

Synergistic Effects of Benzoselenadiazole Core and Alkoxy Side Chain Substitution on the Photovoltaic Performance of Non-Fullerene Acceptors

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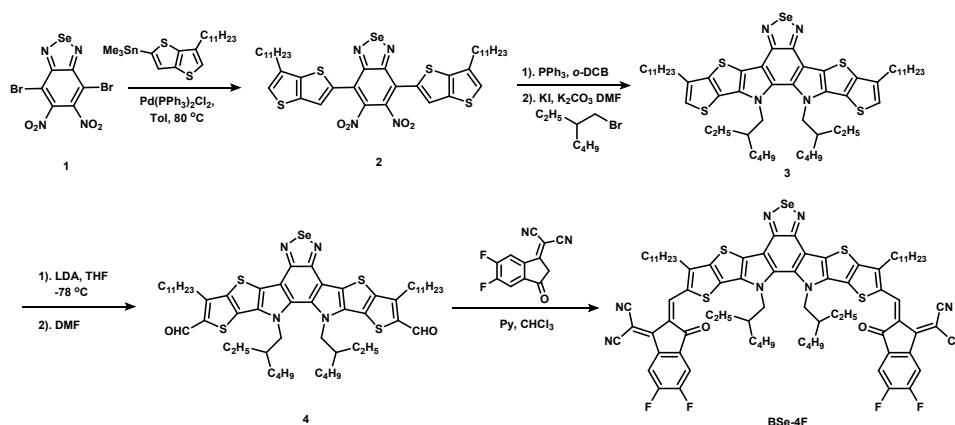
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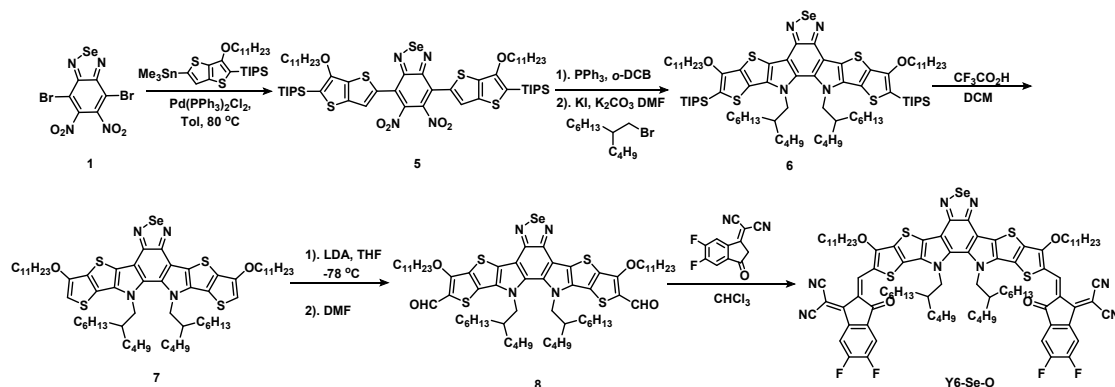
[⊥]These authors contributed equally.

Materials and synthesis

All chemicals, unless otherwise specified, were purchased from Aldrich or other commercial resources and used as received. PM6 (Mn=24.2 kDa) was purchased from Solarmer Energy Inc. Y6-Se was synthesized according to literature.¹ Toluene and THF were distilled from sodium benzophenone under nitrogen before using.

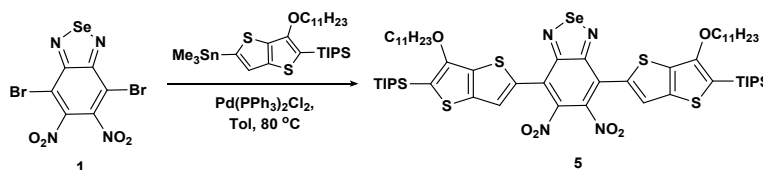


Scheme S1. The synthetic routes of Y6-Se



Scheme S2. The synthetic routes of Y6-Se-O

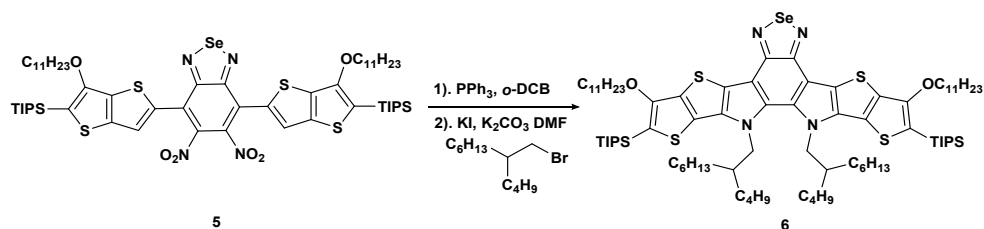
Synthesis of **5,6-dinitro-4,7-bis(5-(triisopropylsilyl)-6-(undecyloxy)thieno[3,2-b]thiophen-2-yl)benzo[*c*][1,2,5]selenadiazole (5)**



A mixture of **compound 1** (115.0 mg, 0.267 mmol), Pd(PPh₃)₂Cl₂ (9.0 mg, 0.013 mmol), triisopropyl(5-(trimethylstannyl)-3-(undecyloxy)thieno[3,2-b]thiophen-2-yl)silane (504.0 mg,

0.801 mmol) was dissolved in anhydrous toluene (10 mL) under N₂ atmosphere. The reaction mixture was then stirred for 12 hours at 80 °C. Then, the reaction mixture was cooled to room temperature and poured into an aqueous KF solution. The mixture was extracted with dichloromethane (3 x 25 mL). The combined organic phase was washed with water followed by brine. Then the solution was dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (stationary phase: silica gel, eluent: *n*-hexane: CH₂Cl₂ = 2:1) to get the product as a violet solid (222 mg, 69%). **¹H NMR** (400 MHz, CDCl₃, ppm): δ = 7.53 (s, 2H), 4.34-4.32 (m, 4H), 1.82-1.78 (m, 4H), 1.50-1.41 (m, 8H), 1.37-1.28 (m, 32H), 1.15-1.14 (m, 30H), 0.90-0.86 (m, 6H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ = 156.75, 154.81, 143.59, 142.10, 133.81, 131.56, 123.68, 122.46, 118.13, 71.46, 31.96, 30.06, 29.69, 29.62, 29.40, 29.37, 25.94, 22.74, 18.80, 14.17, 12.17; **MALDI-TOF MS**: calcd for C₅₈H₉₀N₄O₆S₄SeSi₂ (M⁺), 1202.75; found, 1202.44.

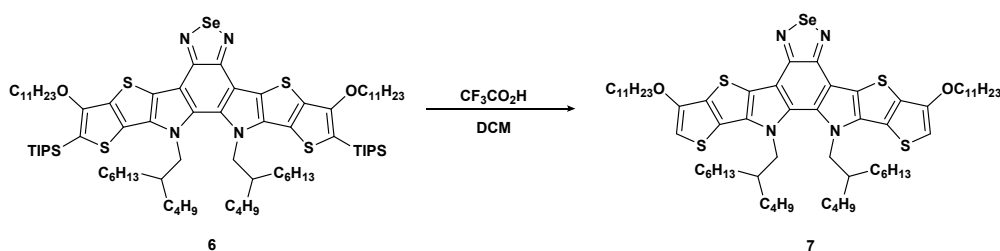
Synthesis of **12,13-bis(2-butyloctyl)-2,10-bis(triisopropylsilyl)-3,9-bis(undecyloxy)-12,13-dihydro-[1,2,5]selenadiazolo[3,4-*e*]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[2',3':4,5]thieno[3,2-*b*]indole (6)**



Compound 5 (217.1 mg, 0.176 mmol) and triethyl phosphate (461.6 mg, 1.76 mmol) were dissolved in anhydrous 1,2-dichlorobenzene (*o*-DCB, 10 mL) under N₂ atmosphere and the reaction mixture was then stirred overnight at 180 °C. After cooling to room temperature, methanol was added to precipitate the residue and the residue was filtered under reduced pressure to obtain a red residue. Subsequently, the red residue was mixed with 1-bromo-2-butyl-octane (1.49 g, 5.981 mmol), potassium carbonate (688.8 mg, 4.984 mmol) and potassium iodide (992.8 mg, 5.981 mmol) in DMF (20 mL) under N₂ atmosphere. The reaction mixture was refluxed overnight at 80 °C. After cooling down to room temperature, the residue was poured into water and extracted with ethyl acetate (3 x 25 mL). The combined organic phase was washed with water followed by brine.

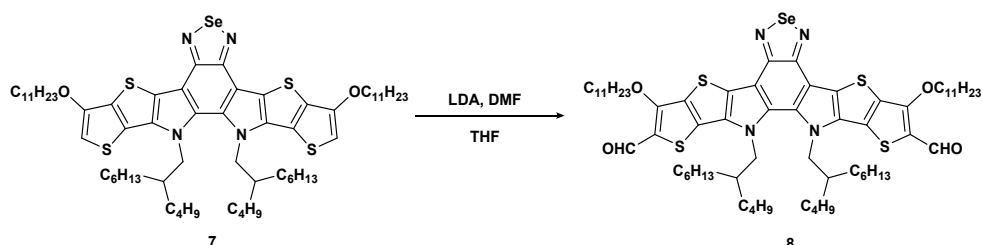
Then the solution was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (stationary phase: silica gel, eluent: *n*-hexane: $\text{CH}_2\text{Cl}_2=3:1$, v/v) to get the product as orange oil (104.2 mg, 37%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): $\delta = 4.54\text{-}4.52$ (m, 4H), 4.47-4.44 (m, 4H), 2.13-2.11 (m, 2H), 1.87-1.80 (m, 4H), 1.55-1.46 (m, 8H), 1.31-1.26 (m, 28H), 1.19-0.87 (m, 80H), 0.78-0.61 (m, 12H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm): $\delta = 156.43, 153.73, 135.98, 131.88, 128.67, 124.70, 124.64, 113.11, 110.84, 71.53, 54.84, 38.55, 31.95, 31.63, 30.41, 30.26, 30.19, 30.09, 29.68, 29.63, 29.61, 29.39, 29.38, 29.36, 29.32, 28.16, 27.89, 25.92, 25.31, 25.02, 22.76, 22.73, 22.71, 22.49, 18.85, 14.15, 14.01, 13.80, 13.74, 12.22$; **MALDI-TOF MS**: calcd for $\text{C}_{82}\text{H}_{138}\text{N}_4\text{O}_2\text{S}_4\text{SeSi}_2$ (M^+), 1475.56; found, 1475.83.

Synthesis of **12,13-bis(2-butylloctyl)-3,9-bis(undecyloxy)-12,13-dihydro-[1,2,5]selenadiazolo[3,4-*e*]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[2',3':4,5]thieno[3,2-*b*]indole (7)**



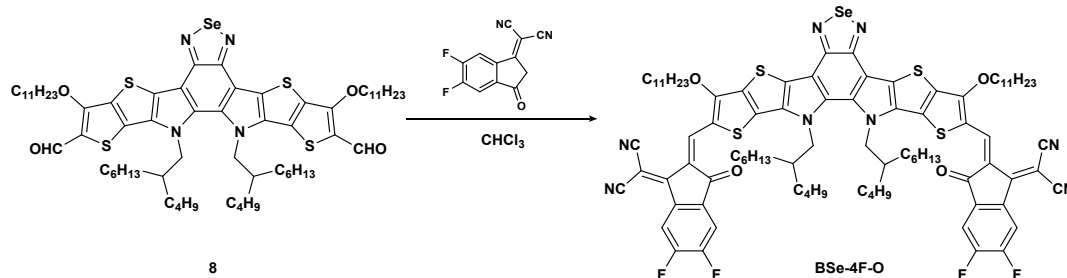
Compound 6 (104.2 mg, 0.069mmol) was dissolved in chloroform (5mL) and trifluoroacetic acid (31.5mg, 0.276mmol) was added into reaction mixture. The reaction mixture was stirred at room temperature until there is no reminding enol silane. The reaction conversion was monitored with TLC. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (stationary phase: silica gel, eluent: *n*-hexane: $\text{CH}_2\text{Cl}_2=3:1$, v/v) to obtain the product as red residue (58.4mg, 75%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): $\delta = 6.28$ (s, 2H), 4.56-4.46 (m, 4H), 4.17-4.14 (m, 4H), 2.11-2.08 (m, 2H), 1.91-1.84 (m, 4H), 1.55-1.48 (m, 4H), 1.41-1.28 (m, 30H), 1.15-0.87 (m, 36H), 0.61 (m, 12H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm): $\delta = 153.64, 151.25, 136.46, 132.54, 131.80, 123.94, 122.15, 113.43, 95.66, 70.75, 55.01, 38.70, 31.95, 31.58, 30.41, 30.30, 30.18, 29.67, 29.65, 29.64, 29.43, 29.39, 29.36, 29.23, 28.02, 27.87, 26.05, 25.37, 25.21, 22.80, 22.76, 22.73, 22.48, 22.46, 14.16, 13.98, 13.96, 13.79, 13.76$; **MALDI-TOF MS**: calcd for $\text{C}_{64}\text{H}_{98}\text{N}_4\text{O}_2\text{S}_4\text{Se}$ (M^+), 1162.71; found, 1162.60.

Synthesis of **12,13-bis(2-butyloctyl)-3,9-bis(undecyloxy)-12,13-dihydro-[1,2,5]selenadiazolo[3,4-e]thieno[2'',3''':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-dicarbaldehyde (8)**



To a solution of **compound 7** (58.4 mg, 0.05 mmol) in THF (10 mL), 2.0 M lithium diisopropylamide in hexane (1 mL, 0.200 mmol) was added dropwise slowly at $-78\text{ }^{\circ}\text{C}$ under N_2 . The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h, and then anhydrous DMF (2 mL) was added. The mixture was stirred overnight at room temperature. Brine was added and the mixture was extracted with ethyl acetate (3 x 25mL). The combined organic phase was washed with water followed by brine. Then the solution was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: *n*-hexane: CH_2Cl_2 = 1:4, v/v) to get the product as orange solid (57.9 mg, 95%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ = 10.09 (s, 2H), 4.69-4.66 (m, 4H), 4.55-4.49 (m, 4H), 2.05-2.02 (m, 2H), 1.96-1.89 (m, 4H), 1.56-1.52 (m, 4H), 1.41-1.27 (m, 30H), 1.10-0.87 (m, 36H), 0.69-0.62 (m, 12H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm): δ = 181.11, 158.65, 153.12, 136.33, 133.21, 130.08, 129.31, 128.89, 121.70, 114.01, 55.22, 38.97, 31.91, 31.51, 30.34, 30.20, 30.04, 29.90, 29.62, 29.58, 29.54, 29.34, 29.28, 27.93, 27.78, 25.78, 25.25, 25.06, 22.76, 22.73, 22.69, 22.47, 14.13, 13.96, 13.75, 13.72; **MALDI-TOF MS**: calcd for $\text{C}_{66}\text{H}_{98}\text{N}_4\text{O}_4\text{S}_4\text{Se}$ (M^+), 1218.73; found, 1218.57.

Synthesis of Y6-Se-O



To a solution of **compound 8** (57.9 mg, 0.0475 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (**IC-2F**) (65.6 mg, 0.285 mmol) in dry chloroform (10 mL) was added pyridine (0.2 mL) under N_2 atmosphere. The reaction mixture was refluxed for 16 hours at $65^\circ C$. After cooling down to room temperature, the reaction mixture was poured into methanol (100 mL) and filtered, the residue left in filter paper was dissolved by $CHCl_3$. After removing the solvent, the residue was purified using column chromatography on silica gel (eluent: *n*-hexane: CH_2Cl_2 = 1:1, v/v), yielding a red solid (57.8 mg, 65%). 1H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.28 (s, 2H), 8.48-8.44 (m, 2H), 7.64-7.60 (m, 2H), 4.80-4.66 (m, 8H), 2.18-2.13 (m, 2H), 2.05-1.98 (m, 4H), 1.59-1.53 (m, 8H), 1.32-0.86 (m, 62H), 0.76-0.66 (m, 12H); MALDI-TOF MS: calcd for $C_{90}H_{102}F_4N_8O_4S_4Se$ (M^+), 1643.05; found, 1643.61.

Measurements

General information: ^1H and ^{13}C NMR spectra were obtained with a Bruker AV-400 MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm, δ). ^1H and ^{13}C NMR spectra were referenced to tetramethylsilane (0 ppm) for CDCl_3 . Mass spectra were collected on a MALDI Micro MX mass spectrometer, or an API QSTAR XL System.

Optical characterizations: Film UV-Vis absorption spectra were acquired on a Perkin Elmer Lambda 20 UV/VIS Spectrophotometer. All film samples were spin-cast on ITO substrates. UV-Vis absorption spectra were collected from the solution of three small molecules with the concentration of 1.0×10^{-5} M in chloroform. A cuvette with a stopper (Sigma Z600628) was used to avoid volatilization during the measurement.

Electrochemical characterizations: Cyclic voltammetry was carried out on a CHI610E electrochemical workstation with the three electrodes configuration, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the supporting electrolyte. The polymer and small molecules were drop-cast onto the glassy carbon electrode from chloroform solutions (5 mg/mL) to form thin films. Potentials were referenced to the ferrocenium/ferrocene couple by using ferrocene as external standards in acetonitrile solutions. The scan rate is 100 mV s^{-1} . The conversion of reduction/oxidation onsets and LUMO/HOMO energy levels can be described as: $E_{\text{LUMO}} = -[e(E^{\text{red}} - E^{\text{Fc/Fc}^+}) + 4.8]$; $E_{\text{HOMO}} = -[e(E^{\text{ox}} - E^{\text{Fc/Fc}^+}) + 4.8]$.

AFM analysis: AFM measurements were performed by using a Scanning Probe Microscope Dimension 3100 in tapping mode. All film samples were spin-cast on ITO substrates.

Device fabrication and characterization: OSCs were made with a device structure of ITO (indium tin oxide)/PEDOT: PSS(poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate))/PM6: acceptor/ PNDIT-F3N ([9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-5,5'-bis(2,2'-thiophene)-2,6-naphthalene-1,4,5,8-

tetracarboxylic-N,N'-di(2-ethylhexyl)imide)] /Ag. The patterned ITO-coated glass was scrubbed by detergent and then cleaned inside an ultrasonic bath by using deionized water, acetone, and isopropyl alcohol sequentially and dried overnight in an oven. Before use, the glass substrates were treated in a UV-Ozone Cleaner for 20 min to improve its work function and clearance. A thin PEDOT: PSS (Heraeus Clevious P VPA 4083) layer with a thickness of about 40 nm was spin-coat onto the ITO substrates at 5000rpm for 30 s, and then dried at 150 °C for 10 min in air. The PEDOT: PSS coated ITP substrates were transferred to a N₂-filled glove box for further processing. The donor: acceptor blends with weight ratio of 1:1.2 and total concentration of 16.5mg/mL dissolved in chloroform. 1-chloronaphthalene (CN) was used as an additive in the concentration of (0.5%, v/v) to optimum device performance. Then the solution was stirred overnight for intensive mixing in a nitrogen-filled glove box. The blend solution was spin-cast on the top of PEDOT: PSS layer at 3500 rpm for 40 s. Then it was annealed at 100 °C for 5 min to remove the solvent to achieve better film morphology. A PNDIT-F3N (~ 10 nm) and Ag layer (~ 100 nm) were sequentially evaporated under vacuum of 5×10⁻⁵ Pa through a shadow mask. The optimal blend thickness measured on a Bruker Dektak XT stylus profilometer was about 100nm. The current-voltage (*J-V*) characteristic curves of all packaged devices were measured by using a Keithley 2400 Source Meter in air. Photocurrent was measured under AM 1.5G (100 mW cm⁻²) using a Newport solar simulator in an Air. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement) to bring spectral mismatch to unity.

EQE measurements. EQE spectra were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.

Hole-mobility measurements. The hole mobilities were measured using the space charge limited current (SCLC) method, employing a device architecture of ITO/PEDOT:PSS/blend film/MoO₃/Ag. The mobilities were obtained by taking current-voltage curves and fitting the results to a space charge limited form, where the SCLC is described by:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu(V_{appl} - V_{bi} - V_s)^2}{8L^3}$$

Where ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material (assumed to

be 3), μ is the hole mobility and L is the thickness of the film. From the plots of $J^{1/2}$ vs $V_{appl} - V_{bi} - V_s$, hole mobilities can be deduced.

Electron mobility measurements. The electron mobilities were measured using the SCLC method, employing a device architecture of ITO/ZnO/blend film/PNDIT-F3N/Ag. The mobilities were obtained by taking current-voltage curves and fitting the results to a space charge limited form, where the SCLC is described by:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu(V_{appl} - V_{bi} - V_s)^2}{8L^3}$$

Where ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material (assumed to be 3), μ is the electron mobility and L is the thickness of the film. From the plots of $J^{1/2}$ vs $V_{appl} - V_{bi} - V_s$, electron mobilities can be deduced.

GIWAXS Characterization. Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were conducted at Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, Berkeley, CA at beamline 7.3.3. Data were acquired at the critical angle (0.13°) of the film with a hard X-ray energy of 10 keV. X-ray irradiation time was 10 s, dependent on the saturation level of the detector. Samples were prepared on Si substrates using identical blend solutions as those used in devices. The coherence length was calculated using the Scherrer equation: $CL = 2\pi K/\Delta q$, where Δq is the full-width at half-maximum of the peak and K is a shape factor (1 was used here).^{2,3}

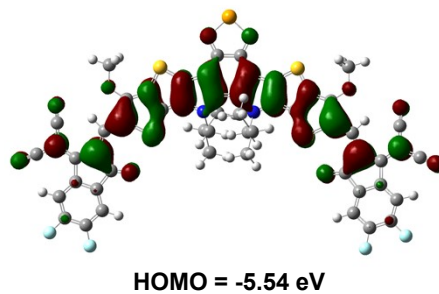
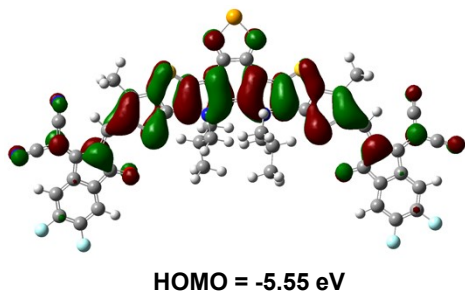
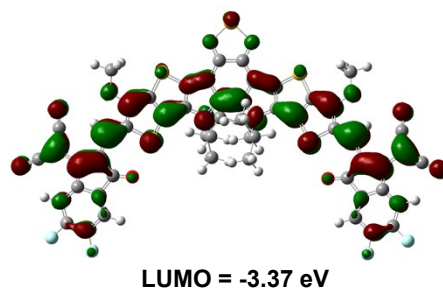
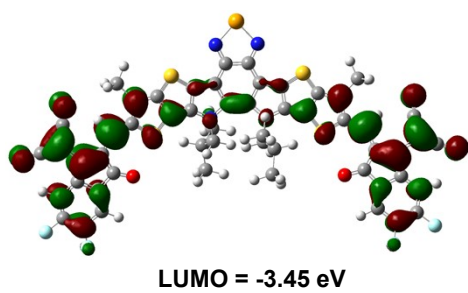
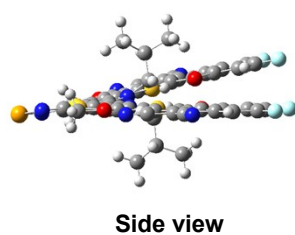
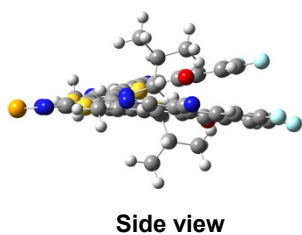
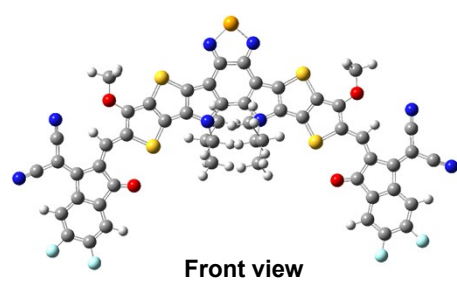
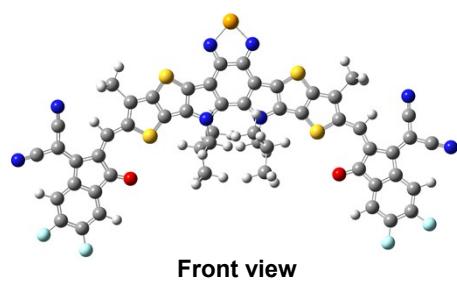


Figure S1. Theory calculation results of Y6-Se and Y6-Se-O.

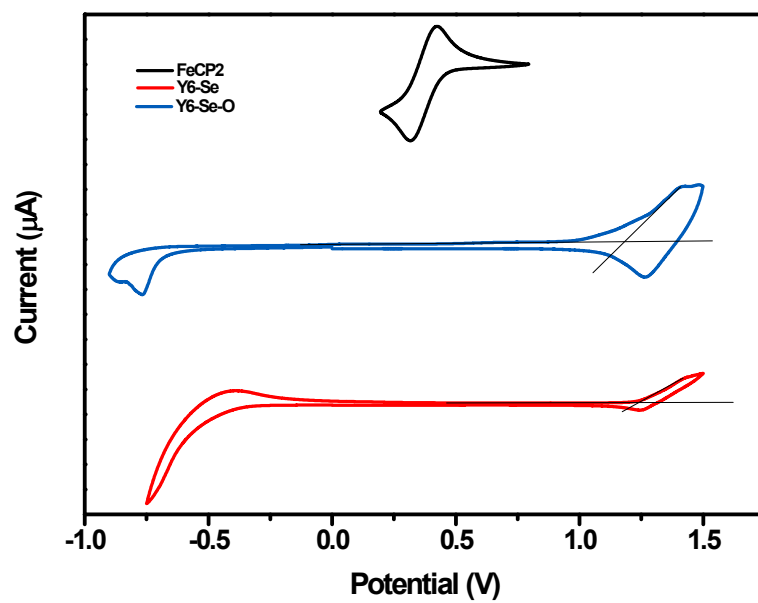


Figure S2. Cyclic Voltammetry curves of Y6-Se and Y6-Se-O.

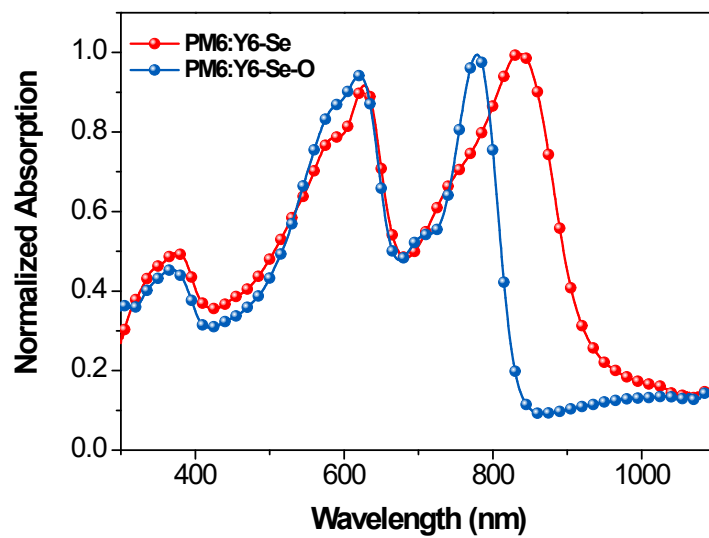


Figure S3. Normalized UV-Vis absorption spectra of PM6:Y6-Se and PM6:Y6-Se-O blend film.

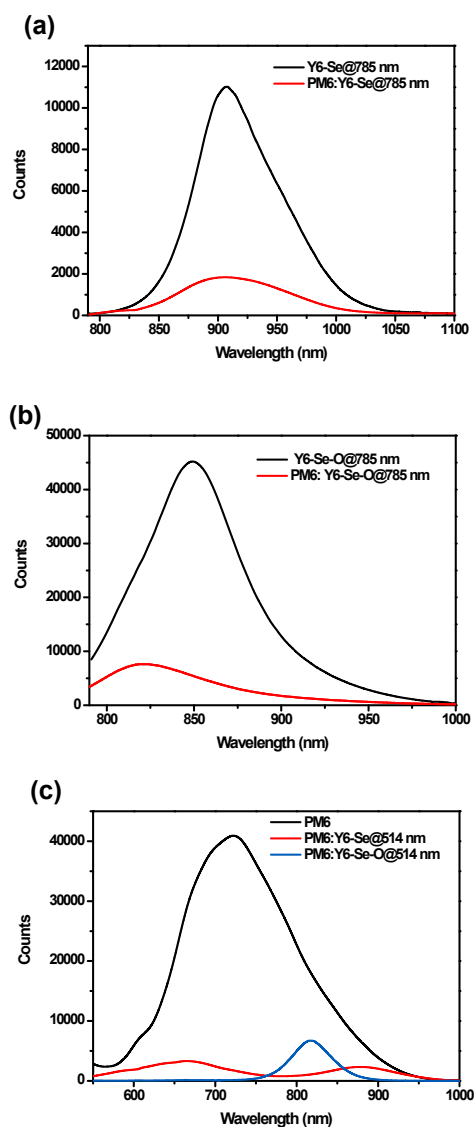


Figure S4. Photoluminescence quenching experiment of (a) the pristine Y6-Se film and PM6:Y6-Se blend films excited at 785 nm; (b) the pristine Y6-Se-O film and PM6:Y6-Se-O blend films excited at 785 nm; (c) the pristine PM6 film, the PM6:Y6-Se, and the PM6:Y6-Se-O blend films excited at 514 nm.

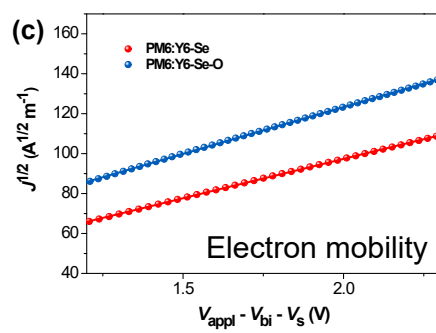
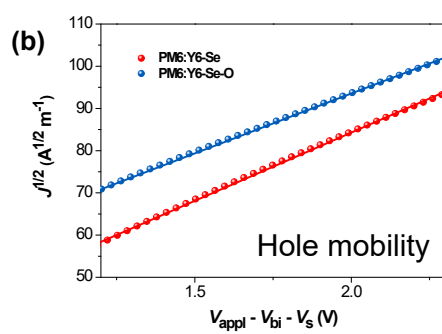
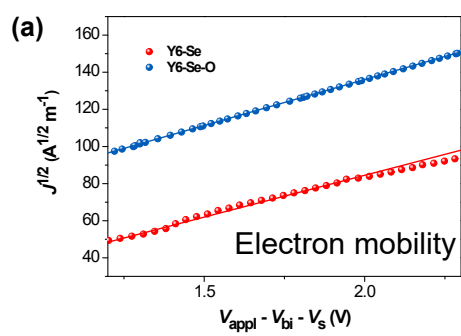


Figure S5. (a) the hole motilities in PM6: Y6-O and PM6: Y6 film; (b) the electron motilities in PM6: Y6-O and PM6:Y6 film.

Table S1. The electron mobilities of the Y6-Se and Y6-Se-O-based devices; the electron and hole mobilities of PM6:Y6-Se and PM6:Y6-Se-O-based devices.

Material Combination	μ_e ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_h ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_e/μ_h
Y6-Se	5.2×10^{-4}		
Y6-Se-O	7.1×10^{-4}		
PM6:Y6-Se	4.8×10^{-3}	3.6×10^{-3}	1.33
PM6:Y6-Se-O	5.2×10^{-3}	4.4×10^{-3}	1.18

Table S2. Morphology parameters extracted from the GIWAXS measurements.

Sample	<u>π-π stacking distance (010)</u>		<u>π-π stacking coherence (010)</u>	
	q_z (\AA^{-1})	$d_{\pi-\pi}$ (\AA)	w (\AA^{-1})	CCL (\AA)
Y6-Se	1.77	3.54	0.23	27
Y6-Se-O	1.87	3.34	0.19	33
PM6:Y6-Se	1.76	3.57	0.22	29
PM6:Y6-Se-O	1.77	3.54	0.24	26

Table S3. Detailed E_{loss} parameters of the all-PSCs based on the three material systems.

Material	E_g	$qV\frac{SQ}{oc}$	$qV\frac{rad}{oc}$	qV_{oc}	E_{loss}	ΔE_1	ΔE_2^c	ΔE_3^d
Combination	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)
PM6:Y6-Se	1.385	1.125	1.077	0.828	0.506	0.260	0.048	0.258
PM6:Y6-Se-O	1.535	1.266	1.198	0.952	0.578	0.269	0.068	0.241

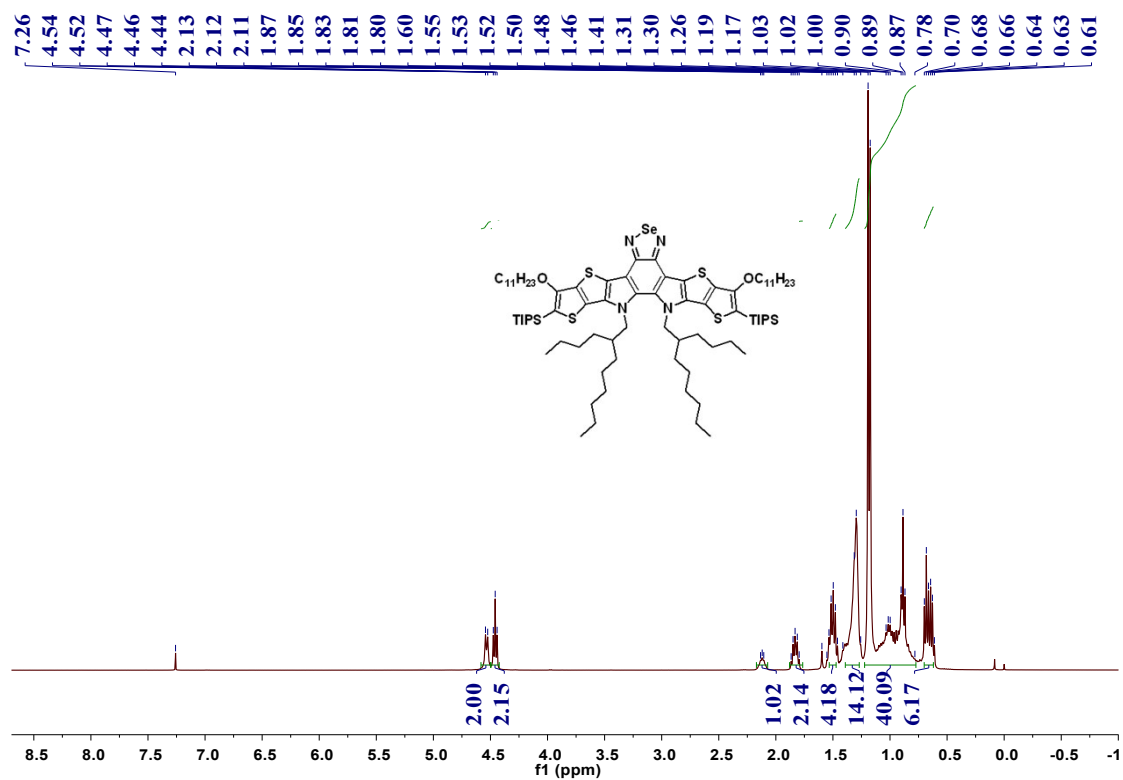


Figure S8. ¹H NMR spectrum of compound 6 (400 MHz, CDCl₃).

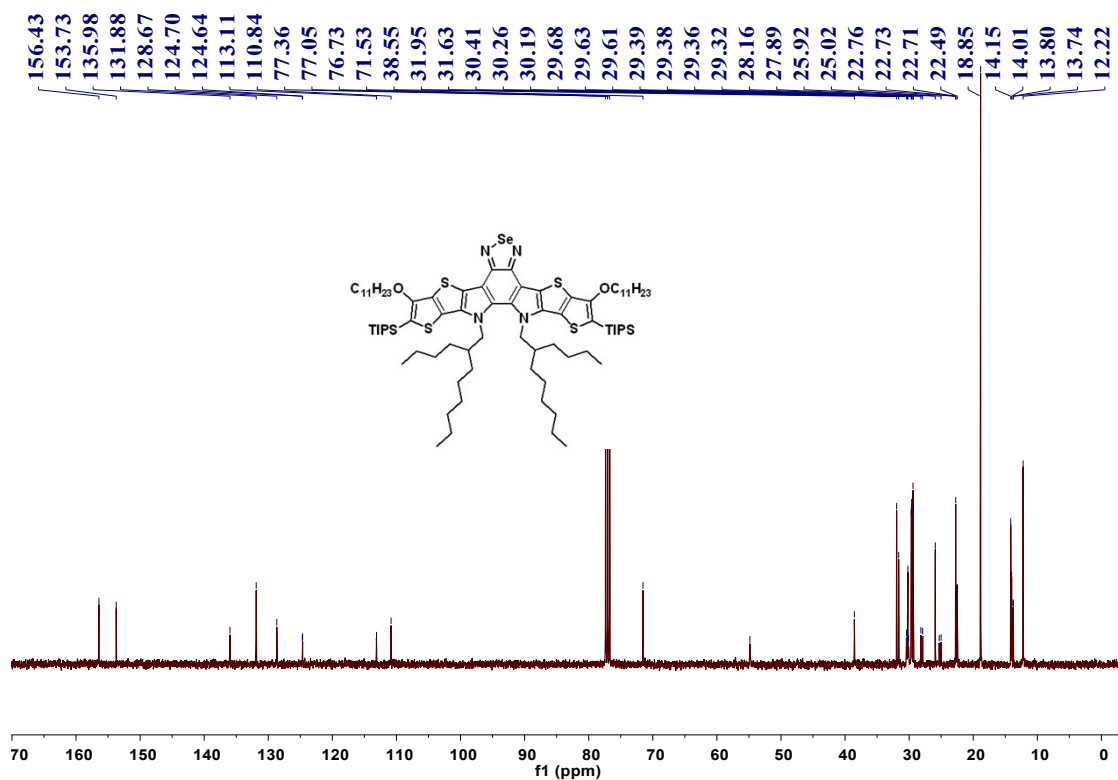


Figure S9. ¹³C NMR spectrum of compound 6 (100 MHz, CDCl₃).

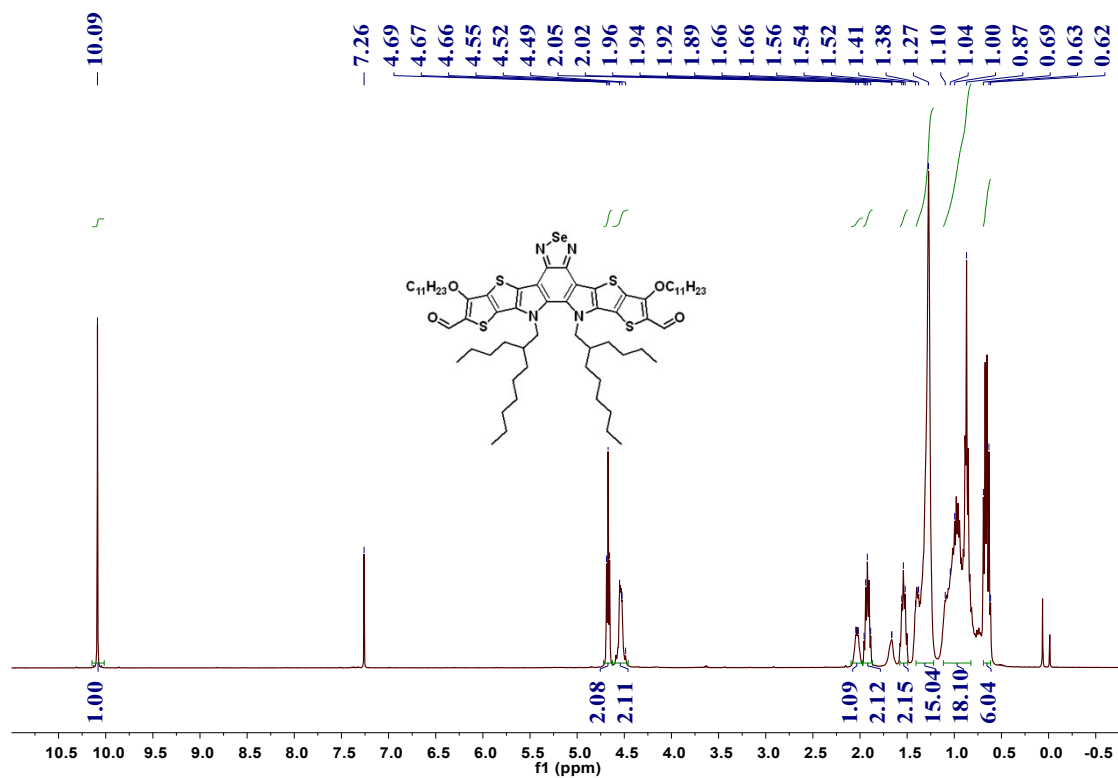


Figure S12. ^1H NMR spectrum of compound **8** (400 MHz, CDCl_3).

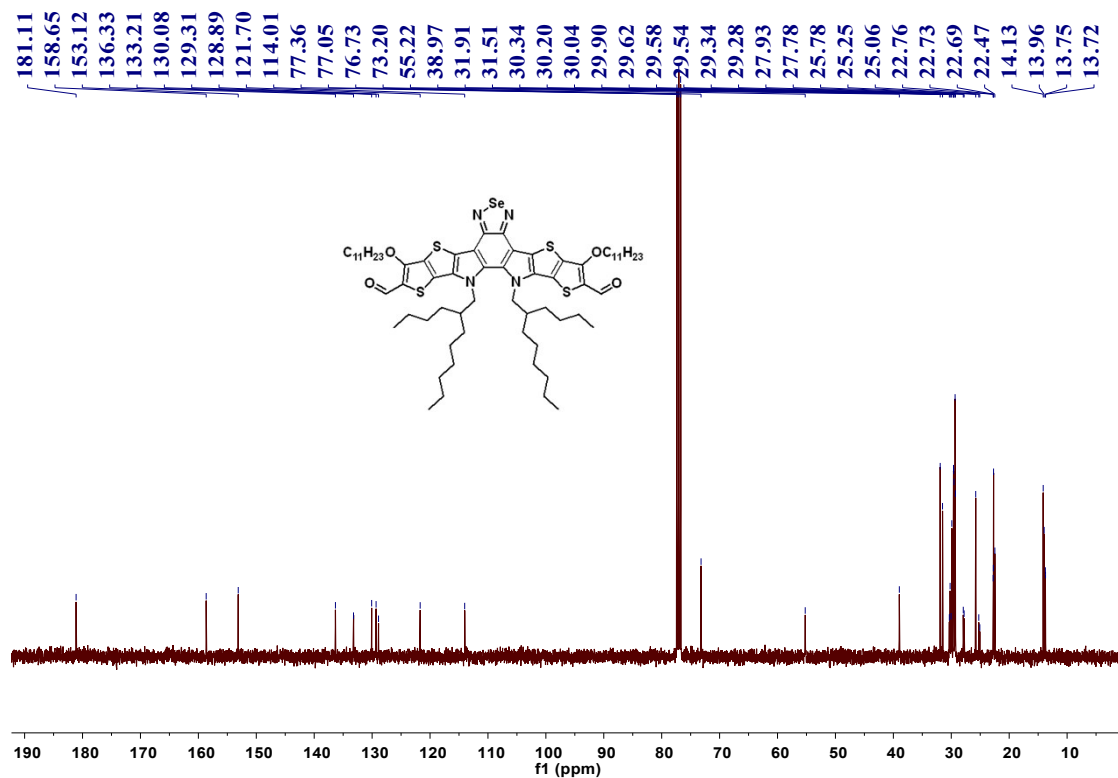


Figure S13. ^{13}C NMR spectrum of compound **8** (100 MHz, CDCl_3).

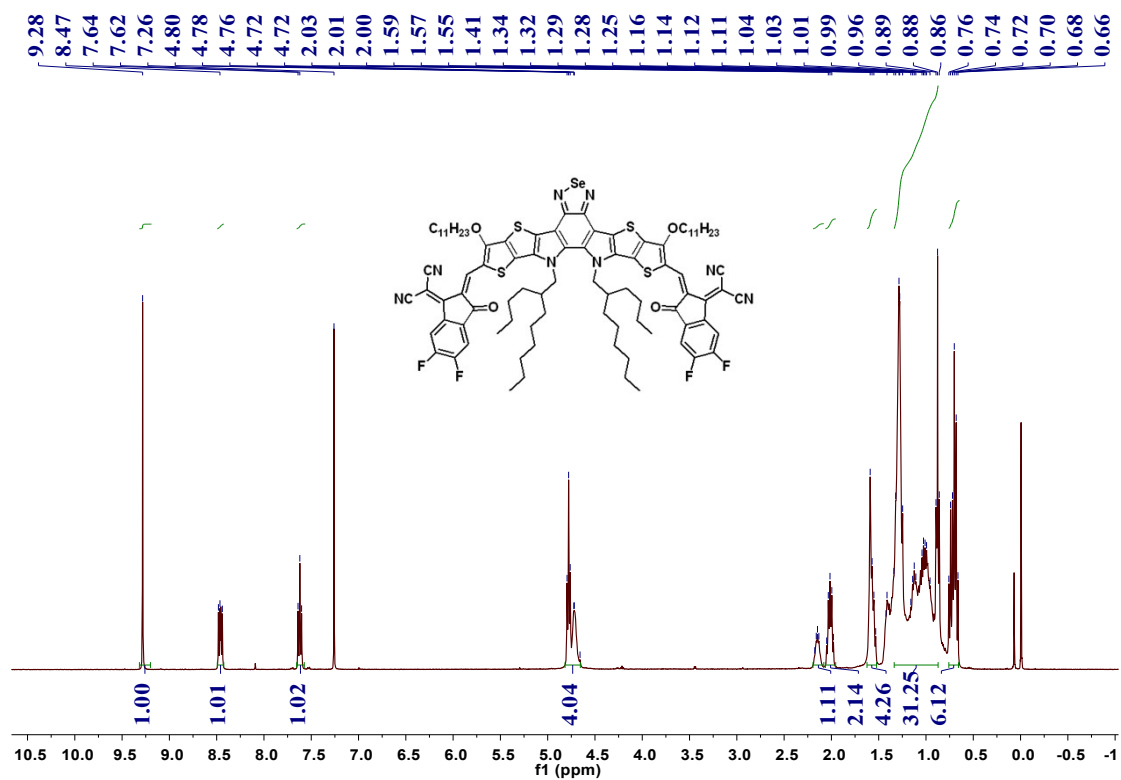


Figure S14. ^1H NMR spectrum of BSe-4F-O (400 MHz, CDCl_3).

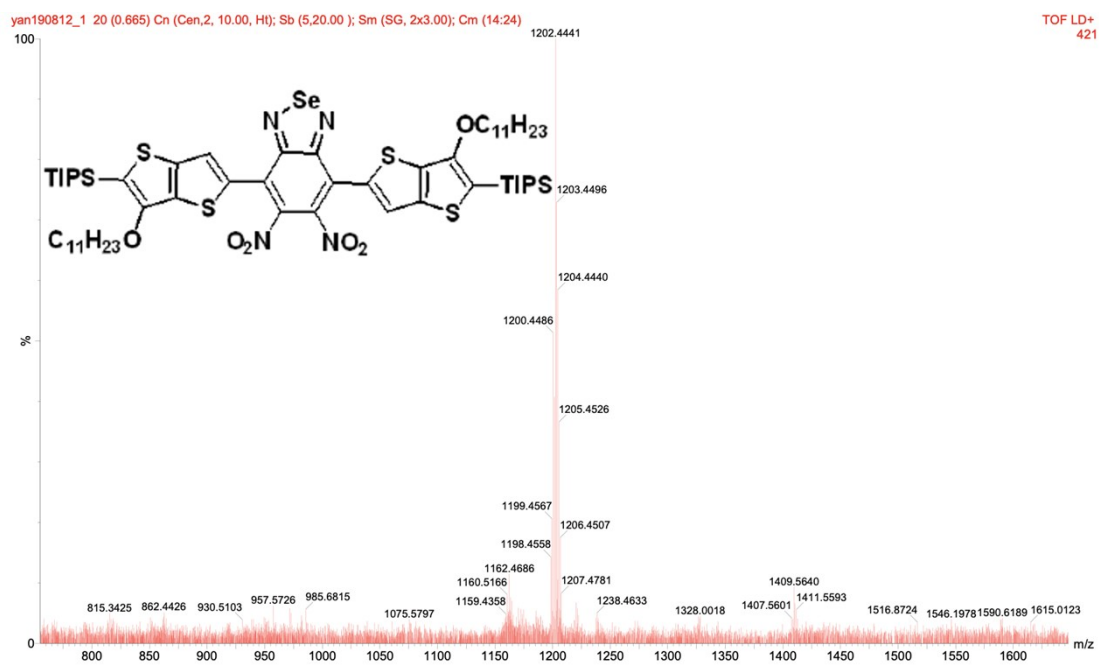
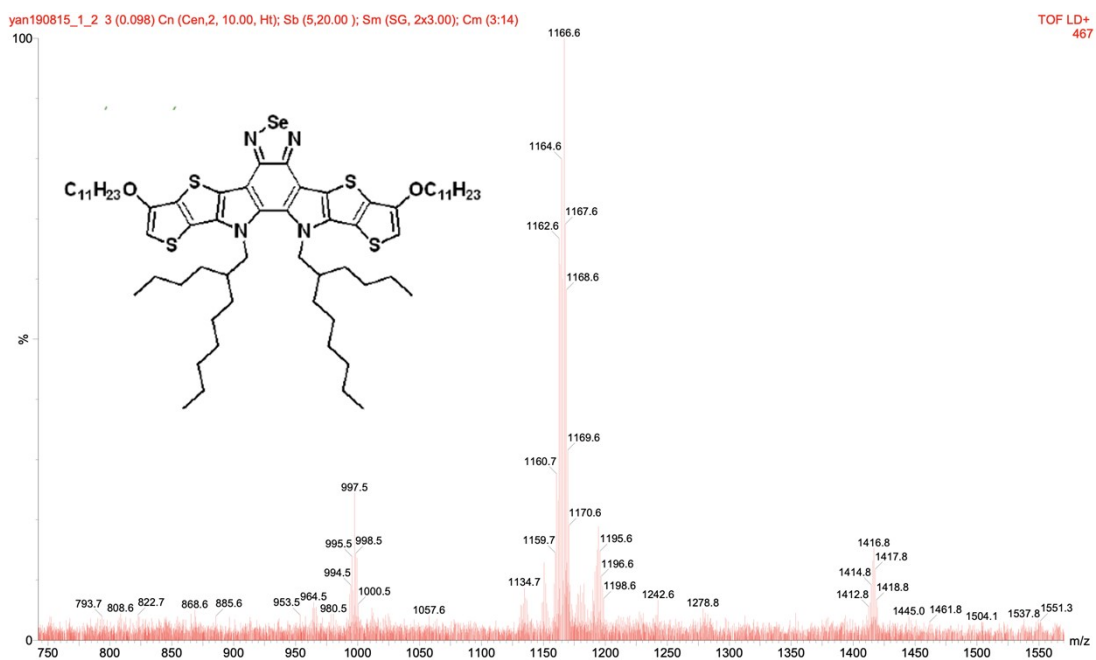
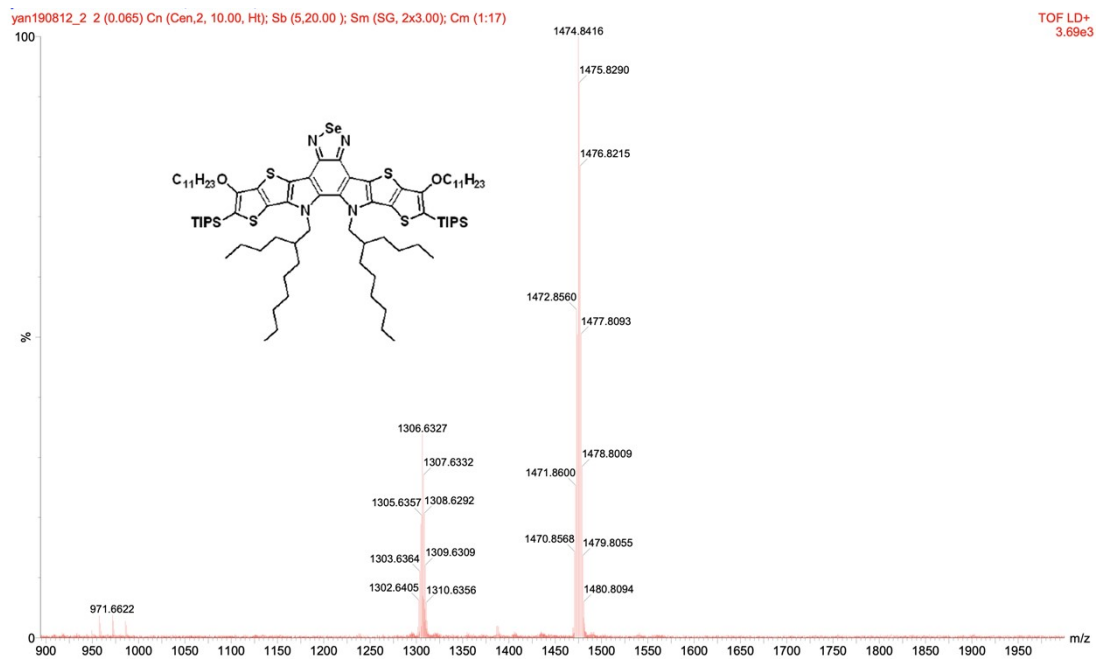
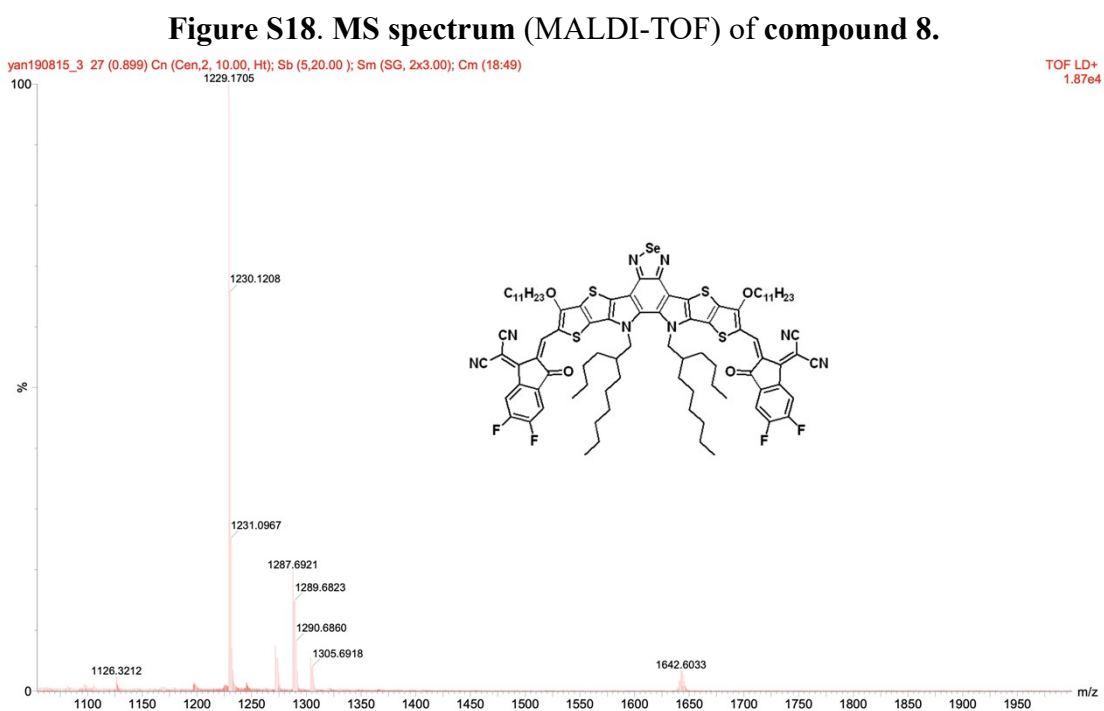
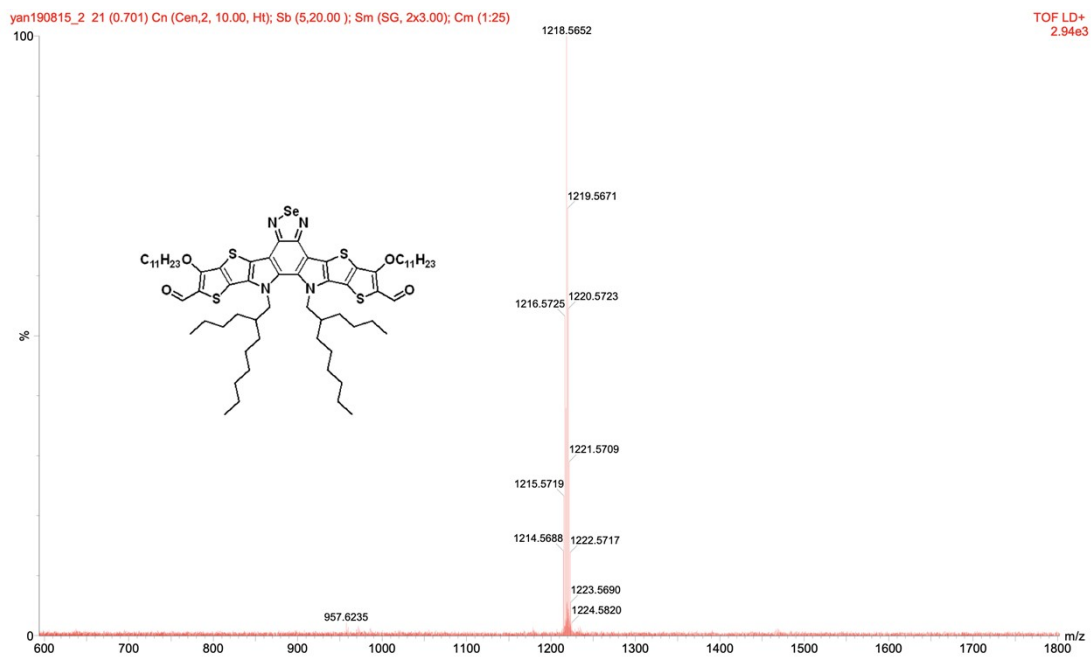


Figure S15. MS spectrum (MALDI-TOF) of compound 5.





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