

## Supporting Information

### **Multiple Fused Ring-based Near-Infrared Nonfullerene Acceptors with Interpenetrated Charge Transfer Network**

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## GENERAL METHODS

**Instruments.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AV 400/500 MHz spectrometer in  $\text{CDCl}_3$  with tetramethylsilane (TMS) as an internal standard. Preparative gel permeation chromatography purification was performed with a JAI LC-9104 recycling preparative high performance liquid chromatography, and the eluent was chloroform. Elemental analysis was performed by a Flash EA1112 elemental analysis system. Cyclic voltammetry (CV) measurements were performed on a CHI 660E potentiostat/galvanostat (Shanghai Chenhua Instrumental Co., Ltd. China) to determine the HOMO and LUMO levels of the polymers, in an acetonitrile solution of  $0.1 \text{ mol L}^{-1}$  tetrabutylammonium hexafluorophosphate ( $[n\text{-Bu}_4\text{N}]^+[\text{PF}_6]^-$ ) at a potential scan rate of  $100 \text{ mV s}^{-1}$  with an  $\text{Ag}/\text{Ag}^+$  reference electrode and a platinum wire counter electrode under a argon atmosphere. Solution and film UV-Vis absorption spectra were recorded on a Shimadzu UV3600 spectrometer. Thermogravimetric analysis (TGA) plots were measured with a Discovery series instrument under a nitrogen atmosphere at heating and cooling rates of  $10 \text{ }^\circ\text{C min}^{-1}$ . Different scanning calorimetry (DSC) measurements were performed on a Discovery series thermal analyzer at a scanning rate of  $10 \text{ }^\circ\text{C min}^{-1}$  in  $\text{N}_2$ . Atom force microscopy (AFM) images were taken on a NanoScopeIIIa controller (Veeco Metrology Group/Digital Instruments, Santa Barbara, CA), using built-in software (version V6.13R1) to capture images. Transmission electron microscopy (TEM) images were acquired using a HITACHI H-7650 electron microscope operating at an

acceleration voltage of 100 kV. All  $J$ - $V$  curves were captured under an AAA solar simulator (SAN-EI) calibrated by a standard single-crystal Silicon photovoltaic cell (certificated by National Institute of Metrology). All EQE data were gained through the measurement of solar cell spectral response measurement system QE-R3011 (Enli Technology Ltd., Taiwan).

**Fabrication and Characterization of OSCs.** The fabrication and measurement methods of OSCs devices are as follows: After a thorough cleaning of the indium-tin oxide (ITO)-coated glass substrate with detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 minutes each and subsequently dried in an oven for 1 minute at 80 °C under vacuum. The ITO glass substrates were treated with UV-ozone for 15 minutes and then the sol-gel-derived ZnO films were spin-coated onto the ITO substrates followed by thermal treatment at 200 °C for 30 min. The concentration of the PBDB-T: Acceptor blend solution for spin-coating was 10 mg mL<sup>-1</sup> with chlorobenzene as the processing solvent. The additive, 1,8-diiodooctane (DIO) was added into solution 30 minutes before the spin-coating process. The blend was stirred at room temperature in the glove box overnight. The active layer was spin-coating at 800 rpm for 30 s to get neat film. A 10 nm MoO<sub>3</sub> layer and a 100 nm Ag layer were subsequently evaporated through a shadow mask to define the active area of the devices. The integrated device structure is ITO/ZnO/PBDB-T:Acceptor/MoO<sub>3</sub>/Ag. An Oriel 150W solar simulator with an AM 1.5G filter was used as a light source to produce an intensity of 100 mW cm<sup>-2</sup> for the

illumination of the photovoltaic cells. The light intensity was calibrated by a 2 cm × 2 cm calibrated silicon solar cell with KG-3 visible color filter. A shadow mask with a single aperture (4.15 mm<sup>2</sup>) was placed onto the devices in order to accurately define the photoactive area.

**Electron-only and hole-only devices fabrication.** Electron-only devices were fabricated with the device structure of ITO/ZnO/PBDB-T:Acceptor/Ca/Al, while the hole-only devices were fabricated with the device structure of ITO/PEDOT:PSS/blends/MoO<sub>3</sub>/Ag. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC,<sup>1,2</sup> which is described by the equation:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_h \frac{V^2}{d^3} \quad (1)$$

where  $J$  is the current,  $\mu_h$  is the zero-field mobility,  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  is the relative permittivity of the material,  $d$  is the thickness of the active layer, and  $V$  is the effective voltage.

## EXPERIMENTAL SECTION

**Materials:** Compound 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene, trimethyl-(thieno[3,2-b]thiophen-2-yl)stannane and **6** were synthesized according previously reported approaches.<sup>3-5</sup> All the other chemicals were purchased as reagent grade from J&K, Energy, Macklin, and Sigma-Aldrich, and used without further purification. All solvents for reactions were freshly distilled immediately prior to use.

**Compound 2** A mixture of **1** (4.50 g, 11.84 mmol), tributyl(thiophen-2-yl)stannane (4.42 g, 11.84 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (137 mg, 0.12 mmol) in 100 mL toluene was refluxed 24 hours under Argon. The reaction mixture was then cooled to room temperature and then extracted with ether. The organic layer was washed with brine and dried over MgSO<sub>4</sub>. The crude product was purified by flash column chromatography with petroleum ether and ethyl acetate (30:1) as eluent to get the product as white solid (3.24 g, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.99 (s, 1H), 7.85 (s, 1H), 7.39 (dd, *J* = 4.0 Hz, 1.6 Hz, 1H), 7.08-7.04 (m, 2H), 4.42 (dd, *J* = 11.2 Hz, 5.6 Hz, 2H), 4.21 (dd, *J* = 11.2 Hz, 5.6 Hz, 2H), 1.41 (t, *J* = 5.6 Hz, 3H), 1.16 (t, *J* = 5.6 Hz, 3H).

**Compound 3** A mixture of **2** (1.71 g, 4.46 mmol), 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (1.04 g, 2.23 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (41 mg, 0.045 mmol), and (*o*-tolyl)<sub>3</sub>P (55 mg, 0.18 mmol) in 50 mL toluene was refluxed 24 hours under Argon. The reaction mixture was then cooled to room temperature and then extracted with dichloromethane. The organic layer was washed with brine and dried over MgSO<sub>4</sub>. The crude product was purified by flash column chromatography with petroleum ether and dichloromethane (1:1) as eluent to get the product as yellow solid (1.30 g, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.88 (s, 2H), 7.85 (s, 2H), 7.41 (dd, *J* = 4.0 Hz, 0.8 Hz, 2H), 7.29 (s, 2H), 7.13-7.07 (m, 4H), 4.29-4.21 (m, 8H), 1.20-1.14 (m, 12H).

**Compound 4** To a solution of 4-hexyl-1-bromobenzene (6.31 g, 26.18 mmol) in THF

(100 mL) at -78 °C was added *n*-BuLi (11.63 mL, 27.92 mmol, 2.4 M) and the mixture was kept at -78 °C for 2 h. A solution of compound 3 (1.30 g, 1.75 mmol) in THF (50 mL) was then added slowly. Then the mixture was stirred at room temperature overnight and then poured into water and extracted twice with ethyl acetate. The organic layer was washed with brine and dried over MgSO<sub>4</sub>. After removing the solvent, the crude product was charged into two-neck flask. THF (80 mL) and concentrated H<sub>2</sub>SO<sub>4</sub> (2.0 mL) were added and the mixture was refluxed for 3 h. Then the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with brine and dried over MgSO<sub>4</sub>. The crude product was purified by flash column chromatography with petroleum ether and dichloromethane (30:1) as eluent to get the product as yellow solid (2.0 g, 65%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.46 (s, 2H), 7.31 (s, 2H), 7.23 (d, *J* = 4.0 Hz, 2H), 7.17-7.14 (m, 8H), 7.12-7.08 (m, 8H), 7.07-7.04 (m, 8H), 7.03-7.00 (m, 8H), 6.99 (d, *J* = 4.0 Hz, 2H), 2.56-2.50 (m, 16H), 1.61-1.52 (m, 16H), 1.35-1.22 (m, 48H), 0.90-0.81 (m, 24H).

**Compound 5** A solution of 4 (0.50 g, 0.28 mmol) in dry THF (80 mL) under argon was cooled to -78 °C and *n*-butyllithium (0.35 mL, 0.84 mmol, 2.4 M) was added dropwise. The resulting solution was stirred at -78 °C for 2 hours, following which DMF (0.5 mL) was added. The reaction mixture was then allowed to warm to room temperature and stirred overnight. Water was added to quench the reaction, and then extracted with dichloromethane. The organic layer was washed with brine and dried over MgSO<sub>4</sub>. The crude product was purified by flash column chromatography with

petroleum ether and dichloromethane (1:1) as eluent to get the product as orange solid (230 g, 45%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 9.79 (s, 2H), 7.63 (s, 2H), 7.58 (s, 2H), 7.35 (s, 2H), 7.16-7.02 (m, 32H), 2.58-2.52 (m, 16H), 1.62-1.53 (m, 16H), 1.36-1.23 (m, 48H), 0.90-0.82 (m, 24H).

**Compound 7** A mixture of **1** (1.00 g, 2.63 mmol), trimethyl(thieno[3,2-b]thiophen-2-yl)stannane (0.80 g, 2.63 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (30 mg, 0.026 mmol) in 80 mL toluene was refluxed 24 hours under Argon. The reaction mixture was then cooled to room temperature and then extracted with ether. The organic layer was washed with brine and dried over MgSO<sub>4</sub>. The crude product was purified by flash column chromatography with petroleum ether and ethyl acetate (30:1) as eluent to get the product as green solid (0.71 g, 61%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.02 (s, 1H), 7.91 (s, 1H), 7.40 (d, *J* = 4.0 Hz, 1H), 7.27-7.24 (m, 2H), 4.43 (dd, *J* = 11.2 Hz, 5.6 Hz, 2H), 4.23 (dd, *J* = 11.2 Hz, 5.6 Hz, 2H), 1.42 (t, *J* = 5.6 Hz, 3H), 1.13 (t, *J* = 5.6 Hz, 3H).

**Compound 8** A mixture of **7** (1.05 g, 2.39 mmol), 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene (0.53 g, 1.14 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (21 mg, 0.023 mmol), and (*o*-tolyl)<sub>3</sub>P (28 mg, 0.092 mmol) in 100 mL toluene was refluxed 24 hours under Argon. The reaction mixture was then cooled to room temperature and then extracted with chloroform. The organic layer was washed with brine and dried over MgSO<sub>4</sub>. The crude product was purified by flash column chromatography with petroleum ether and dichloromethane (1:1) as eluent to get the

product as yellow solid (0.87 g, 89%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.91 (s, 4H), 7.41 (d,  $J = 4.4$  Hz, 2H), 7.31 (s, 4H), 7.29 (d,  $J = 4.0$  Hz, 2H), 4.31-4.23 (m, 8H), 1.20-1.11 (m, 12 H).

**Compound 9** To a solution of 4-hexyl-1-bromobenzene (3.38 g, 14.0 mmol) in THF (100 mL) at  $-78$  °C was added  $n\text{-BuLi}$  (6.2 mL, 14.9 mmol, 2.4 M) and the mixture was kept at  $-78$  °C for 2 h. A solution of compound 8 (0.80 g, 0.93 mmol) in THF (50 mL) was then added slowly. Then the mixture was stirred at room temperature overnight and then poured into water and extracted twice with ethyl acetate. The organic layer was washed with brine and dried over  $\text{MgSO}_4$ . After removing the solvent, the crude product was charged into two-neck flask. THF (80 mL) and concentrated  $\text{H}_2\text{SO}_4$  (1.0 mL) were added and the mixture was refluxed for 3 h. Then the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with brine and dried over  $\text{MgSO}_4$ . The crude product was purified by flash column chromatography with petroleum ether and dichloromethane (30:1) as eluent to get the product as yellow solid (0.51 g, 29%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.46 (s, 2H), 7.38 (s, 2H), 7.27-7.23 (m, 4H), 7.21-7.16 (m, 8H), 7.14-7.11 (m, 8H), 7.110-7.06 (m, 8H), 7.05-7.01 (m, 8H), 2.57-2.48 (m, 16H), 1.64-1.52 (m, 16H), 1.36-1.21 (m, 48H), 0.90-0.80 (m, 24H).

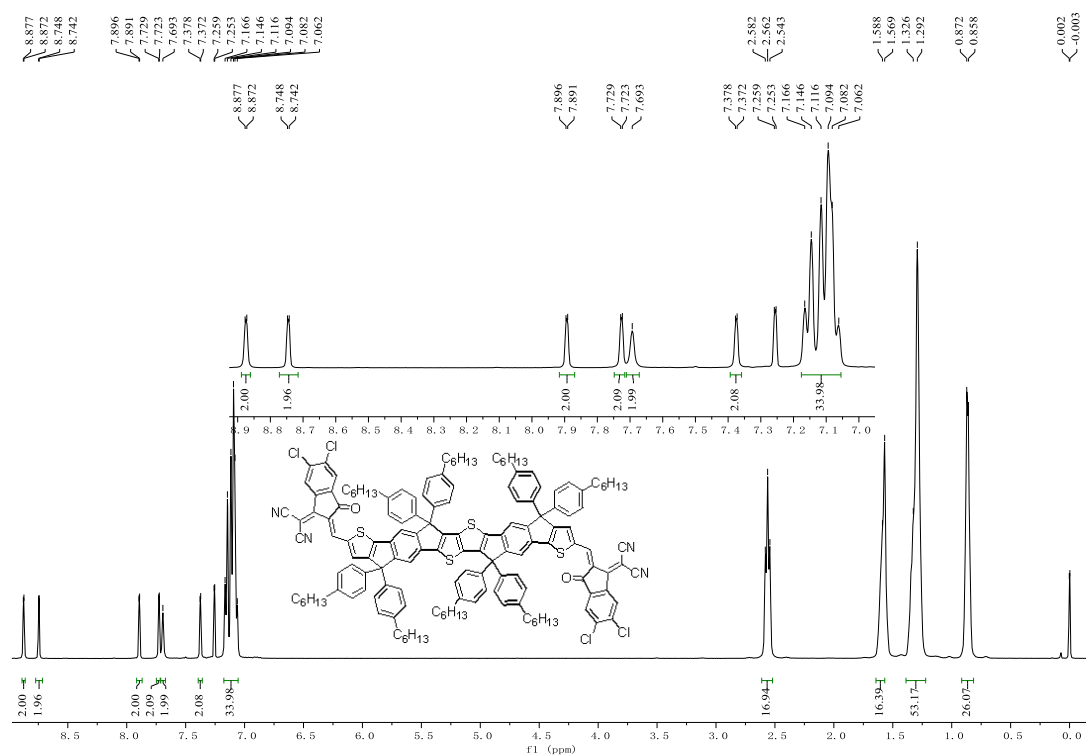
**Compound 10** A Vilsmeier reagent, which was prepared with  $\text{POCl}_3$  (0.19 g, 1.21 mmol) in DMF (4 mL), was added to the solution of compound 9 (0.23 g, 0.12 mmol) in 1,2-dichloroethane (20 mL) at  $0$  °C under nitrogen. The mixture was refluxed



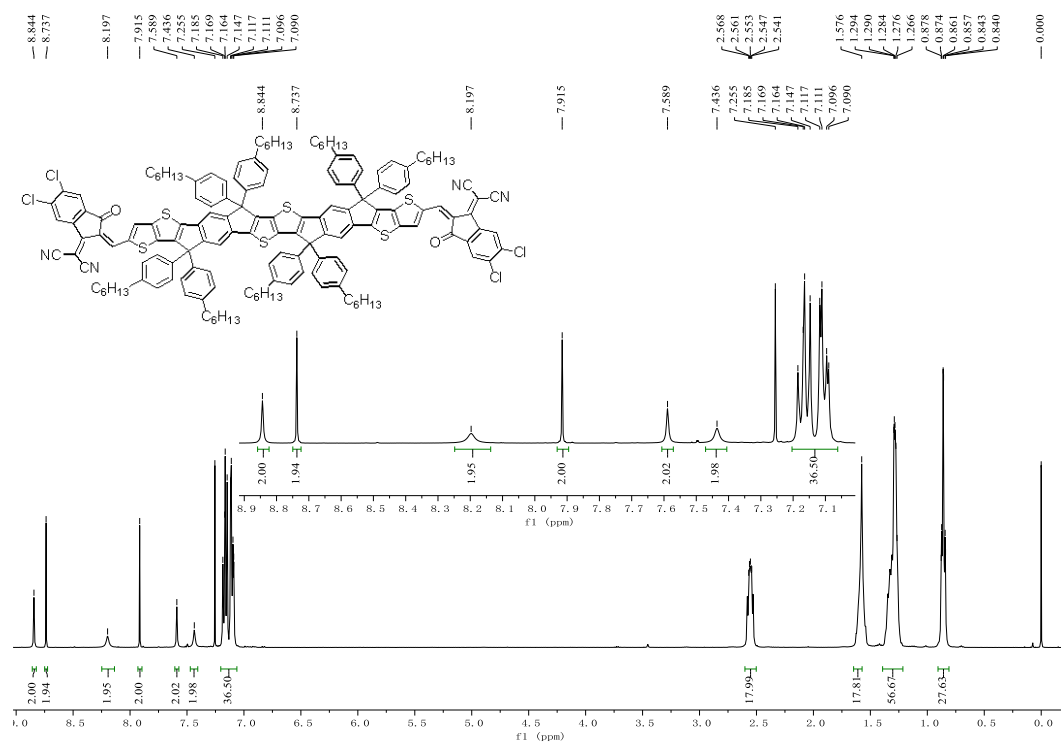
overnight and then poured into water and extracted twice with dichloromethane. The organic layer was washed with brine and dried over  $\text{MgSO}_4$ . The crude product was purified by flash column chromatography with petroleum ether and dichloromethane (1:1) as eluent to get the product as orange solid (0.19 g, 82%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 9.87 (s, 2H), 7.92 (s, 2H), 7.54 (s, 2H), 7.42 (s, 2H), 7.20-7.03 (m, 32H), 2.58-2.50 (m, 16H), 1.62-1.51 (m, 16H), 1.36-1.22 (m, 48H), 0.88-0.81 (m, 24H).

**Compound R10-4Cl** A mixture of 5 (142 mg, 0.077 mmol), 6 (101 mg, 0.385 mmol), in chloroform/pyridine (10 mL/0.5 mL) was refluxed 24 hours under Argon. The reaction mixture was then cooled to room temperature and then extracted with chloroform. The organic layer was washed with brine and dried over  $\text{MgSO}_4$ . The crude product was purified by flash column chromatography with chloroform as eluent and further purified with cycling preparative HPLC to get the product as black solid (115 mg, 64%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.87 (s, 2H), 8.75 (s, 2H), 7.89 (s, 2H), 7.73 (s, 2H), 7.69 (s, 2H), 7.37 (s, 2H), 7.18-7.05 (m, 32H), 2.61-2.52 (m, 16H), 1.63-1.52 (m, 16H), 1.37-1.22 (m, 48H), 0.91-0.81 (m, 24H).  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 186.1, 162.5, 158.3, 157.6, 156.9, 154.3, 149.0, 143.8, 142.3, 140.6, 140.3, 140.2, 139.4, 139.2, 138.6, 137.4, 136.0, 133.6, 128.7, 127.9, 127.6, 126.9, 125.0, 120.3, 119.7, 117.4, 114.5, 68.8, 63.0, 62.8, 35.6, 35.5, 31.7, 31.3, 31.2, 29.1, 22.6, 14.1. HRMS (MALDI+) calcd for  $\text{C}_{152}\text{H}_{148}\text{Cl}_4\text{N}_4\text{O}_2\text{S}_4$  ( $\text{M}^+$ ): 2329.9239, found: 2329.9211. Elemental analysis (%) calcd for  $\text{C}_{152}\text{H}_{148}\text{Cl}_4\text{N}_4\text{O}_2\text{S}_4$ : C 78.26, H 6.39, N 2.40, S 5.50, found: C 77.99, H 6.21, N 2.31, S 5.38.

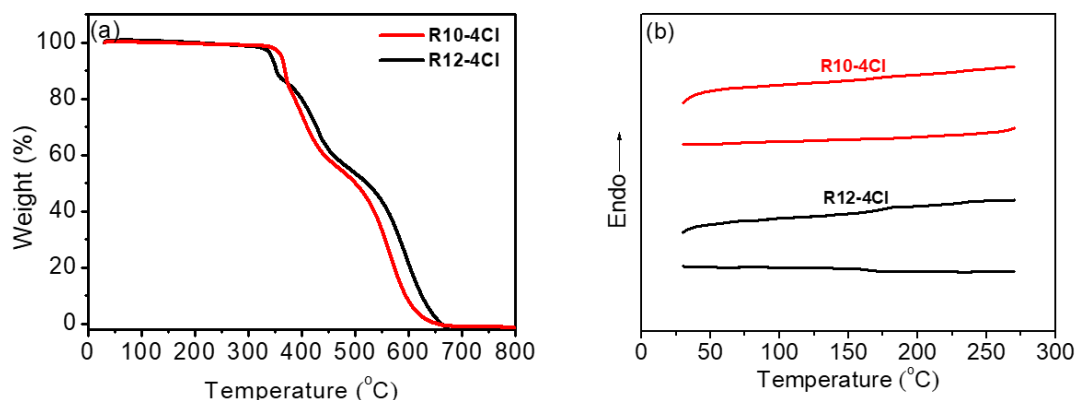
**Compound R12-4Cl** A mixture of 10 (93.3 mg, 0.048 mmol), 6 (100.4 mg, 0.382 mmol), in chloroform/pyridine (10 mL/0.5 mL) was refluxed 24 hours under Argon. The reaction mixture was then cooled to room temperature and then extracted with chloroform. The organic layer was washed with brine and dried over MgSO<sub>4</sub>. The crude product was purified by flash column chromatography with chloroform as eluent and further purified with cycling preparative HPLC to get the product as black solid (65 mg, 55%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 8.84 (s, 2H), 8.74 (s, 2H), 8.20 (s, 2H), 7.92 (s, 2H), 7.59 (s, 2H), 7.44 (s, 2H), 7.20-7.06 (m, 32H), 2.60-2.50 (m, 16H), 1.63-1.52 (m, 16H), 1.37-1.22 (m, 48H), 0.90-0.81 (m, 24H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ: 185.9, 158.2, 155.8, 155.5, 148.4, 143.6, 142.4, 142.2, 139.6, 139.5, 139.2, 139.0, 138.7, 137.8, 136.9, 136.0, 128.8, 128.6, 128.0, 127.8, 126.9, 125.1, 121.0, 117.0, 114.4, 69.2, 63.1, 35.6, 31.7, 31.2, 29.2, 22.6, 14.1. HRMS (MALDI+) calcd for C<sub>156</sub>H<sub>148</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>2</sub>S<sub>6</sub> (M<sup>+</sup>): 2441.8681, found: 2441.8671. Elemental analysis (%) calcd for C<sub>156</sub>H<sub>148</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>2</sub>S<sub>6</sub>: C 76.63, H 6.10, N 2.29, S 7.87, found: C 76.46, H 6.04, N 2.31, S 7.75.



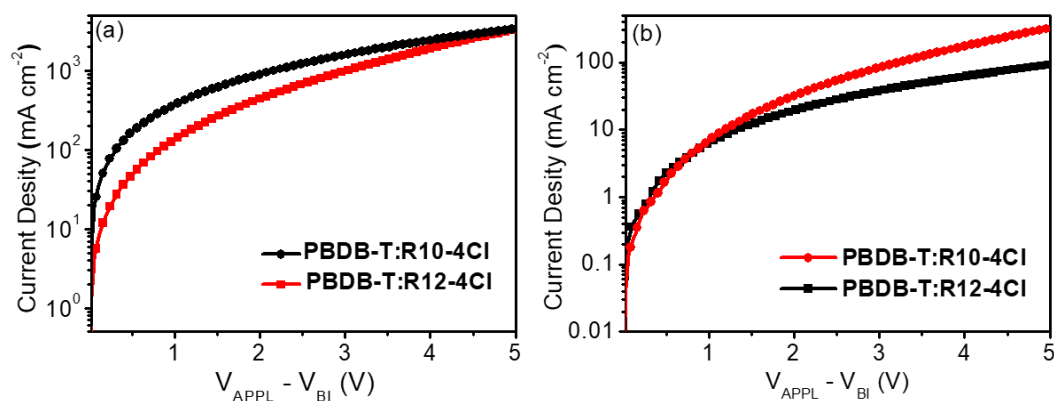
**Figure S1.  $^1\text{H}$  NMR of R10-4Cl in  $\text{CDCl}_3$ .**



**Figure S2.  $^1\text{H}$  NMR of R12-4Cl in  $\text{CDCl}_3$ .**



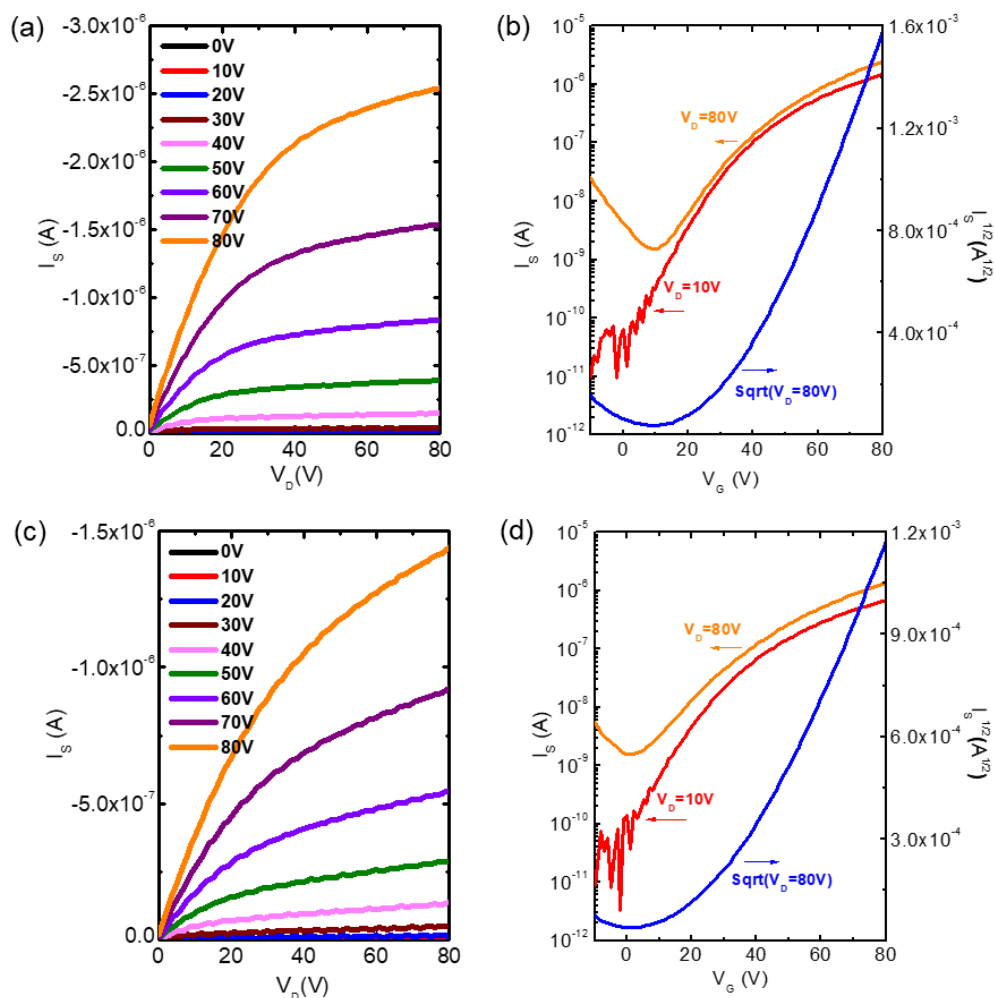
**Figure S3.** (a) Thermogravimetric analysis (TGA) results of R10-4Cl and R12-4Cl with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  under nitrogen purge. (b) Differential scanning calorimetry (DSC) results of R10-4Cl and R12-4Cl with heating and cooling rates of  $10\text{ }^{\circ}\text{C min}^{-1}$  under nitrogen purge.



**Figure S4.** Double logarithmic plots of the current density ( $J$ ) versus voltage ( $V$ ) curves for the hole-only (a) and electron-only (b) of R10-4Cl and R12-4Cl-based devices.

The OFET mobilities of the two small molecules were measured by fabricating the

top-gate/bottom-contact (TG/BC) OFET devices with the structure of glass/Au/active layer/CYTOP/Al. The output and transfer plots of the devices showed typical n-type OFET characteristics (Figure S5 and Table S1). The electron mobilities are calculated from the transfer characteristics of the devices in the saturation regime. R10-4Cl and R12-4Cl exhibited the electron mobilities of  $2.36 \times 10^{-3}$  and  $5.59 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The higher electron mobility of R10-4Cl is in accordance with the SCLC result, indicating the interpenetrating network is beneficial for the charge transfer.



**Figure S5.** OTFT output and transfer characteristics of (a, b) R10-4Cl and (c, d) R12-4Cl-based devices

**Table S1. TG/BC OTFT performance parameters of R10-4Cl and R12-4Cl.**

| Materials | $\mu$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ) | V <sub>T</sub> (V) | I <sub>on</sub> /I <sub>off</sub> |
|-----------|--|--------------------|-----------------------------------|
| R10-4Cl   | 2.36 × 10 <sup>-3</sup> (1.46 × 10 <sup>-3</sup> )       | 32                 | 10 <sup>3</sup>                   |
| R12-4Cl   | 5.59 × 10 <sup>-3</sup> (5.50 × 10 <sup>-3</sup> )       | 31                 | 10 <sup>3</sup>                   |

## REFERENCES

- (1) Mihailetchi, V. D.; Wildeman, J.; Blom, P. W. Space-Charge Limited Photocurrent. *Phys. Rev. Lett.* **2005**, *94*, 126602-126605.
- (2) Davids, P. S.; Campbell, I. H.; Smith, D. L. Device Model for Single Carrier Organic Diodes. *J. Appl. Phys.* **1997**, *82*, 6319-6325.
- (3) Lin, Y.; Wang, J.; Zhang, Z. G.; Bai, H.; Li, Y.; Zhu, D.; Zhan, X. An Electron Acceptor Challenging Fullerenes for Efficient Polymer Solar Cells. *Adv. Mater.* **2015**, *27*, 1170-1174.
- (4) Yao, H.; Cui, Y.; Yu, R.; Gao, B.; Zhang, H.; Hou, J. Design, Synthesis, and Photovoltaic Characterization of a Small Molecular Acceptor with an Ultra-Narrow Band Gap. *Angew. Chem. Int. Ed.* **2017**, *56*, 3045-3049.
- (5) Li, Y.; Lin, J. D.; Che, X.; Qu, Y.; Liu, F.; Liao, L. S.; Forrest, S. R. High Efficiency Near-Infrared and Semitransparent Non-Fullerene Acceptor Organic Photovoltaic Cells. *J. Am. Chem. Soc.* **2017**, *139*, 17114-17119.