

Incorporation of selenophene into thienoazacoronene-based non-fullerene acceptor: Impact on photophysical and photovoltaic properties

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Experimental

Instruments. ^1H NMR and ^{13}C NMR spectra were measured with a JEOL JNM-EX400 NMR spectrometer. ^1H , ^{13}C , HSQC, and HMBC NMR spectra of **Se-TACIC** were recorded with a Bruker 18.8 T AVANCE-III NMR spectrometer (^1H and ^{13}C Larmor frequencies were 800 MHz and 201MHz, respectively) equipped with a 5-mm CPTCI triple resonance inverse detection cryoprobe. High-resolution mass spectra were measured on a Thermo Fisher Scientific EXACTIVE (APCI) and LTQ orbitrap XL (MALDI). Attenuated total reflectance (ATR) FT-IR spectra were recorded on a ThermoFisher Scientific Nicolet 6700 FT-IR. Thermogravimetric analysis (TGA) measurements were conducted with a SHIMADZU TG-50 under flowing nitrogen at a scan rate of $10\text{ }^\circ\text{C min}^{-1}$. Differential scanning calorimetry (DSC) analysis was made on a SHIMADZU DSC-60 at a scan rate of $10\text{ }^\circ\text{C min}^{-1}$. UV–vis–near infrared (NIR) absorption spectra were obtained on a SHIMADZU UV-3600i Plus spectrometer. Steady-state fluorescence spectra were recorded on a HORIBA NanoLog spectrofluorometer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed using an ALS 630A electrochemical analyzer in dichloromethane containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) as a supporting electrolyte. Time-correlated single photon counting (TCSPC) measurements using a HORIBA NanoLOG-TCSPC were conducted for fluorescence lifetime measurements on the nanosecond time-scale. Absolute photoluminescence quantum efficiencies were determined using a HAMAMATSU PHOTONICS Quantaurus-QY Plus Absolute PL quantum yield spectrometer C13534-01. The time resolution was ca. 200 ps. Photoemission yield spectroscopy in air (PYSA) measurements were performed using an AC-3 (Riken Keiki).

Photocurrent-voltage characteristics were measured by Keithley 2400 SourceMeter under a nitrogen atmosphere and simulated solar light (100 mW cm^{-2} , AM1.5) with OTENTO-SUN III solar simulator (Bunkoukeiki). Photocurrent action spectra were recorded with CEP-2000RR (Bunkoukeiki). Current–voltage characteristics of the electron- and hole-only devices for space charge-limited current (SCLC) measurements were conducted using Keithley 2400 SourceMeter under a nitrogen atmosphere. Dynamic light scattering (DLS) measurements were performed using a Horiba LB550 particle size analyzer. Atomic force microscopy (AFM) analyses were carried out with an Asylum Technology MFP-3D-SA in the AC mode. Film thicknesses were measured using DektakXT stylus profiler (Bruker).

Theoretical calculations. Geometry optimization and electronic structure calculations were performed using density functional theory (DFT) at the RB3LYP/6-31G(d) level. Calculations were carried out using the Gaussian 16 program.^{S1} All structures were fully optimized without any symmetry restriction.

SCLC measurements. The hole and electron mobilities were measured using the SCLC method by using devices with the configurations of ITO/PEDOT:PSS/PBDB-T:NFA/MoO₃/Au for hole and ITO/ZnO/PBDB-T:NFA/Al for electron by taking current–voltage curves and fitting the results to a space charge limited form, where the SCLC is described by:

$$J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$$

where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the polymer, μ is the charge mobility, V is the voltage drop across the device, and L is the thickness of the blend film. The dielectric constant ε_r is assumed to be 3, which is a typical value for organic semiconductors.

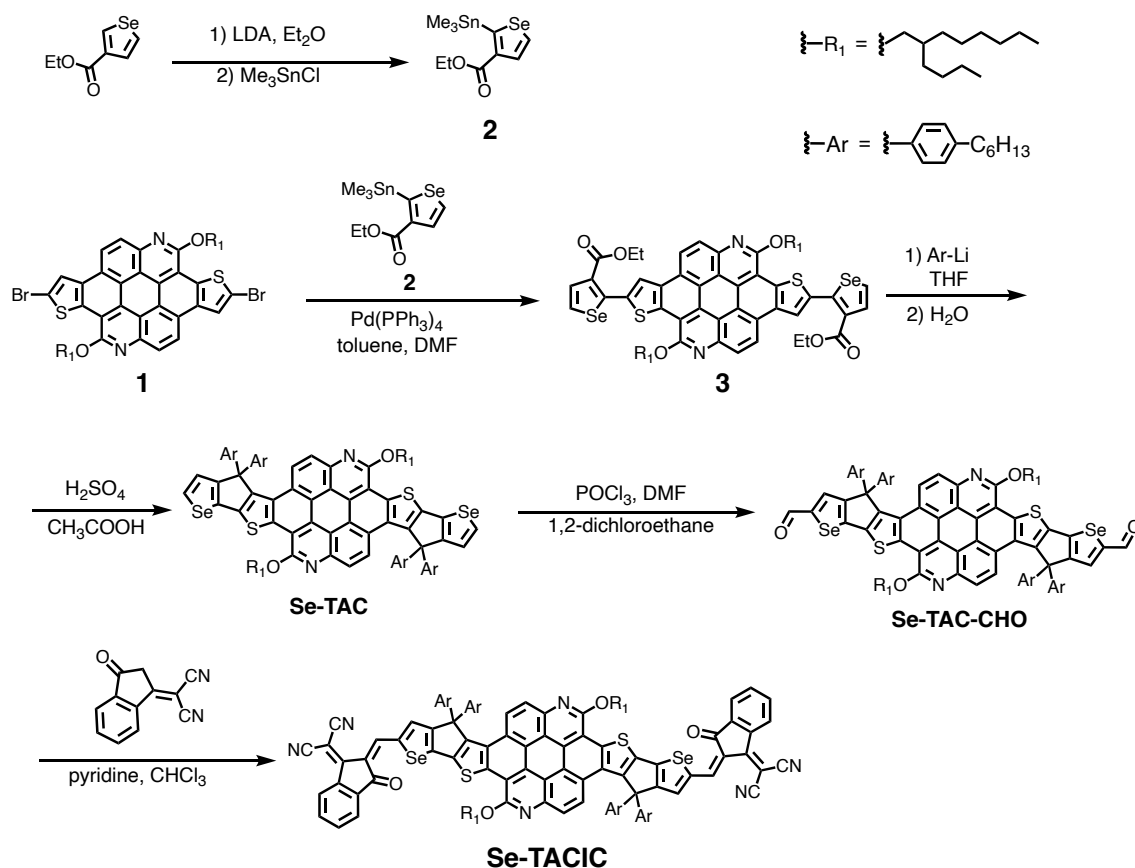
Grazing incidence small-angle X-ray scattering (GIWAXS) measurements. Samples were prepared by spin-coating the NFA or PBDB-T:NFA solution on the ITO/ZnO substrate as conducted in the OPV device fabrications. GIWAXS measurements were conducted at the SPring-8 on beamline BL19B2. The sample was irradiated at a fixed incident angle on the order of 0.12 ° through a Huber diffractometer with X-ray energy of 12.398 keV (X-ray wavelength $\lambda = 0.10002$ nm), and the GIWAXS patterns were recorded with a 2D image detector (Pilatus 300 K) with the sample-to-detector distances of 173.8 mm.

OPV fabrication. OPV devices were prepared on patterned indium tin oxide (ITO) substrates which were cleaned by ultra-sonication in deionized water, CHCl₃, acetone, and tetramethylammonium hydroxide aqueous solution for 15 min each, and then deionized water for 25 min, followed by 2-propanol and ethanol for 15 min each. They were subsequently dried under nitrogen flow, and treated in a UV–ozone cleaner for 25 min. A solution of Zn(OAc)₂·2H₂O (55 mg), 2-methoxyethanol (1 mL), ethanolamine (15.6 μ L) was stirred at room temperature, and was spin-coated on substrates at 3000 rpm for 20 s. The ZnO layer was dried at 200 °C for 30 min, and then transferred into a glove box filled with dried N₂ gas to coat the active layer. A blend solution of PBDB-T with **E-TACIC** ([PBDB-T] = 6 mg mL^{−1} and [E-TACIC] = 5.4 mg mL^{−1}, i.e., [S-TACIC] = 2.7 μ mol mL^{−1} and [Se-TACIC] = 2.5 μ mol mL^{−1}) in chloroform with 1-chloronaphthalene (0.4 vol.%) was prepared and stirred on a hotplate at 50 °C for 3 h. The active layer was spin-coated at 2250 rpm for 20 s on the top of the ZnO layer, and the samples were annealed at 100 °C for 5 min. The thicknesses of the photoactive layers were measured to be ca. 100 nm by a stylus profiler. All samples were finally transferred to an evaporation chamber for MoO₃ deposition (~10 nm) at a rate of 0.1–0.3 Å s^{−1} and Ag deposition (~100 nm) at a rate of 1–2 Å s^{−1} before extracting their J – V characteristics (under AM 1.5 conditions). OPV devices had

the architecture of ITO/ZnO/**PBDB-T:E-TACIC**/MoO₃/Ag.

Synthetic Procedures

Materials. Ethyl selenophene-3-carboxylate,^{S2} compound **1**,^{S3} and 1,1-dicyanomethylene-3-indanone (IC)^{S4} were synthesized according to the literature procedures. Preparations of **S-TACIC** were reported in the previous manuscript.^{S3} PBDB-T was purchased from 1-Material. All other chemicals were purchased from commercial supplier and used without further purification.



Scheme S1. Synthesis routes of **Se-TACIC**.

Compound 2. To a solution of diisopropylamine (0.81 mL, 5.8 mmol, 1.1 equiv.) in dry ether (25 mL) at -78°C , *n*-BuLi (1.6 M in hexane, 3.61 mL, 5.8 mmol, 1.1 equiv.) was added dropwise under nitrogen to form lithium diisopropylamide (LDA). A solution of ethyl selenophene-3-carboxylate (1.07 g, 5.26 mmol, 1.0 equiv.) in dry ether (5 mL) was then added dropwise to the formed LDA slowly and the resulting solution was kept stirring at -78°C for 2 h. To the reaction mixture was added trimethyltin chloride (2.30 g, 11.6 mmol, 2.2 equiv.) in dry THF (3 mL) in one portion via syringe injection at -78°C . Then the cooling bath was removed, and the mixture was gradually warmed to room temperature. After stirring overnight at room temperature, the reaction

solution was quenched with H₂O. The solvent was removed under reduced pressure, and the crude product was purified by neutral silica gel column chromatography with hexane/CHCl₃ = 1/1 as eluent. Compound **2** was obtained as pale-yellow oil (1.87 g, 97.1%)

¹H-NMR (400 MHz, CDCl₃, ppm) δ 8.23 (d, J = 5.3 Hz, 1H), 7.99 (d, J = 5.3 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H), 0.38 (s, 9H). **¹³C-NMR** (100 MHz, CDCl₃, ppm) δ 165.0, 161.4, 142.4, 135.7, 132.3, 61.1, 14.8, -6.4. **HRMS** (p APCI) calcd for [C₁₀H₁₇O₂SeSn]⁺ ([M+H]⁺): 368.9410; found: 368.9415. **IR** (ATR, cm⁻¹): $\nu_{\max}$ 2978, 2913, 1694, 1498, 1455, 1417, 1395, 1368, 1305, 1248, 1216, 1137, 1112, 1026, 969, 887, 858, 766, 706, 618, 528, 511.

Compound 3. A solution of compound **1** (480 mg, 0.510 mmol, 1.0 equiv.) and **2** (1.86 g, 5.10 mmol, 10 equiv.) in toluene (20 mL) and DMF (5 mL) was deoxygenated with N₂ for 30 min. After Pd(PPh₃)₄ (58.9 mg, 0.0510 mmol, 0.1 equiv.) was added, the reaction mixture was stirred overnight at 110°C. The reaction was quenched with KF aq., extracted with CHCl₃, and the organic phase was dried over Na₂SO₄. After filtration, the solvent was removed under reduced pressure and resulting residue was purified by column chromatography with hexane/CHCl₃ = 1/4 to 0/1 as eluent to give a solid, which was further purified by reprecipitation with CHCl₃/methanol. Compound **3** was obtained as an orange solid (522.8 mg, 85.1%).

¹H-NMR (400 MHz, CDCl₃, ppm) δ 8.26 (s, 2H), 8.10 (d, J = 8.7 Hz, 2H), 7.92 (brs, 4H), 7.89 (brs, 2H), 4.77 (d, J = 4.1 Hz, 4H), 4.47 (q, J = 7.2 Hz, 4H), 2.25 (q, J = 5.8 Hz, 2H), 2.02–1.95 (m, 2H), 1.91 (d, J = 5.5 Hz, 2H), 1.78–1.66 (m, 8H), 1.53 (t, J = 7.3 Hz, 8H), 1.45–1.34 (m, 8H), 1.25 (s, 6H), 1.09 (t, J = 7.1 Hz, 8H), 0.93–0.88 (m, 8H). **¹³C-NMR** (201 MHz, CDCl₃, ppm) δ 165.0, 162.1, 157.0, 148.1, 142.9, 140.7, 135.9, 131.0, 128.7, 127.0, 124.8, 123.8, 123.0, 118.6, 118.0, 114.0, 110.0, 70.7, 61.4, 38.4, 32.4, 32.0, 31.8, 30.4, 30.1, 29.7, 27.5, 23.8, 23.2, 14.9, 14.8, 14.6. **HRMS** (p APCI) calcd for [C₆₄H₇₁O₆S₂Se₂]⁺ ([M+H]⁺): 1187.3078; found: 1187.3077.

Se-TAC. To a solution of 1-bromo-4-hexylbenzene (0.46 mL, 2.24 mmol, 19 equiv.) in THF (9 mL) at -78 °C, *n*-BuLi (1.60 M, 1.40 mL, 2.24 mmol, 19 equiv.) was added under N₂ atmosphere, before stirred at -78°C for 1 h. A solution of compound **3** (138.3 mg, 0.12 mmol, 1.0 equiv.) in THF (18 mL) was added slowly. After the addition, the mixture was stirred at -78 °C for 1 h and then at room temperature for 3 h. The reaction was quenched with NH₄Cl aq., extracted with CHCl₃, and combined organic phase was dried over Na₂SO₄. After filtration, the solvent was removed under reduced pressure. To a solution of crude product in acetic acid (56 mL), H₂SO₄ (0.56 mL) was added, before stirred at 80 °C for 30 min. The reaction was quenched with Na₂CO₃ aq., extracted with CHCl₃, and combined organic phase was dried over Na₂SO₄. After filtration, the solvent was removed under reduced pressure, and the resulting residue was purified by column chromatography with hexane/CHCl₃ = 4/1 to 2/1 as eluent. Se-TAC was obtained a red solid and

used in the next step without further purification.

Se-TAC-CHO. POCl₃ (0.23 mL, 2.47 mmol, 100 equiv.) was added to solution of DMF (0.19 mL) at 0 °C and stirred at 0 °C for 1 h under N₂ atmosphere. To a solution of Se-TAC (42.2 mg, 0.025 mmol, 1.0 equiv.) in 1,2-dichloroethane (5.74 mL), the Vilsmeier reagent (3.71 mL) was added dropwise at 0°C. The mixture was stirred at room temperature for 2 h and then at 80 °C for 2 h. After cooling down to room temperature, the reaction was quenched with NaOAc aq., extracted with CHCl₃, and the organic phase was dried over Na₂SO₄. After filtration, the solvent was removed under reduced pressure, and resulting residue was purified by column chromatography with hexane/CHCl₃ = 1/1 to 0/1 as eluent to give a solid. The crude product of Se-TAC-CHO was obtained as an orange solid and used in the next step without further purification.

Se-TACIC. A solution of Se-TAC-CHO (47.5 mg, 0.027 mmol, 1.0 eq.) and IC (63.9 mg, 0.27 mmol, 10 eq.) in CHCl₃ (5.5 mL) was deoxygenated with N₂ for 30 min before 1 drop of pyridine was added. After overnight refluxing, the solvent was removed under reduced pressure, and resulting residue was purified by column chromatography with hexane/CHCl₃ = 1/2 as eluent, reprecipitated with CHCl₃/EtOH. Se-TACIC was obtained as a dark blue solid (56.2 mg, 20.7 %, 3 steps).

¹H-NMR (400 MHz, CDCl₃, ppm) δ 8.99 (d, J = 9.1 Hz, 2H), 8.99 (s, 2H), 8.59 (brs, 2H), 8.41 (d, J = 9.1 Hz, 2H), 8.00 (s, 2H), 7.80 (brs, 2H), 7.63 (brs, 2H), 7.58 (d, J = 8.4 Hz, 8H), 7.09 (d, J = 8.4 Hz, 8H), 5.06 (d, J = 5.4 Hz, 4H), 2.54–2.50 (m, 8H), 2.38–2.34 (m, 2H), 1.93–1.90 (m, 4H), 1.80–1.73 (m, 4H), 1.37–1.35 (m, 6H), 1.26–1.21 (m, 42H), 1.02 (t, J = 7.2 Hz, 6H), 0.88 (t, J = 7.0 Hz, 10H), 0.80 (t, J = 6.8 Hz 18H). **¹³C-NMR** (201 MHz, CDCl₃, ppm) δ 188.1, 165.9, 159.5, 159.1, 157.4, 157.06, 144.2, 142.5, 141.5, 141.0, 140.1, 140.1, 138.6, 138.5, 135.6, 133.8, 133.2, 133.0, 131.2, 128.4, 128.0, 127.7, 126.7, 126.1, 124.1, 124.1, 122.3, 120.0, 119.3, 114.5, 114.0, 113.9, 111.4, 69.9, 67.0, 64.3, 36.9, 34.5, 31.0 30.8, 30.6, 30.5, 30.1, 28.8, 28.2, 28.0, 26.0, 22.2, 21.7, 21.5, 13.3, 13.2, 13.0. **HRMS** (p APCI) calcd for [C₁₃₄H₁₃₅N₆O₄S₂Se₂]⁺ ([M+H]⁺): 2115.8311; found: 2115.8329. **IR** (ATR, cm⁻¹) : $\nu_{\max}$ 2922, 2853, 2217, 1695, 1588, 1557, 1538, 1479, 1398, 1308, 1289, 1247, 1223, 1177, 1155, 1129, 1092, 1020, 981, 912, 829, 770, 720, 689, 648, 622, 602 514. T_d (decomposition temperature) = 369 °C. No T_m (melting point) was observed < 369 °C.

Table S1. Optical parameters of **Se-TACIC** and **S-TACIC** in chloroform and film states.

Sample	$\lambda_{\text{abs,sol}}$ / nm	ε_{max} / $10^5 \text{ M}^{-1} \text{ cm}^{-1}$	$\lambda_{\text{PL, sol}}$ / nm	$E_{\text{g,sol}}^{\text{opt}}$ / eV	$\lambda_{\text{abs,film}}$ / nm	$\lambda_{\text{PL,film}}$ / nm	$E_{\text{g,film}}^{\text{opt}}$ / eV	$\tau_{\text{S1,sol}}$ / ps	$\tau_{\text{S1,film}}$ / ps
Se-TACIC	703	3.2	744	1.71	735	787	1.62	499	<200
S-TACIC	686	3.2	718	1.75	716	778	1.66	220	1590

Table S2. Singlet exciton lifetime (τ_{S1}),^a photoluminescence quantum yield (Φ_{PL}),^b radiative rate constant (k_{r}),^c and nonradiative rate constant (k_{nr})^c of **Se-TACIC** and **S-TACIC** in chloroform and film states.

Sample	τ_{S1} / ps	Φ_{PL}	k_{r} / s^{-1}	k_{nr} / s^{-1}
Se-TACIC sol.	499	0.172	3.4×10^8	1.7×10^9
Se-TACIC film	—	0.036	—	—
S-TACIC sol.	220	0.082	3.7×10^8	4.2×10^9
S-TACIC film	1590	0.082	5.2×10^7	5.8×10^8

^a Estimated by the fluorescence decay measurements. ^b Estimated by the integrated sphere method.^c k_{r} and k_{nr} are calculated from the experimental data of Φ_{PL} and τ_{S1} , according to the following equations; $\Phi_{\text{PL}} = k_{\text{r}} \times (k_{\text{r}} + k_{\text{nr}})^{-1}$ and $\tau_{\text{S1}} = (k_{\text{r}} + k_{\text{nr}})^{-1}$.**Table S3.** Photovoltaic parameters of the PBDB-T:Se-TACIC-based devices under various fabrication conditions.

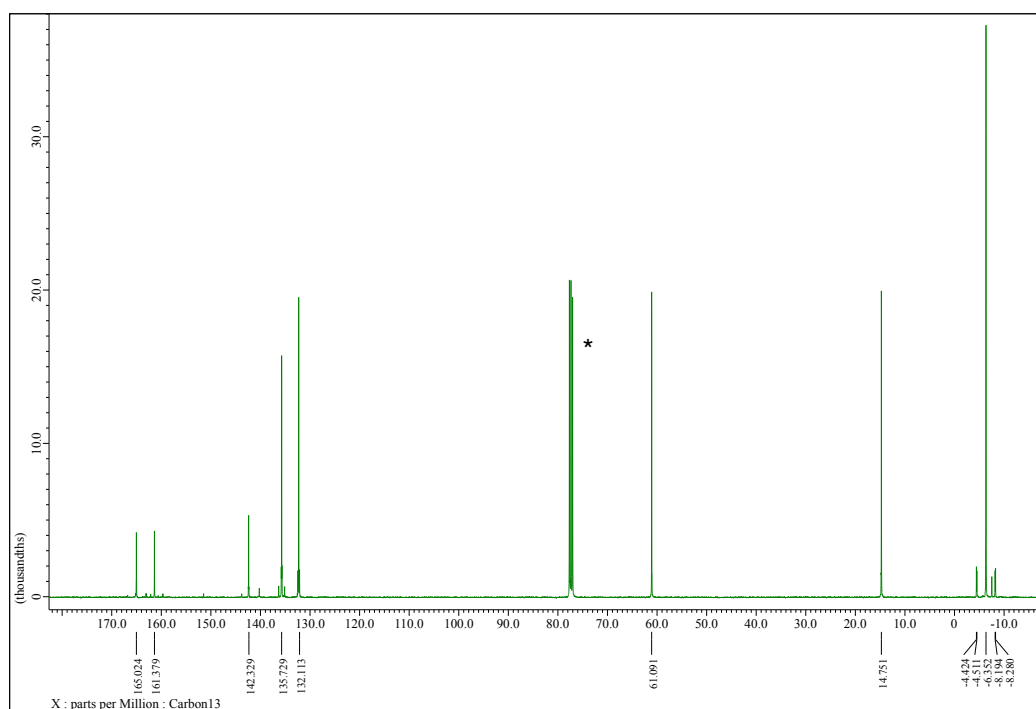
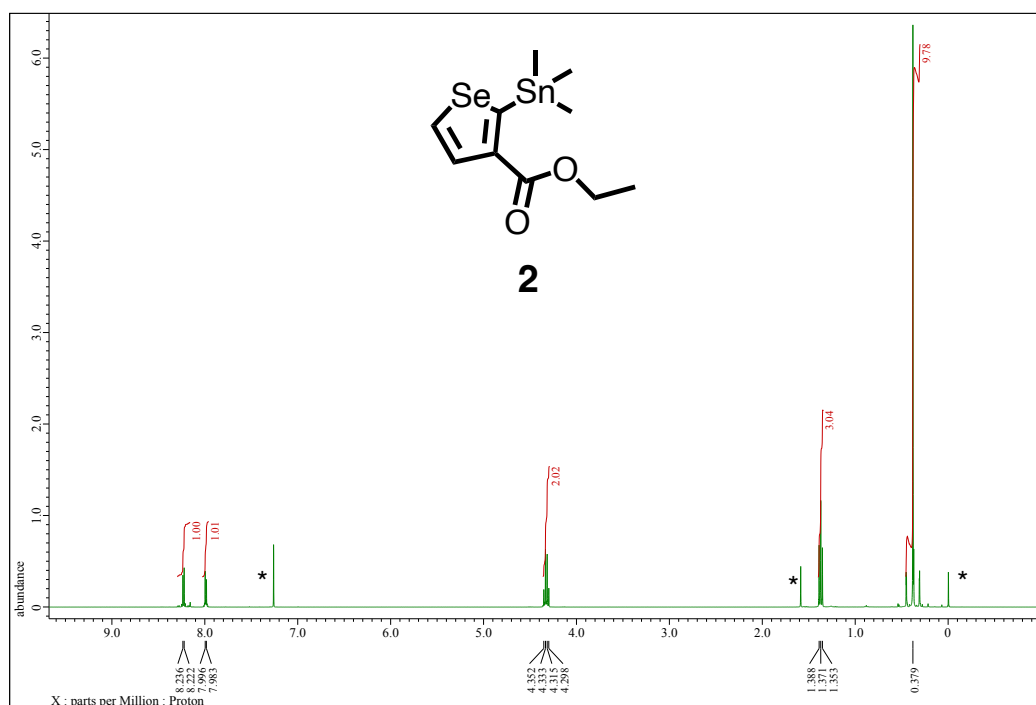
PBDB-T:Se-TACIC weight ratio	annealing	additive concentration / vol%	J_{SC} / mA cm^{-2}	V_{OC} / V	FF / %	PCE / %
1:1	100 °C, 5 min	0.4	11.7	0.845	44.0	4.35
0.9:1	100 °C, 5 min	0.4	9.43	0.823	42.7	3.31
1:0.9	No annealing	0.4	11.4	0.890	48.7	4.93
1:0.9	100 °C, 5 min	0.4	11.8	0.908	52.2	5.58
1:0.9	100 °C, 5 min	1.0	9.53	0.902	38.5	3.32

Table S4. Charge mobilities (μ_e and μ_h) and charge mobility balances (μ_e/μ_h) of the PBDB-T:NFA blend films.

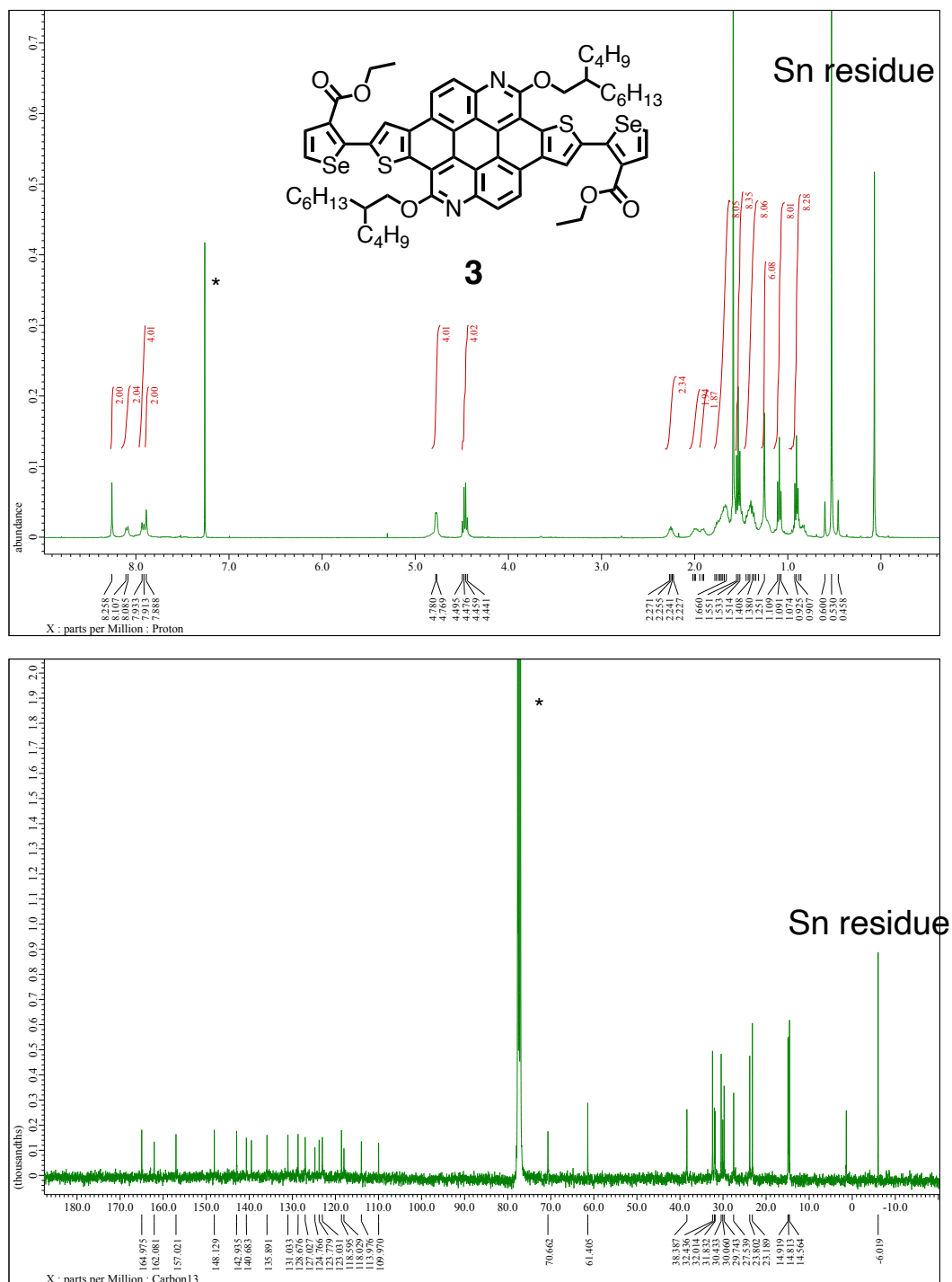
NFA	$\mu_e^a / \times 10^{-4} \text{ cm}^{-2} \text{ V}^{-1} \text{ s}^{-1}$	$\mu_h^b / \times 10^{-4} \text{ cm}^{-2} \text{ V}^{-1} \text{ s}^{-1}$	μ_e/μ_h
Se-TACIC	1.1	3.4	0.32
S-TACIC	1.2	2.6	0.46

^a Measured by SCLC with the device configuration of ITO/PEDOT:PSS/**PBDB-T:NFA**/MoO₃/Au. ^b Device configuration; ITO/ZnO/**PBDB-T:NFA**/Al.

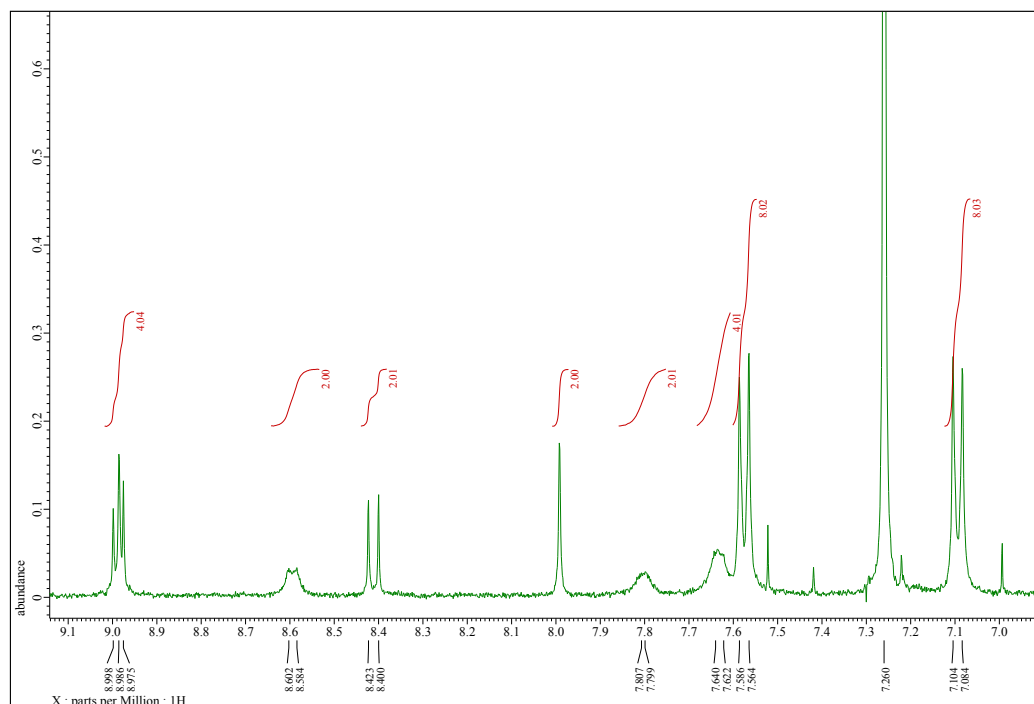
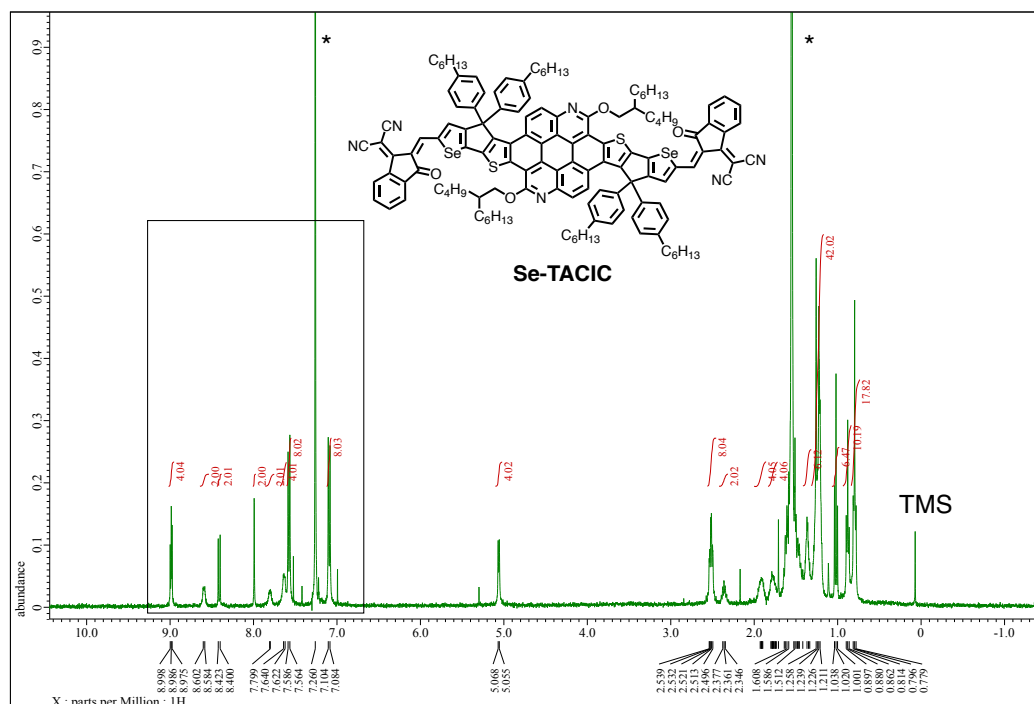
(a)



(b)



(c)



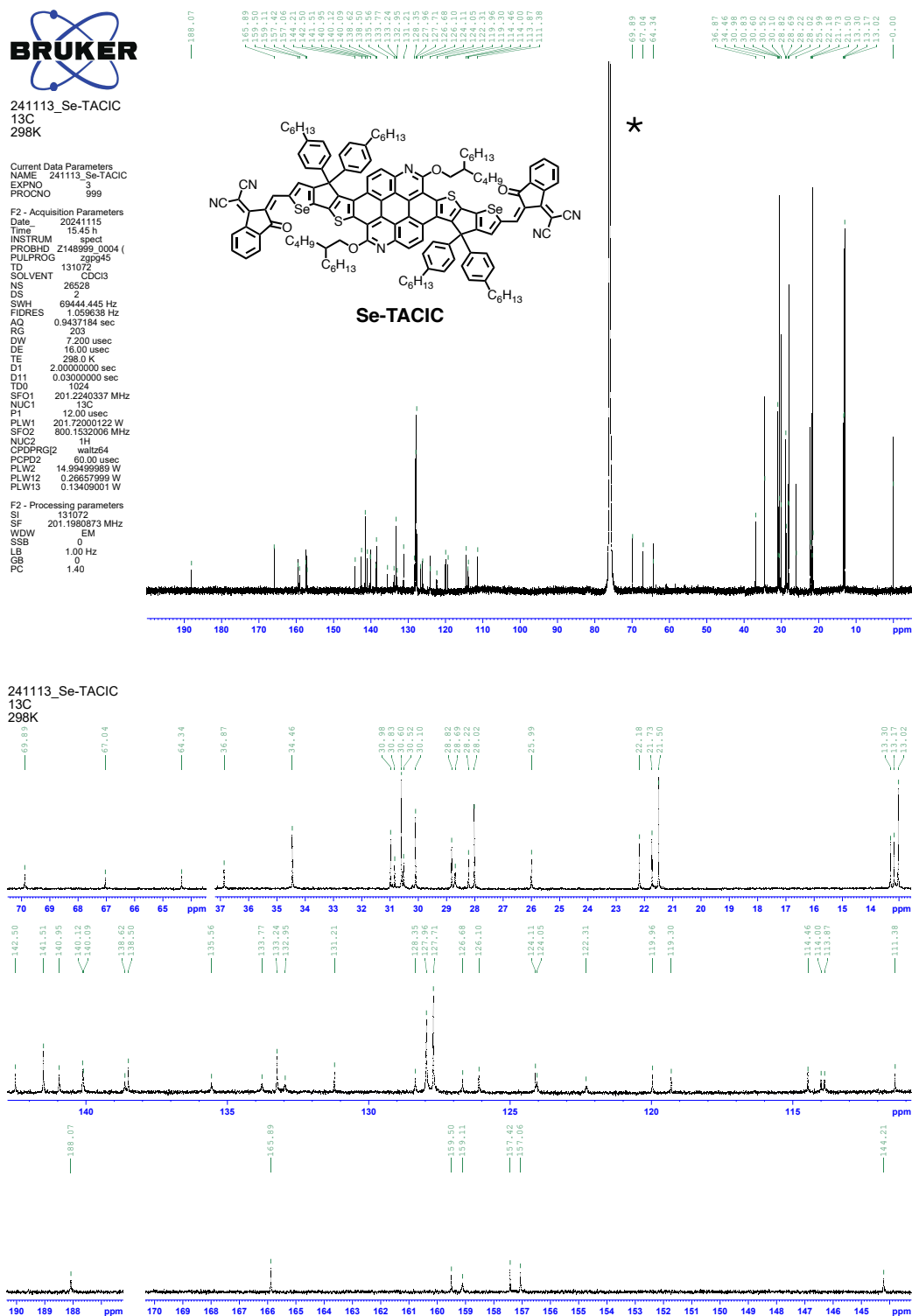


Fig. S1. ¹H (upper) and ¹³C (lower) NMR spectra of (a) **2**, (b) **3**, and (c) **Se-TACIC** in CDCl₃. Peaks marked with * arise from residual solvents.

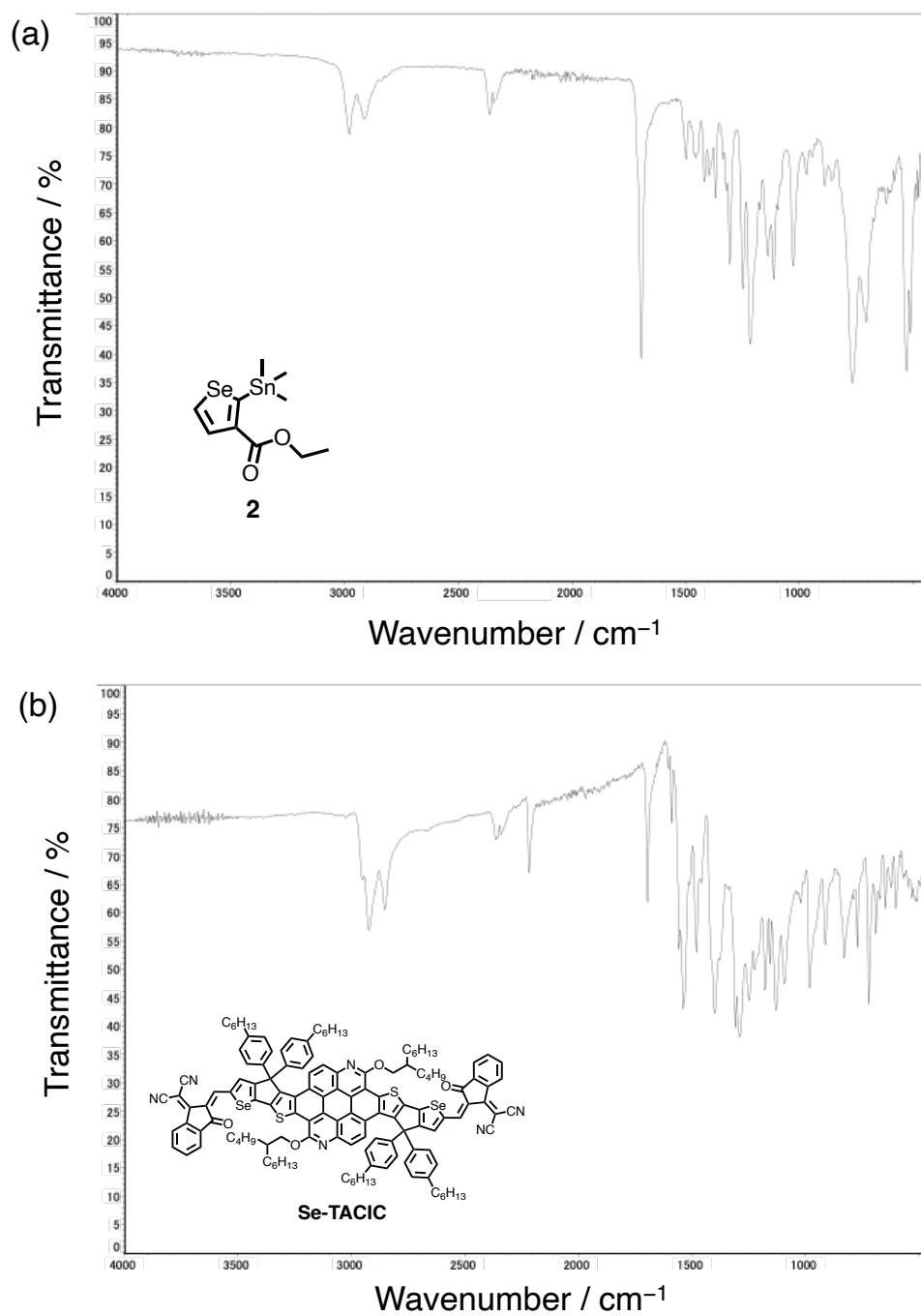


Fig. S2. ATR FT-IR spectra of (a) **2** and (b) **Se-TACIC**.

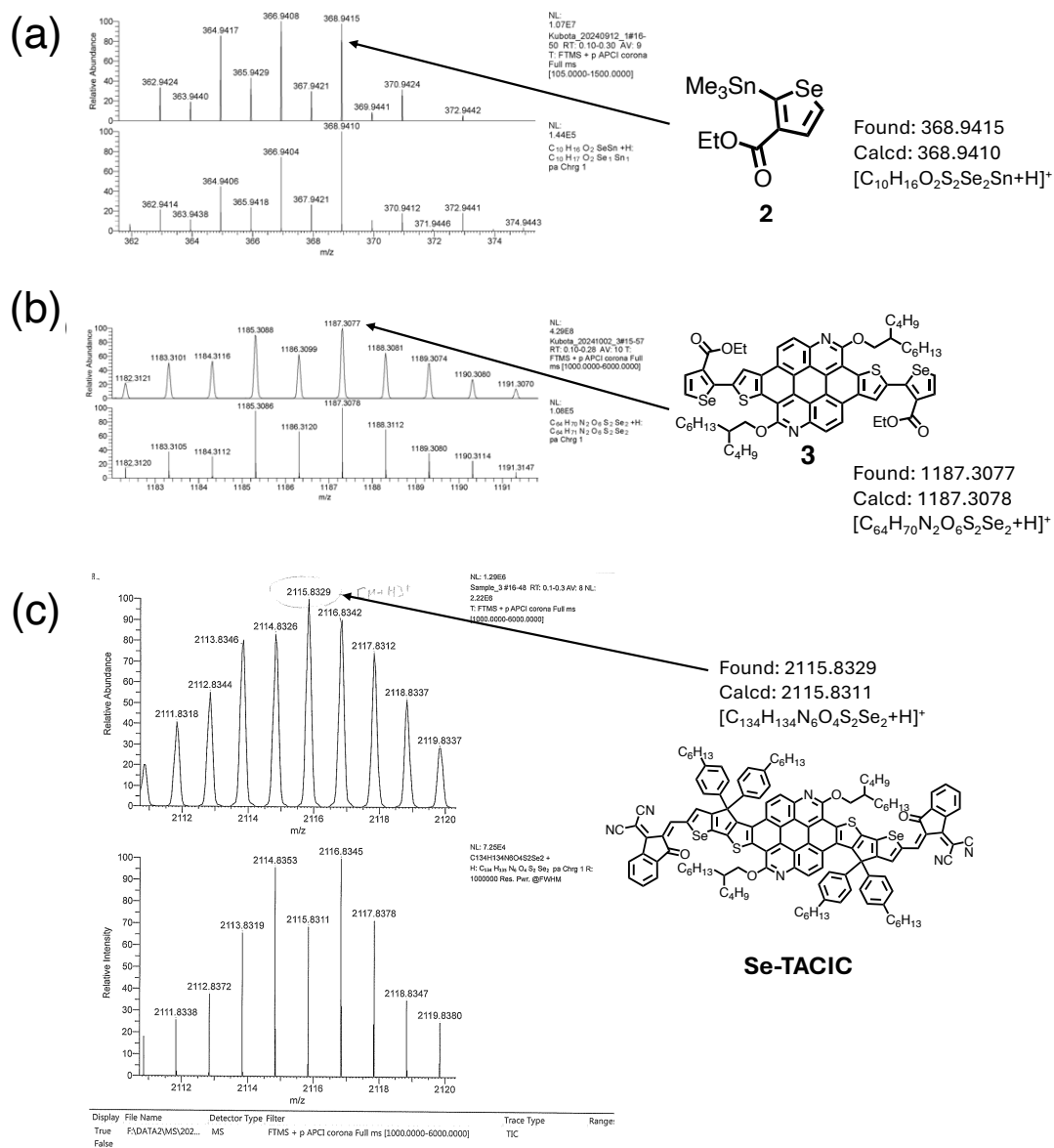


Fig. S3 High-resolution mass spectra of (a) **2**, (b) **3**, and (c) **Se-TACIC**.

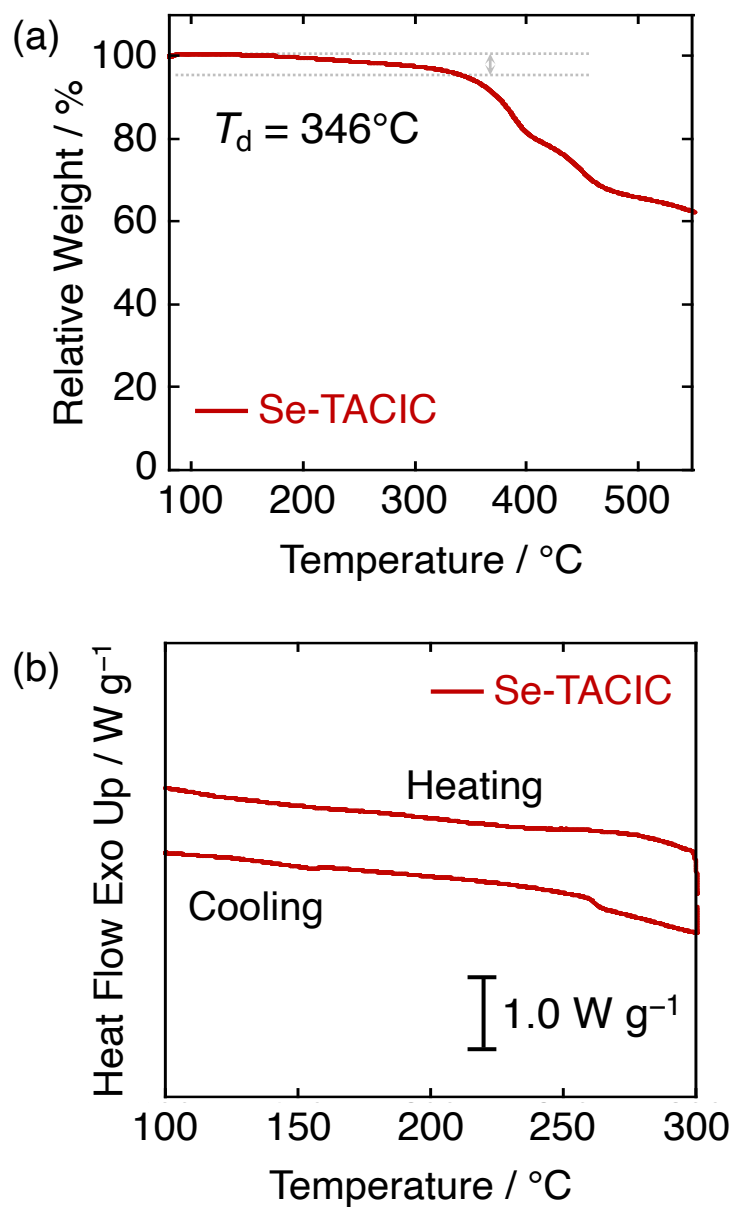


Fig. S4. (a) TGA curve of **Se-TACIC**. Decomposition temperature (T_d , 5% weight loss) is 346 °C. (b) DSC curve of **Se-TACIC**. The analyses were performed under flowing nitrogen at a scan rate of 10 °C min⁻¹.

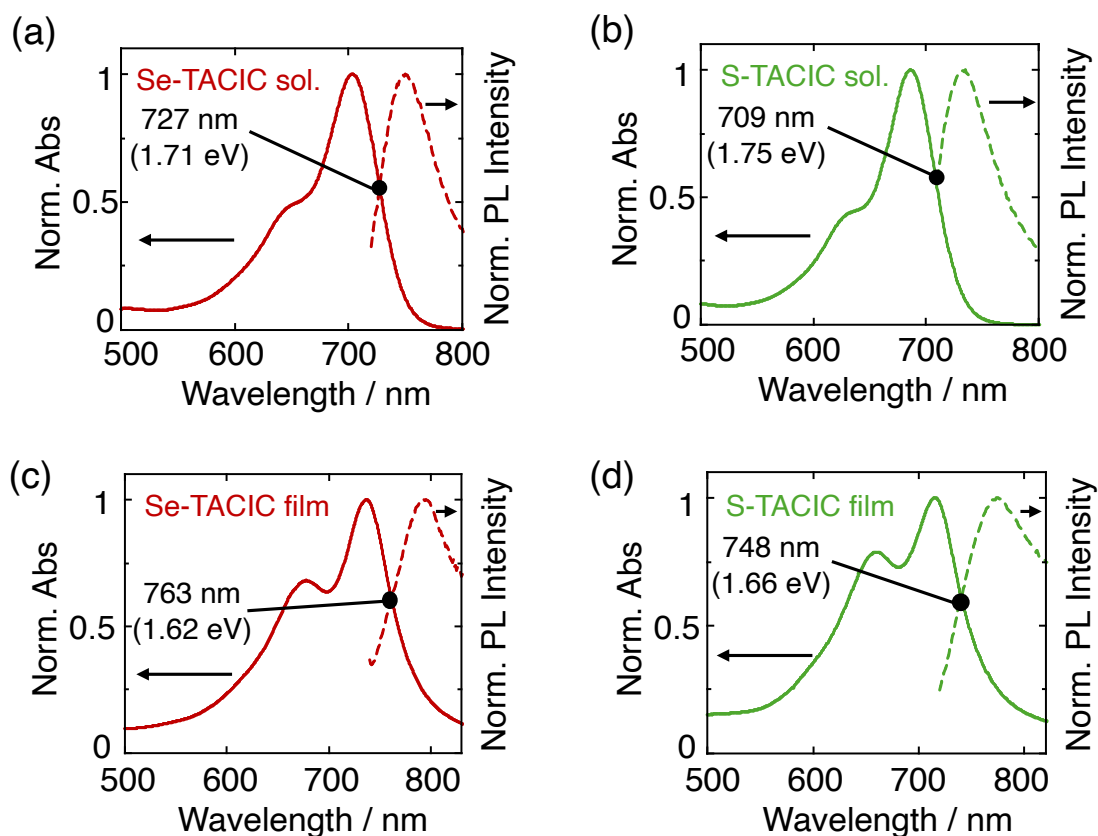


Fig. S5. (a,b) Normalized UV-vis-NIR absorption and fluorescence spectra of (a) **Se-TACIC** and (b) **S-TACIC** in chloroform (excited at 685 nm). (c,d) Normalized UV-vis-NIR absorption and fluorescence spectra of (c) **Se-TACIC** and (d) **S-TACIC** films (excited at 710 nm). The wavelengths and energies at the intersection points are shown in the figures.

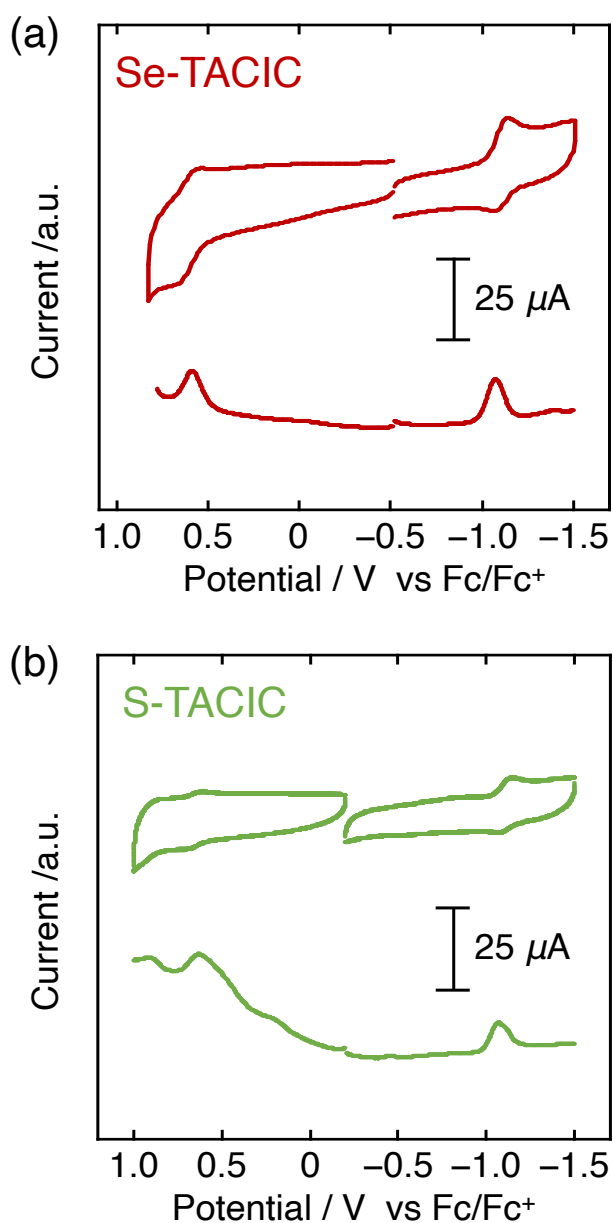


Fig. S6. Cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) of (a) **Se-TACIC** and (b) **S-TACIC** in dichloromethane containing 0.1 M Bu₄NPF₆. Sweep rate: 0.1 V s⁻¹; reference electrode, Ag/AgNO₃ (0.01 M AgNO₃, 0.09 M Bu₄NPF₆ in acetonitrile).

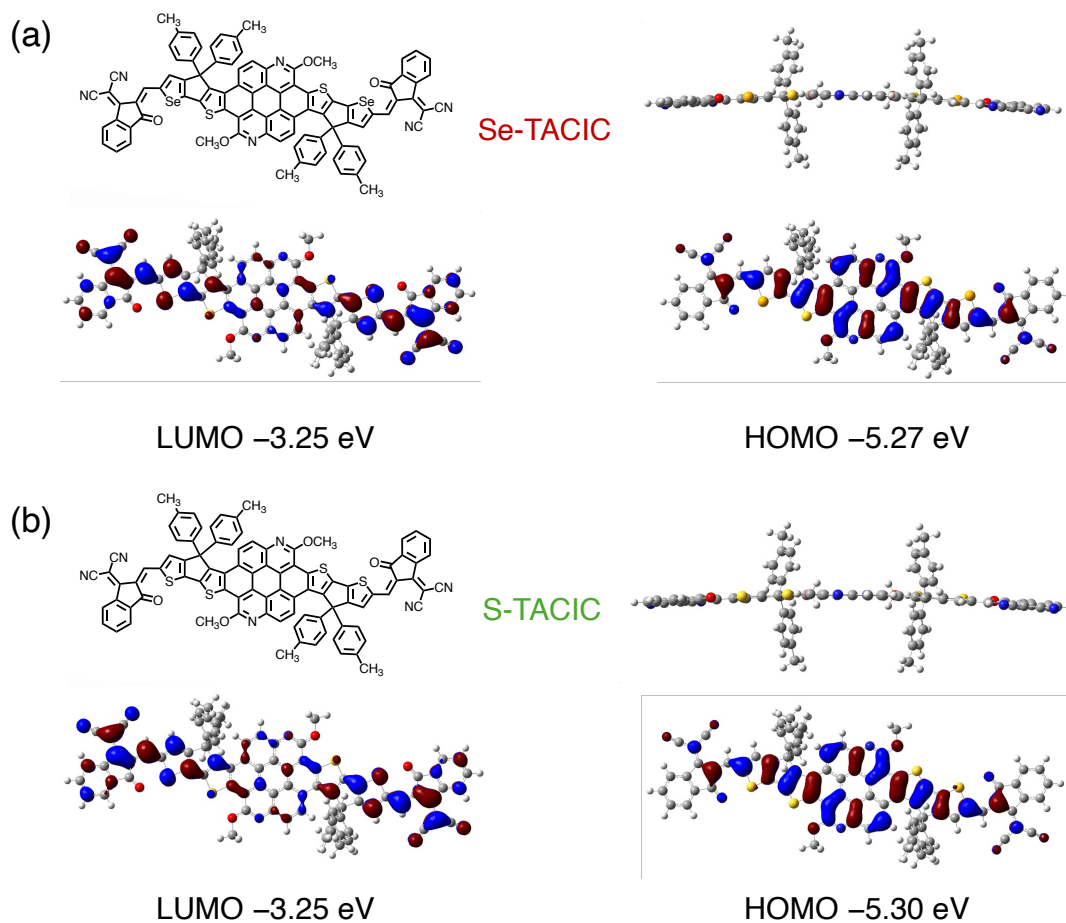


Fig. S7. Chemical structures, optimized structures (side view), and contour plots of frontier molecular orbitals simulated by the DFT calculations using the B3LYP/6-31G(d) model for simplified (a) **Se-TACIC**, and (b) **S-TACIC**. Alkyl chains were simplified to methyl groups. The calculated energy levels are shown below the corresponding depictions.

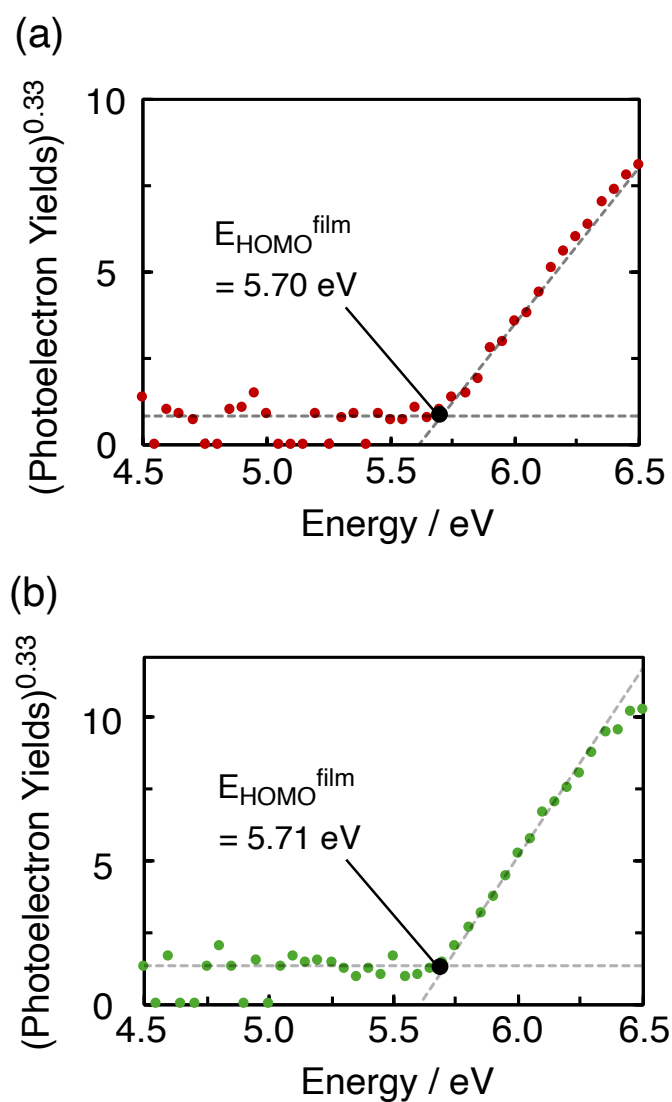


Fig. S8. Photoemission yield spectroscopy in air (PYSA) of (a) **Se-TACIC** and (b) **S-TACIC**.

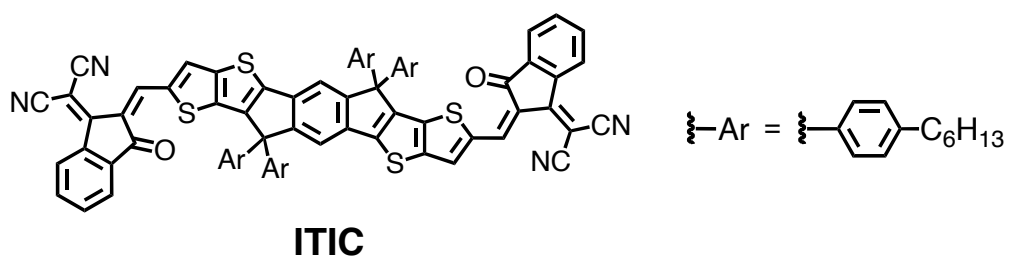


Fig. S9. Chemical structure of **ITIC**.

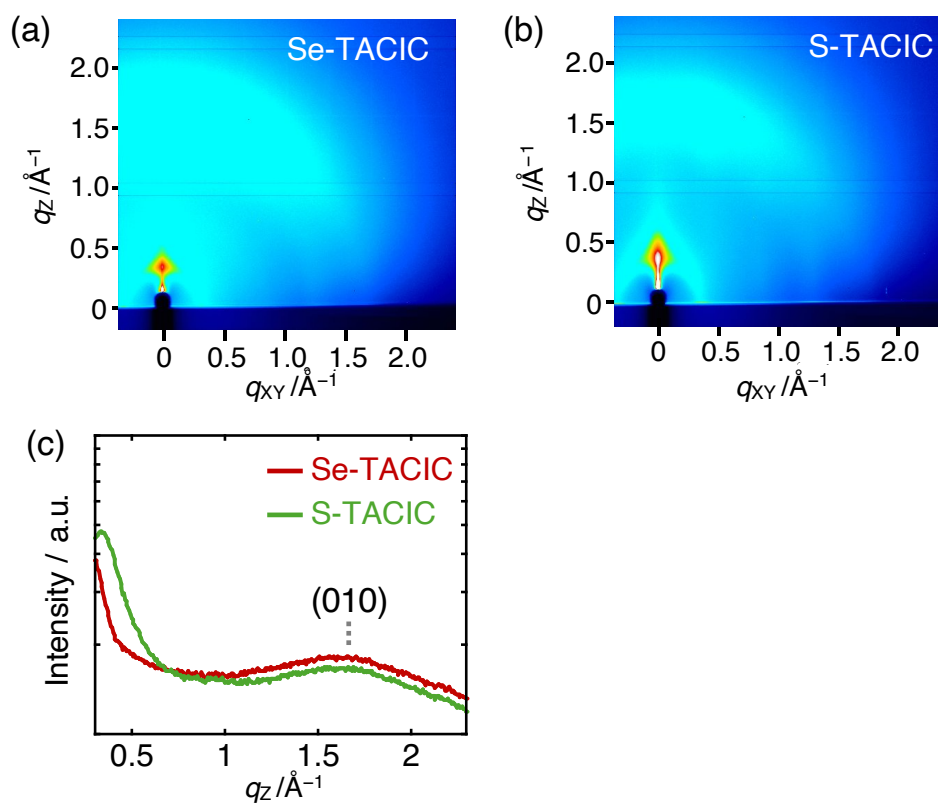


Fig. S10. Two dimensional GIWAXS plots of (a) **Se-TACIC** and (b) **S-TACIC** neat films on glass substrate. (c) Out-of-plane GIWAXS profiles for **Se-TACIC** and **S-TACIC** neat films.

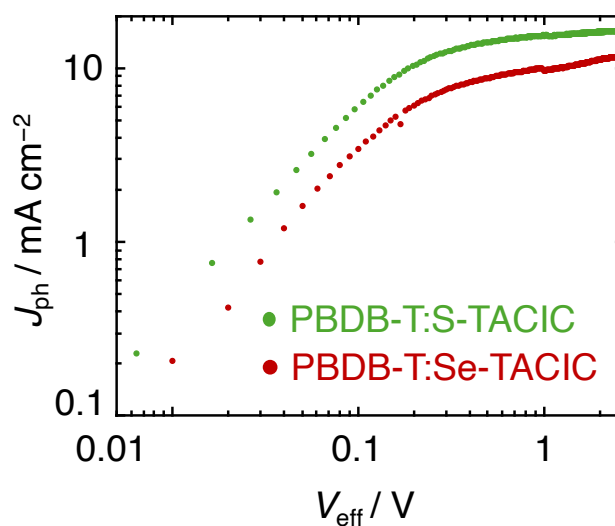


Fig. S11. Photocurrent density vs. effective voltage ($J_{\text{ph}}-V_{\text{eff}}$) characteristics for devices with **PBDB-T:Se-TACIC** and **PBDB-T:S-TACIC**. J_{ph} is derived from $J_{\text{ph}} = J_{\text{L}} - J_{\text{D}}$, where J_{L} and J_{D} are the current densities under illumination and in the dark, respectively. V_{eff} is expressed as $V_{\text{eff}} = V_0 - V_{\text{a}}$, where V_0 is the voltage when J_{ph} is zero, and V_{a} is the applied voltage. For both devices, J_{ph} initially showed a linear dependence and then reached saturation (J_{sat}) in the high reverse voltage region ($V_{\text{eff}} > 2$ V), indicating efficient charge dissociation into free charges and their subsequent collection by the electrodes. The ratios of $J_{\text{ph}}/J_{\text{sat}}$ under short-circuit conditions and at the maximal power points can be used to estimate η_{dis} and η_{col} of the devices.^{S5,S6}

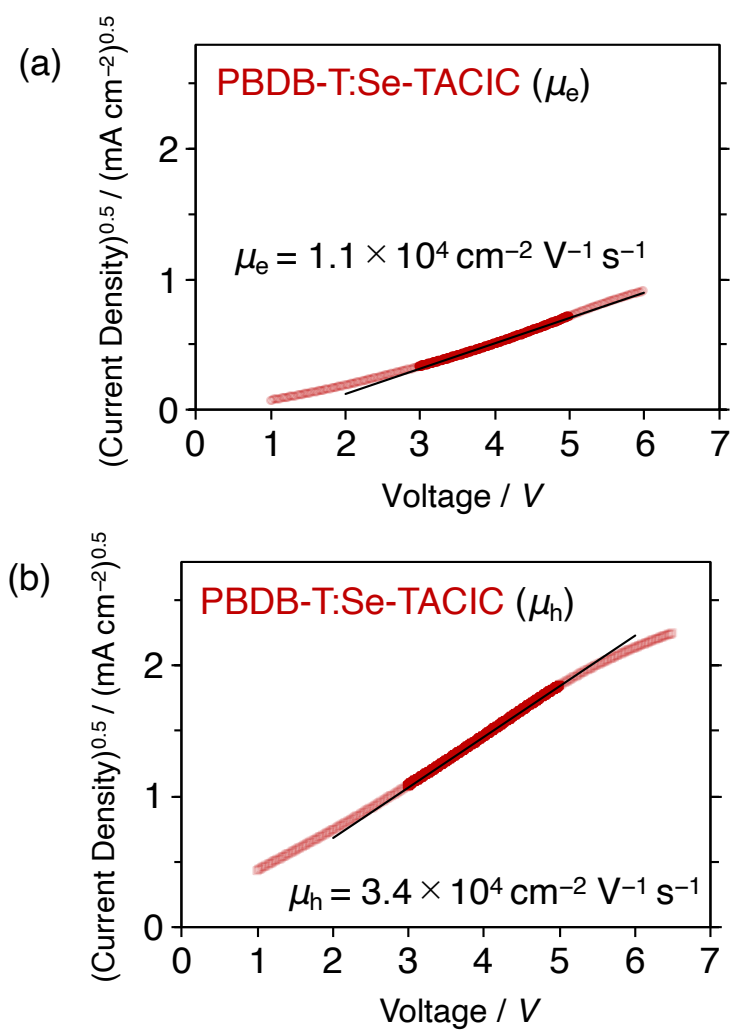


Fig. S12. $J^{0.5}$ - V plots for (a) electron-only and (b) hole-only devices based on PBDB-T:Se-TACIC.

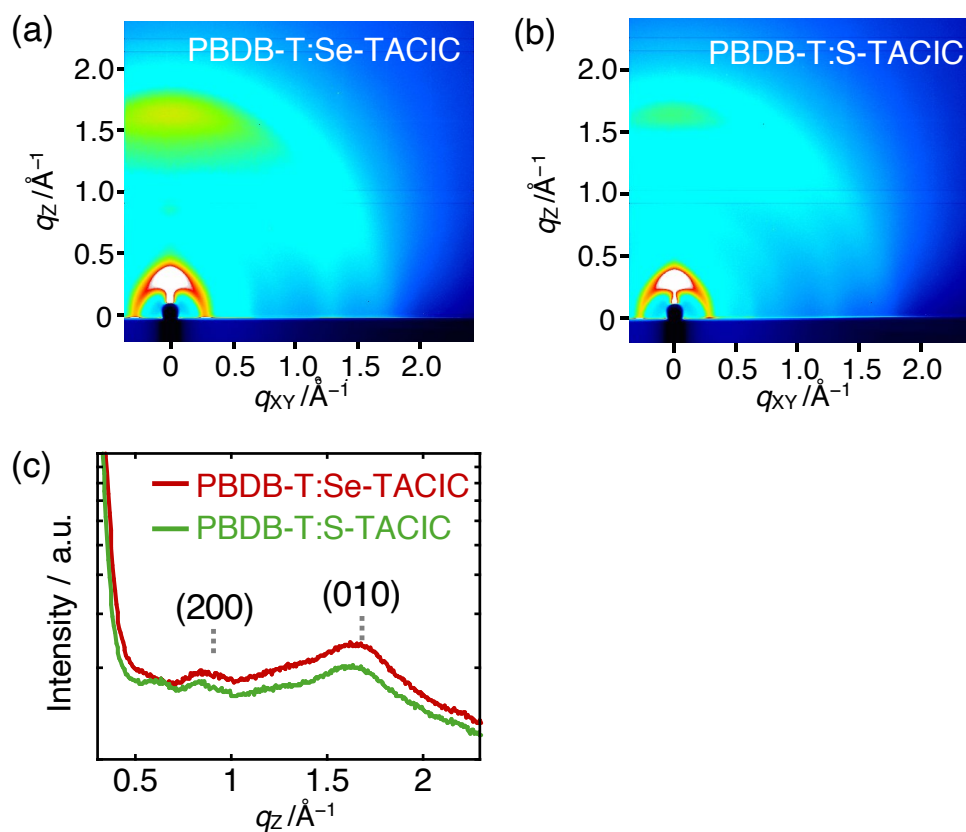


Fig. S12. Two dimensional GIWAXS plots of (a) **PBDB-T:Se-TACIC** and (b) **PBDB-T:S-TACIC** blend films. (c) Out-of-plane GIWAXS profiles for **PBDB-T:Se-TACIC** and **PBDB-T:S-TACIC**.

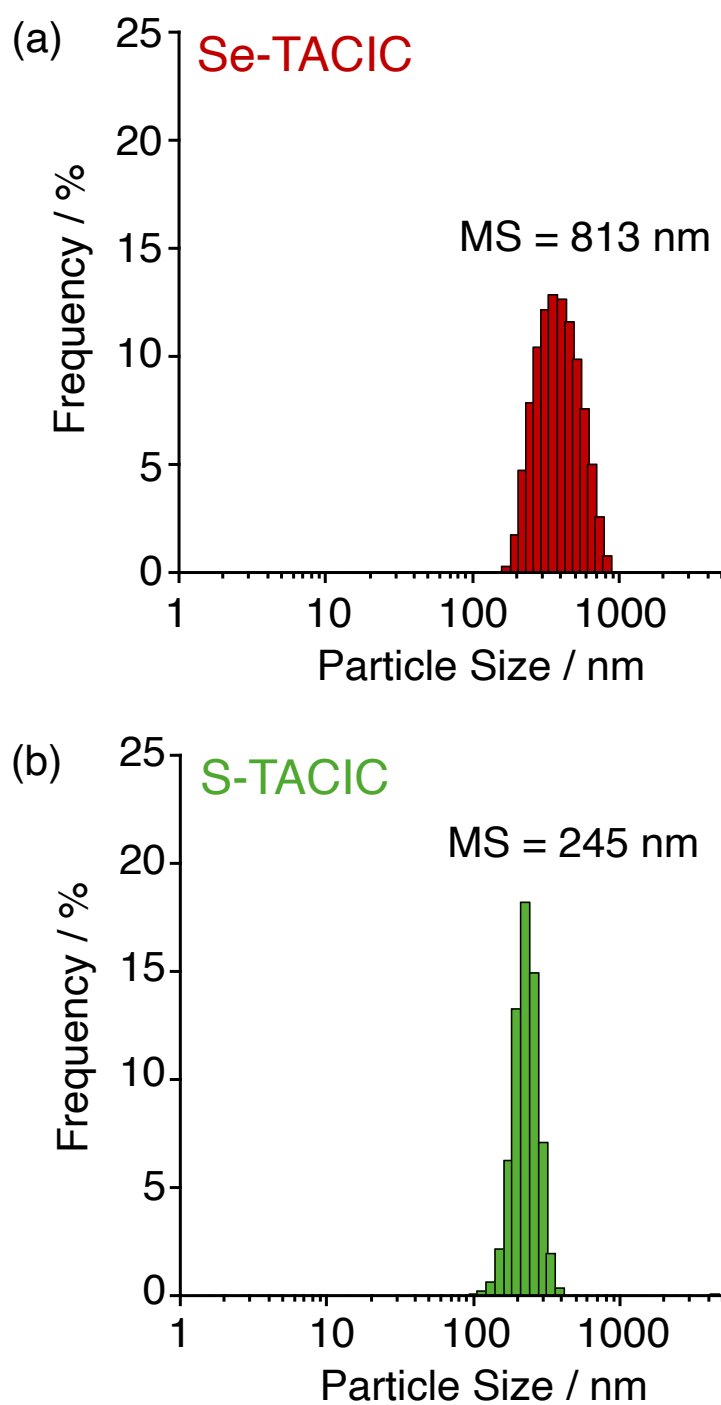


Fig. S13. Particle size distributions of (a) **Se-TACIC** and (b) **S-TACIC** in chloroform at room temperature determined by DLS. Concentration: $[\text{Se-TACIC}] = [\text{S-TACIC}] = 6 \text{ mg mL}^{-1}$. Median size (M.S.) values are shown.

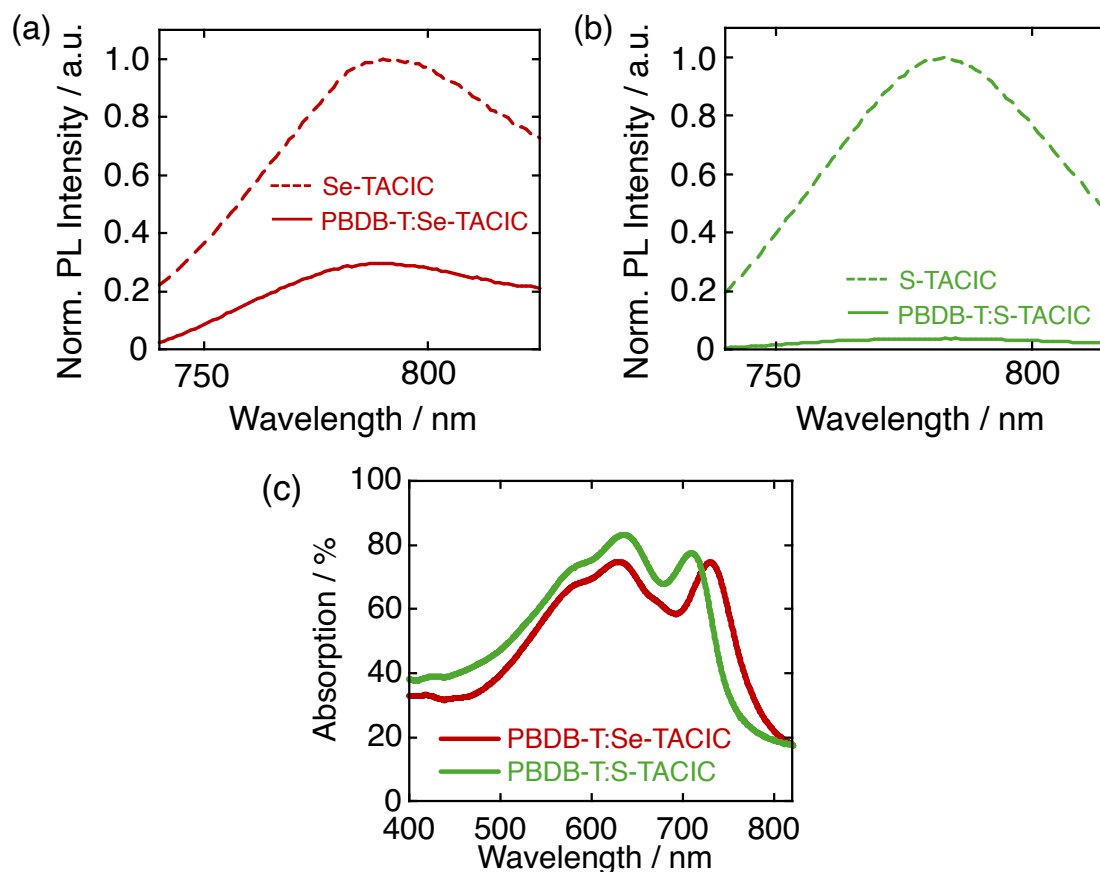


Fig. S14. Photoluminescence spectra of (a) **Se-TACIC** single component film (red dotted line) and **PBDB-T:Se-TACIC** (red solid line) and (b) **S-TACIC** single component film (green dotted line) and **PBDB-T:S-TACIC** (green solid line). The samples were excited at 730 nm and 710 nm, respectively, where the NFAs were predominantly excited. The emission intensities are normalized by those of the acceptor single component films to account for difference in absorbance of the **PBDB-T:NFA** films at the excitation wavelength. (c) UV-vis-NIR absorption spectra of **PBDB-T** blend films with **SeTACIC** and **S-TACIC** on ITO/ZnO substrates. Note that the total absorption of the ITO/ZnO/**PBDB-T:E-TACIC**/MoO₃/Ag devices is higher than the values shown here due to reflection from the Ag electrode.

References

- [S1] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.
- [S2] P. Franchetti, L. Cappellacci, G. A. Sheikha, H. N. Jayaram, V. V. Gurudutt, T. Sint, B. P. Schneider, W. D. Jones, B. M. Goldstein, G. Perra, A. De Montis, A. G. Loi, P. La Colla, M. Grifantini, *J. Med. Chem.* **1997**, *40*, 1731.
- [S3] T. Umeyama, K. Igarashi, D. Sasada, Y. Tamai, K. Ishida, T. Koganezawa, S. Ohtani, K. Tanaka, H. Ohkita, H. Imahori, *Chem. Sci.* **2020**, *11*, 3250.
- [S4] Y. Cui, H. Ren, J. Yu, Z. Wang, G. Qian, *Dyes Pigm.* **2009**, *81*, 53.
- [S5] M. L. Keshtov, S. A. Kuklin, A. R. Khokhlov, Z. Xie, C. Dou, Y. Zou, I. E. Ostapov, E. E. Makhaeva, R. Suthar, G. D. Sharma, *ACS Appl. Energy Mater.* **2020**, *3*, 495.
- [S6] X. Chen, B. Kan, Y. Kan, M. Zhang, S. B. Jo, K. Gao, F. Lin, F. Liu, X. Peng, Y. Cao, A. K. Y. Jen, *Adv. Funct. Mater.* **2020**, *30*, 1909535.