Supporting Information

Chlorinated Effects of the Non-fullerene Acceptor Based on Selenium Heterocyclic Core for High-Efficiency Organic Solar Cells

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1. Detailed experimental procedure

(1) Materials:

lithium diisopropylamide (LDA) and pyridine all purchased from J&K Scientific. 1-bromo-2butyloctane, 1-Cl-IC, 1-Cl-IC-mix and 2-Cl-IC all purchased from Hyper, Inc. All other solid pharmaceuticals and solvents were purchased from commercial sources and used directly without further purification. In our previous studies, we synthesized compound 1¹.

(2) Synthesis:



Scheme S1. The synthetic route of compound 2.

Synthesis of compound **2**. Under the protection of nitrogen, compound **1** (3 g, 3.5 mmol) and triphenyl phosphorus (9 g, 34 mmol) were added to 1,2-dichlorobenzene (o-DCB, 30 mL) within a 50 mL double neck bottle. The mixture was stirred at 200 °C for 6 h. After cooled to room

temperature, the mixture was precipitated in methanol (100 mL) for 3 h. Then the purple- red solid 2 was obtained by vacuum filtration (2.08 g, 75%).



Scheme S2. The synthetic route of compound 3.

Synthesis of compound **3**. Compound **2** (2.08 g, 2.62 mmol), K_2CO_3 (3.62 g, 26.24 mmol) and potassium iodide (4.35 g, 26.24 mmol) were added to anhydrous DMF (50 mL) within a 100 mL reaction flask under the protection of nitrogen, the solution was stirred and heated to 80 °C for 30 min, then 1-bromo-2-butyloctane (4.23 g, 17.03 mmol) was added into the mixture, which would be stirred 12 h. The mixture was transferred to a 500 mL beaker after cooled to room temperature and poured with water (200 mL), then it was extracted with dichloromethane. The lower organic phase was dried over anhydrous Na₂SO₄, then the dichloromethane solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography with dichloromethane/petroleum ether (1:1, v/v) to get compound 3 as a red solid (2.51 g, 85%). ¹H NMR (400 MHz, CDCl₃) δ 6.99 (s, 2H), 4.55 (d, J = 7.6 Hz, 4H), 2.81 (t, J = 7.5 Hz, 4H), 2.09 (s, 2H), 1.90-1.80 (m, 4H), 1.58 (s, 4H), 1.37-0.80 (m, 66H), 0.68-0.59 (m, 12H).



Scheme S3. The synthetic route of compound 4.

Synthesis of compound **4**. Compound **3** (1 g, 0.88 mmol) was dissolved in tetrahydrofuran that had been dehydrated (30 mL) within a 100 mL cryogenic reaction flask, then the mixture was cooled to 0 °C. Under the nitrogen, LDA (4 mmol, 2 M) and DMF (0.6 mL, 8.0 mmol) were slowly added dropwise sequentially. The mixture was stirred at 25 °C for 12 hours. Water (80 mL)

was added to terminate the reaction, the mixture was extracted with dichloromethane. The anhydrous MgSO₄ was added to the lower organic phase. Then the organic solvent was evaporated under reduced pressure. The crude product was purified with column chromatography on silica gel and the silica gel using dichloromethane/petroleum ether (2:1, V/V) as the eluent to obtain the orange-red solid 4 (0.56 g, 80%). ¹H NMR (400 MHz, CDCl₃) δ 10.13 (s, 2H), 4.57 (d, J = 7.4 Hz, 4H), 3.19 (t, J = 7.6 Hz, 4H), 2.05 (s, 2H), 1.91 (dd, J = 14.9, 7.3 Hz, 4H), 1.48- 1.41 (m, 4H), 1.31- 0.84 (m, 66H), 0.68- 0.60 (m, 12H).



Scheme S4. The synthetic route of compound BTSeIC-2Cl- γ .

Synthesis of **BTSeIC-2CI-** γ . Compound **4** (100 mg, 0.084 mmol) and 1-CI-IC (115 mg, 0.504 mmol) were mixed in anhydrous chloroform (30 mL) under the protection of nitrogen. Then the pyridine (0.7 mL) was slowly added dropwise to the mixture. The resulting solution was heated and stirred at 60 °C for 12 hours. The solution was precipitated in methanol for 3 h, then the precipitate was filtered and collected. The crude product was then purified by column chromatography (dichloromethane: petroleum ether =2:1, V/V, 91 mg, 67%). ¹H NMR (400 MHz, CDCl₃) δ 9.18 (s, 2H), 8.65 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 2.1 Hz, 2H), 7.71 (dd, J = 8.4, 2.1 Hz, 2H), 4.73 (s, 4H), 3.26- 3.21 (m, 4H), 2.14 (s, 2H), 1.90- 1.84 (m, 4H), 1.52 (d, J = 10.1 Hz, 4H), 1.27- 0.84 (m, 66H), 0.72- 0.64 (m, 12H). ¹³C NMR (400 MHz, CDCl₃) δ 187.17 (s), 153.84 (s), 153.19 (s), 145.32 (s), 138.66 (s), 137.50 (s), 136.04 (s), 133.51 (s), 129.55 (s), 120.15 (s), 115.72-115.52 (m), 77.42 (d, J = 11.5 Hz), 77.16 (s), 76.84 (s), 68.30 (s), 32.03 (s), 31.80 (s), 31.36 (s), 29.98 (s), 29.62 (dd, J = 17.0, 11.3 Hz), 22.78 (dd, J = 23.6, 6.8 Hz), 14.39- 14.08 (m), 13.92 (s), 1.18 (s). MALDI-TOF-MS m/z: [M] calcd. for C90H104Cl2N802S4Se, 1606.57, found 1606.35.



Scheme S5. The synthetic route of compound BTSeIC-2Cl-mix.

Synthesis of **BTSeIC-2CI-mix**. **BTSeIC-2CI-mix** and **BTSeIC-2CI-** γ were synthesized in a similar manner. ¹H NMR (400 MHz, CDCl₃) δ 9.18 (s, 2H), 8.70 (d, J = 1.5 Hz, 1.14H), 8.66 (d, J = 8.5 Hz, 0.86H), 7.89 (s, 0.86H), 7.88 (d, J = 4.6 Hz, 1.14H), 7.74 - 7.70 (m, 2H), 4.74 (s, 4H), 3.24 (t, J = 7.8 Hz, 4H), 2.16 (s, 2H), 1.92 - 1.84 (m, 4H), 1.52 (s, 4H), 1.28 - 0.88 (m, 51H), 0.72 - 0.65 (m, 10H). ¹³C NMR (400 MHz, CDCl₃) δ 176.50 (s), 153.01 (s), 140.15 (d, J = 300.9 Hz), 104.08 - 94.81 (m), 77.58 - 77.12 (m), 77.12 - 77.06 (m), 76.84 (s), 32.03 (s), 29.98 (s), 29.62 (dd, J = 16.9, 11.3 Hz), 22.84 (s), 14.29 (s), 1.18 (s). MALDI-TOF-MS m/z: [M] calcd. for C90H104Cl2N8O2S4Se, 1606.57, found 1606.35.



Scheme S6. The synthetic route of compound BTSeIC-4Cl.

Synthesis of **BTSeIC-4Cl**. **BTSeIC-4Cl** and **BTSeIC-2Cl-** γ were synthesized in a similar manner. ¹H NMR (400 MHz, CDCl₃) δ 9.17 (s, 2H), 8.80 (s, 2H), 7.95 (s, 2H), 4.73 (s, 4H), 3.23 (t, J = 6.9 Hz, 4H), 2.16- 2.10 (m, 2H), 1.90- 1.84 (m, 4H), 1.52 (d, J = 11.5 Hz, 4H), 1.27- 0.88 (m, 66H), 0.70- 0.64 (m, 12H). ¹³C NMR (400 MHz, CDCl₃) δ 186.34 (s), 154.25 (s), 153.14 (s), 145.51 (s), 139.41 (d, J = 36.6 Hz), 133.65 (s), 117.81 (d, J = 413.4 Hz), 219.56- 31.39 (m), 77.48 (s), 77.16 (s), 76.84 (s), 71.47- 68.78 (m), 68.68 (s), 29.74- 29.37 (m), 22.75 (d, J = 18.9 Hz), 1.17 (s). MALDI-TOF-MS m/z: [M] calcd. for C90H104Cl4N8O2S4Se, 1674.49, found 1674.21.

(3) Spectral charts of nuclear magnetic resonance



Figure S2. The ¹H NMR spectrum of compound 4 in CDCl₃.





Figure S6. The ¹³C NMR spectrum of BTSeIC-2Cl-mix in CDCl₃.



Figure S8. The ¹³C NMR spectrum of BTSeIC-4Cl in CDCl₃.

2. Material characterization

(1) Electrochemical characterization

At room temperature, the CV traces of films conducted on electrochemical workstation by using a scan rate of 100 mV s⁻¹ with conventional three-electrode configuration (consisting of the working electrode, Pt-C electrode and a Ag/AgCl reference electrode) in acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu4NPF6) (after deoxygenation). The potential of ferrocene is used as internal standard. On the basis of 4.8 eV below vacuum for the energy level of Fc/Fc⁺, the HOMO and LUMO levels of the **BTSeIC-2Cl-** γ , **BTSeIC-2Cl-mix** and **BTSeIC-4Cl** acceptors were calculated from the onset oxidation potentials (E_{onset}^{ox}) and onset reduction potentials (E_{onset}^{red}) respectively according to the following equations:

$$HOMO = -e(E_{onset}^{ox} - E_{Fc/Fc}^{+} + 4.8V)$$
(S1)

$$LUMO = -e(E_{onset}^{red} - E_{Fc/Fc}^{+} + 4.8V)$$
(S2)





Figure S9. Thermal gravity analyzes (TGA) of **BTSeIC-2Cl-***γ*, **BTSeIC-2Cl-mix** and **BTSeIC-4Cl** with a heating rate of 10 °C/min under nitrogen conditions.





Figure S10. UV-vis-NIR spectra of (a) BTSeIC-2Cl-γ, BTSeIC-2Cl-mix and BTSeIC-4Cl in CF solution and (b) PM6: BTSeIC-2Cl-γ, PM6: BTSeIC-2Cl-mix and PM6: BTSeIC-4Cl films.
(4)



Figure S11. The cyclic voltammetry (CV) spectra of BTSeIC-2Cl-γ, BTSeIC-2Cl-mix, and BTSeIC-4Cl.

(5) Optimized geometries



Figure S12. Optimized geometries with the dihedral angles of **BTSeIC-2Cl-**γ, **BTSeIC-2Cl-**β, and **BTSeIC-4Cl** by DFT calculation.

(6) Contact angle



Figure S13. Contact angle images of neat PM6, BTSeIC-2Cl-γ, BTSeIC-2Cl-mix, and BTSeIC-4Cl films with water and glycerol droplet on top.

Table S1. Contact angle and surface Energy Data of the PM6, BTSeIC-2Cl-γ, BTSeIC-2Cl-mix, and BTSeIC-4Cl pure substance films.

Materials	$ heta_{ m H2O}$	$\theta_{\rm C3H8O3}$	γ	γ^{d}	$\gamma^{\mathbf{p}}$	
	[deg]	[deg]	[mN ⁻¹]	[mN • m ⁻¹]	[mN • m ⁻¹]	λΡΜ6-SMAs
PM6	101.2	89.7	21.61	15.14	6.45	
BTSeIC-2Cl-γ	86.9	82.7	26.18	9.59	16.59	0.22
BTSeIC-2Cl-mix	90.2	82.9	24.38	15.21	9.18	0.14
BTSeIC-4Cl	94.6	83.7	25.79	19.70	6.09	0.09

3. Photovoltaic Device Fabrication

Positive device Fabrication: Devices in this study were fabricated with the positive structure (glass/indium tin oxide (ITO)/poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) (4083) (PEDOT: PSS)/active layers/PDINO/Ag). The ITO high-transparency glass substrate was cleaned with cleaning solution, and then sonicated with deionized water, acetone, and anhydrous ethanol in turn (each 15 min). And then dried by nitrogen gun. ITO was treated plasma for 6 min. PEDOT: PSS was filtered through a PTFE filter and spin-coated onto ITO at 3500 rpm for 40 s, subsequently, PEDOT: PSS film was heated at 135 °C for 10 min. Notably, at this point the substrate was transferred to the nitrogen-filled glove box. The polymer donor PM6: acceptor (D: A = 1: 1.2, 17.6 mg mL⁻¹) was dissolved beforehand in chloroform (CF) with the addition of the solvent additive 1,8-diiodooctane (DIO) (0.5%, v/v) or 1-chloronaphthalene (CN) (0.5%, v/v). The mixed solution was spin-coated on the top of the PEDOT: PSS film at 3000 rpm for 40 s to form the photoactive layer of about 100 nm. Then the active layer thin film was annealed at 100 °C for 10 min. PDINO (dissolved in methanol at 1 mg mL⁻¹) was spin-coated onto the active layer at 3000 rpm for 40 s to form the electron transport layer. After that, the semi-finished devices were transferred to the high-vacuum evaporator, the Ag anode (100 nm) was deposited under the pressure of 4×10^{-4} Pa. The current density-voltage (J-V) curves of all devices were measured using a Keithley 2400 Source Meter under AM 1.5G (100 mW cm⁻²). The light intensity was calibrated using a standard silicon solar cell provided by PV Measurements. The typical active area is 0.043 cm^2 as defined by a metal mask with an aperture. The external quantum efficiency (EQE) spectra were measured by QE-R3011 system (150 W xenon lamp fitted with a monochromator as a monochromatic light source). The film thicknesses were measured using Bruker DektakXT stylus profiling system.

(1) Device Optimized Data

 Table S2. The photovoltaic parameters of the BTSeIC-2Cl-γ, BTSeIC-2Cl-mix and BTSeIC-4Cl

 based OSCs.

A accentor	PM6: acceptor	Additive	Annealing	V _{OC}	$J_{ m SC}$	FF	PCE
Acceptor	w/w	(%)	(°C)	(V)	(mA cm ⁻²)	(%)	(%)
BTSeIC-2Cl-γ	1:1	-	-	0.89	21.26	69.76	13.17
	1:1.2	-	-	0.89	21.29	69.57	13.21
	1:1.2	0.5 CN	-	0.87	21.97	70.69	13.54
	1:1.2	0.5 DIO	-	0.85	23.18	72.63	14.32
	1:1.2	0.5 DIO	100	0.86	23.72	73.08	14.91
	1:1.2	0.5 DIO	120	0.85	23.65	72.79	14.50
BTSeIC-2Cl-mix	1:1	-	-	0.87	22.37	67.01	13.02
	1:1.2	-	-	0.87	21.93	69.87	13.32
	1:1.2	0.5 CN	-	0.87	22.63	67.87	13.35
	1:1.2	0.5 DIO	-	0.84	22.38	72.90	13.64
	1:1.2	0.5 DIO	100	0.85	23.20	71.91	14.21
	1:1.2	0.5 DIO	120	0.84	22.98	72.45	13.93
BTSeIC-4Cl	1:1	-	-	0.83	23.65	71.22	14.10
	1:1.2	-	-	0.84	23.83	71.71	14.32
	1:1.2	0.5 CN	-	0.85	23.88	72.89	14.79
	1:1.2	0.5 DIO	-	0.82	25.76	72.06	15.28
	1:1.2	0.5 DIO	100	0.82	26.92	73.11	16.14
	1:1.2	0.5 DIO	120	0.82	26.16	72.90	15.53



(3) The optimized BTSeIC-2Cl-y, BTSeIC-2Cl-mix and BTSeIC-4Cl-based devices

Fig. S14. The *J-V* curves of **BTSeIC-2Cl-** γ , **BTSeIC-2Cl-mix** and **BTSeIC-4Cl** based OSCs with (a) different ratios of donor to acceptor, (b) different contents of DIO or CN as additives and (c) different annealing temperature under AM 1.5 G illumination at intensity of 100 mW cm⁻².



(4) SCLC method to calculate the electron/hole mobility curve

Figure S15. The ln (JL $^3/V^2$) versus (V/L) $^{0.5}$ curves of (a) hole-only and (b) electron-only

BTSeIC-2Cl-y, BTSeIC-2Cl-mix and BTSeIC-4Cl based OSCs.

(5) Device stability test



Figure S16. The long-term stability tests of the **BTSeIC-2Cl-***γ*, **BTSeIC-2Cl-mix** and **BTSeIC-4Cl**-based devices (stored and tested in the glove box).

(6) The summary of the reported NFAs containing both selenium heterocycle and chlorinated end group in the binary OSCs



Figure S17. Molecular structure and information of NFAs containing both selenium heterocycles and chlorinated end groups that had been reported in binary OSCs.

References

1. E. Zhu, L. Fu, Y. Lu, W. Jiang, M. H. Jee, R. Liu, Z. Li, G. Che, H. Y. Woo and C. Liu, *ACS Appl. Mater. Interfaces*, 2022, **14**, 7082-7092.