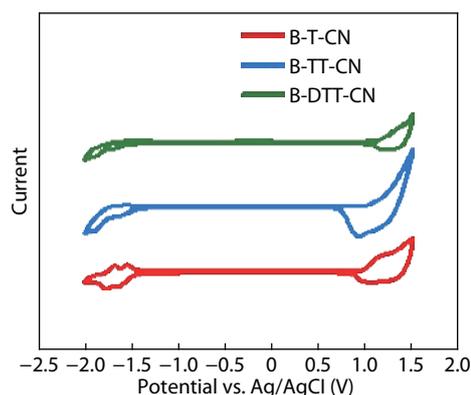


Fig. S4. (Color online) Cyclic voltammogram of B-T-CN, B-TT-CN, and B-DTT-CN thin films.

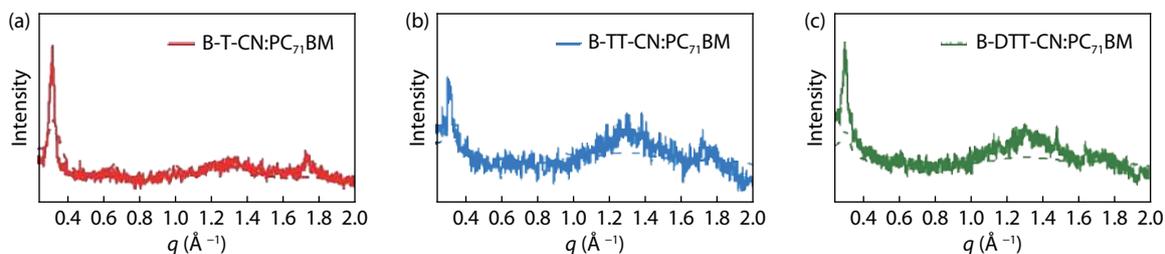


Fig. S5. (Color online) Out-of-plane (solid line) and in-plane (imaginary line) scattering profiles of three materials in blend films.

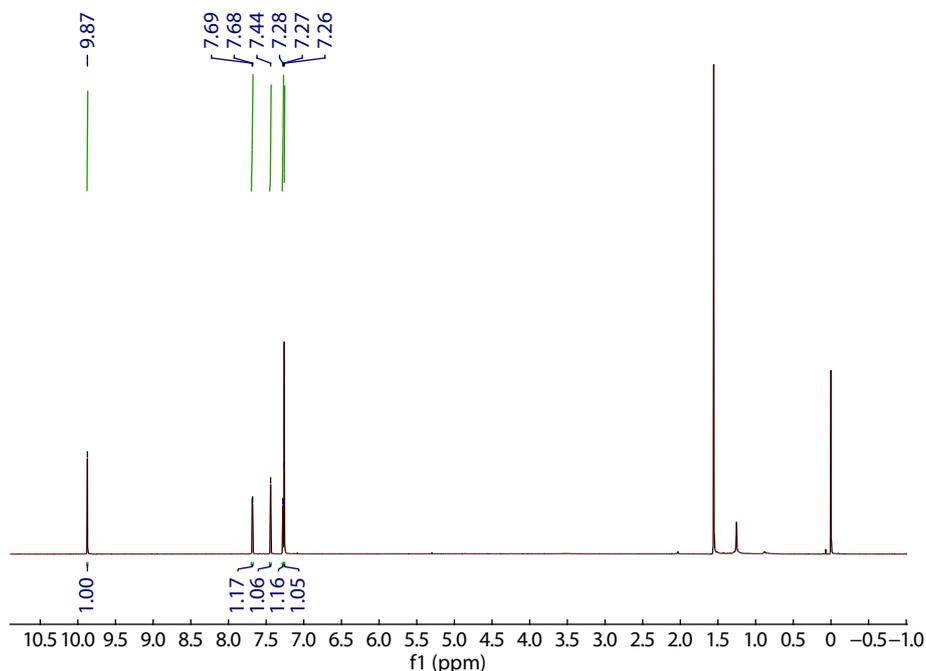
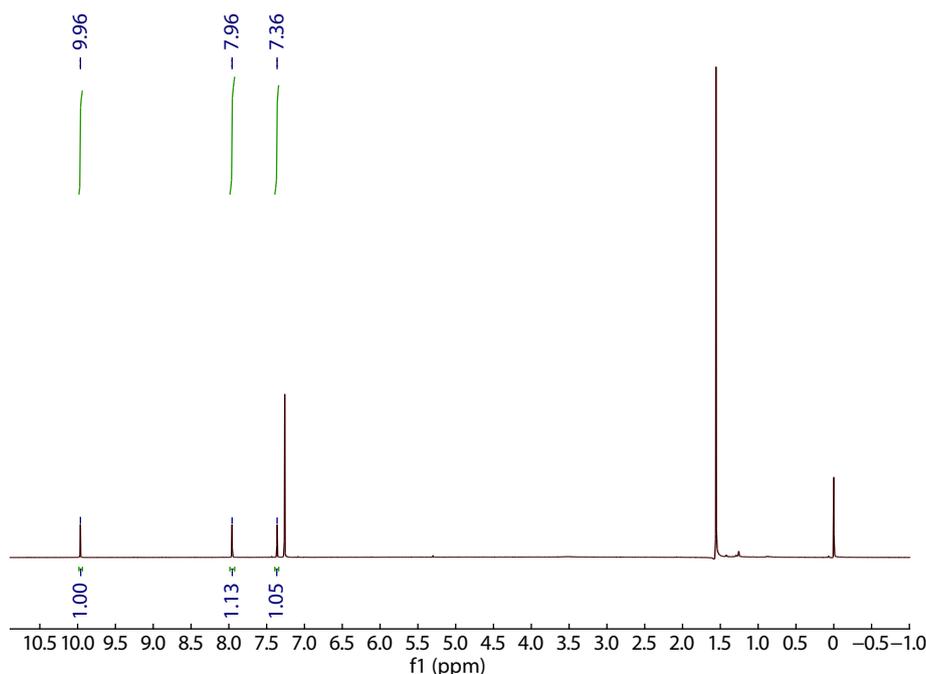
Synthesis and characterization

All reagents and intermediates were commercially available and used without further purification unless otherwise specified. The compound 1a was synthesized as reported in the previously literature^[1].

Synthesis of compounds 2b and 2c: Compounds 2a (300 mg, 2.14 mmol) were dissolved by a mixture solvent of chloroform (10 mL) and acetic acid (10 mL) in a 50 mL round bottomed flask. In dark condition, the NBS (418.3 mg, 2.35 mmol) were added in portions over 1 h at 0 °C and then the solution was stayed in ice bath for 30 min. Then the reaction mixture was stirred overnight at room temperature. The mixture was washed with aqueous sodium hydrogen carbonate, water and extracted by CH₂Cl₂ three times. The organic layer was collected and dried by anhydrous sodium sulfate, then

the solvent was removed under vacuum. The crude product was quickly rushed by silica column chromatography (pure petroleum spirit 40–60 °C Rf 0.8) to give 2b as a faint yellow liquid. Then, in a 100 mL reaction tube, compound 2b (427 mg, 1.95 mmol), 5-formyl-2-thiopheneboronic acid (304 mg, 1.95 mmol), tetrahydrofuran (15 mL) and Pd(PPh₃)₄ (200 mg) were added in turn under a nitrogen atmosphere. Then the K₂CO₃ aqueous solution (2 M, 1.5 mL) was added and the reaction mixture was stirred overnight at 70 °C. The reaction mixture was washed with water and extracted by CH₂Cl₂ three times. The organic layer was collected and dried by anhydrous sodium sulfate, then the solvent was removed under vacuum. The crude product was purified by silica column chromatography (petroleum spirit 40–60 °C : dichloromethane = 1 : 1 Rf 0.4) to give 2c as a dark yellow solid (207 mg, 0.83 mmol, 42.6% yield). ¹H NMR (600 MHz, CDCl₃) δ 9.88 (s, 1H), 7.69 (d, J = 3.8 Hz, 1H), 7.55 (s, 1H), 7.46 (d, J = 5.2 Hz, 1H), 7.29 (d, J = 3.8 Hz, 1H), 7.26 (d, J = 5.4 Hz, 1H).

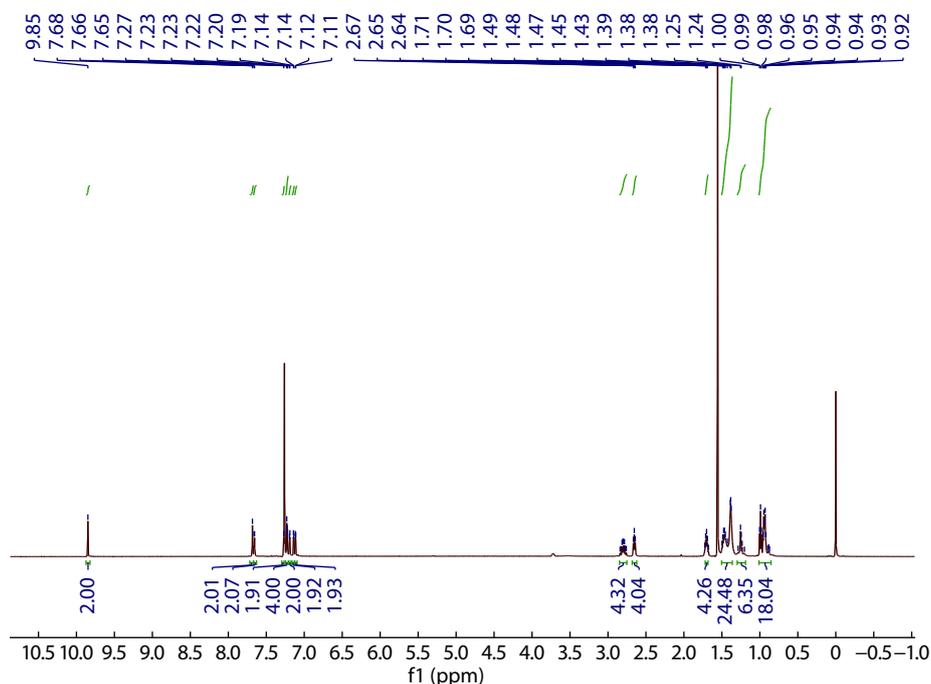
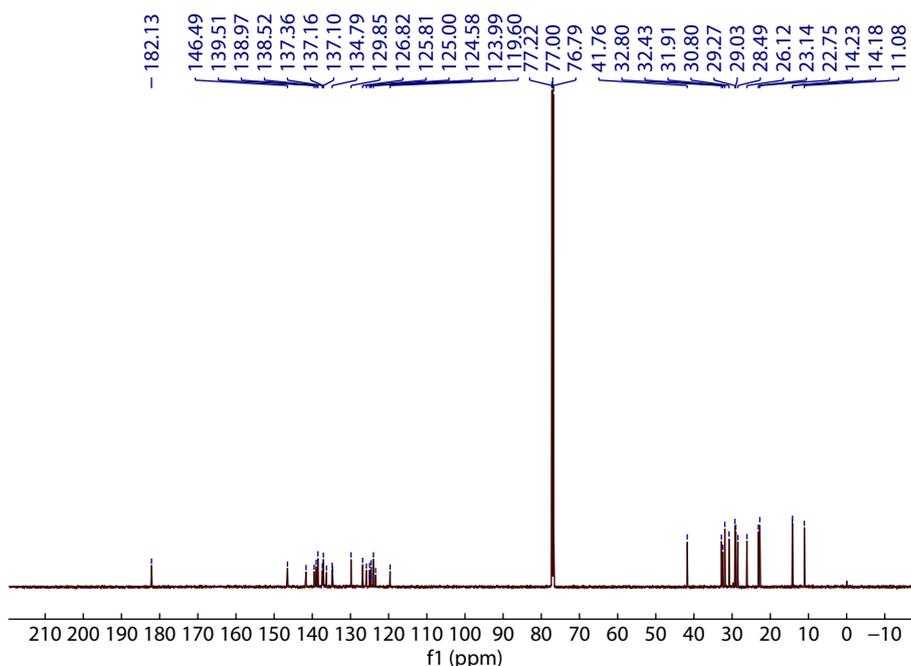
Synthesis of compound 2: The compounds 2c (207 mg,

¹H NMR spectrum of compound 2 (CDCl₃)¹H NMR spectrum of compound 3 (CDCl₃)

0.83 mmol) were dissolved in a mixture solvent of chloroform (10 mL) and acetic acid (10 mL) in a 50 mL round bottomed flask. In dark condition, the NBS (164 mg, 0.92 mmol) was added to the reaction in portions over 1 h at 0 °C and the solution was stayed in ice bath for 30 min. Then the reaction mixture was stirred overnight at room temperature. The mixture was washed with aqueous sodium hydrogen carbonate, water and extracted by CH₂Cl₂ three times. The organic layer was collected and dried by anhydrous sodium sulfate, then the solvent was removed under vacuum. The crude product was purified by silica column chromatography (petroleum spirit 40–60 °C : dichloromethane = 1 : 1 R_f 0.6) to give 2 as a faint yellow solid (246 mg, 0.75 mmol, 90.4% yield). ¹H NMR

(600 MHz, CDCl₃) δ 9.87 (s, 1H), 7.68 (d, *J* = 3.9 Hz, 1H), 7.44 (s, 1H), 7.27 (d, *J* = 3.9 Hz, 1H), 7.26 (s, 1H).

Synthesis of compound 3b: In a 100 mL dried reaction tube, the POCl₃ (280 mg, 1.83 mmol) were added to the dried DMF (1.7 mL) at 0 °C under N₂ atmosphere obtained the Vilsmeier reagents. After 1 h, the 1,2-dichloroethane (10 mL) solution of compound 3a (300 mg, 1.53 mmol) was added to the above mixture and the reaction mixture was stirred for 30 min in ice bath. Then the reaction tube was removed to the oil bath and stirred overnight at 70 °C. The solution was quenched with ice water and washed with aqueous sodium hydrogen carbonate to pH = 7. The organic layer was collected and the solvent removed by vacuum. Then the crude product

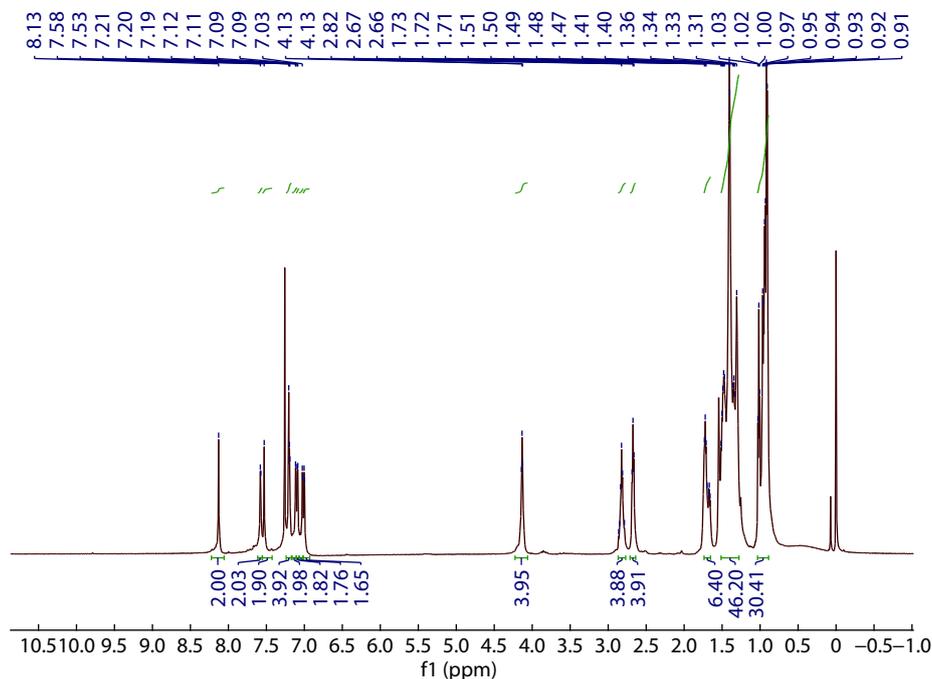
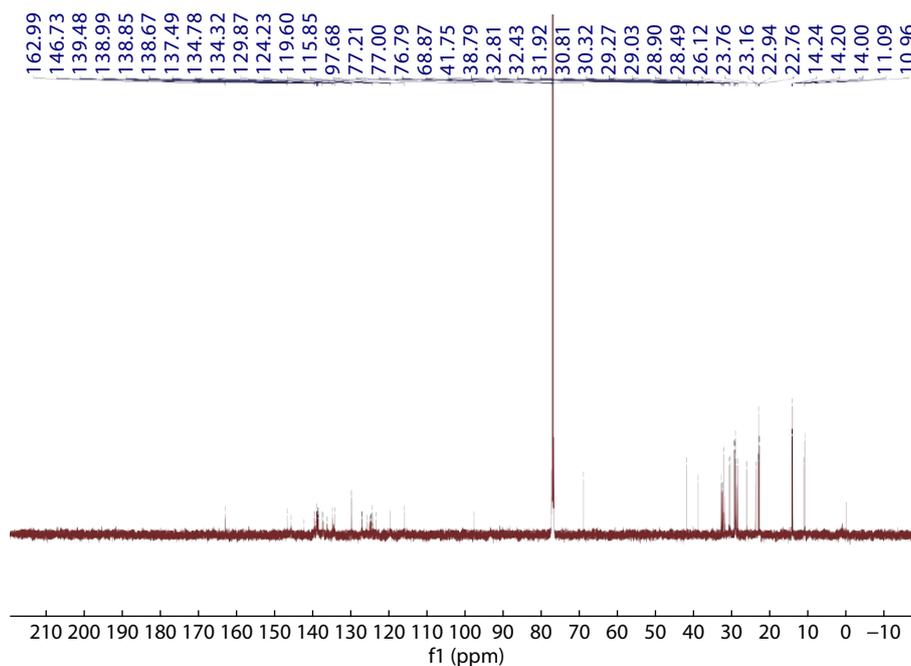
¹H NMR spectrum of compound B-T-CHO (CDCl₃)¹³C NMR spectrum of compound B-T-CHO (CDCl₃)

was washed with water and petroleum three times to give a white solid (293 mg, 1.31 mmol, 71.6% yield) without further purification. ¹H NMR (600 MHz, CDCl₃) δ 9.96 (s, 1H), 7.97 (s, 1H), 7.57 (d, *J* = 5.2 Hz, 1H), 7.35 (d, *J* = 5.2 Hz, 1H).

Synthesis of compound 3: The compound 3b (293 mg, 1.31 mmol) were dissolved in a mixture solvent of chloroform (10 mL) and acetic acid (10 mL) in a 50 mL round bottomed flask. In dark condition, NBS (256 mg, 1.44 mmol) were added to the reaction in portions over 1 h at 0 °C and the solution was stayed in ice bath for 30 min. Then the reaction mixture was stirred overnight at room temperature. The mixture was washed with aqueous sodium hydrogen carbonate, water and extracted by CH₂Cl₂ three times. The organic lay-

er was collected and dried by anhydrous sodium sulfate, then the solvent was removed under vacuum. The crude product was purified by silica column chromatography (petroleum spirit 40–60 °C : dichloromethane = 1 : 1 Rf 0.5) to give 3 as a faint yellow solid (324 mg, 1.07 mmol, 81.7% yield). ¹H NMR (600 MHz, CDCl₃) δ 9.96 (s, 1H), 7.96 (s, 1H), 7.36 (s, 1H).

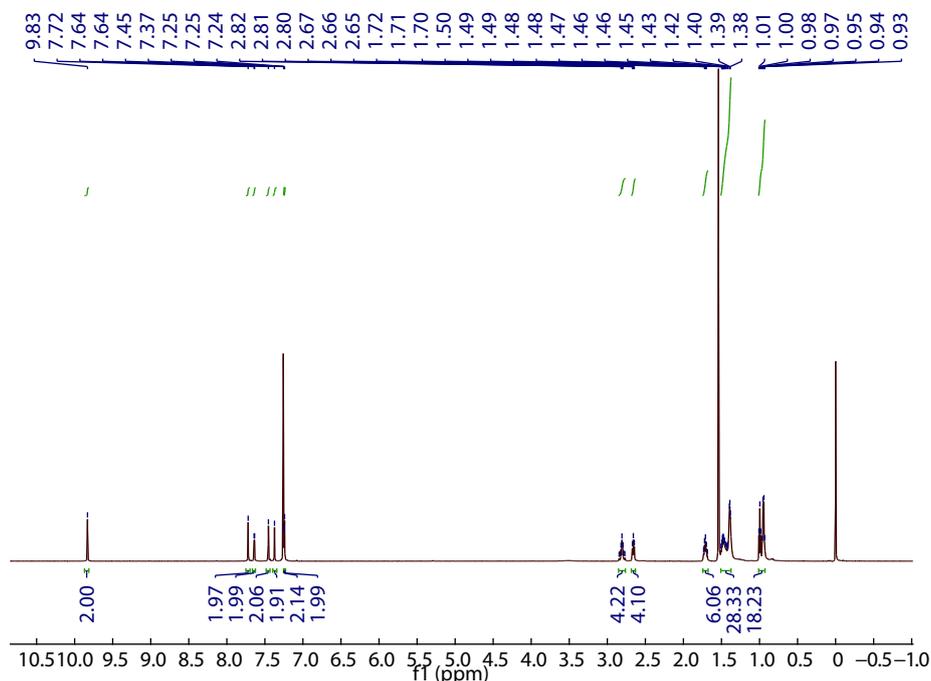
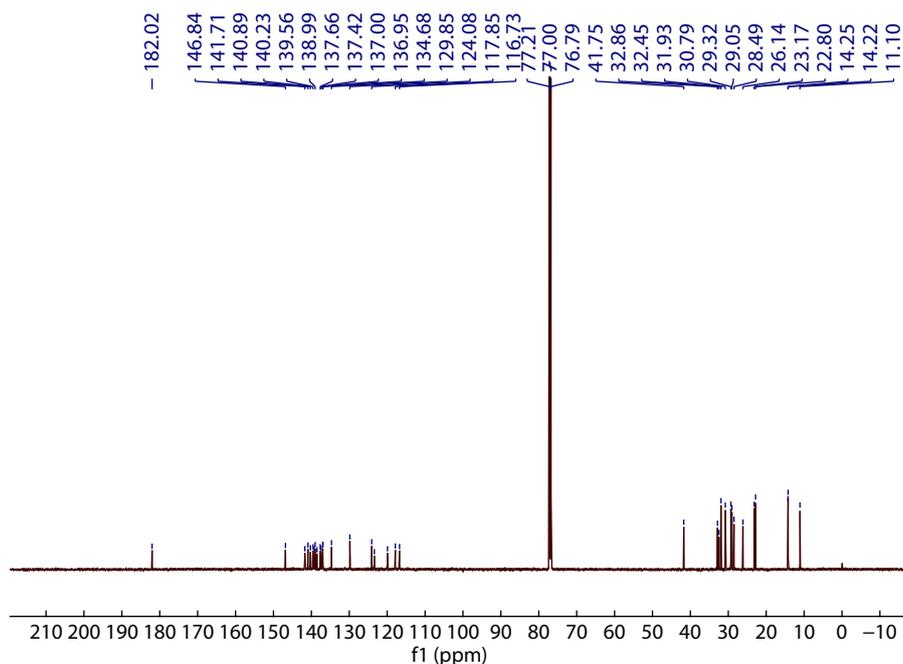
Synthesis of compound B-T-CHO: Compound 1 (195 mg, 0.55 mmol) and compound 4 BDT (268 mg, 0.25 mmol) were dissolved by toluene (20 mL) in reaction tube, the solution was degassed by bubbling N₂ for 15 min, then the Pd(PPh₃)₄ (29 mg, 0.025 mmol) were added and then the N₂ was continue bubbling for 10 min. Then the mixture was heated to 120 °C and refluxed overnight under N₂ atmosphere. The

¹H NMR spectrum of compound B-T-CN (CDCl₃)¹³C NMR spectrum of compound B-T-CN (CDCl₃)

solvent was removed by vacuum, then the crude product was purified by silica column chromatography (petroleum spirit 40–60 °C : dichloromethane = 1 : 1.5 Rf 0.4) to give B-T-CHO as a red solid (272 mg, 0.21 mmol, 84% yield). ¹H NMR (600 MHz, CDCl₃) δ 9.85 (s, 2H), 7.68 (s, 2H), 7.66 (d, *J* = 3.9 Hz, 2H), 7.27 (s, 2H), 7.25–7.21 (m, 4H), 7.19 (d, *J* = 3.7 Hz, 2H), 7.14 (d, *J* = 3.7 Hz, 2H), 7.11 (d, *J* = 3.7 Hz, 2H), 2.84–2.76 (m, 4H), 2.65 (t, *J* = 7.5 Hz, 4H), 1.72–1.68 (m, 4H), 1.50–1.36 (m, 24H), 1.30–1.19 (m, 6H), 1.00–0.92 (m, 18H). ¹³C NMR (151 MHz, CDCl₃) δ 182.13, 146.49, 141.64, 139.51, 138.97, 138.52, 137.36, 137.16, 137.10, 136.29, 134.79, 134.68, 129.85, 126.82, 125.81, 125.05, 125.00, 124.62, 124.58, 123.99, 123.42, 119.60, 77.22, 77.00, 76.79, 41.76, 32.80, 32.43, 31.91, 30.80, 29.27, 29.03,

28.49, 26.12, 23.14, 22.75, 14.23, 14.18, 11.08. MS *m/z*: [M⁺] calculated for C₇₂H₇₈O₂S₁₀, 1294.3209; found, 1294.3217.

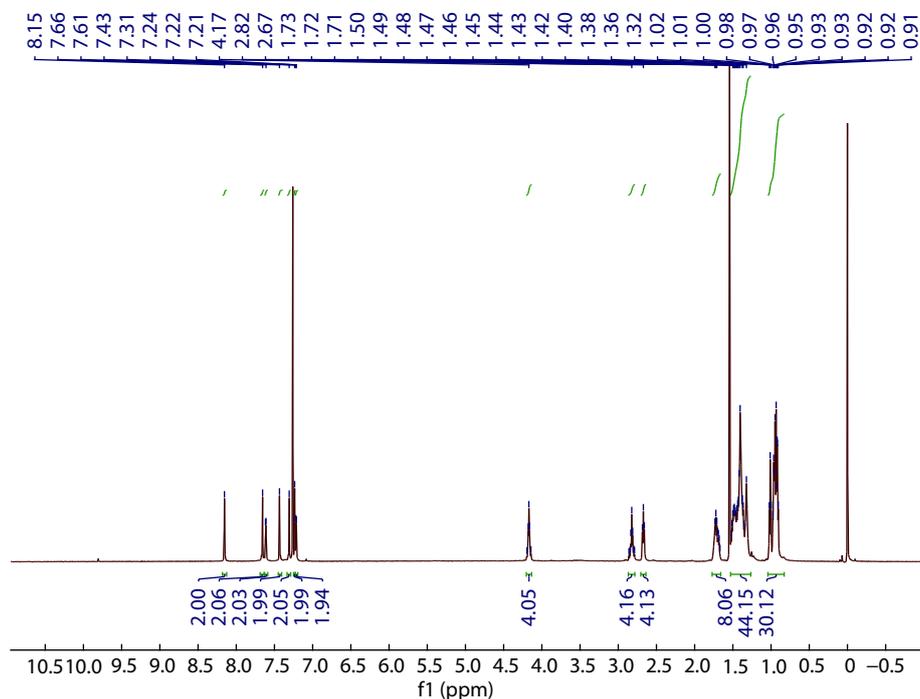
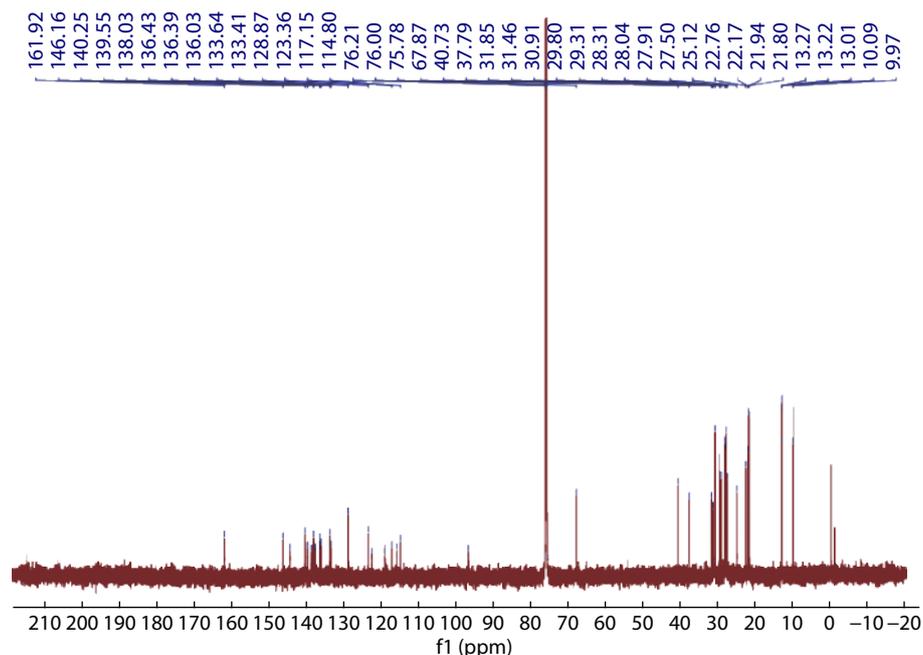
Synthesis of compound B-T-CN: Under N₂ protection, compound B-T-CHO (100mg, 0.077 mmol) and 2-ethylhexyl cyanoacetate (152 mg, 0.77 mmol) were dissolved in dried chloroform (20 mL) and then added NEt₃ 0.5 mL at room temperature. After 6 h, the reaction was stopped by put the mixture into methanol. The solvent was removed by vacuum. Washed the mixture three times with methanol, n-hexane and acetone, the black solid was collected to give B-T-CN (117 mg, 0.071 mmol, 92.2% yield). ¹H NMR (600 MHz, CDCl₃) δ 8.13 (s, 2H), 7.58 (d, *J* = 3.7 Hz, 2H), 7.53 (s, 2H), 7.24–7.17 (m, 4H), 7.11 (d, *J* = 3.7 Hz, 2H), 7.09 (d, *J* = 3.4 Hz, 2H), 7.02 (d, *J* =

 ^1H NMR spectrum of compound B-TT-CHO (CDCl_3) ^{13}C NMR spectrum of compound B-TT-CHO (CDCl_3)

3.4 Hz, 2H), 7.00 (*d*, $J = 3.4$ Hz, 2H), 4.23–4.06 (m, 4H), 2.87–2.77 (m, 4H), 2.71–2.64 (m, 4H), 1.74–1.65 (m, 6H), 1.51–1.28 (m, 46H), 1.03–0.89 (m, 30H). ^{13}C NMR (151 MHz, CDCl_3) δ 162.99, 146.73, 145.56, 142.24, 139.48, 138.99, 138.85, 138.67, 138.48, 137.49, 137.13, 136.25, 134.78, 134.32, 129.87, 127.14, 125.86, 125.13, 124.70, 124.23, 123.36, 119.63, 119.60, 115.85, 97.68, 77.21, 77.00, 76.79, 68.87, 41.75, 38.79, 32.81, 32.43, 31.92, 30.81, 30.32, 29.27, 29.03, 28.90, 28.49, 26.12, 23.76, 23.16, 22.94, 22.76, 14.24, 14.20, 14.00, 11.09, 10.96. MS m/z : [M^+] calculated for $\text{C}_{94}\text{H}_{112}\text{N}_2\text{O}_4\text{S}_{10}$, 1652.5829; found, 1652.5836.

Synthesis of compound B-TT-CHO: As the similar meth-

ods described at B-T-CHO, B-TT-CHO were synthesized by compound 2 (246 mg, 0.75 mmol) and compound 4 BDT (365 mg, 0.34 mmol) as a red solid (352 mg, 0.28 mmol, 82.3% yield). ^1H NMR (600 MHz, CDCl_3) δ 9.83 (s, 2H), 7.72 (s, 2H), 7.64 (*d*, $J = 3.9$ Hz, 2H), 7.45 (s, 2H), 7.37 (s, 2H), 7.25 (*d*, $J = 3.9$ Hz, 2H), 7.24 (s, 2H), 2.85–2.76 (m, 4H), 2.66 (*t*, $J = 7.6$ Hz, 4H), 1.75–1.68 (m, 6H), 1.50–1.38 (m, 28H), 1.01–0.93 (m, 18H). ^{13}C NMR (151 MHz, CDCl_3) δ 182.02, 146.84, 141.71, 140.89, 140.23, 139.56, 139.28, 138.99, 138.51, 137.66, 137.42, 137.00, 136.95, 134.68, 129.85, 124.08, 123.38, 119.91, 117.85, 116.73, 77.21, 77.00, 76.79, 41.75, 32.86, 32.45, 31.93, 30.79, 29.32, 29.05, 28.49, 26.14, 23.17, 22.80, 14.25, 14.22, 11.10. MS m/z :

¹H NMR spectrum of compound B-TT-CN (CDCl₃)¹³C NMR spectrum of compound B-TT-CN (CDCl₃)

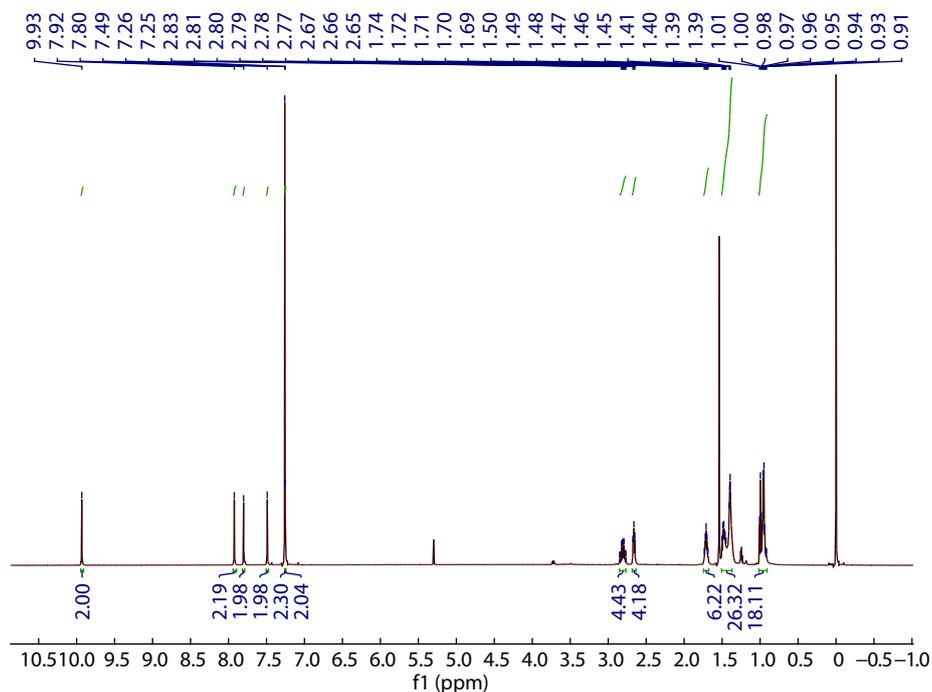
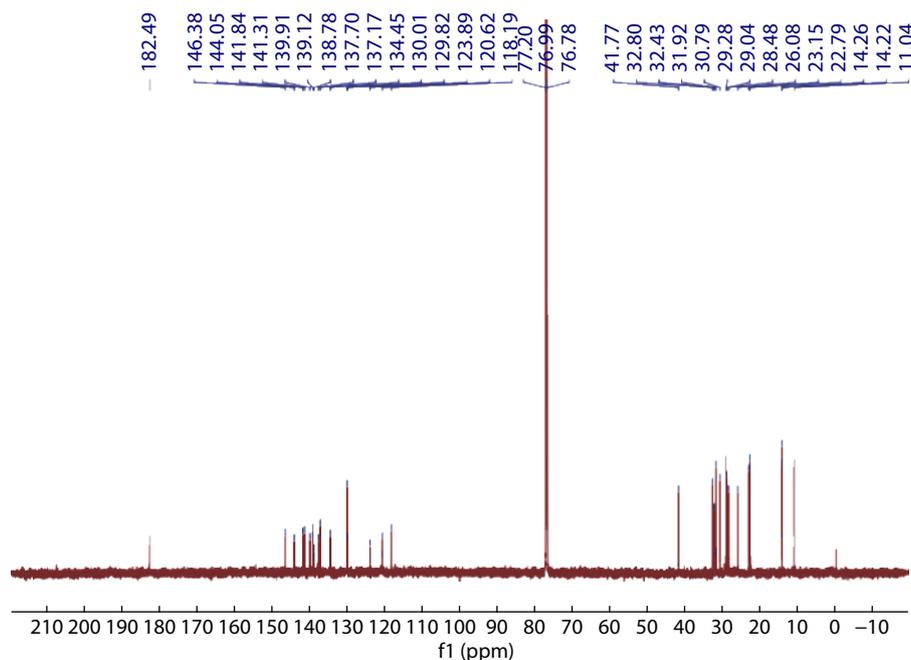
[M⁺] calculated for C₆₈H₇₄O₂S₁₀, 1242.2896; found, 1242.2302.

Synthesis of compound B-TT-CN: As the similar methods described at B-T-CN, B-TT-CN were synthesized by B-TT-CHO (100 mg, 0.08 mmol) and 2-ethylhexyl cyanoacetate (158 mg, 0.8 mmol) as a black solid (117 mg, 0.073 mmol, 91% yield).

¹H NMR (600 MHz, CDCl₃) δ 8.15 (s, 2H), 7.66 (s, 2H), 7.61 (d, *J* = 3.9 Hz, 2H), 7.43 (s, 2H), 7.31 (s, 2H), 7.24 (s, 2H), 7.22 (d, *J* = 3.9 Hz, 2H), 4.17 (p, *J* = 10.7 Hz, 4H), 2.87–2.78 (m, 4H), 2.67 (t, *J* = 7.6 Hz, 4H), 1.77–1.66 (m, 8H), 1.50–1.32 (m, 44H), 1.02–0.91 (m, 30H). ¹³C NMR (151 MHz, CDCl₃) δ 161.92, 146.16, 144.39, 140.25, 139.55, 138.60, 138.52, 138.03, 137.58, 136.43, 136.39, 136.03, 133.64, 133.41, 128.87, 123.36, 122.42,

119.00, 117.15, 115.76, 114.80, 96.79, 67.87, 40.73, 37.79, 31.85, 31.46, 30.91, 29.80, 29.31, 28.31, 28.04, 27.91, 27.50, 25.12, 22.76, 22.17, 21.94, 21.80, 13.27, 13.22, 13.01, 10.09, 9.97. MS *m/z*: [M⁺] calculated for C₉₀H₁₀₈N₂O₄S₁₀, 1600.5516; found, 1600.5508.

Synthesis of compound B-DTT-CHO: As the similar methods described at B-T-CHO and B-TT-CHO, B-DTT-CHO were synthesized from compound 3 (200 mg, 0.66 mmol) and compound 4 BDT (322 mg, 0.3 mmol) as a red solid (262 mg, 0.22 mmol, 73% yield). ¹H NMR (600 MHz, CDCl₃) δ 9.93 (s, 2H), 7.92 (s, 2H), 7.80 (s, 2H), 7.49 (s, 2H), 7.26 (s, 2H), 7.25 (s, 2H), 2.83–2.78 (m, 4H), 2.66 (t, *J* = 7.6 Hz, 4H), 1.74–1.68 (m, 6H),

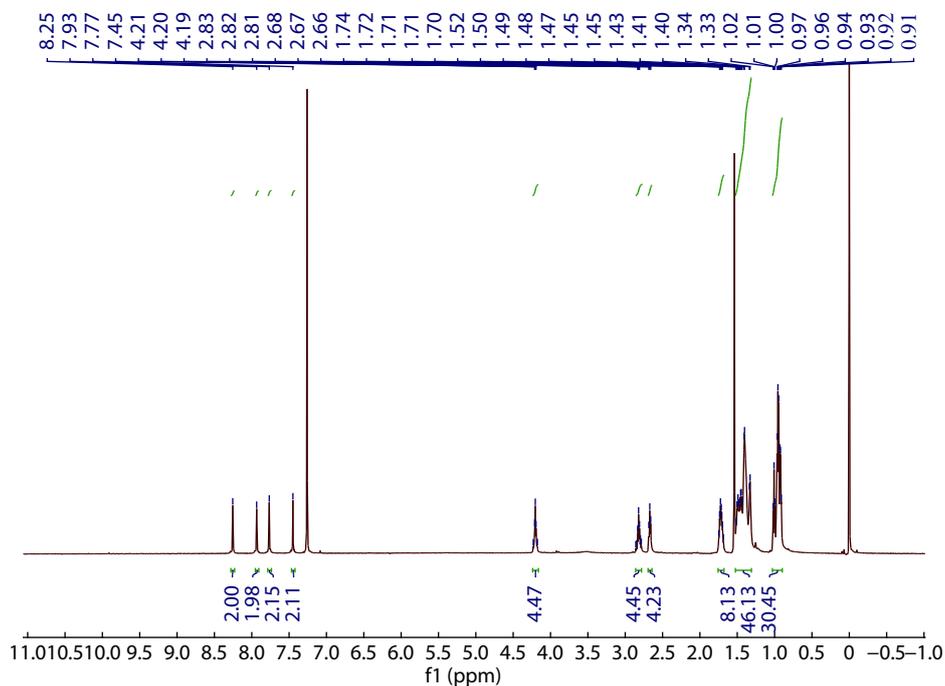
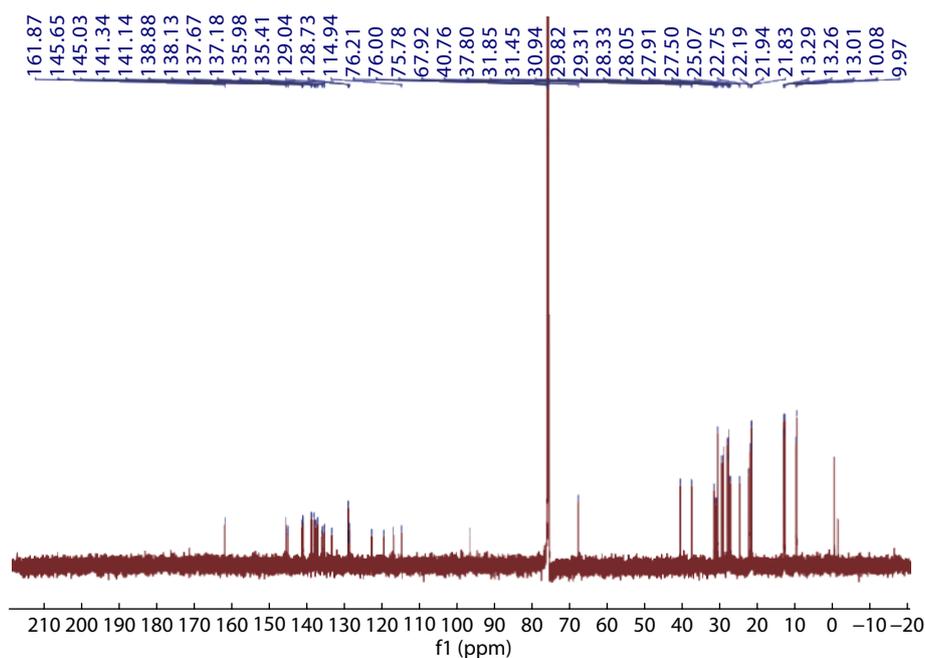
¹H NMR spectrum of B-DTT-CHO (CDCl₃)¹³C NMR spectrum of compound B-DTT-CHO (CDCl₃)

1.51–1.37 (m, 26H), 1.01–0.91 (m, 18H). ¹³C NMR (151 MHz, CDCl₃) δ 182.49, 146.38, 144.05, 141.84, 141.31, 139.91, 139.12, 138.81, 138.78, 137.70, 137.17, 134.45, 130.01, 129.82, 123.89, 120.66, 120.62, 118.19, 41.77, 32.80, 32.43, 31.92, 31.80, 30.79, 29.28, 29.04, 28.48, 26.08, 23.15, 22.79, 14.26, 14.22, 14.14, 11.04. MS m/z: [M⁺] calculated for C₆₄H₇₀O₂S₁₀, 1190.2583; found, 1190.2578.

Synthesis of compound B-DTT-CN: As the similar methods described at B-T-CN and B-TT-CN, B-DTT-CN was synthesized by B-DTT-CHO (100 mg, 0.084 mmol) and 2-ethylhexyl cyanoacetate (165 mg, 0.84 mmol) as a black solid (118 mg, 0.076 mmol, 90.5% yield). ¹H NMR (600 MHz, CDCl₃) δ 8.25 (s,

2H), 7.93 (s, 2H), 7.77 (s, 2H), 7.45 (s, 2H), 4.20 (p, J = 10.6 Hz, 4H), 2.86–2.78 (m, 4H), 2.67 (t, J = 7.5 Hz, 4H), 1.76–1.68 (m, 8H), 1.52–1.31 (m, 46H), 1.03–0.90 (m, 30H). ¹³C NMR (151 MHz, CDCl₃) δ 161.87, 145.65, 145.04, 145.03, 141.34, 141.14, 138.88, 138.13, 137.67, 137.18, 136.06, 135.98, 135.41, 133.42, 129.04, 128.99, 128.92, 128.73, 122.78, 119.61, 117.07, 114.94, 96.78, 76.21, 76.00, 75.78, 67.92, 40.76, 37.80, 31.85, 31.45, 30.94, 29.82, 29.31, 28.33, 28.05, 27.91, 27.50, 25.07, 22.75, 22.19, 21.94, 21.83, 13.29, 13.26, 13.01, 10.08, 9.97. MS m/z: [M⁺] calculated for C₈₆H₁₀₄N₂O₄S₁₀, 1548.5203; found, 1548.5208.

Supporting methods

¹H NMR spectrum of B-DTT-CN (CDCl₃)¹³C NMR spectrum of compound B-DTT-CN (CDCl₃)

Material characterization: ¹H NMR and ¹³C NMR spectra were measured by AVANCE550 nuclear resonance (NMR) 600 and 151 MHz spectroscopy. High resolution MALDI TOF mass spectrometry were tested on a Bruker Daltonics Solari X MALDI-TOF-MS. UV-Vis absorption spectra were obtained with a Perkin Eimer Lambda 365 spectrophotometer. Cyclic voltammetry were measured by CH Instruments Ins. 600E electrochemical workstation with three electrode system which using glassy carbon electrode as working electrode, platinum wire electrode as counter electrode, and Ag/AgCl electrode as reference electrode. The 0.1 M acetonitrile solution of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) were employed as electrolyte. The CV curves versus the potential of ref-

erence electrode were recorded, which was calibrated by the ferrocene-ferrocenium (Fc/Fc⁺) redox couple (4.8 eV below the vacuum level). The working electrode were burnished by the alpha alumina powder (0.3 μm) and sanding paper. And the materials were measured by coating a film on the working electrode surface. Before the electrochemical workstation working, the electrolyte were degassed by bubbling N₂ for 5 min. And as the testing process, the N₂ were still injected at the top liquid surface. The details about measured parameters as following: Scan rate (V/s): 0.05; Segment: 3; Sample interval (V): 0.001; Quiet time (s): 4; Sensitivity (A/V): 10⁻⁵. Thermo gravimetric analysis (TGA) was carried out on a METTLER TOLEDO TGA thermo gravimetric analyzer with thermal

balance under protection of nitrogen at a heating rate of 10 °C/min.

Device fabrication and characterization: Patterned ITO glasses with a sheet resistance of 15 Ω/□ were washed sequentially by detergent, deionized water, acetone, and isopropyl alcohol in an ultrasonic bath sequentially for 30 min, and further treated with UV-ozone for 15 min. A thin layer (ca. 30 nm) of PEDOT:PSS (Clevios P VP Al 4083) was spin coated on at 4000 rpm and baked at 120 °C for 10 min under ambient conditions. The substrates were then transferred into a nitrogen-filled glove box. The optimized overall concentration was 20 mg/mL in chloroform solution with D/A ratio of 1 : 1 (w/w) for both B-T-CN:PC₇₁BM, B-TT-CN:PC₇₁BM and B-DTT-CN:PC₇₁BM based devices. Active layer was spin coated at 3000 rpm, after that, 10 s of solvent vapor annealing by tetrahydrofuran was performed. Then Phen-NaDPO was spin-coated on the active layer by 2000 rpm from isopropyl alcohol solution with a concentration at 0.5 mg/mL. Then, the films were transferred into a thermal evaporator, 100 nm of Ag was deposited through a shadow mask with 0.11 cm² of active area under a base pressure of 2 × 10⁻⁶ Torr.

SCLC mobility measurements: The carrier mobility (hole and electron mobilities) of photoactive layer was determined by fitting the dark current of hole-/electron-only diodes to the SCLC model. Hole-only diode configuration: Glass/ITO/MoO₃/active layer/MoO₃/Ag; electron-only diode configuration: Glass/ITO/ZnO/Phen-NaDPO/active layer/Phen-NaDPO/Ag; the active layer thickness was determined by a Tencor surface profilometer. The electric-field-dependent SCLC mobility was estimated using the following equation:

$$J(V) = \frac{9}{8} \epsilon_0 \epsilon_r \mu_0 e^{0.98\beta} \sqrt{\frac{V-V_{bi}}{L}} \frac{(V-V_{bi})^2}{L^3}. \quad (1)$$

Photocurrent density–voltage (J – V) characteristics was recorded with a Keithley 2400 source meter under AM 1.5G illumination provided by a 300 W xenon arc solar simulator (Oriel) calibrated by a silicon reference cell. The external quantum efficiency (EQE) was performed using certified IPCE

equipment (Zolix Instruments, Inc, Solar Cell Scan 100).

Thin-film characterizations: Topographic images of the films were obtained on a Bruker atomic force microscopy (AFM) with the type of dimension edge with Scan Asyst™ in the tapping mode using an etched silicon cantilever at a nominal load of ~ 2 nN, and the scanning rate for a 2 × 2 μm² image size was 0.8 Hz. The GIWAXS characterization of the thin films was performed at the PLS-II 6A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea. Thin-film samples were prepared under device conditions on the Si/PEDOT:PSS substrates. The X-rays coming from the in-vacuum undulator (IVU) were monochromated (wavelength λ = 1.10994 Å) using a double crystal monochromated and focused both horizontally and vertically (450 (H) × 60 (V) μm² in FWHM @ the sample position) using K-B type mirrors. The grazing incidence wide-angle X-ray scattering sample stage was equipped with a 7-axis motorized stage for the fine alignment of sample, and the incidence angles of the X-beam was set to be 0.11°–0.13° for the neat and blend films. The GIWAXS patterns were recorded with a 2D CCD detector (Rayonix SX165) and an X-ray irradiation time within 100 s, dependent on the saturation level of the detector. Diffraction angles were calibrated using a sucrose standard (monoclinic, P21, $a = 10.8631$ Å, $b = 8.7044$ Å, $c = 7.7624$ Å, and $\beta = 102.938^\circ$) and sample-to-detector distance was ~231 mm.

DFT calculations: All density functional theory (DFT) calculations were carried out by the Gaussian 09 program. Considering the computational cost and the potential effects of the substituent groups, all the alkyl substituent groups were replaced by methyl groups to simplify the calculation. Geometry optimizations were performed at the rb3lyp/6-31g(d,p) level. Frequency analysis calculations were conducted at the same level as for the geometry optimizations, to confirm that they are local minima (no imaginary frequencies).

References

- [1] Feng Q, Lu X, Zhou G, et al. Synthesis and photovoltaic properties of organic sensitizers incorporating a thieno[3,4-c]pyrrole-4,6-dione moiety. *Phys Chem Chem Phys*, 2012, 14, 7993