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Supporting Information

Synergistic effect of selenophene-containing central core and the regioisomeric monochlorinated terminals on molecular packing, crystallinity, film morphology, and photovoltaic performance of selenophene-based nonfullerene acceptors

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General procedures and experimental details

Measurement: All air and water-sensitive reactions were carried out under N₂. Toluene and THF were dried by Na and then freshly distilled before using. The other precursors were used as the common commercial level. ¹H and ¹³C NMR spectra were carried out on the Bruker Ascend-400 and 700 NMR spectrometer. All chemical shifts were reported in ppm. Chemical shifts in ¹H NMR were referenced to TMS and in ¹³C NMR were referenced to CDCl₃. Mass spectra were recorded on a Bruker BIFLEX III mass spectrometer and a Bruker Solarix XR mass spectrometer. Thermogravimetric analysis (TGA) was performed using a TA Instrument Q600 analyzer under nitrogen gas flow with a heating rate of 10 °C min⁻¹. The calculations were performed using the Gaussian 09 software package. UV-vis absorption spectra were taken on a Hitachi UH5300 UV-vis spectrometer. The electrochemical cvclic voltammetry was carried out on CHI electrochemical workstation with glass carbon disk, Ag/Ag⁺ electrode, and Pt wire, as working electrode, reference electrode, and counter electrode, respectively, in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. During CV measurements, the films were drop-cast on the glass carbon working electrode from chloroform solution. Single crystals data collection was performed at 170 K for TSeIC-M-Cl on a SuperNova diffractometer, using graphite-monochromated Cu Ka radiation (λ =1.54184 Å). Data of **TSeIC-P-Cl** was performed at 293 K on a Bruker SMART CCD area detector, using graphite-monochromated Mo K α radiation (λ =0.71073 Å). All calculations were performed using the SHELXL and the crystallographic software package. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1964587 and 1964586, respectively. The single crystal X-ray crystallographic data were summarized in Table S1. Atomic force microscopy (AFM) measurements were taken on a Bruker Inova atomic microscope in tapping mode. Transmission electron microscope (TEM) measurements were performed on a JEOL JEM-1400 transmission electron microscope. GIWAXS measurements were performed at the PLS-II 9A U-SAXS beamline of the Korean Pohang Accelerator Laboratory.

Crystal Growth: **TSeIC-P-Cl** or **TSeIC-M-Cl** (5 mg) were dissolved in CH_2Br_2 (1 mL) in a small dram vial. This vial was placed into a large dram vial containing *n*-heptane (5 mL). The large vial was then sealed tightly and left undisturbed at room temperature until crystal growth occurred.

Space-Charge-Limited Current (SCLC) measurements: The hole and electron mobility were measured using the SCLC method with device architecture of ITO/PEDOT:PSS/active layer/MoO3/Ag and ITO/ZnO/active layer/PFN/Al, respectively. The current density–voltage (J-V) characteristics of the hole or electron only devices are fitted by the Mott–Gurney law: $J = (9/8)\varepsilon_r\varepsilon_0\mu(V^2/L^3)$, where J is the current density, ε_r is the dielectric permittivity of the active layer, ε_0 is the vacuum permittivity, L is the thickness of the active layer, μ is the mobility. $V=V_{app}-V_{bi}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage (V_{bi} is 0 V here). The mobility can be calculated from the slope of the $J^{0.5} \sim V$ curves.

Solar cell fabrication and characterization: bulk-hetero junction organic solar cells (BHJ-OSCs) were fabricated with a conventional architecture of ITO/PEDOT:PSS/active layer/ZrAcac/Al. After cleaning according to the procedure reported previously, the indium tin oxide (ITO)-coated glass substrates were ready for use. A 40 nm thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (HeraeusClevios P VP A 4083) layer was firstly spin-casting on top of the ITO substrates and then annealed on a hotplate at 150 °C for 10 min under the ambient condition. The donor **PBT1-C** ($M_n = 34.2 \text{ k}$, PDI =1.8) was mixed with **TSeIC-M-Cl** or **TSeIC-P-Cl** at a blending ratio of 1:1 and DIO content of 0.25% in CHCl₃. The polymer concentration is fixed at 7 mg/mL. Then they were spun cast on the top of the PEDOT:PSS to form the active layer. After annealing at 100 °C for 5 min in a glove box, the optimal thickness of the active layers is 110 nm measured using an Ambios Technology XP-2 surface profilometer. A thin layer (~ 5 nm) of ZrAcac in ethanol

with a concentration of 1.4 mg/mL was spin-casting on the top of the active layer at a spin coating rate of 3500 rpm and functions as the cathode interfacial layer. Finally, a 100 nm-thick Al electrode was successively deposited on top of the active layers. The active area of devices is 4.50 mm². Current density-voltage (J-V) characteristics were measured using a Keithley2400 Source Measure Unit. Solar cell performance used an Air Mass 1.5 Global (AM1.5 G) solar simulator (Class AAA solar simulator, Model 94063A, Oriel) with an irradiation intensity of 100 mW cm⁻², which was measured by a calibrated silicon solar cell and a readout meter (Model 91150V, Newport). EQE spectra were measured by using a QEX10 Solar Cell IPCE measurement system (PV measurements, Inc.).

1. Synthetic procedures of new compounds



IC-M-Cl and IC-P-Cl: In a 100 mL flask, compound 1 (0.518 g, 2.37 mmol) and malononitrile (0.314 g, 4.75 mmol) were added to absolute ethanol (10 mL) at room temperature. Anhydrous sodium acetate (0.290 g, 3.56 mmol) was further added to the reaction. The reaction mixture was stirred at room temperature for 3 h. Then, the mixture was poured into water (30 mL) and acidified to pH 1-2 with HCl, and the precipitate was filtered and washed with water and petroleum ether. The crude product was further purified by flash column chromatography, eluting with petroleum ether and dichloromethane (v:v = 1:1) and then recrystallized by petroleum ether to obtain the isomer **IC-M-Cl** as a pale yellow solid (0.162 g, 30%, Rf = 0.50) and the other isomer **IC-P-Cl** as a pale yellow solid (0.178 g, 33%, Rf = 0.57).

¹H NMR of **IC-M-Cl** (CDCl₃, 400 MHz, ppm): δ 8.61-8.60 (d, J = 2.0 Hz, 1H, Ph-*H*), 7.93-7.91 (d, J = 8.2 Hz, 1H, Ph-*H*), 7.81-7.79 (dd, J = 8.2, 2.0 Hz, 1H, Ph-*H*), 3.75 (s, 2H, CH₂). ¹³C NMR of **IC-M-Cl** (CDCl₃, 175 MHz, ppm): δ 193.3, 164.7, 143.5, 143.2, 143.1, 138.6, 136.0, 125.8, 125.7, 111.6, 80.4, 43.2. FT-ICR-MS of **IC-M-Cl** (*m*/*z*): calcd. for C₁₂H₅ClN₂O: 228.0090 (100%). Found: 228.0083 (M⁺, 100 %).

¹H NMR of **IC-P-Cl** (CDCl₃, 400 MHz, ppm): δ 8.59-8.57 (d, J = 8.6 Hz, 1H, Ph-*H*), 7.94-7.93 (d, J = 2.0 Hz, 1H, Ph-*H*), 7.84-7.82 (dd, J = 8.6, 2.0 Hz, 1H, Ph-*H*), 3.76 (s, 2H, CH₂). ¹³C NMR of **IC-P-Cl** (CDCl₃, 175 MHz, ppm): δ 193.4, 164.8, 142.9, 141.8, 140.5, 136.2, 127.0, 124.7, 112.0, 111.8, 79.5, 43.4. FT-ICR-MS of **IC-P-Cl** (*m*/*z*): calcd. for C₁₂H₅ClN₂O: 228.0090 (100%). Found: 228.0086 (M⁺, 100%).



TSeIC-M-CI: In a 100 mL flask, IC-M-CI (0.172 g, 0.754 mmol) and IDTSe-2CHO (0.147 g, 0.126 mmol) was added. The reaction mixture was evacuated and backfilled with N₂ three times. Then freshly degassed chloroform (40 mL) and pyridine (1 mL) were added into the reaction mixture. The reaction was stirred for 8 h at room temperature. Then the solution was poured into methanol and the precipitate was filtered off and washed with methanol. The residue was directly purified by silica gel column chromatography by using petroleum ether and dichloromethane (v:v = 1:1) as the eluent to yield the product as a purple solid (0.174 g, 86%, Rf = 0.72). ¹H NMR of **TSeIC-M-Cl** (CDCl₃, 400 MHz, ppm): δ 9.02 (s, 2H, CH=C), 8.64 (s, 2H, Ph-*H*), 8.27 (s, 2H, Se-*H*), 7.82-7.80 (d, *J* = 8.0 Hz, 2H, Ph-*H*), 7.70-7.68 (d, *J* = 6.8 Hz, 4H, Ph-*H*), 7.20-7.18 (d, *J* = 8.0 Hz, 8H, Ph-*H*), 7.14-7.12 (d, *J* = 8.0 Hz, 8H, Ph-*H*), 2.58-2.54 (t, J = 7.9 Hz, 8H, CH_2), 1.60-1.55 (m, 8H, CH_2), 1.35-1.26 (m, 24H, CH_2), 0.87-0.84 (m, 12H, CH₃). ¹³C NMR of **TSeIC-M-Cl** (CDCl₃, 175 MHz, ppm): δ 187.8, 158.5, 156.2, 153.4, 151.7, 150.8, 145.1, 142.5, 141.9, 141.7, 141.2, 141.0, 138.9, 137.1, 134.8, 134.4, 128.9, 127.9, 125.4, 124.6, 121.0, 118.8, 114.3, 114.2, 69.9, 63.1, 35.6, 31.7, 31.3, 29.7, 29.1, 22.6, 14.1. MALDI-TOF MS (m/z): calcd. for C94H80Cl2N4O2S2Se2: 1590.3 (100%). Found: 1590.5 (M⁺, 100%). Elemental Analysis: calcd for C₉₄H₈₀Cl₂N₄O₂S₂Se₂: C, 70.98; H, 5.07; N, 3.52. Found: C, 70.75; H, 5.13; N, 3.41.



TSeIC-P-CI: In a 100 mL flask, IC-P-CI (0.145 g, 0.636 mmol) and IDTSe-2CHO (0.120 g, 0.106 mmol) was added. The reaction mixture was evacuated and backfilled with N₂ three times. Then freshly degassed chloroform (40 mL) and pyridine (1 mL) were added into the reaction mixture. The reaction was stirred for 10 h at room temperature. Then the solution was poured into methanol and the precipitate was filtered off and washed with methanol. The residue was directly purified by silica gel column chromatography using petroleum ether and dichloromethane (v:v = 1:1) as the eluent to yield the product as a purple solid (0.140 g, 83%, Rf = 0.66). ¹H NMR of **TSeIC-P-Cl** (CDCl₃, 400 MHz, ppm): δ 9.02 (s, 2H, CH=C), 8.60-8.58 (d, J = 8.4 Hz, 2H, Ph-H), 8.26 (s, 2H, Se-H), 7.81-7.80 (d, J = 2.0 Hz, 2H, Ph-H), 7.69-7.66 (dd, J = 8.4, 2.0 Hz, 4H, Ph-H), 7.21-7.19 (d, J = 8.1 Hz, 8H, Ph-H), 7.16-7.14 (d, J = 8.1 Hz, 8H, Ph-H), 2.59-2.55 (t, J = 7.8 Hz, 8H, CH₂), 1.65-1.56 (m, 8H, CH₂), 1.36-1.24 (m, 24H, CH₂), 0.90-0.82 (m, 12H, CH₃). ¹³C NMR of **TSeIC-P-Cl** (CDCl₃, 175 MHz, ppm): δ 187.6, 158.9, 156.2, 153.4, 151.7, 150.7, 145.1, 142.5, 141.7, 141.2, 141.1, 141.0, 138.9, 138.1, 137.9, 137.1, 135.0, 128.9, 127.9, 126.4, 123.7, 121.0, 118.8, 114.5, 114.4, 69.3, 63.1, 35.7, 31.7, 31.2, 29.1, 22.6, 14.1. MALDI-TOF MS (*m/z*): calcd. for C₉₄H₈₀Cl₂N₄O₂S₂Se₂: 1590.3 (100%). Found: 1590.2 (M⁺, 100 %). Elemental Analysis: calcd for C₉₄H₈₀Cl₂N₄O₂S₂Se₂: C, 70.98; H, 5.07; N, 3.52. Found: C, 70.28; H, 5.14; N, 3.39.

3. Additional characterization of TSeIC-M-Cl, TSeIC-P-Cl, PBT1-C:TSeIC-M-Cl and PBT1-C:TSeIC-P-Cl blend films.



Figure S1. The thin layer chromatography (TLC) of IC-M-Cl, IC-P-Cl and IC-Cl-m in the mixture of petroleum ether and dichloromethane (v:v=1:1).



Figure S2. Thermal gravity analyse (TGA) of **TSeIC-M-Cl** and **TSeIC-P-Cl** with a heating rate of 10 °C/min under N₂ atmosphere.



Figure S3. The configuration and conformation isomers of **TSeIC-M-Cl** calculated by DFT theory. And the corresponding total energy were also provided. The red marked isomer represents the optimal geometry of **TSeIC-M-Cl**.



Figure S4. The configuration and conformation isomers of **TSeIC-P-Cl** calculated by DFT theory. And the corresponding total energy were also provided. The red marked isomer represents the optimal geometry of **TSeIC-P-Cl**.



Figure S5. HOMO and LUMO distributions and energy levels of **TSeIC-M-Cl** and **TSeIC-P-Cl** calculated by DFT B3LYP/6-31G(d,p), where the *p*ara-hexyl phenyl groups were simplified as phenyl groups to shorten the computational time.



Figure S6. The simulated half moecular dipole moments of **TSeIC-M-Cl** and **TSeIC-P-Cl** using a DFT method.

Compound		TSeIC-M-Cl	TSeIC-P-Cl	
Temperature		170 K	293 K	
Bond precision		C-C = 0.0183 Å	C-C = 0.0151 Å	
		Wavelength = 1.54184 Å	Wavelength = 1.54178 Å	
	a (Å)	10.3138 (2)	11.0576 (3)	
	b (Å)	21.5968 (4)	27.0950 (9)	
0.11	c (Å)	32.3938 (5)	27.5989 (5)	
Cell	α (°)	98.034 (2)	98.151 (2)	
	β (°)	93.346 (2)	96.438 (2)	
	γ (°)	96.126 (2)	97.703 (2)	
Volume		7084.24 (20)	8038.59 (40)	
Crystal system		Triclinic	Triclinic	
Space group		<i>P</i> -1	<i>P</i> -1	
Hall group		-P 1	-P 1	
Formula		$C_{94}H_{80}Cl_2N_4O_2S_2Se_2$	$C_{94}H_{80}Cl_2N_4O_2S_2Se_2$	
Molecular Weight		1590.56	1590.56	
Dx, g cm ⁻³		1.118	0.986	
Ζ		3	3	
μ (mm ⁻¹)		2.254	1.986	
F000		2466.0	2466.0	
h, k, lmax		12, 25, 38	13, 32, 32	
Data completeness		0.996	0.990	
Theta(max)		66.594	66.050	
R(reflections)		0.1305 (17403)	0.1481 (16755)	
wR2(reflections)		0.3009 (24945)	0.3888 (27747)	
S		1.008	1.360	
Npar		1516	1458	

Table S1 Check CIF report of XRD data of single crystal of isomers **TSeIC-M-Cl** (CCDC 1964587) and **TSeIC-P-Cl** (CCDC 1964586).



Figure S7. The comparison of the relevant intermolecular interaction of **TSeIC-M-Cl** and **TSeIC-P-Cl** in π - π stacking direction (a, b) and molecular slipped stacking direction (c, d).



Figure S8. The schematic diagrams of (a) d_p and P along the molecular long axis and (b) d_r and R along the molecular short axis.

Table S2. The detail slipped stacking information of TSeIC-M-Cl and TSeIC-P-Cl calculated from the single crystals.

	TSeIC-M-Cl	TSeIC-P-Cl
The longitudinal length (Å)	31.43	28.68
The longitudinal shift (d _p , Å)	27.09	22.16
The length of longitudinal overlap (Å)	4.34(13.81%) ^a	6.52(22.73%) ^a
The transverse length (Å)	7.21	10.83

The transverse shift (d_r, A)	3.70	4.20
The length of transverse overlap (Å)	3.51(48.68%) ^a	6.63(61.22%) ^a
the pitch angle (P)	83.07°	80.68°
the roll angle (R)	48.24°	49.23°

^{a)}The percentages in the bracket represent the ratios of overlap part in the entire length.



Figure S9. Absorption spectra of TSeIC-M-Cl and TSeIC-P-Cl in diluted CHCl₃ solution.



Figure S10. Cyclic voltammograms of **TSeIC-M-Cl** and **TSeIC-P-Cl** films on Pt electrode in CH₃CN solution with Bu_4NPF_6 (0.1 M) with a scan rate of 100 mV/s.



Figure S11. (a) The dark $J^{0.5}$ -V plots of electron-only devices based on neat TSeIC-M-Cl and TSeIC-P-Cl films; (b) The dark $J^{0.5}$ -V plots of electron-only devices based on PBT1-C:TSeIC-M-Cl and PBT1-C:TSeIC-P-Cl blend films. (c) The dark $J^{0.5}$ -V plots of hole-only devices based on PBT1-C:TSeIC-M-Cl and PBT1-C:TSeIC-P-Cl blend films.



Figure S12. GIWAXS patterns of pure donor PBT1-C film.



Figure S13. The comparison of 1D GIWAXS patterns of (a) **TSeIC-M-Cl** and (b) **TSeIC-P-Cl** in neat films and the simulated data between structure factor F and q (hkl) based on the information of single crystals. The slight difference was caused by the temperature.

4. Copies of ¹H NMR, ¹³C NMR, and MALDI-TOF MS Spectra.





$\begin{pmatrix} 9.023 \\ -8.641 \\ -8.641 \\ 7.197 \\ 7.797 \\ 7.692 \\ 7.692 \\ 7.199 \\ 7.179 \\ 7.124 \\ 7.124 \end{pmatrix}$



¹³C NMR spectrum of **TSeIC-M-Cl**

9.017 8.605 8.605 8.584 8.564 7.806 7.601 7.601 7.666 7.666 7.666 7.661 7.661 7.661 7.193 7.138

2.5592 2.5533 2.5533 2.5533 2.5533 2.5533 1.597 1.597 1.596 1.1596 1.1288 1.1289 1.128







