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Electronic Supporting information

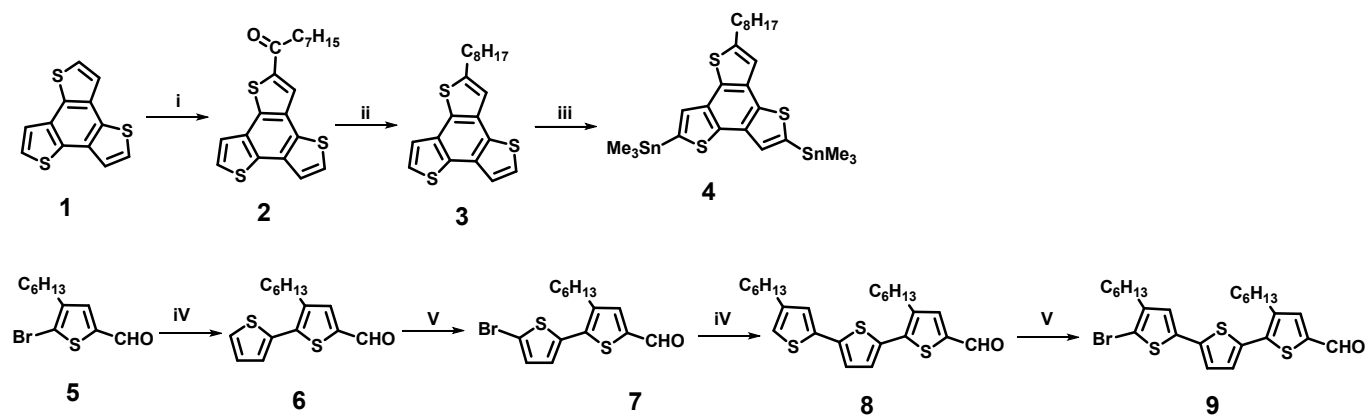
Novel solution-processible small molecules based on benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene for effective organic photovoltaics with high open-circuit voltage

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1. Synthetic routes of the intermediates



Scheme S1. Synthesis of the intermediates. Reagents and conditions: (i) AlCl_3 , $\text{C}_7\text{H}_{15}\text{COCl}$, $0\text{ }^\circ\text{C}$; (ii) KOH , $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$, diethyleneglycol, $180\text{ }^\circ\text{C}$; (iii) THF, $n\text{-BuLi}$, $-78\text{ }^\circ\text{C}$, SnMe_3Cl ; (iv) $\text{Pd}(\text{PPh}_3)_4$, toluene, reflux; (v) NBS, chloroform: AcOH (1:1), $0\text{ }^\circ\text{C}$ then RT.

The synthesis routes of the intermediates are shown in Scheme S1.

2-octanoylbenzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophen (**2**)

To an iced-cooled solution of **1** (1.5 g, 6.1 mmol) and octanoylchloride (1.1 mL, 6.7 mmol) in dichloromethane (30 mL), aluminum chloride (1.072 g, 8.0 mmol) was slowly added. The reaction mixture was stirred for 2h and then quenched with iced hydrochloric acid (2 M, 20 mL). The mixture was extracted with dichloromethane, then the organic layer was dried over anhydrous magnesium sulfate and concentrated to afford the crude product. Finally, the crude product was purified by column chromatography (dichloromethane/petroleum ether = 1/1, v/v) to obtain a white solid product. (1.9 g, 83.7% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.22 (s, 1H), 7.67 – 7.64 (m, 2H), 7.58 (t, $J = 5.36\text{ Hz}$, 2H), 3.08 (t, $J = 7.40\text{ Hz}$, 2H), 1.92 – 1.78 (m, 2H), 1.48 – 1.28 (m, 8H), 0.89 (t, $J = 6.46\text{ Hz}$, 3H).

2-octylbenzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophen (**3**)

To a suspension of **2** (1.25 g, 3.4 mmol) in diethylene glycol (100 mL), hydrazine monohydrate (6 mL, 0.12 mol) and potassium hydroxide (6 g, 0.11 mol) was added, and the reaction mixture was stirred at $190\text{ }^\circ\text{C}$ overnight. The cooled reaction mixture was poured into water, extracted with dichloromethane. Then the organic layer was dried over anhydrous magnesium sulfate and concentrated to afford the crude product. Purification by column chromatography (petroleum ether) afforded the title compounds as a white solid. (1.1 g, 91.7% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.62 (d, $J = 5.28\text{ Hz}$, 1H), 7.57 (d, $J = 5.32\text{ Hz}$, 1H), 7.51 (d, $J = 5.28\text{ Hz}$, 2H), 7.30 (s, 1H), 3.11 (t, $J = 7.50\text{ Hz}$, 2H), 1.90 – 1.84 (m, 2H), 1.47 – 1.29 (m, 10H), 0.88 (t, $J = 6.84\text{ Hz}$, 3H). MALDI-TOF MS ($\text{C}_{20}\text{H}_{22}\text{S}_3$) m/z : calcd for 358.09, found 358.16.

5,8-di(trimethylstannyl)-2-octylbenzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophen (4)

A two-neck round-bottom flask containing **3** (1 g, 2.8 mmol) was evacuated and filled with N₂ three times, and then anhydrous tetrahydrofuran was injected (THF, 30 mL). *n*-Butyllithium (2.5 M in hexane, 3.4 mL, 8.4 mmol) was added drop wise into flask at -78 °C, then the mixture was warmed to room temperature and stirred for 2h. The reaction mixture was cooled to -78 °C again, trimethyltinchloride (2 M in hexane, 4.5 mL, 9mmol) was added, and then the mixture was warmed to room temperature overnight. The reaction was quenched through the addition of water. The reaction mixture was extracted with hexane (3×100 mL), then the organic layer was dried over anhydrous magnesium sulfate and concentrated to afford a light yellow solid. The crude product was used without further purification. (1.5 g, 78.9% yield) ¹H NMR (400 MHz, CDCl₃): δ 7.67 (s, 1H), 7.60 (s, 1H), 7.30 (s, 1H), 2.99 (t, J = 7.20 Hz, 2H), 1.91 – 1.74 (m, 2H), 1.40 - 1.13 (m, 10H), 0.88 (t, J = 6.36 Hz, 3H), 0.47 (s, 18H). MALDI-TOF MS(C₂₆H₃₈S₃Sn₂) m/z: Calcd. for 684.02 , found 684.03.

2-thienyl-3-hexyl-5-thenaldehyde(6)

A solution of **5** (4.7 g, 17.13 mmol) and 2-tributylstannylthiophene (6.4 g, 17.13 mmol) in toluene (30 mL) was evacuated and filled with N₂ three times, followed by the addition of Pd(PPh₃)₄ (3 mol%). After being stirred at 110 °C for 24 h, the cooled reaction mixture was poured into water, extracted with dichloromethane, the organic layer was dried over anhydrous magnesium sulfate and concentrated to afford the crude product. Purification by column chromatography (dichloromethane/ petroleum ether =1/3, v/v) to yield a red solid product. (3.6 g, 75.8% yield) ¹H NMR (400 MHz, CDCl₃): δ 9.83 (s, 1H), 7.60 (s, 1H), 7.43 (d, J = 4.96 Hz, 1H), 7.28 (d, J = 3.12 Hz, 1H), 7.16 – 7.09 (m, 1H), 2.84 – 2.75 (t, J = 7.46 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.43 – 1.26 (m, 6H), 0.90 (t, J = 6.32 Hz, 3H).

Compound 7

N-Bromosuccinimide (2.4 g, 13.48 mmol) was added in small portions to a solution of **6** (3.6 g, 13.08mol) in chloroform and acetic (80 mL, 1:1, v/v) at 0 °C. After being stirred for 6h at room temperature, the reaction mixture was poured into water, extracted with dichloromethane, then the organic layer was dried over anhydrous magnesium sulfate and concentrated to afford the crude product. Purification by column chromatography (dichloromethane/ petroleum ether =1/3, v/v) to yield a yellow solid product. (3.5 g, 75.9% yield) ¹H NMR (400 MHz, CDCl₃): δ 9.82 (s, 1H), 7.62 (s, 1H), 7.05(d, J = 3.52 Hz, 1H), 7.03(d, J = 3.60 Hz, 1H), 2.75 (t, J=7.60 Hz, 2H), 1.81-1.61 (m, 2H), 1.45-1.18 (m, 6H), 0.90 (t, J = 6.34 Hz, 3H).

Compound 8

A solution of **7** (1 g, 2.81 mmol) and 2-tributylstannyl-4-hexylthiophene (1.93 g, 4.21 mmol) in toluene (30 mL) was evacuated and filled with N₂ three times, followed by the addition of Pd(PPh₃)₄ (3 mol%). After being stirred at 110 °C for 24 h, the cooled reaction mixture was poured into water, extracted with dichloromethane, then the organic layer was dried over anhydrous magnesium sulfate and concentrated to afford the crude product. Purification by column chromatography (dichloromethane/ petroleum ether =1/3, v/v) to yield a red solid product. (1.0 g, 83.3% yield) ¹H NMR (400 MHz, CDCl₃): δ 9.83 (s, 1H), 7.60 (s, 1H), 7.19 (d, J = 3.62 Hz, 1H), 7.13 (d, J = 3.50 Hz, 1H), 7.07 (s, 1H), 6.86

(s, 1H), 2.82 (t, $J = 7.62$ Hz, 2H), 2.60 (t, $J = 7.58$ Hz, 2H), 1.79 – 1.61 (m, 4H), 1.47 – 1.20 (m, 12H), 0.90 (s, 7H), 0.90 (t, $J = 6.36$ Hz, 3H).

Compound 9

N-Bromosuccinimide (1.28 g, 7.19 mmol) was added in small portions to a solution of **8** (3.2 g, 7.19 mmol) in chloroform and acetic (80 mL, 1:1, v/v) at 0 °C. After being stirred for 6 h at room temperature, the reaction mixture was poured into water, extracted with dichloromethane, the organic layer was dried over anhydrous magnesium sulfate and concentrated to afford the crude product. Purification by column chromatography (dichloromethane/ petroleum ether = 1/3, v/v) to yield a yellow solid product. (3.5 g, 93.1% yield) ^1H NMR (400 MHz, CDCl_3): δ 9.85 (s, 1H), 7.62 (s, 1H), 7.20 (d, $J = 3.52$ Hz, 1H), 7.10 (d, $J = 3.60$ Hz, 1H), 6.93 (s, 1H), 2.82 (t, $J = 7.69$ Hz, 2H), 2.57 (t, $J = 7.60$ Hz, 2H), 1.78 – 1.68 (m, 2H), 1.51 – 1.25 (m, 12H), 0.92 (t, $J = 6.40$ Hz, 3H).

Compound 11

A solution of **4** (0.5 g, 0.73 mmol) and **10** (0.71 g, 1.61 mmol) in toluene (20 mL) was evacuated and filled with N_2 three times, followed by the addition of $\text{Pd}(\text{PPh}_3)_4$ (3 mol%). After being stirred at 110 °C for 24 h, the cooled reaction mixture was poured into water, extracted with dichloromethane, then the organic layer was dried over anhydrous magnesium sulfate and concentrated to afford the crude product. Purification by column chromatography (dichloromethane/ petroleum ether = 1/1, v/v) to yield a red solid product. (0.4 g, 50.8% yield) ^1H NMR (400 MHz, CDCl_3): δ 9.85 (s, 2H), 7.63-7.60 (s, 2H), 7.59(s, 2H), 7.29(s, 1H), 7.19 (s, 2H), 3.02 (t, $J = 7.40$ Hz, 2H), 2.95 – 2.89 (t, $J = 7.70$ Hz, 4H), 2.89 – 2.83 (t, $J = 7.80$ Hz, 4H), 1.89 – 1.80 (m, 2H), 1.79 – 1.67 (m, 8H), 1.50 – 1.40 (m, 10H), 1.40 – 1.26 (m, 24H), 0.97 – 0.82 (m, 15H). MALDI-TOF MS ($\text{C}_{62}\text{H}_{78}\text{O}_2\text{S}_7$) m/z : Calcd. for 1078.41, found 1078.56.

Compound 12

A solution of **4** (0.5 g, 0.73 mmol) and **9** (0.84 g, 1.61 mmol) in toluene (20 mL) was evacuated and filled with N_2 three times, followed by the addition of $\text{Pd}(\text{PPh}_3)_4$ (3 mol%). After being stirred at 110 °C for 24 h, the cooled reaction mixture was poured into water, extracted with dichloromethane, then the organic layer was dried over anhydrous magnesium sulfate and concentrated to afford the crude product. Purification by column chromatography (dichloromethane/ petroleum ether = 1/1, v/v) to yield a red solid product. (0.4 g, 44.0% yield) ^1H NMR (400 MHz, CDCl_3): δ 9.84 (s, 2H), 7.61(s, 2H), 7.56 (s, 2H), 7.54 (s, 1H), 7.22 (d, $J = 3.36$ Hz, 2H), 7.19 (d, $J = 3.36$ Hz, 2H), 7.11 (s, 2H), 3.01 (t, $J = 7.38$ Hz, 2H), 2.95 - 2.78 (m, 8H), 1.90 - 1.80 (m, 2H), 1.80-1.65 (m, 8H), 1.53 – 1.41 (m, 10H), 1.41 – 1.14 (m, 24H), 0.98 – 0.85 (m, 15H). MALDI-TOF MS ($\text{C}_{70}\text{H}_{82}\text{O}_2\text{S}_9$) m/z : Calcd. for 1242.38, found 1242.49.

Compound D1

A solution of **11** (0.3 g, 0.28 mmol) and 3-ethylrhodanine (0.45 g, 2.8 mmol) in chloroform (20 mL) was evacuated and filled with N_2 three times, followed by the addition of piperidine (0.5 mL). The mixture was refluxed and stirred overnight under N_2 . The cooled reaction mixture was poured into water, extracted with chloroform. Then the organic layer was dried over anhydrous magnesium sulfate and concentrated to afford the crude product. Purification by column

chromatography (chloroform/petroleum ether =1/1, v/v) to yield a red black product. (0.32 g, 84.2% yield) ^1H NMR (400 MHz, CDCl_3): δ 7.73 (s, 2H), 7.52 (s, 1H), 7.51 (s, 1H), 7.23 (s, 1H), 7.18 (s, 2H), 7.13 (s, 2H), 4.29 – 4.09 (m, 4H), 3.00 (t, J = 7.36 Hz, 2H), 2.95 – 2.87 (t, J = 7.60 Hz, 4H), 2.82 (t, J = 7.50 Hz, 4H), 1.89 – 1.81 (m, 2H), 1.80 – 1.73 (m, 4H), 1.73 – 1.67 (m, 4H), 1.54 – 1.42 (m, 10H), 1.42 – 1.33 (m, 14H), 1.33 – 1.25 (m, 16H), 1.00 – 0.83 (m, 15H). ^{13}C NMR (100 MHz, CDCl_3): δ 191.89, 167.13, 146.52, 140.89, 140.83, 139.54, 137.20, 134.90, 134.75, 134.53, 133.47, 132.35, 131.72, 131.26, 131.11, 130.72, 130.31, 129.63, 124.68, 120.34, 119.79, 119.69, 118.61, 39.84, 31.88, 31.72, 31.37, 30.81, 30.40, 30.03, 29.69, 29.54, 29.41, 29.30, 22.71, 22.68, 14.17, 14.11, 12.29. MALDI-TOF MS ($\text{C}_{72}\text{H}_{88}\text{N}_2\text{O}_2\text{S}_{11}$) m/z : calcd for 1364.38, found 1364.44. m.p. 202 °C. Elemental Analysis: calcd for C, 63.30; H, 6.49; N, 2.05; S, 25.82; found C, 63.06; H, 7.04; N, 2.03; S, 25.50.

Compound D2

D2 was prepared from **12** (0.24 g, 0.19 mmol) and 3-ethylrhodanine (0.31 g, 1.9 mmol) using the same procedure described for the preparation of **D1**. A black liquid was obtained after purification by column chromatography (chloroform/ petroleum ether =1/1, v/v). (0.24 g, 81.4% yield) ^1H NMR (400 MHz, CDCl_3): δ 7.74 (s, 2H), 7.51 (s, 1H), 7.49 (s, 1H), 7.23 (s, 1H), 7.19 (d, J = 3.38 Hz, 2H), 7.16 (d, J = 3.32 Hz, 2H), 7.08 (s, 2H), 4.26-4.09 (m, 4H), 3.01 (t, J = 7.30 Hz, 2H), 2.88 (t, J = 7.62 Hz, 4H), 2.80 (t, J = 7.64 Hz, 4H), 1.90-1.82 (m, 2H), 1.80-1.72 (m, 4H), 1.71 – 1.65 (m, 4H), 1.53 – 1.32 (m, 10H), 1.33 – 1.24 (m, 30H), 1.03-0.86 (m, 15H). ^{13}C NMR (100 MHz, CDCl_3): δ 191.78, 166.97, 145.94, 140.52, 140.45, 140.22, 139.76, 138.25, 138.20, 136.99, 135.10, 134.69, 134.47, 134.26, 133.77, 130.91, 130.59, 130.20, 126.91, 126.62, 124.46, 123.64, 119.96, 118.36, 39.79, 31.96, 31.91, 31.86, 31.78, 29.63, 29.54, 29.52, 29.46, 29.38, 22.88, 22.84, 22.76, 22.75, 14.35, 14.29, 14.23, 14.22, 14.18, 12.30. MALDI-TOF MS ($\text{C}_{80}\text{H}_{92}\text{N}_2\text{O}_2\text{S}_{13}$) m/z : calcd for 1528.35, found 1528.41. m.p. 72 °C. Elemental Analysis: calcd for C, 62.78; H, 6.06; N, 1.83; S, 27.24; found C, 62.49; H, 6.61; N, 2.32; S, 26.78.

2. The optimized molecular geometries

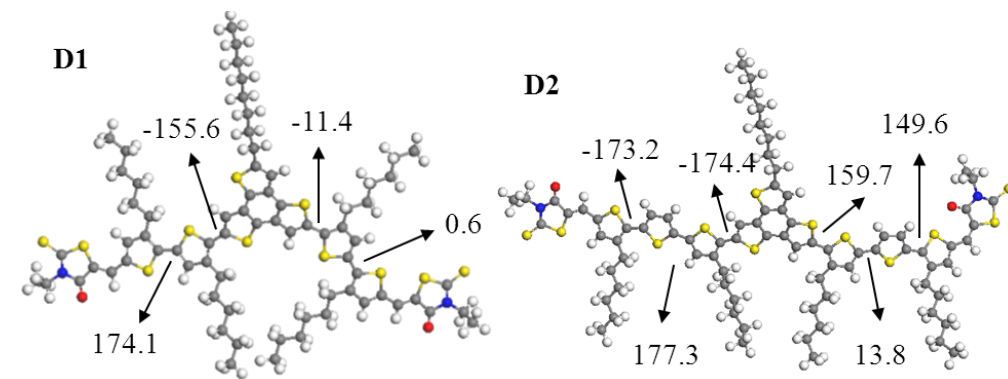


Fig. S1 The optimized molecular geometries of two small molecules.

3. Photovoltaic properties

Table. S1. Photovoltaic properties and the thickness of **D1** and **D2** composite film.

Device	D:A (w:w)	Solvent	V_{oc} (V)	J_{sc} (mAcm ⁻²)	FF	PCE (%)	Thickness (nm)
D1-CB	D1(1:0.5)	CB	-	-	-	-	-
D2-CB	D2(1:2)	CB	0.80	2.48	0.25	0.50	85
D1-CB	D1(1:2)	CB	0.99	2.77	0.30	0.82	82
D1-CF	D1(1:0.5)	CF	1.07	3.84	0.35	1.45	103
D1-CF	D1(1:0.5)	CF	1.10	4.25	0.45	2.10	112
D1-CF	D1(1:0.5)	CF	1.12	3.92	0.35	1.55	145
D2-CF	D2(1:0.5)	CF	0.53	0.27	0.12	0.13	119
D2-CF	D2(1:0.5)	CF	0.62	0.88	0.24	0.13	101
D1-CF	D1(1:0.8)	CF	1.00	3.47	0.38	1.32	120

4. Hole Mobility Device Fabrication and Characterization

The SCLC devices were fabricated with the configuration of ITO/PEDOT:PSS (25 nm)/polymer:PC₆₁BM/MoO₃(20 nm)/Al(100 nm), and the hole mobilities of the active layers were calculated according the equation¹.

$$\ln(JL^3/V^2) \cong 0.89(1/E_0)^{0.5}(V/L)^{0.5} + \ln(9\epsilon\epsilon_0\mu_0/8)$$

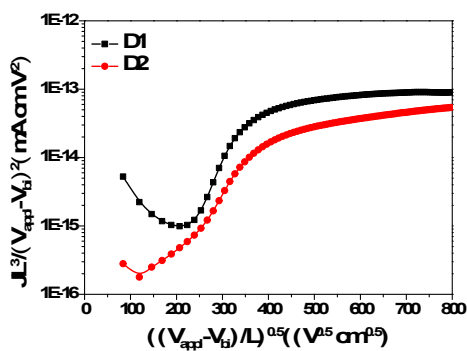


Fig. S2. Current-voltage curves of the SCLC devices

5. IPCE curves

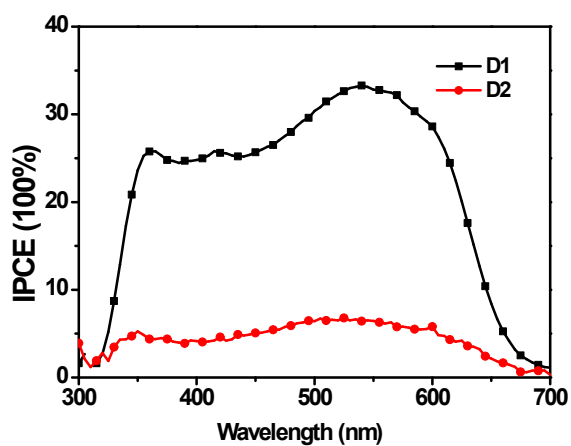


Fig. S3. IPCE plots of the for **D1-CF** and **D2-CF** OPV devices (1:0.5 w/w).

1. G. G. Malliaras, J. R. Salem, P. J. Brock and C. Scott, *Physical Review B*, 1998, **58**, 13411.