Supporting Information

Fine-Tuning Device Performances of Small Molecule Solar Cells via the More Polarized DPP-Armed Donor Units

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1. Experimental section

1.1. Materials

PC₆₁BM was purchased from American Dye Source (ADS) Inc. All other reagents and chemicals were purchased from commercial sources (TCI, Acros, Sigma, or Alfa) and used without further ⁵ purification except statements. Solvents (toluene and tetrahydrofuran) were distilled by standard procedures before used.

1.2. Instruments, methods and measurements

¹H NMR and ¹³C NMR spectrums were recorded by a Bruker DMX-400 spectrometer with CDCl₃ as a solvent and tetramethylsilane as an internal reference. MALDI-TOF mass spectra were recorded by ¹⁰ a Bruker BIFLEXIII. Absorption spectra were taken on a Hitachi U-3010 UV-vis spectrophotometer. The pristine films on quartz plate used for the UV measurements were prepared by spin-coating a 1 mg/mL chloroform solution of the samples. To compare with the EQE characteristics of the best devices, the blending films used for absorption spectrum measurements were prepared on ITO/PEDOT: PSS substrate under the same conditions (e.g. donor/acceptor ratio, spin-coating speed, 15 solvent) to the preparation of photovoltaic devices that afford the best performances. The electrochemical cyclic voltammetry (CV) was performed using a Zahner IM6e electrochemical workstation in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) dichloromethane (DCM) solution with a scan speed at 0.1 V/s. A Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The concentration of **DPPT**, **DPPSe** and **DPPTT** is adjusted as 1 20 mg/mL in chromatographic pure DCM solution) for the measurements cyclic voltammetry (CV). XRD samples were prepared under the same conditions to the preparation of photovoltaic active-layers (e.g. donor/acceptor ratio, spin-coating speed, solvent) that afford the best performances with silica as substrates. The film thickness was measured as about 150 nm. Atom force microscopy (AFM) was investigated by SPI 3800N using tapping-mode with a scan speed of 1Hz.

25 1.3. Fabrication and characterizations of OSCs

OSCs with a typical configuration of ITO/PEDOT: PSS/**DPPT** (**DPPSe** or **DPPTT**): PC₆₁BM/Ca/Al was fabricated as follows. The ITO glass was pre-cleaned with deionized water, CMOS grade acetone and isopropanol in turn for 15 min. The organic residues were further removed by treating

with UV-ozone for 1 h. Then the ITO glass was modified by spin-coating PEDOT: PSS (poly(3,4ethylenedioxythiophene)- poly(styrenesulfonate) layer, 45 nm) on it. After the ITO glasses were dried in oven at 150°C for 15 m in, the active layer was spin-coated on the ITO/PEDOT:PSS using a blend solution of **DPPT**, **DPPSe** and **DPPTT**, respectively, and PC₆₁BM (40 mg/mL in o-⁵ dichlorobenzene (o-CB) for **DPPT** and **DPPSe** and CHCl₃ for **DPPTT**, variants with donor/acceptor weight ratio of 1:2, 1:1, 2:1, 3:1 and 4:1, respectively). Ca (12 nm) and Al (120 nm) electrode was then subsequently thermally evaporated on the active layer under the vacuum of 1×10^{-6} Torr. The active area of the device was 0.04 cm², and the thickness of the active films were in the range of $70 \sim 200$ nm. The devices were characterized in nitrogen atmosphere under the illumination of is simulated AM 1.5 G, 100 mW/cm² using a xenon-lamp-based solar simulator. The current-voltage (*I-V*) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. The IPCE measurements of the encapsulated devices were performed in air (PV Measurements Inc., Model QEX7).

1.4. Tests of the hole mobilities of the small molecule and PC61BM blending films

¹⁵ The devices were fabricated with configuration of ITO/PEDOT:PSS/small molecule: PC₆₁BM/Au with the donor/acceptor ratio of 3:1 (**DPPT**:PC₆₁BM), 3:1 (**DPPSe**:PC₆₁BM), and 2:1 (**DPPTT**:PC₆₁BM). The active layers were spin-coated under the conditions that afford the best photovoltaic results. The following equation was applied to estimate the hole mobilities:^{1, 2} $Ln(JL^3V^2)$ = $0.89(1/E_0)^{0.5}(V/L)^{0.5}+Ln(9\varepsilon c_0\mu_0/8)$, where ε is the dielectric constant of the polymer, ε_0 the ²⁰ permittivity of the vacuum, μ_0 the zero-field mobility, E_0 the characteristic field, *J* the current density, *L* the thickness of the films, and $V = V_{appl}-V_{bi}$; V_{appl} is the applied potential, and V_{bi} the built-in potential which results from the difference in the work function of the anode and the cathode (in this device structure, $V_{bi} = 0.2$ V). The $\ln(JL^3/V^2)$ vs $(V/L)^{0.5}$ plots of the small molecules based on SCLC method is are shown in Figure 3. The hole mobility of the blending films were deduced from the ²⁵ intercept value $Ln(9\varepsilon c_0\mu_0/8)$. Herein ε is 3, ε_0 is 8.85419×10⁻¹² CV⁻¹m⁻¹.

2. Synthesis



Scheme S1 The synthetic routes toward the DPP-based small molecules.

2.1 Synthesis of protocols

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The synthetic routes towards **DPPT**, **DPPSe**, and **DPPTT** are showed in Scheme S1.

Trimethyl(5-octylthieno[3,2-b]thiophen-2-yl)stannane (2): 2-octylthiophene (**1**, 400 mg, 2 mmol) and 10 ml anhydrous tetrahydrofuran (THF) were put into to a flask tube in nitrogen atmosphere and ¹⁵ cooled down to -78°C. Subsequently, butylithium (1 ml, 2.2 M in hexane) was added to the flask tube dropwise. After stirred at -78 °C for 30 min, trimethyltin chloride (2.2 ml, 1 M in hexane) was added in one portion. And then the reaction was stirred at room temperature for another 2 h and then was poured into water and extracted by diethyl ether twice. After being dried by anhydrous magnesium sulfate (MgSO₄) and removing the solvent, the product of **2** was used in the next step ²⁰ without any further purification.

1-(Selenophen-2-yl)octan-1-one (4): Aluminum chloride (AlCl₃, 400 mg, 3 mmol) was added to a solution of selenophene (**3**, 262 mg, 2 mmol) in anhydrous DCM. The solution was stirred at room

temperature for 1 h, then cooled to 0 °C. Octanoyl chloride (358 mg, 2.2 mmol) was carefully added to the solution for 10 min. After the addition was completed, the mixture was stirred at room temperature for another 2 h. Water was added to the reaction solution to quench the reaction and then the solution was extracted with DCM. The organic phase was dried with anhydrous MgSO₄ and solvent was removed under vacuum. The crude residue was purified by silica gel chromatography (petroleum ether) to yield **4** (340 mg, 1.3 mmol, 65%). ¹H NMR (400 MHz, CDCl₃): 8.35(d, 1H, J=5.32Hz), 7.91(d, 1H, J=3.28 Hz), 7.38(t, 1H, J=4.44 Hz), 2.90(t, 2H, J=7.4 Hz), 1.74(m, 2H), 1.28–1.34(m, 8H), 0.87(m, 3H). ¹³C NMR (100 MHz, CDCl₃): 194.2, 151.6, 139.5, 134.0, 130.7, 38.8, 31.7, 29.3, 29.1, 25.0, 22.6, 14.1.

- ¹⁰ **2-Octylselenophene (5):** AlCl₃(400 mg, 3 mmol) was carefully added to a solution of LiAlH₄ (285 mg, 7.5 mmol) in anhydrous ether (10 ml) at 0 °C, then 1-(selenophen-2-yl)octan-1-one (**4**, 271 mg, 1 mmol) was added to the solution. Then the mixture was stirred at room temperature for 1 h. Cool water was added slowly to the solution in ice-bath to quench the reaction and then the solution was extracted with DCM. The organic phase was dried with anhydrous MaSO₄ and solvent was removed ¹⁵ under vacuum. The crude residue was purified by silica gel chromatography (petroleum ether) to
- produce **5** (155 mg, 0.6 mmol, 60%). ¹H NMR (400 MHz, CDCl₃): 7.79(d, 1H, *J*=5.35Hz), 7.13(t, 1H, *J*=3.78Hz), 6.95(d, 1H, *J*=3.62Hz), 2.89(t, 2H, *J*=7.40Hz), 1.69(m, 2H), 1.28—1.38(m, 10H), 0.89(m, 3H). ¹³C NMR (100 MHz, CDCl₃): 153.5, 129.1, 127.9, 126.2, 32.7, 32.6, 31.9, 29.4, 29.2, 29.1, 22.7, 14.1.
- ²⁰ Trimethyl (5-octylselenophen-2-yl) stannane (6): The experimental procedure is similar to that of
 2 except for altering the starting material to 2-octylselephene (5, 260 mg, 1 mmol) and the product 6 was used in the next step without any further purification.

1-(Thieno[3,2-b]thiophen-2-yl)octan-1-one (8): The experimental procedure is similar to that of 4 except for altering the starting material to thieno[3,2-b] thiophene (7, 280 mg, 2 mmol). The crude
²⁵ residue was purified by silica gel chromatography (petroleum ether) to yield 8 (400 mg, 1.5 mmol, 75%). ¹H NMR (400 MHz, CDCl₃): 7.90(s, 1H), 7.61(d, 2H, *J*=5.12Hz), 7.29(d, 2H, *J*=5.08Hz), 2.92(t, 2H, *J*=7.36Hz), 1.77(m, 2H), 1.37-1.29(m, 8H), 0.87(t, 3H). ¹³C NMR (100 MHz, CDCl₃): 193.8, 145.5, 144.6, 138.5, 131.8, 123.7, 119.6, 38.6, 31.2, 28.9, 28.6, 24.5, 22.1, 13.6.

2-Octylthieno[3,2-b]thiophene (9): The experimental procedure is similar to that of 5 except for altering the starting material to 1-(selenophen-2-yl)octan-1-one (8, 266 mg, 1 mmol). The crude residue was purified by silica gel chromatography (petroleum ether) to yield 9 (200 mg, 0.8 mmol, 80%). ¹H NMR (400 MHz, CDCl₃): 7.24(d, 1H, *J*=4.52Hz), 7.19(t, 1H, *J*=4.28Hz), 6.96(s, 1H), 5 2.88(t, 2H, *J*=7.48Hz), 1.72(m, 2H), 1.38-1.27(m, 10H), 0.88(m, 3H). ¹³C NMR (100 MHz, CDCl₃): 148.6, 138.8, 137.3, 119.5, 116.2, 31.9, 31.6, 31.2, 29.4, 29.2, 29.1, 22.7, 14.1.

Trimethyl(5-octylthieno[3,2-b]thiophen-2-yl)stannane (10): The experimental procedure is similar to that of 2 except for altering the starting material to 2-octylthieno[3, 2-b]thiophene (9, 252 mg, 1 mmol) and the product 10 was used in the next step without any further purification.

¹⁰ 2.2 Synthesis of DPPT, DPPSe and DPPTT

A general synthetic procedure for synthesis of **DPPT**, **DPPS**e and **DPPTT** is as follows. A 10 ml anhydrous toluene solution of 3,6-bis(5-bromothiophen-2-yl)-2-(2-ethylheptyl)-5-(2-ethylhexyl) pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione (**11**, 134 mg, 0.2 mmol) ³ and Trimethyl stannane compounds (**2**, **6**, or **10**) in a molar ratio of 1: 2.2 were put into a flask under nitrogen atmosphere. ¹⁵ After 10 min nitrogen-blowing of the solution, catalyst of Pd(PPh₃)₄ (0.1 eq) was added to the reaction and the reactant was heated to reflux at 130 °C for 24 h. Then the reactant was cooled to room temperature. Subsequently, the solvent was removed under vacuum and the reactant was purified by silica gel chromatography (petroleum ether: DCM=2:1).

2,5-Bis(2-ethylhexyl)-3,6-bis(5'-octyl-[2,2'-bithiophen]-5-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-

²⁰ dione (DPPT): DPPT is obtained as a dark blue powder (146 mg, 0.16 mmol, 80%). ¹H NMR (400 MHz, CDCl₃): 8.91(d, 2H, *J*=3.24Hz), 7.26(d, 2H, *J*=4.32Hz), 7.17(d, 2H, *J*=3.20Hz), 6.90(d, 2H, *J*=3.62Hz), 4.03(m, 4H), 2.88(m, 4H), 1.92(m,2H), 1.69(m, 4H), 1.26-1.38(m, 36H), 0.88(m, 18H).
¹³C NMR (100 MHz, CDCl₃): 161.7, 147.8, 143.4, 139.4, 136.8, 136.7, 127.5, 125.4, 125.0, 124.0, 108.2, 46.0, 39.3, 31.9, 31.6, 30.4, 30.3, 29.3, 29.2, 29.1, 28.3, 26.8, 23.7, 23.1, 22.7, 14.1, 10.6.
²⁵ MALDI-TOF MS: 913.4 (M+H⁺). Elemental Analysis for C₅₄H₇₆N₂O₂S₄: Calcd: C, 71.00%; H, 8.39%; N, 3.07%. Found: C, 70.72%; H, 8.39%; N, 2.93%.

2,5-Bis(2-ethylhexyl)-3,6-bis(5-(5-octylselenophen-2-yl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-

1,4(2H,5H)-dione (DPPSe): DPPSe is obtained as a dark green powder (171 mg, 0.17 mmol, 85%). ¹H NMR (400 MHz, CDCl₃): 8.91(d, 2H, *J*=3.26Hz), 7.26(d, 2H, *J*=3.66Hz), 7.17(d, 2H, *J*=3.20Hz), 6.90(d, 2H, *J*=3.16Hz), 4.03(m, 4H), 2.88(t, 4H), 1.92(m, 2H), 1.69(m, 4H). ¹³C NMR(100 MHz, ⁵ CDCl₃): 161.7, 155.6, 145.5, 139.5, 138.4, 136.8, 127.7, 127.5, 127.1, 124.8, 108.3, 46.0, 39.3, 33.0, 32.5, 31.9, 30.4, 29.7, 29.3, 29.2, 29.1, 28.6, 23.7, 23.1, 22.7, 14.1,10.6. MALDI-TOF MS: 1007.8 (M+H⁺). Elemental Analysis for C₅₄H₇₆N₂O₂S₂Se₂: Calcd: C, 64.39%; H, 7.61%; N, 2.78%. Found: C, 64.00%; H, 7.52%; N, 2.79%.

2,5-Bis(2-ethylhexyl)-3,6-bis(5-(5-octylthieno[3,2-b]thiophen-2-yl)thiophen-2-yl)pyrrolo[3,4-

¹⁰ c]pyrrole-1,4(2H,5H)-dione (DPPTT): DPPTT is obtained as a dark blue powder (174 mg, 0.17 mmol, 83%). ¹H NMR (400 MHz, CDCl₃): 8.94(d, 2H, *J*=1.36Hz), 7.38(s, 2H), 7.26(d, 2H, *J*=2.40Hz), 6.91(s, 2H), 4.02(m, 4H), 2.86(m, 4H), 1.93(m, 2H), 1.71(m, 4H), 1.38-1.28(m, 36H), 0.92(m, 18H). ¹³C NMR(100 MHz, CDCl₃): 161.6, 150.3, 143.3, 139.2, 139.0, 128.1, 136.8, 135.9, 127.9, 124.3, 117.3, 116.4, 108.3, 46.0, 39.3, 39.3, 31.9, 31.5, 31.3,30.4,29.3, 29.2, 29.1, 28.6, 23.7,
 ¹⁵ 23.2, 22.7, 14.1, 10.6. MALDI-TOF MS: 1025.4 (M+H⁺). Elemental Analysis for C₅₈H₇₆N₂O₂S₆: Calcd: C, 67.92%; H, 7.47%; N, 2.73%; Found: C, 67.81%; H, 7.16%; N, 2.43%.

3. Supporting figures

²⁰ Figure S1. Performances of standard P3HT/PCBM device.



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Figure S2. Tapping mode AFM images of **DPPT** (a), **DPPSe** (b), and **DPPTT** (c) pristine films. Note: scan area: $5 \times 5 \mu m$, R_q roughness = 1.30 nm (a), 1.43 nm (b), and 6.15 nm (c).

4. Supporting tables

5 Table S1 optoelectronic properties of the DPP-based small molecules.

compounds	$\lambda^a_{max} (nm)^a$	solution $\varepsilon_{\max}/10^3$ fw	fwhm	fwhm λ^a_{max} (nm) ^a	film <i>fwhm</i>	$\lambda^a_{edge}(nm)^d / E_g^{opt}$	Electrochemical properties $E_{ox}(V)^{f}/HOMOE_{red}(V)^{f}/LUMO E_{g}^{elec}(eV)^{g}$		
DPPT DPPSe	583, 621 589, 627	(M cm ⁻) ⁶ 44.8, 47.6 46.1, 48.0	(cm ⁻) ^e 3078.1 3117.4	597, 659 606, 669	(cm ⁻) ² 4036.8 4229.6	(ev) 737/1.68 746/1.66	0.66/-5.06	-1.02/-3.38 -1.02/-3.38	1.68 1.63
DPPTT	601, 639	47.1, 48.6	3145.1	617, 680	4452.2	778/1.59	0.58/-4.98	-1.02/-3.38	1.60

Note: ^{*a*} absorption maximum; ^{*b*} molar extinction coefficient; ^{*c*} the full width at half maximum (fwhm) is calculated following this equation of fwhm = $1/\lambda_{hm}^1 - 1/\lambda_{hm}^2$, where λ_{hm}^1 and λ_{hm}^2 are the wavelengths at the half maxima of the absorption, respectively, localizing at the blue and the red edge of the absorption band; ^{*d*} absorption edge; ^{*e*} optical bandgap calculated from the absorption edge with $1240/\lambda_{edge}$; ^{*f*} onset voltage of the oxidation/reduction processes; ^{*g*} and calculated from the onset of oxidation/reduction voltage; ^{*h*} electrochemical bandgaps calculated from LUMO-HOMO.

Table S2. XRD diffraction peaks and *d*-spacing of the pristine small molecule films and small molecule/PC61BM blending films with the donor/acceptor ratio of 3:1 (**DPPT**:PC₆₁BM), 3:1 (**DPPSe**:PC₆₁BM), and 2:1 (**DPPTT**:PC₆₁BM), respectively.

		2θ (deg) (<i>a</i> -spacing (A))		
Film	а	b	с	$I_{\rm a}/I_{\rm b}$
DPPT	4.47 (19.7)	7.27 (12.1)	23.86 (3.72)	3.97
DPPSe	4.45 (19.8)	6.95 (12.7)	23.22 (3.83)	2.89
DPPTT	4.86 (18.2)	6.78 (13.0)	21.78 (4.08)	17.12
DPPT:PCBM	4.45 (19.8)	7.29 (12.1)	23.60 (3.76)	14.66
DPPSe:PCBM	4.48 (19.7)	6.97 (12.6)	23.80 (3.73)	3.51
DPPTT:PCBM	4.65 (19.0)	6.60 (13.4)	20.43 (4.03)	3.46

Note: **a**, **b**, and **c** represent the different packing direction as shown in Figure 7b; I_a/I_b denotes the relative intensity ratio of **a** reflection versus **b** ¹⁵ reflection.

5. References

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