Supplementary Information

Regulating Crystallinity of Dimeric Acceptors via Central Core Engineering for Efficient Ternary Organic Solar Cells

Bigui Zhou¹, Binhang Shao¹, Bin Fan¹, Weikun Chen¹, Qinhao Shi¹, Yijie Nai¹, Hui Yang¹, Jun Yuan¹, Yingping Zou^{1, 2*}

¹College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, Hunan, P. R. China

²National Engineering Research Centre of Advanced Energy Storage Materials, Changsha 410199, Hunan, P. R.

China

* E-mail: yingpingzou@csu.edu.cn

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1. Instruments and characterization

¹H NMR and ¹³C NMR spectra were recorded using a Bruker AV-400 spectrometer in a deuterated chloroform solution at 298 K, unless specified otherwise. Chemical shifts are reported as δ values (ppm) with tetramethylsilane (TMS) as the internal reference. The molecular mass was confirmed using an Autoflex III matrix-assisted laser desorption ionization mass spectrometer (MALDI-TOF-MS). Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA-7 with a heating rate of 10 K/min under nitrogen. UV-*Vis* absorption spectra were recorded on the SHIMADZU UV-2600 spectrophotometer. The cyclic voltammetry results were obtained with a computer-controlled CHI 660E electrochemical workstation.

The morphologies of the PM6/acceptor blend films were investigated by atomic force microscopy (AFM, Agilent Technologies, 5500 AFM/SPM System, USA) in contacting mode with a 5 µm scanner. Transmission electron microscopy (TEM) measurements were performed in a JEOL/JEM-F200. Samples for the TEM measurements were prepared as following: The active layer films were spin-cast on ITO/PEEDOT:PSS substrates, and the substrates with active layers were submerged in deionized water to make the active layers float onto the air-water interface. Then, the floated films were picked upon an unsupported 200 mesh copper grids for the TEM measurements. The density functional theory (DFT) was applied using the Gauss software package on B3LYP/6-31G* level.

Device fabrication and characterization:

The optimized solar cell devices were fabricated with a conventional structure of ITO glass/2PACz/PM6:SMAs/PNDIT-F3N/Ag. Pre-patterned ITO-coated glass substrates (purchased from Advanced Election Technology Co., Ltd) were washed with deionized water and isopropyl alcohol in an ultrasonic bath for 15 minutes each. After blowdrying with high-purity nitrogen, all ITO substrates are cleaned in the ultraviolet ozone cleaning system for 25 minutes. Subsequently, a thin layer of 2PACz (Xi'an Polymer Light Technology Corp 4083) was deposited through spin-coating on pre-cleaned ITOcoated glass at 3000 rpm for 30 s and dried subsequently at 100°C for 15 minutes in atmospheric air. Then the photovoltaic layers were spin-coated in a nitrogen filled glovebox from a blend solution of PM6:BTP-4Cl (1:1.2), PM6:BTP-4Cl:S-EDOT, and PM6:BTP-4Cl:Se-EDOT (14mg/mL with 0. 5vol% 1-chloronaphthalene (CN)) in CF. The optimal active layers were fabricated by spin-coating at about 3000 rpm for the 30s. Then the PM6:BTP-4Cl, PM6:BTP-4Cl:S-EDOT, and PM6:BTP-4Cl:Se-EDOT films were treated with thermal annealing at 100°C for 10 minutes. After cooling to room temperature, a PNDIT-F3N layer via a solution concentration of 1 mg/mL was deposited at the top of the active layer at a rate of 3000 rpm for 30 s. Finally, the top Ag electrode of 100 nm thickness was thermally evaporated through a mask onto the cathode buffer layer under a vacuum of 1.5×10^{-4} mbar. The thickness of optimal active layer measured by a Bruker Dektak XT stylus profilometer was about 100 nm. Current density-voltage (*J-V*) curves of the devices were performed by a Keithley 2400 source meter in a glove box. The simulated sunlight was calibrated by an AM 1.5G solar simulator (Enlitech, SS-F5, Taiwan), which was measured with a calibrated Si diode from the National Renewable Energy Laboratory.

Electron mobility and hole mobility measurements:

The electron and hole mobility of PM6:BTP-4Cl, PM6:BTP-4Cl:S-EDOT and PM6:BTP-4Cl:Se-EDOT blend films were measured by using the method of spacecharge limited current (SCLC). The electron-only SCLC device was a stack of ITO/ZnO/active layer/ PNDIT-F3N /Ag, and the hole-only SCLC device was a stack of ITO/PEDOT:PSS/active layer/MoO₃/Ag. The electron-only and hole-only SCLC device fabricating methods were the same as those for OSCs. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8d^3$, where J is the current density, d is the film thickness of the active layer, μ is the charge carrier mobility, ε_r is the relative dielectric constant of the transport medium, and ε_0 is the permittivity of free space. $V = V_{app}-V_{bi}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage. The carrier mobility can be calculated from the slope of the $J^{1/2} - V$ curves.

2. Experimental Procedures

2.1 Materials

Anaerobic reactions described in this work are carried out under an argon atmosphere. Unless otherwise stated, ultra-dry reagents and all other reagents are commercially available and can be used without further purification. Column chromatography is generally carried out on silica gel (200-300 mesh) and reaction was monitored by thin layer chromatography (TLC) using silica gel GF254 plate with UV light to visualize the course of reaction. BTP-S-2FBr and BTP-Se-2FBr were synthesized according to the reported literature.¹

2.2 General procedures



Figure S1. Synthetic routes of S-EDOT and Se-EDOT.

Synthesis of S-EDOT

In a 100 mL three-necked round-bottomed flask, BTP-S-2FBr (180 mg, 0.095 mmol), 2,5-bis(tributylstannyl)-3,4-ethenedioxythiophene (32.4 mg, 0.045 mmol), Pd₂(dba)₃ (6.5 mg, 0.007 mmol), and P(o-tol)₃ (24.6 mg, 0.081 mmol) were added. The reaction system was evacuated-argon-filled three times and then 50 mL of toluene that had been deoxygenated for 20 min was added, and then the reaction was allowed to react at 110 °C for 2 h. The progress of the reaction was monitored by TLC. At the end of the reaction, the reaction solution was poured into 100 mL of methanol for settling, filtered, and the obtained solid was separated and purified by silica gel column chromatography (PE/DCM, 1/2, v/v), and further recrystallized from methanol and chloroform to obtain the target product S-EDOT, which was dried to give 96 mg of black solid (0.026 mmol, 58% yield). ¹H NMR (400 MHz, Chloroform-d) δ 9.13 (s, 4H), 8.73 (d, J = 8.4 Hz, 2H), 8.57 (dd, J = 9.8, 6.5 Hz, 2H), 8.32 (s, 2H), 8.08 (s, 2H), 7.64 (t, J = 7.4 Hz, 2H), 4.82 $(d, J = 7.8 \text{ Hz}, 8\text{H}), 4.60 \text{ (s, 4H)}, 3.25-3.02 \text{ (m, 8H)}, 2.23-2.04 \text{ (m, 8H)}, 1.50-0.95 \text{ (m, 8H)$ 184H), 0.89-0.74 (m, 50H). ¹³C NMR (600 MHz, CDCl₃) δ 185.89, 153.51, 152.65, 147.53, 145.25, 145.22, 141.68, 138.28, 138.08, 137.60, 137.44, 135.95, 134.36, 134.09, 129.93, 129.90, 125.74, 119.83, 117.00, 115.21, 114.65, 113.84, 113.25, 112.36, 77.23, 77.02, 76.81, 68.57, 64.87, 55.90, 40.02, 39.85, 39.15, 35.93, 34.65, 33.57, 33.31, 33.26, 31.95, 31.92, 31.88, 31.87, 31.82, 30.55, 29.79, 29.70, 29.67, 29.64, 29.61, 29.56, 29.54, 29.49, 29.39, 29.33, 29.32, 29.26, 29.20, 28.85, 27.22, 26.60, 25.55, 23.02, 22.70, 22.67, 22.64, 14.13, 14.11, 14.08. MALDI-TOF m/z calcd for [M⁺] C₂₂₂H₂₈₂F₄N₁₆O₆S₁₁ 3697.9184, found 3697.7511.

Synthesis of Se-EDOT

A 100 mL three-necked round-bottomed flask was charged with BTP-Se-2FBr (182 mg, 0.095 mmol), 2,5-bis(tributylstannyl)-3,4-ethylenedioxythiophene (32.4 mg, 0.045 mmol), Pd₂(dba)₃ (6.5 mg, 0.007 mmol), and P(o-tol)₃ (24.6 mg, 0.081 mmol), the reaction system was evacuated-argon-filled three times and then 50 mL of toluene that was deoxygenated for 20 min was added, and then the reaction was allowed to react at 110 °C for 2 h. The progress of the reaction was monitored by TLC. At the end of the reaction, the reaction solution was poured into 100 mL of methanol for settling, filtered, and the resulting solid was separated and purified by silica gel column chromatography using PE/DCM (1/2, v/v) as eluent. The crude product was further recrystallized from methanol and chloroform to obtain Se-EDOT, which was dried to give 117 mg of black solid (0.031 mmol, 69% yield). ¹H NMR (400 MHz, Chloroform-d) δ 9.10 (s, 4H), 8.71 (s, 2H), 8.55 (s, 2H), 8.08 (s, 1H), 7.64 (t, *J* = 7.4 Hz, 2H), 4.72 (d, *J* = 69.1 Hz, 12H), 3.07 (s, 8H), 2.31-2.15 (m, 4H), 2.04 (s, 4H), 1.38-1.03 (m, 184H), 0.82 (m, 50H). ¹³C NMR (600 MHz, CDCl₃) & 185.87, 155.25, 153.51, 153.11, 145.33, 138.14, 137.87, 137.49, 137.14, 136.57, 136.05, 134.44, 134.02, 115.91, 115.27, 114.71, 77.28, 77.02, 76.77, 68.35, 64.88, 55.81, 39.96, 39.18, 34.60, 33.54, 33.29, 31.95, 31.93, 31.86, 31.83, 30.60, 29.72, 29.68, 29.65, 29.57, 29.41, 29.39, 29.33, 29.21, 28.83, 27.22, 26.58, 25.61, 23.02, 23.00, 22.70, 22.68, 22.65, 14.14, 14.11, 14.06. MALDI-TOF m/z calcd for [M⁺] C₂₂₂H₂₈₂F₄N₁₆O₆S₉Se₂ 3793.8073, found 3793.8002.

3. Additional Figures



Figure S1. Thermogravimetric analysis curves of S-EDOT and Se-EDOT with a heating rate of 10 $^{\circ}C \cdot min^{-1}$



Figure S2. UV-Vis absorption spectra of S-EDOT, Se-EDOT and BTP-4Cl in CF solution



Figure S3. The C-V curves of S-EDOT
Se-EDOT and BTP-4Cl in solid state.



Figure S4. The C-V curves of PM6 in solid state.



Figure S5. Optimized molecular conformation and electron density distributions of S-EDOT and Se-EDOT.



Figure S6. The electrostatic potential (ESP) of S-EDOT and Se-EDOT.



Figure S7. The contact angle of PM6, BTP-4Cl, S-EDOT and Se-EDOT.



Figure S8. (a) *J-V* curves and (b) EQE curves based on PM6:S-EDOT and PM6:Se-EDOT.



Figure S9. a) Hole mobility. b) Electron mobility of the optimized OSCs based on PM6:BTP-4Cl, PM6:BTP-4Cl;S-EDOT, and PM6:BTP-4Cl:Se-EDOT.



Figure S10. AFM Phase images based on PM6:BTP-4Cl, PM6:BTP-4Cl;S-EDOT, and PM6:BTP-4Cl:Se-EDOT.



Figure S11. 2D-GIWAXS patterns of (a) BTP-4Cl, (b) S-EDOT and (c) Se-EDOT neat films; (d) In plane and out of plane (solid) GIWAXS curves of the corresponding 2D patterns;

4. Additional Tables

Film	θ _w ([°])	θ _{EG} (^o)	γ^{tot} $\gamma^{(mN m^{-1})}$	χ _{PM6:X} (K)	χ _{BTP-4CI:X} (K)	ω x
PM6	104.17	83.27	24.83	-	0.212	-
BTP-4Cl	98.49	72.46	29.64	0.212	-	-
S-EDOT	98.37	68.93	28.66	0.137	0.008	0.608
Se-EDOT	101.69	70.59	28.48	0.125	0.011	0.537

 Table S1. The contact angle data of PM6, BTP-4Cl, S-EDOT and Se-EDOT.

Table S2. Photovoltaic performance of ternary organic solar cells corresponding to two acceptors

 under different optimization conditions.

active layer	D/A	Concentration	additive	V _{oc} (V)	FF (%)	J _{sc} (mA cm-2)	PCE
	1:1.2:0	14mg/mL	1-CN (0.5%)	0.852	72.44	26.74	16.51
	1:1.1:0.1	16mg/mL	DIO (0.25%)	0.836	71.06	26.71	15.87
DM6.DTD ACI	1:1.1:0.1	16mg/mL	1-CN (0.25%)	0.851	71.63	26.41	16.09
S-EDOT	1:1.1:0.1	16mg/mL	1-CN (0.5%)	0.860	71.77	27.52	16.99
	1:1.1:0.1	14mg/mL	1-CN (0.25%)	0.869	74.40	27.43	17.73
	1:1.1:0.1	14mg/mL	1-CN (0. 5%)	0.882	77.57	26.73	18.29
	1:0:1.2	16mg/mL	1-CN (0.5%)	0.946	74.57	21.14	14.95
	1:1.1:0.1	14mg/mL	1-CN (0.25%)	0.858	72.47	26.12	16.24
	1:1.0:0.2	14mg/mL	1-CN (0.25%)	0.872	74.16	25.94	16.78
PM6:BTP-4Cl: Se-EDOT	1:1.0:0.2	14mg/mL	1-CN (0.5%)	0.864	73.91	26.96	17.22
	1:1.0:0.2	14mg/mL	DIO (0.25%)	0.852	73.61	25.98	16.30
	1:0:1.2	16mg/mL	1-CN (0.5%)	0.947	68.27	21.67	13.98

	In plane (100)					
Films	Location ^a <i>d</i> -spacing		FWHM	^b CCL		
	(Å ⁻¹)	(Å)	(Å ⁻¹)	(Å)		
BTP-4Cl	0.290	10.83	0.059	47.39		
S-EDOT	0.297	10.58	0.092	30.39		
Se-EDOT	0.307	10.23	0.128	21.84		
PM6:BTP-4Cl	0.305	20.63	0.096	29.13		
PM6:BTP-4Cl:S-EDOT	0.307	20.46	0.105	26.62		
PM6:BTP-4C1:Se-EDOT	0.304	20.67	0.092	30.39		

Table S3. GIWAXS data of the in plane (100).

Table S4. GIWAXS data of the out of plane (010).

	Out of plane (010)					
Films	Location	cation ^a d-spacing		^b CCL		
	(Å ⁻¹)	(Å)	(Å ⁻¹)	(Å)		
BTP-4Cl	1.797	1.748	0.302	9.26		
S-EDOT	1.737	1.809	0.250	11.18		
Se-EDOT	1.739	1.806	0.239	11.69		
PM6:BTP-4Cl	1.734	1.812	0.259	10.79		
PM6:BTP-4Cl:S-EDOT	1.738	1.807	0.239	11.70		
PM6:BTP-4Cl:Se-EDOT	1.732	1.814	0.233	12.00		

^a Calculated from the equation: $d = 2\pi/q$. ^b Obtained from the Scherrer equation: CCL= $2\pi K/FWHM$, where FWHM is the full-width at half-maximum and K is a shape factor (K= 0.89 here).²

5. ¹H NMR, ¹³C NMR, and MALDI-TOF MS spectra



Figure S12. ¹H NMR spectrum of compound S-EDOT in CDCl₃.



10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 fl (ppm)

Figure S13. ¹³C NMR spectrum of compound S-EDOT in CDCl₃.



Figure S14. The high-resolution mass spectrum (MALDI-TOF) of S-EDOT



Figure S15. ¹H NMR spectrum of compound Se-EDOT in CDCl₃.



Figure S16. ¹³C NMR spectrum of compound Se-EDOT in CDCl₃.



Figure S17. The high-resolution mass spectrum (MALDI-TOF) of Se-EDOT.

6. Reference

1. C. Sun, J. Wang, F. Bi, H. Jiang, C. Yang, Y. Li, J. Chu and X. Bao, Energy Environ. Sci., 2025,

, 862-873.

2. K. Ma, W. Feng, H. Liang, H. Chen, Y. Wang, X. Wan, Z. Yao, C. Li, B. Kan and Y. Chen, *Adv. Funct. Mater.*, 2023, **33**, 2214926.