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Supporting Information for

Tailoring Non-fullerene Acceptors by Selenium-incorporated Heterocycles for Organic Solar Cells with over 16% Efficiency

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General Information.
^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm, δ). ^{1}H NMR 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.

Materials. 4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]selenadiazole **1** and trimethyl(3-undecylselenopheno[3,2-b]thiophen-5-yl)stannane were synthesized according to previous reported literature.[1], [2] PM6 (Mn=24.2 kDa) was purchased from Solarmer Energy Inc. Tetrahydrofuran were freshly distilled before use from sodium using benzophenone as the indicator. All other reagents and chemicals were purchased from commercial sources and used without further purification.

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 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}.

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

Solar cell fabrication and testing. 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-tetracaboxylic-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 even. 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 Clevios P VPA 4083) layer with a thickness of about 40 nm was spin-coat onto the ITO substrates at 4000rmp for 40 s, and then dried at 150 °C for 15 min in air. The PEDOT: PSS coated ITP substrates were transferred to a N_2-filled glove box for further processing. The donor: acceptor blends with weight ratio of 1:1.2 and total concentration of 16mg/mL dissolved in chloroform. 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 immediately after being stirred on a hotplate of 65 °C for 30 minutes at 2500 rpm for 40 s. Then it was annealed at 90 °C for 5 min to remove the solvent. A thin layer of PNDIT-F3N (~10 nm) was cast onto processed active layer, and Ag layer (~100 nm) was deposited in thermal evaporator 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. EQEs 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.

EQE measurements. EQEs 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/MoO_3/Al. 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/Ca/Al. 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 $V_{appl} - V_{bi} - V_s$, electron mobilities can be deduced.

GIWAXS characterization. GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source.[3] Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.13°, which maximized the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 2M photon counting detector. In-plane and out-of-plane sector averages were calculated using the Nika software package.[4] The uncertainty for the peak fitting of the GIWAXS data is 0.3 A. The coherence length was calculated using the Scherrer equation:

$$L_c = \frac{2\pi K}{\Delta q}$$

R-SoXS characterization. R-SoXS transmission measurements were performed at beamline 11.0.1.2 at the Advanced Light Source.[5] Samples for R-SoXS measurement were prepared on a PSS modified Si substrate under the same conditions as those used for device fabrication, and then transferred by floating in water to a 1.5 mm × 1.5 mm, 100 nm thick Si_3N_4 membrane supported by a 5 mm × 5 mm, 200 μm thick Si frame (Norcada Inc.). 2D scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE). The sample detector distance was calibrated from diffraction peaks of a triblock copolymer poly(isoprene-b-styrene-b-2-vinyl pyridine), which has a known spacing of 391 Å. The beam size at the sample is approximately 100 μm by 200 μm.

Photoluminescence (PL) and electroluminescence (EL) measurements: PL data werecollected using a Zolix Flex One Spectrometer. The PL excitation wavelength was set to 639 nm.

Fourier-transform photocurrent spectroscopy external quantum efficiency (FTPS-EQE) measurements: FTPS-EQE spectra were measured by using a Vertex 70 from Bruker optics and QTH lamp. The EL signature was collected with monochromator and detected with Si-CCD detector.

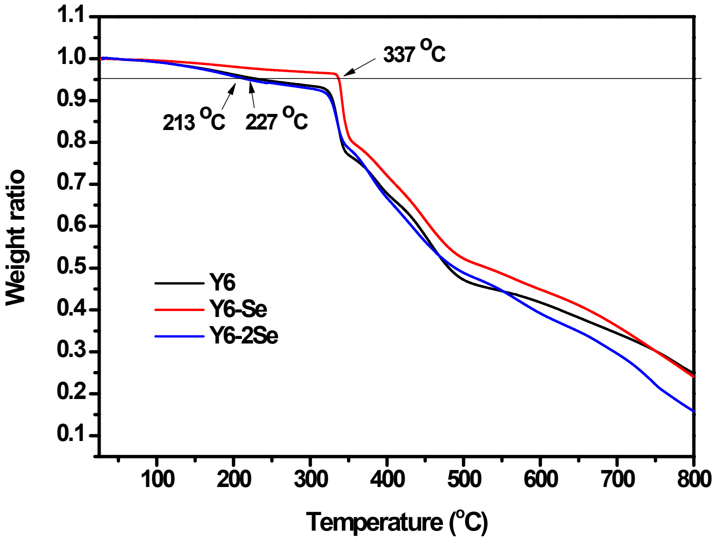


Figure S1. Thermogravimetric curves of Y6, Y6-Se and Y6-2Se. The thermal degradation temperature (T_d at 5% weight loss) of two SMAs are 213, 227 and 337 °C.

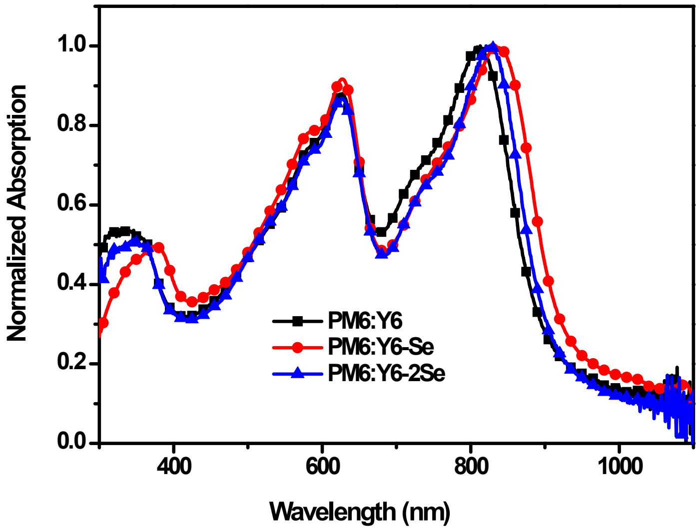


Figure S2. Blend film absorption of PM6:Y6, PM6:Y6-Se and PM6:Y6-2Se.

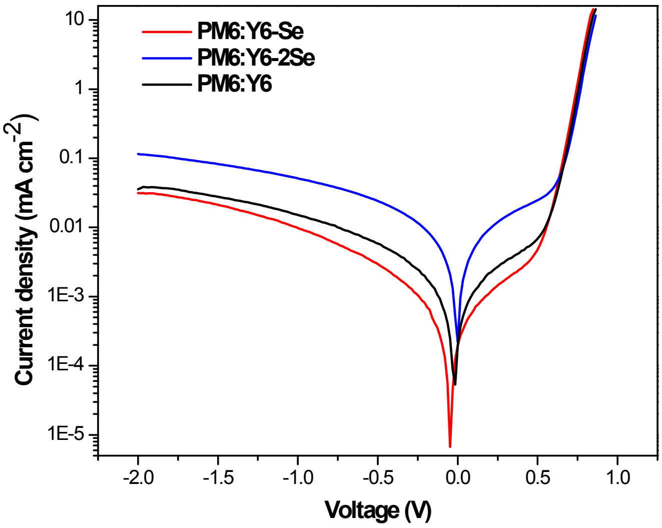


Figure S3. The dark *J–V* curves of the PM6:Y6, PM6:Y6-Se and PM6:Y6-2Se devices.

Table S1. The resistance parameters of the PM6:Y6, PM6:Y6-Se and PM6:Y6-2Se devices.

	PM6:Y6	PM6:Y6-Se	PM6:Y6-2Se
R_S ($\Omega \cdot cm^2$)	5.2	3.9	6.1
R_{Sh} ($k\Omega \cdot cm^2$)	2.0	2.6	1.9

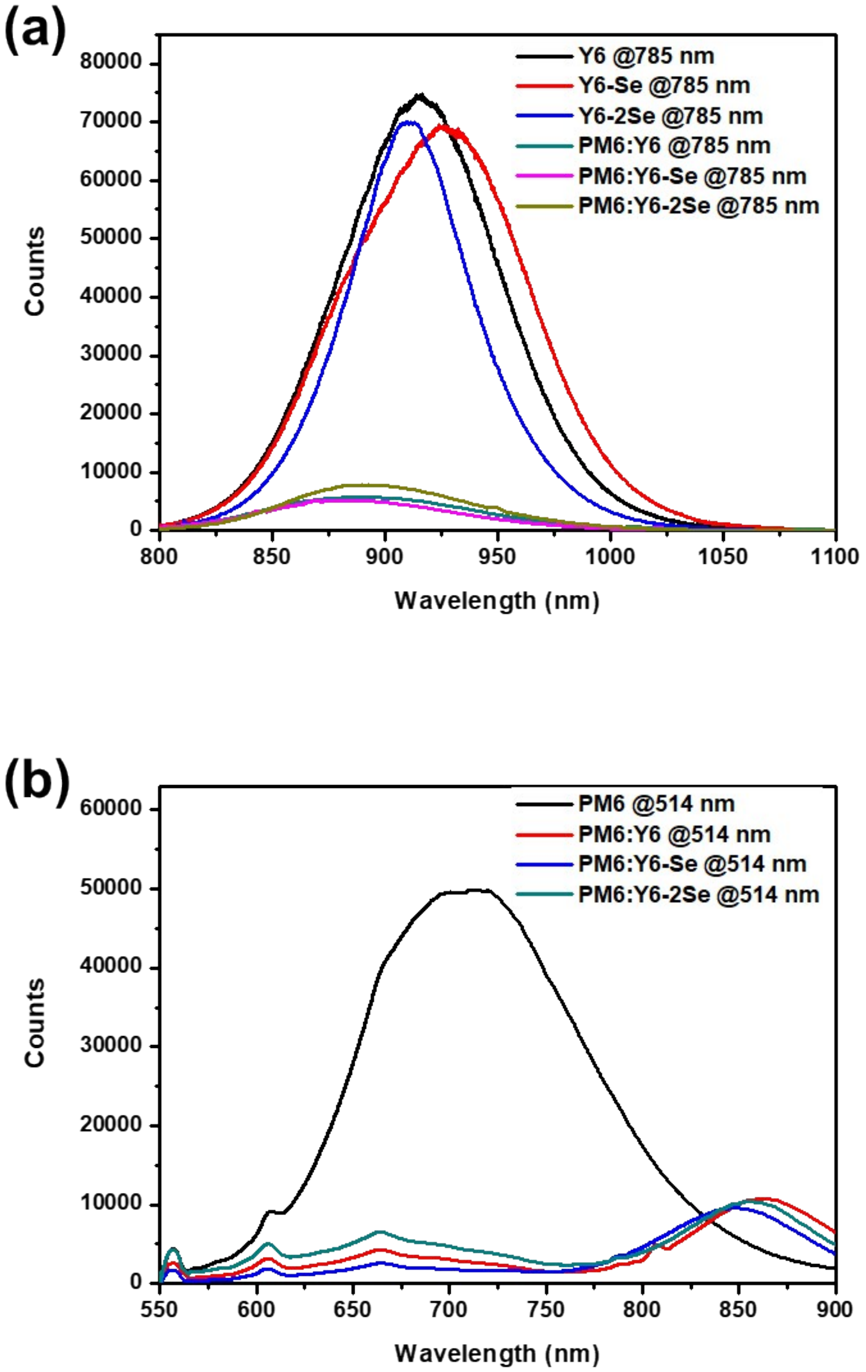


Figure S4. Photoluminescence quenching experiment of (a) the pristine Y6 film and PM6: Y6 blend films excited at 785 nm; the pristine Y6-Se film and PM6: Y6-Se blend films excited at 785 nm; the pristine Y6-2Se film and PM6: Y6-2Se blend films excited at 785 nm (b) the pristine PM6 film, the PM6: Y6, PM6: Y6-Se and PM6: Y6-2Se blend films excited at 514 nm.

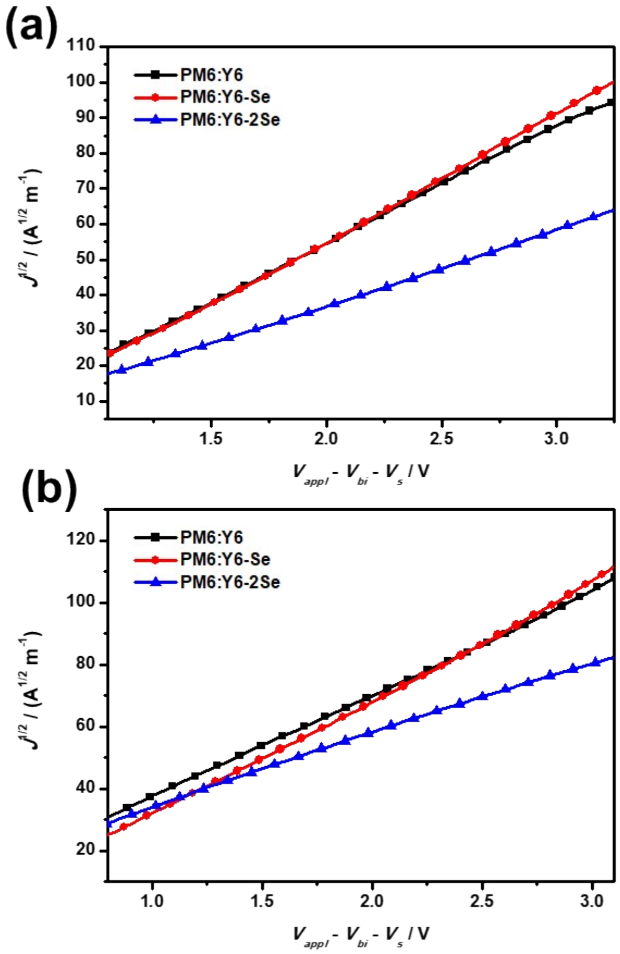


Figure S5. $J^{1/2}$~V characteristics of (a) hole-only devices and (b) electron-only devices of the PM6: Y6, PM6: Y6-Se and PM6: Y6-2Se films.

Table S2. Photovoltaic performance parameters of PM6:Y6-Se at different D/A ratios.

D:A Ratio （*w/w*）	V_{OC} **(V)**	J_{SC} **(mA/cm^2)**	**FF (%)**	**PCE (%)**
1 : 1	0.82	24.74	0.74	15.15
1 : 1.2	0.82	25.99	0.75	16.02
1 : 1.4	0.82	25.19	0.72	14.92

Table S3. Photovoltaic performance parameters of PM6:Y6-2Se at different D/A ratios.

D:A Ratio （*w/w*）	V_{OC} **(V)**	J_{SC} **(mA/cm^2)**	**FF (%)**	**PCE (%)**
1 : 1	0.84	23.56	0.72	14.35
1 : 1.2	0.83	24.65	0.72	14.94
1 : 1.4	0.84	24.39	0.72	14.66

Table S4. Photovoltaic performance parameters of PM6:Y6-Se at 1:1.2 D/A ratios with different contents of additive.

Additive CN (%)	V_{OC} **(V)**	J_{SC} **(mA/cm^2)**	**FF (%)**	**PCE (%)**
0 CN	0.82	25.50	0.65	13.70
0.2 CN	0.82	25.21	0.70	14.64
0.5 CN	0.82	25.99	0.75	16.02
0.7 CN	0.81	18.34	0.67	9.94

Table S5. Photovoltaic performance parameters of PM6:Y6-2Se at 1:1.2 D/A ratios with different contents of additive.

Additive CN (%)	V_{OC} **(V)**	J_{SC} **(mA/cm^2)**	**FF (%)**	**PCE (%)**
0 CN	0.84	23.88	0.69	13.85
0.2 CN	0.84	24.40	0.71	14.51
0.5 CN	0.84	24.65	0.72	14.94
0.7 CN	0.84	23.67	0.67	13.44

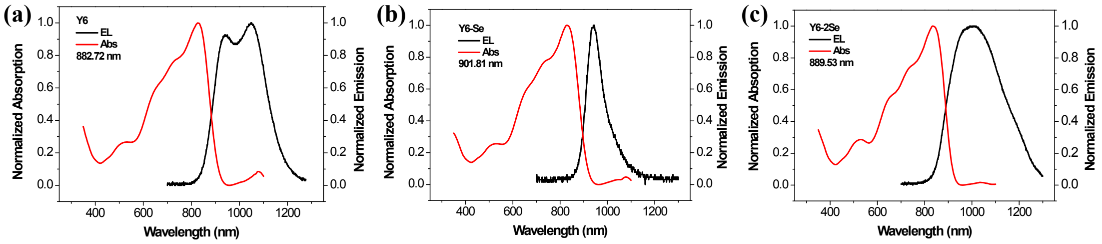


Figure S6. (a-c) Normalized electroluminescence (EL) and Absorption (Abs) spectra of Y6, Y6-Se and Y6-2Se for accurate bandgap calculation.

Table S6. Detailed V_{loss} parameters of the devices based on Y6, Y6-Se and Y6-2Se.

Device	E_{gap} **[eV]**	V_{OC} **[eV]**	V_{loss} **[eV]**	$V_{oc}^{SQ\,a}$ **[eV]**	ΔE_1 **[eV]**	$V_{oc}^{rad\,b}$ **[eV]**	$\Delta E_2\,c$ **[eV]**	$\Delta E_{3\mathrm{d}}$ **[eV]**
PM6:Y6	1.405	0.83	0.575	1.133	0.254	1.068	0.065	0.238
PM6:Y6-Se	1.375	0.82	0.555	1.119	0.256	1.036	0.083	0.216
PM6:Y6-2Se	1.393	0.83	0.563	1.139	0.254	1.065	0.074	0.235

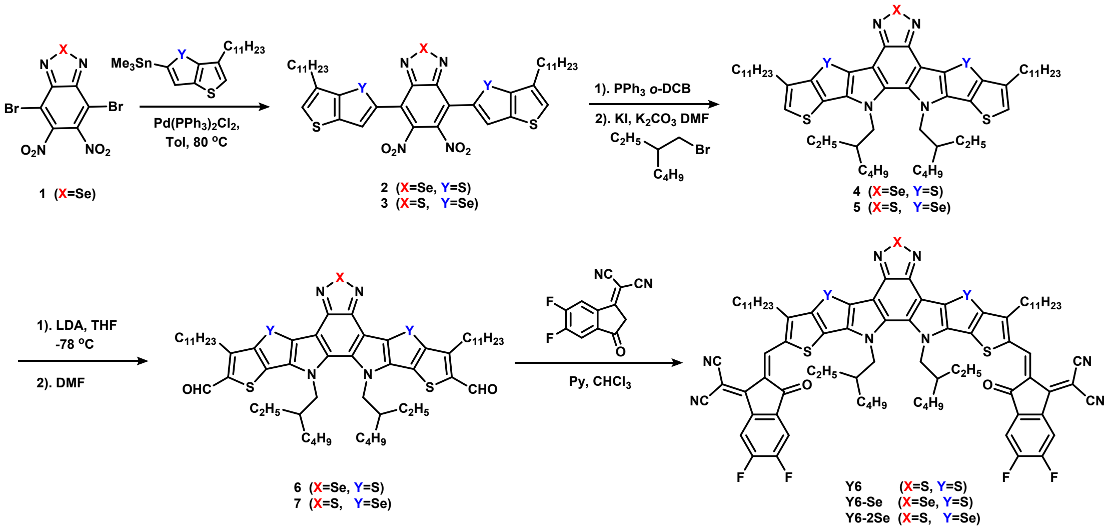
[a] V_{oc}^{SQ} : Schokley-Queisser limit to V_{OC}.

[b] V_{oc}^{rad} : radiative limit to V_{OC}, measured using $\mathrm{EQE}_{\mathrm{EL}}$.

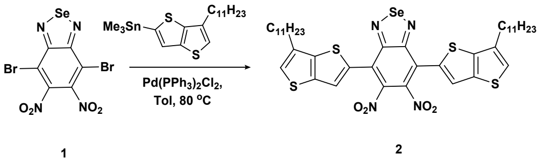
[c] ΔE_2 (ΔV_{oc}^{rad}): voltage losses due to non-ideal absorption (it was calculated from EL and FTPS measurements).

[d] ΔE_3 ($\Delta V_{oc}^{non-rad}$): voltage losses due to non-radiative recombination only.

Synthesis of Y6-Se and Y6-2Se



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

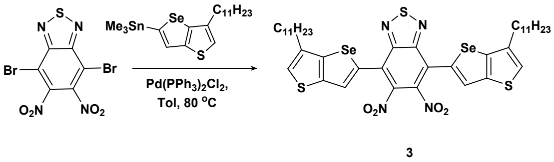


To a mixture of 4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]selenadiazole (**1**, 500 mg, 1.16 mmol), trimethyl(3-undecylthiopheno[3,2-b]thiophen-5-yl)stannane (1.46 g, 2.88 mmol), $Pd_2(dba)_3$ (60 mg, 0.065 mmol) and P(*o*-tol)$_3$ (160 mg, 0.523 mmol) was added anhydrous toluene (10 mL) under N_2. The reaction mixture was stirred for 12 h at 120 ^{o}C. Then, the reaction mixture was cooled and poured into an aqueous potassium fluoride. The mixture was extracted with diethyl ether for three times. 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:dichloromethane = 1:1) to get the product as dark red solid (713 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.16 (s, 2H), 2.77 (t, J = 7.7 Hz, 4H), 1.82-1.75 (m, 4H), 1.41-1.27 (m, 32H), 0.88 (t, J = 6.8 Hz, 6H).

MALDI-TOF MS: cacld for $C_{40}H_{50}N_4O_4S_4Se$ (M+), 858.1880; found, 858.1894.

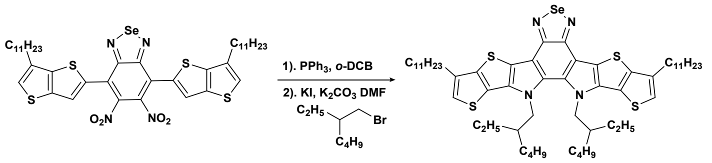
Synthesis of **5,6-dinitro-4,7-bis(3-undecylselenopheno[3,2-b]thiophen-5-yl)benzo[c][1,2,5]thiadiazole (3)**



To a mixture of 4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole (500 mg, 1.31 mmol), trimethyl(3-undecylselenopheno[3,2-b]thiophen-5-yl)stannane (1.46 g, 2.88 mmol), $Pd_2(dba)_3$ (60 mg, 0.065 mmol) and P(*o*-tol)$_3$ (160 mg, 0.523 mmol) was added anhydrous toluene (10 mL) under N_2. The reaction mixture was stirred for 12 h at 120 °C. Then, the reaction mixture was cooled and poured into an aqueous potassium fluoride. The mixture was extracted with diethyl ether for three times. 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:dichloromethane = 1:1) to get the product as dark red solid (973 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.18 (s, 2H), 2.79 (t, J = 7.7 Hz, 4H), 1.85-1.75 (m, 4H), 1.47-1.25 (m, 32H), 0.91 (t, J = 6.8 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.01, 145.78, 140.16, 138.02, 132.49, 126.28, 124.76, 122.43, 31.93, 30.70, 29.68, 29.65, 29.60, 29.40, 29.37, 28.73, 22.71, 14.14.
MALDI-TOF MS: cacld for $C_{40}H_{50}N_4O_4S_3Se_2$ (M+), 906.1325; found, 906.1384.

Synthesis of **12,13-bis(2-ethylhexyl)-3,9-diundecyl-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 (4)**



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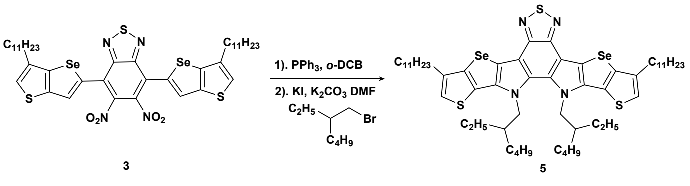
Compound **2** (500 mg, 0.58 mmol) and triphenylphosphine (1.53 g, 5.83 mmol) were dissolved in anhydrous 1,2-dichlorobenzene (*o*-DCB, 3 mL) under argon and the mixture was stirred at 180 °C overnight. After cooling to room temperature, methanol was added and the mixture was filtered under reduced pressure to yield an orange solid. Subsequently, the orange intermediate was then mixed with K_2CO_3 (483 mg, 3.49 mmol), KI (34 mg, 0.58 mmol), 2-ethylhexyl (894 mg, 4.65 mmol) and anhydrous DMF (10 mL) were mixed under argon and stirred at 80 °C overnight. The mixture was extracted with diethyl ether for three times. 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:dichloromethane = 1:1) to give an orange solid (354 mg, 60% yield, two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 2H), 4.63-4.53 (m, 4H), 2.82 (t, J = 7.6 Hz, 4H), 2.09-2.06 (m, 2H), 1.90-1.82 (m, 4H), 1.46-1.28 (m, 36H), 1.13-0.87 (m, 18H), 0.69-0.62 (m, 12H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.77, 142.00, 136.86, 136.64, 131.49, 123.61, 123.48, 119.07, 113.34, 54.86, 39.93, 31.96, 30.33, 29.71, 29.67, 29.65, 29.54, 29.50, 29.39, 28.86, 27.75, 23.13, 23,08, 22.79, 22.73, 14.15, 13.75, 10.09, 10.05.
MALDI-TOF MS: cacld for $C_{56}H_{82}N_4S_4Se$ (M+), 1018.4588; found, 1018.4545.

Synthesis of **12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-**

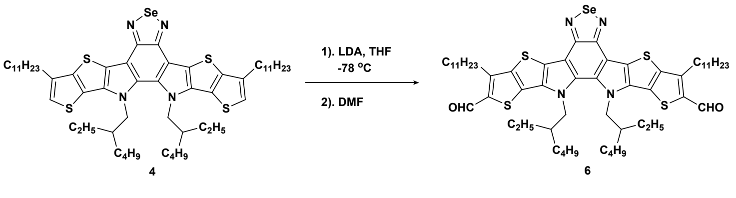
[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5']selenopheno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]selenopheno[3,2-b]indole (5)



Compound **3** (500 mg, 0.55 mmol) and triphenylphosphine (1.45 g, 5.52 mmol) were dissolved in anhydrous 1,2-dichlorobenzene (*o*-DCB, 3 mL) under argon and the mixture was stirred at 180 °C overnight. After cooling to room temperature, methanol was added and the mixture was filtered under reduced pressure to yield an orange solid. Subsequently, the orange intermediate was then mixed with K_2CO_3 (458 mg, 3.31 mmol), KI (32 mg, 0.55 mmol), 2-ethylhexyl (848 mg, 4.41 mmol) and anhydrous DMF (10 mL) were mixed under argon and stirred at 80 °C overnight. The mixture was extracted with diethyl ether for three times. 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:dichloromethane = 1:1) to give an orange solid (377 mg, 64% yield, two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 2H), 4.75-4.58 (m, 4H), 2.84 (t, J = 7.6 Hz, 4H), 2.14-1.99 (m, 2H), 1.95-1.78 (m, 4H), 1.51-1.25 (m, 36H), 1.16-0.86 (m, 18H), 0.67-0.62 (m, 12H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.11, 140.28, 139.19, 137.88, 131.01, 125.27, 119.60, 118.46, 114.14, 54.85, 39.95, 31.95, 30.33, 29.71, 29.67, 29.62, 29.50, 29.39, 28.96, 27.63, 23.06, 22.78, 22.73, 14.15, 13.74, 10.04.
MALDI-TOF MS: cacld for $C_{56}H_{82}N_4S_3Se_2$ (M+), 1067.4105; found, 1067.4094.

Synthesis of **12,13-bis(2-ethylhexyl)-3-undecyl-9-(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 (6)**



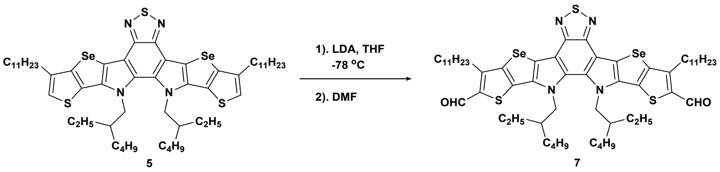
To a solution of compound **4** (200 mg, 0.196 mmol) in THF (10 mL), 2.0 M lithium diisopropylamide in hexane (0.20 mL, 0.400 mmol) was added dropwise slowly at −78 °C under N_2. The mixture was stirred at −78 °C for 1 h, and then anhydrous DMF (1.0 mL) was added. The mixture was stirred overnight at room temperature. Brine was added and the mixture was extracted with ethyl acetate for three times. 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 (160 mg, 75%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 10.13 (s, 2H), 4.64-4.54 (m, 4H), 3.18 (t, *J* = 7.6 Hz, 4H), 2.05-2.00 (m, *J* = 10.7, 4.7 Hz, 2H), 1.95-1.87 (m, 4H), 1.48-1.25 (m, 36H), 1.11-0.84 (m, 18H), 0.70-0.60 (m, 12H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 181.76, 153.32, 146.90, 143.13, 136.85, 136.43, 132.79, 129.63, 128.08, 114.28, 55.10, 40.13, 31.91, 31.60, 30.33, 29.65, 29.60, 29.52, 29.38, 29.33, 28.17, 27.59, 23.08, 22.72, 22.69, 14.13, 13.69, 10.11, 10.08.

MALDI-TOF MS: cacld for $C_{58}H_{82}N_4O_2S_4Se$ (M+), 1074.4486; found, 1074.4462.

Synthesis of **12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5']selenopheno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]selenopheno[3,2-b]indole-2,10-dicarbaldehyde (7)**



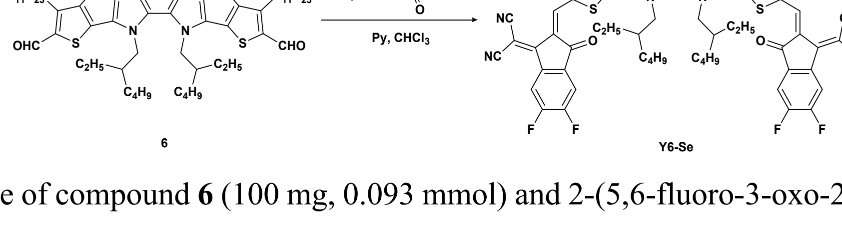
To a solution of compound **5** (200 mg, 0.188 mmol) in THF (10 mL), 2.0 M lithium diisopropylamide in hexane (0.20 mL, 0.400 mmol) was added dropwise slowly at −78 °C under N$_2$. The mixture was stirred at −78 °C for 1 h, and then anhydrous DMF (1.0 mL) was added. The mixture was stirred overnight at room temperature. Brine was added and the mixture was extracted with ethyl acetate for three times. The combined organic phase was washed with water followed by brine. Then the solution was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: *n*-hexane: CH$_2$Cl$_2$= 1:4, v/v) to get the product as orange solid (179 mg, 85%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 10.15 (s, 2H), 4.82-4.62 (m, 4H), 3.18 (t, *J* = 7.6 Hz, 4H), 2.04 (m, *J* = 10.7, 4.7 Hz, 2H), 1.97-1.85 (m, 4H), 1.54-1.21 (m, 36H), 1.14-0.83 (m, 18H), 0.75-0.58 (m, 12H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 181.56, 148.96, 147.90, 141.42, 137.68, 136.04, 132.18, 131.83, 124.51, 115.17, 55.08, 40.14, 31.91, 30.48, 29.63, 29.61, 29.51, 29.47, 29.39, 29.33, 28.86, 27.46, 23.04, 22.72, 22.69, 14.13, 13.69, 10.14, 10.08.

MALDI-TOF MS: cacld for $C_{58}H_{82}N_4O_2S_3Se_2$ (M+), 1122.3930; found, 1122.3947.

Synthesis of **Y6-Se**



A mixture of compound **6** (100 mg, 0.093 mmol) and 2-(5,6-fluoro-3-oxo-2,3-dihydro-

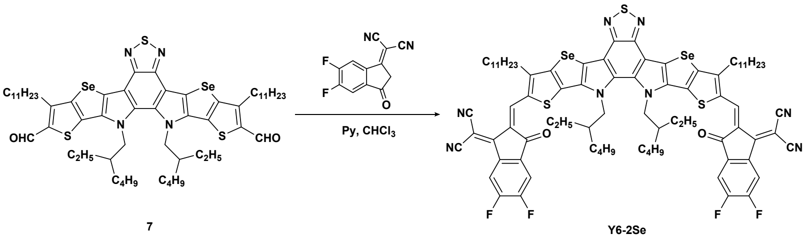
1*H*-inden-1-ylidene)malononitrile (108 mg, 0.465 mmol) in chloroform (10 mL) was degassed before pyridine (1 mL) was added. The reaction was kept at 65 °C under N_2 for 1h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (stationary phase: silica gel; eluent: dichloromethane) to get the product as dark blue solid (100 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 2H), 8.53 (dd, *J* = 9.9, 6.5 Hz, 2H), 7.70 (T, *J* = 7.5 Hz, 2H), 4.82-4.65 (m, 4H), 3.20 (t, *J* = 7.8 Hz, 4H), 2.20-2.06 (m, 2H), 1.92-1.77 (m, 4H), 1.52-1.19 (m, 36H), 1.13-0.83 (m, 18H), 0.81-0.66 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 185.81, 157.43, 155.34, 153.60, 152.89, 152.43, 145.19, 136.68, 136.38, 134.47, 133.82, 132.62, 131.61, 119.31, 115.49, 114.57, 114.42, 112.07, 68.60, 50.20, 37.47, 35.65, 32.85, 31.94, 30.83, 29.85, 29.66, 29.65, 29.54, 29.42, 29.36, 29.00, 25.93, 23.10, 22.71, 14.13, 10.89.

MALDI-TOF MS: cacld for $C_{82}H_{86}F_4N_8O_2S_4Se$ (M+), 1498.4858; found, 1498.4873.

Synthesis of **Y6-2Se**



A mixture of compound **7** (100 mg, 0.079 mmol) and 2-(5,6-fluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (92 mg, 0.395 mmol) in chloroform (10 mL) was degassed before pyridine (1 mL) was added. The reaction was kept at 65 °C under N_2 for 1h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (stationary phase: silica gel; eluent: dichloromethane) to get the product as dark blue solid (92 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 2H), 8.53 (dd, *J* = 10.0, 6.4 Hz, 2H), 7.69 (T, *J* = 7.5 Hz, 2H), 4.87-4.80 (m, 4H), 3.16 (t, *J* = 7.8 Hz, 4H), 2.13-2.06 (m, 2H), 1.89-1.81 (m, 4H), 1.51-1.18 (m, 36H), 1.12-1.02 (m, 12H), 0.88-0.73 (m, 12H), 0.71-0.66 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.12, 158.75, 156.17, 155.68, 155.55, 153.11, 153.05, 152.98, 152.91, 147.92, 143.37, 138.73, 138.53, 136.67, 136.59, 134.89, 134.43, 133.54, 132.44, 128.31, 119.78, 116.48, 115.01, 114.78, 114.59, 112.51, 112.32, 68.48, 55.64, 40.53, 31.91, 31.28, 30.72, 29.82, 29.69, 29.64, 29.62, 29.50, 29.44, 29.34, 27.69, 23.27, 23.23, 22.90, 22.69, 14.12, 13.80, 10.26, 10.18

MALDI-TOF MS: cacld for $C_{82}H_{86}F_4N_8O_2S_3Se_2$ (M+), 1546.4302; found, 1546.4382.

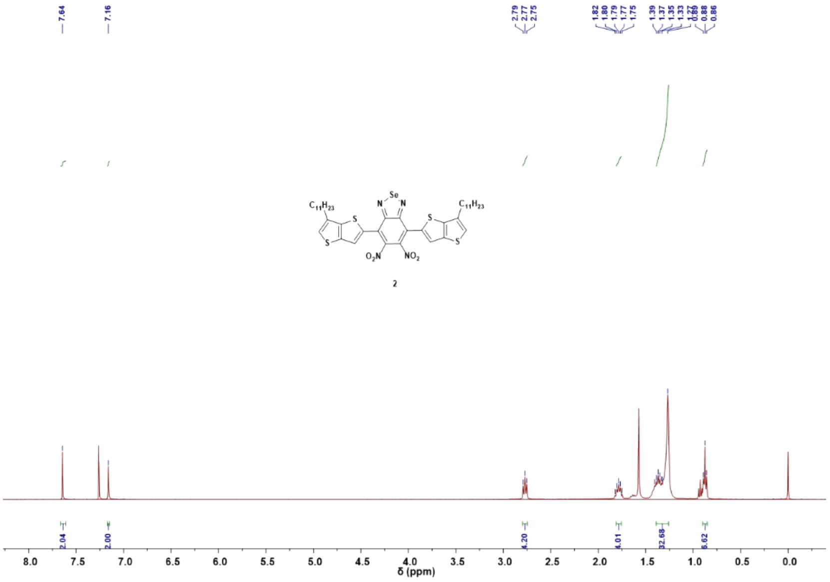


Figure S7. ^{1}HNMR spectrum of compound **2** (400 MHz, $CDCl_3$).

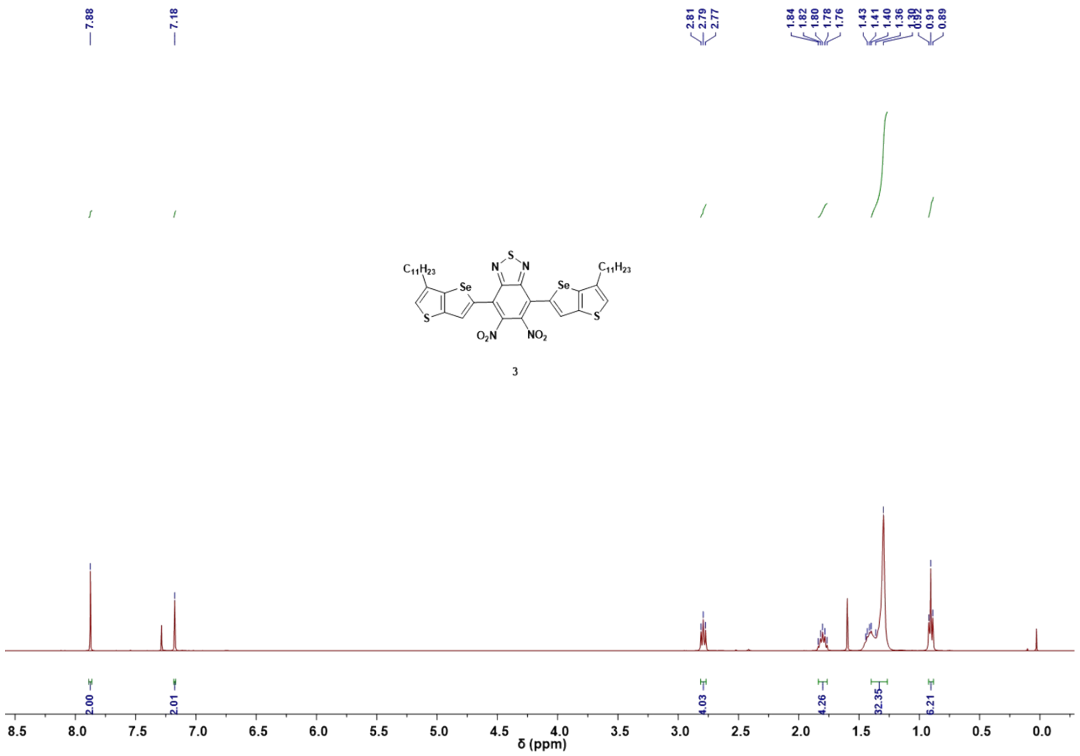


Figure S8. ^{1}HNMR spectrum of compound **3** (400 MHz, $CDCl_3$).

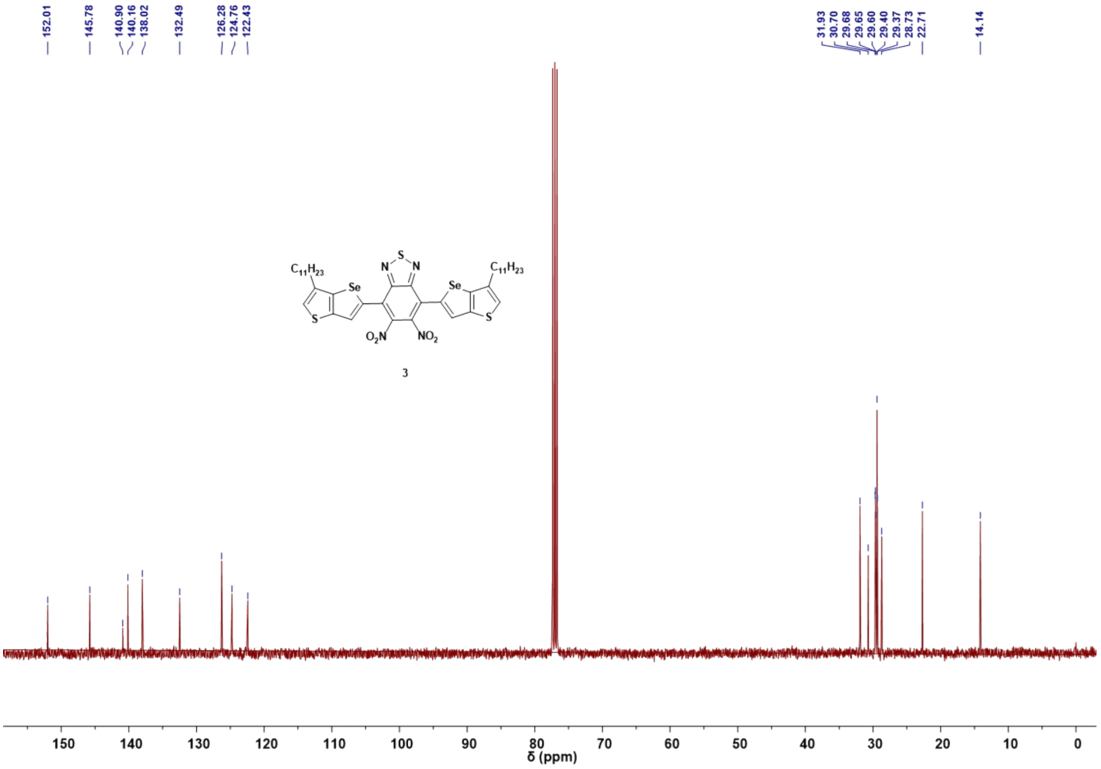


Figure S9. ^{13}CNMR spectrum of compound **3** (100 MHz, $CDCl_3$).

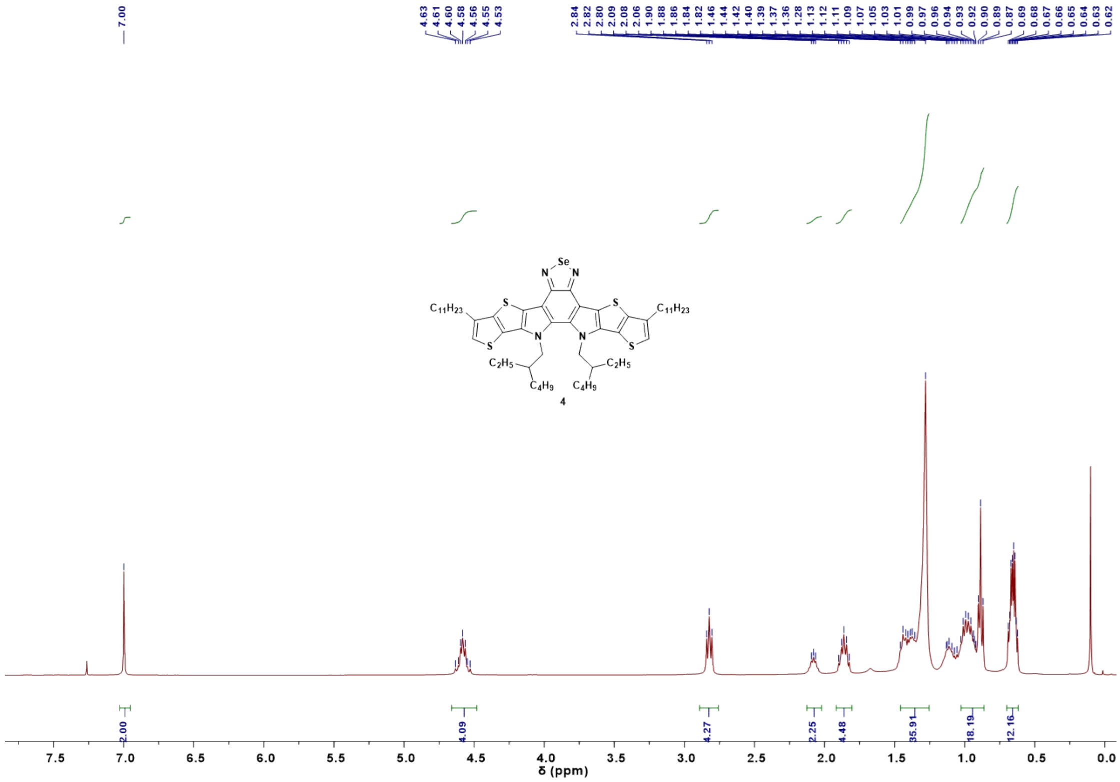


Figure S10. ^{1}HNMR spectrum of compound **4** (400 MHz, $CDCl_3$).

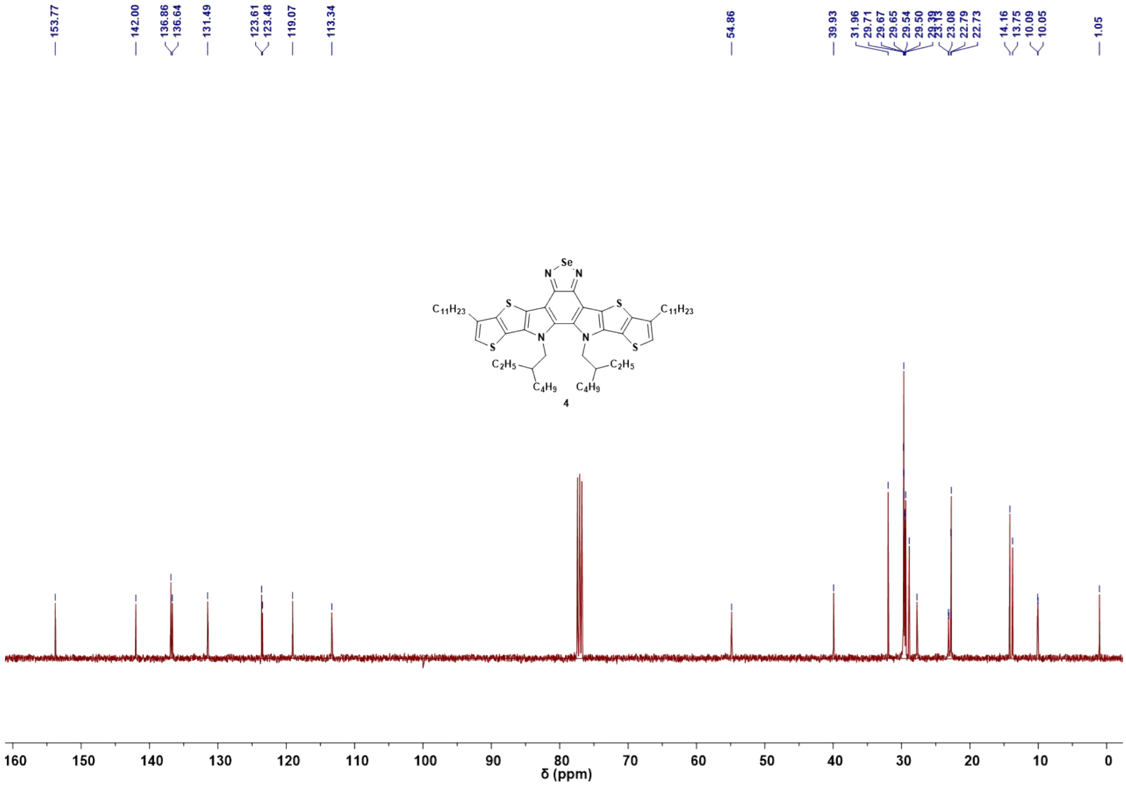


Figure S11. ^{13}CNMR spectrum of compound **4** (100 MHz, $CDCl_3$).

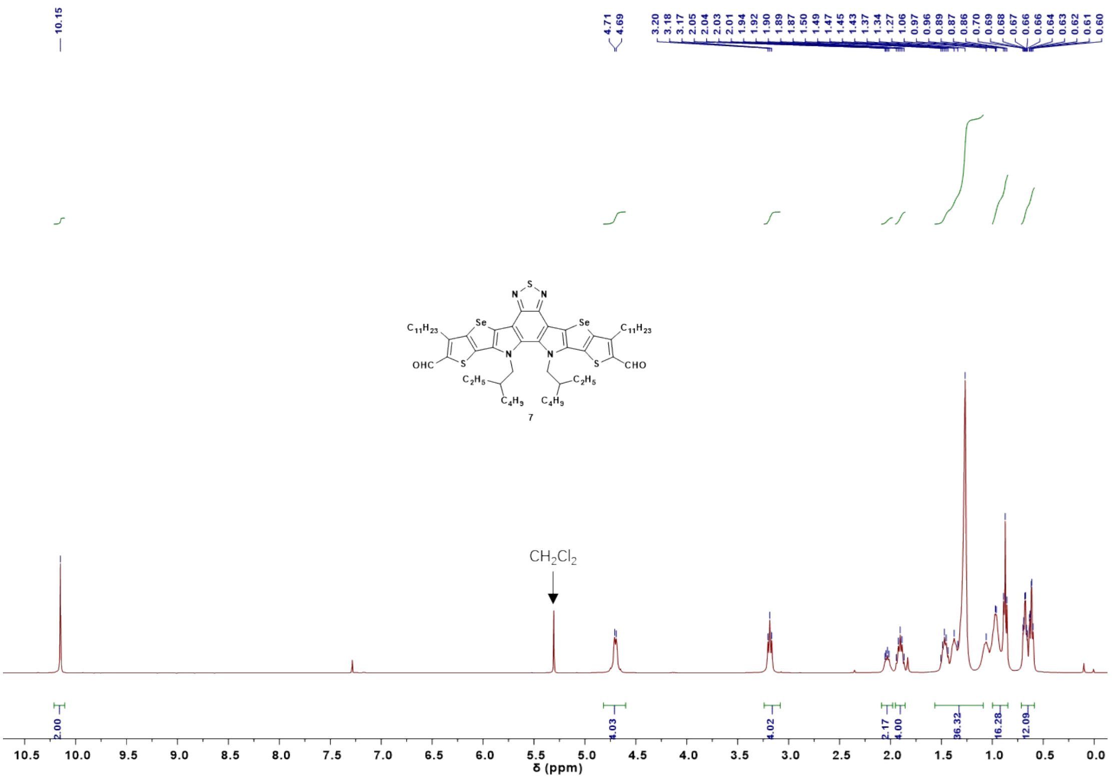


Figure S12. ^{1}HNMR spectrum of compound **5** (400 MHz, $CDCl_3$).

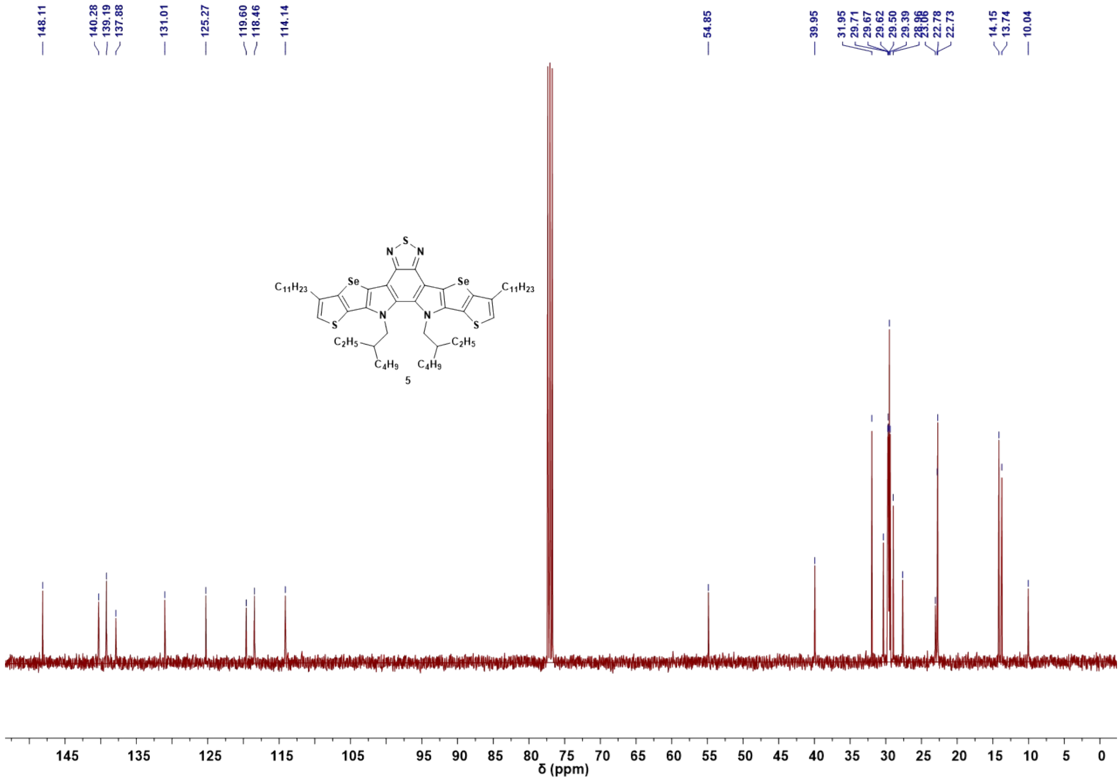


Figure S13. ^{13}CNMR spectrum of compound **5** (100 MHz, $CDCl_3$).

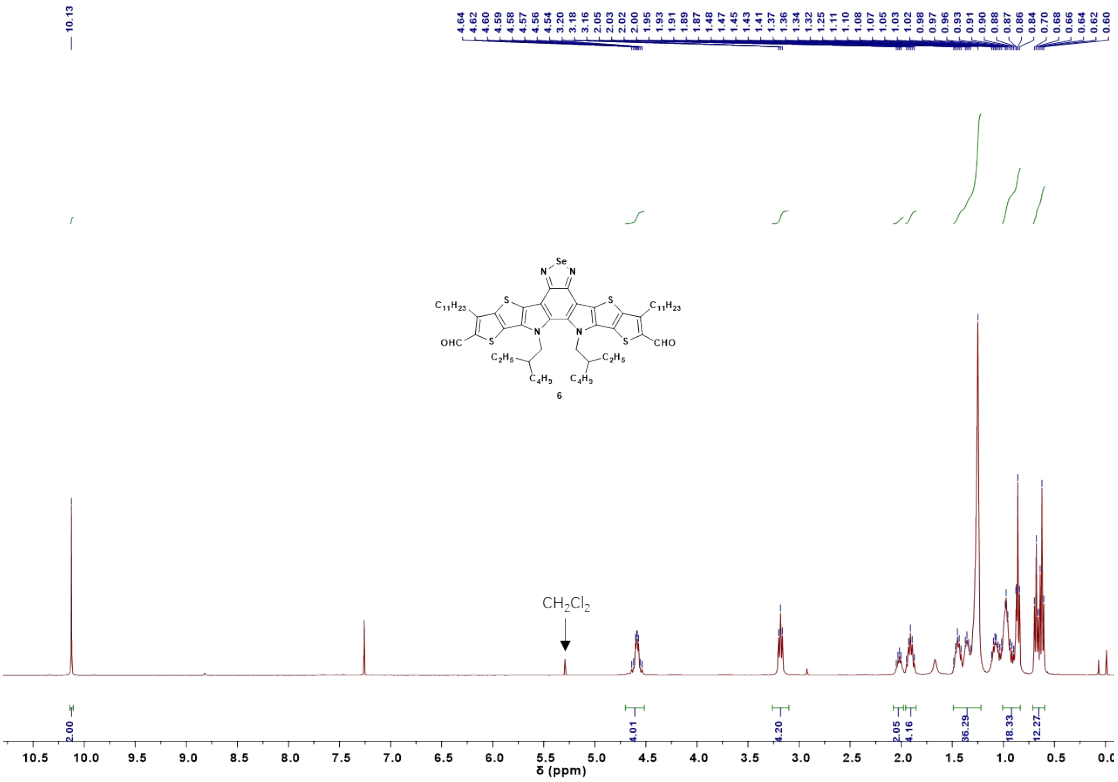


Figure S14. ^{1}HNMR spectrum of compound **6** (400 MHz, $CDCl_3$).

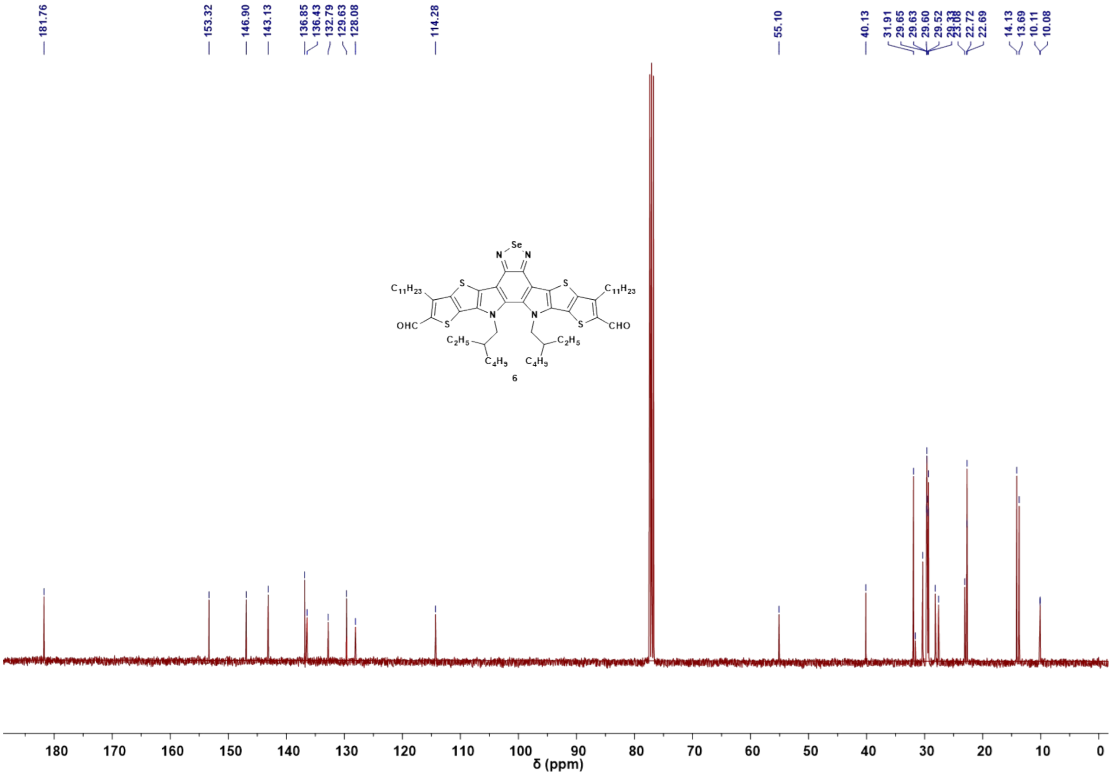


Figure S15. ^{13}CNMR spectrum of compound **6** (100 MHz, $CDCl_3$).

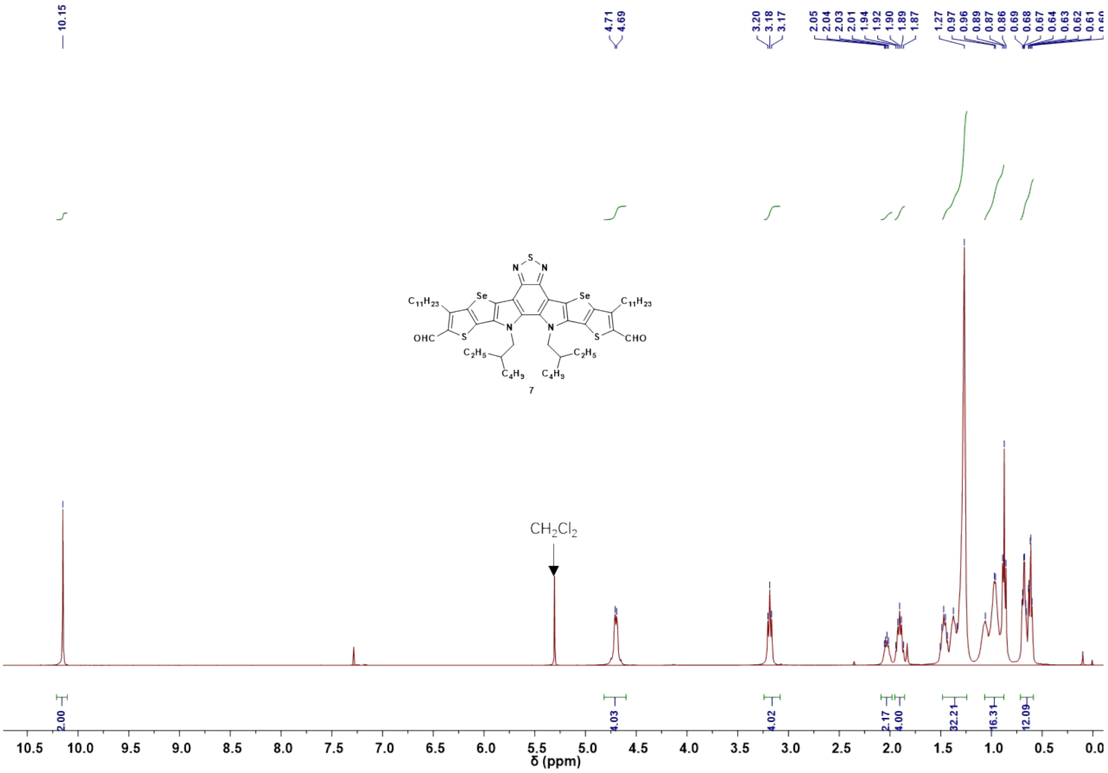


Figure S16. ^{1}HNMR spectrum of compound **7** (400 MHz, $CDCl_3$).

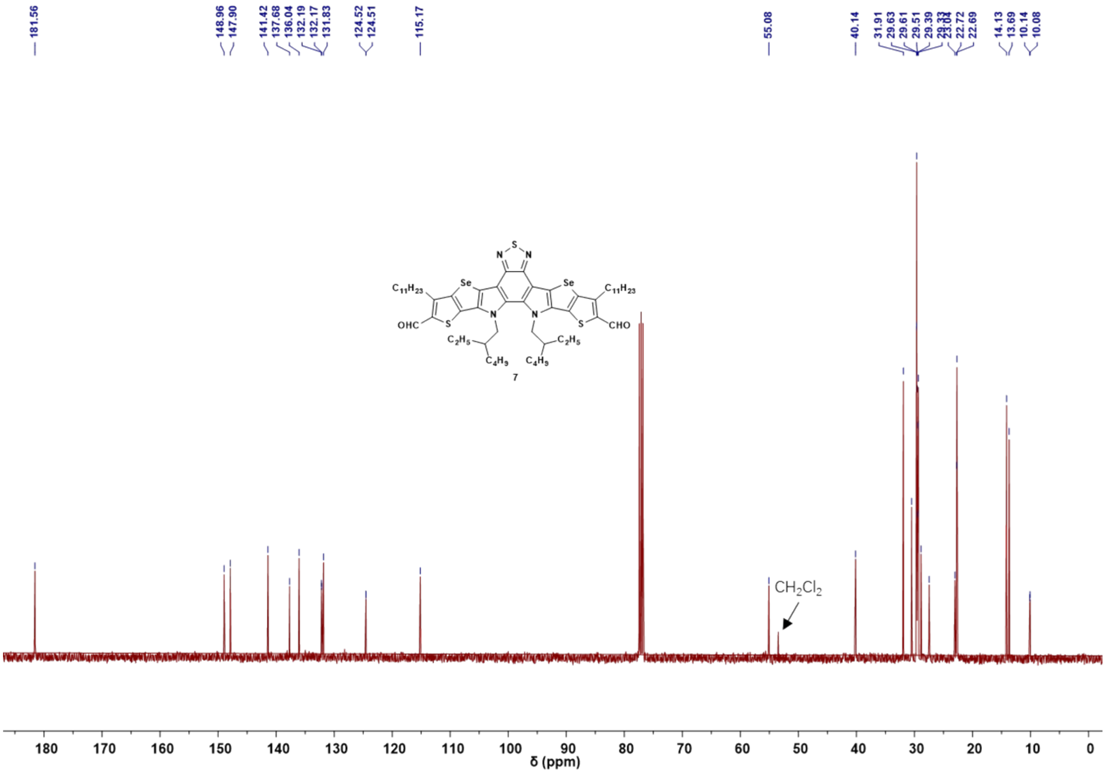


Figure S17. ^{13}CNMR spectrum of compound **7** (100 MHz, $CDCl_3$).

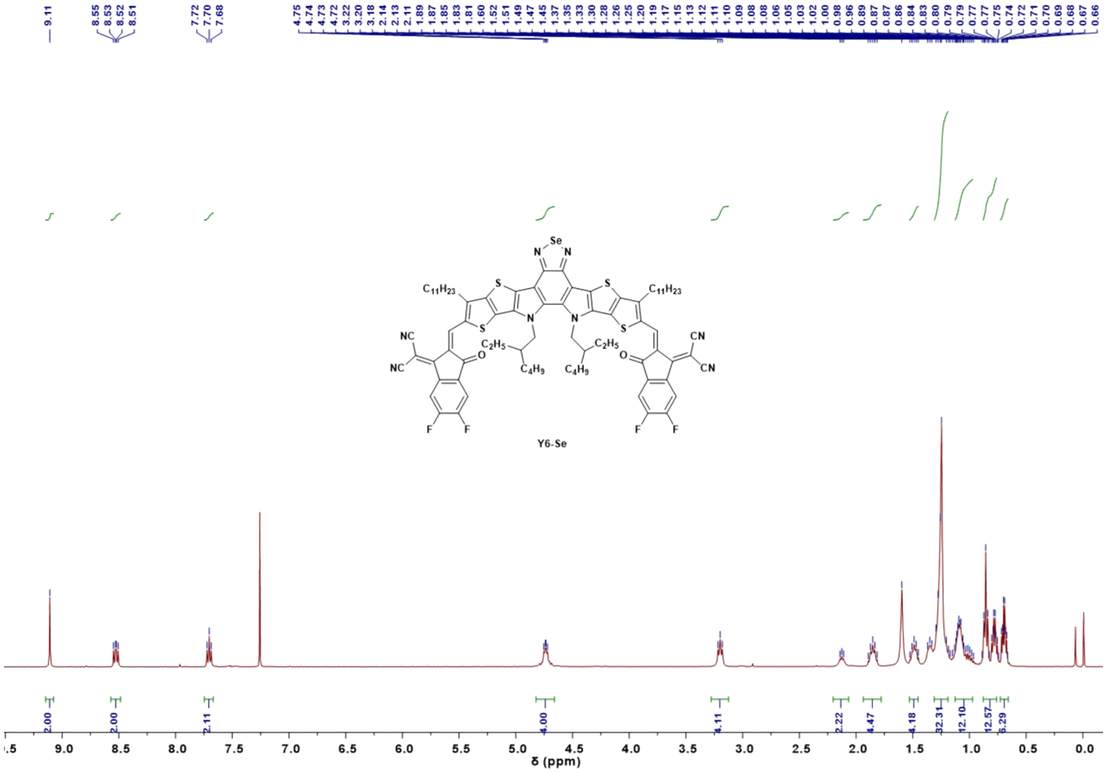


Figure S18. ^{1}HNMR spectrum of **Y6-Se** (400 MHz, $CDCl_3$).

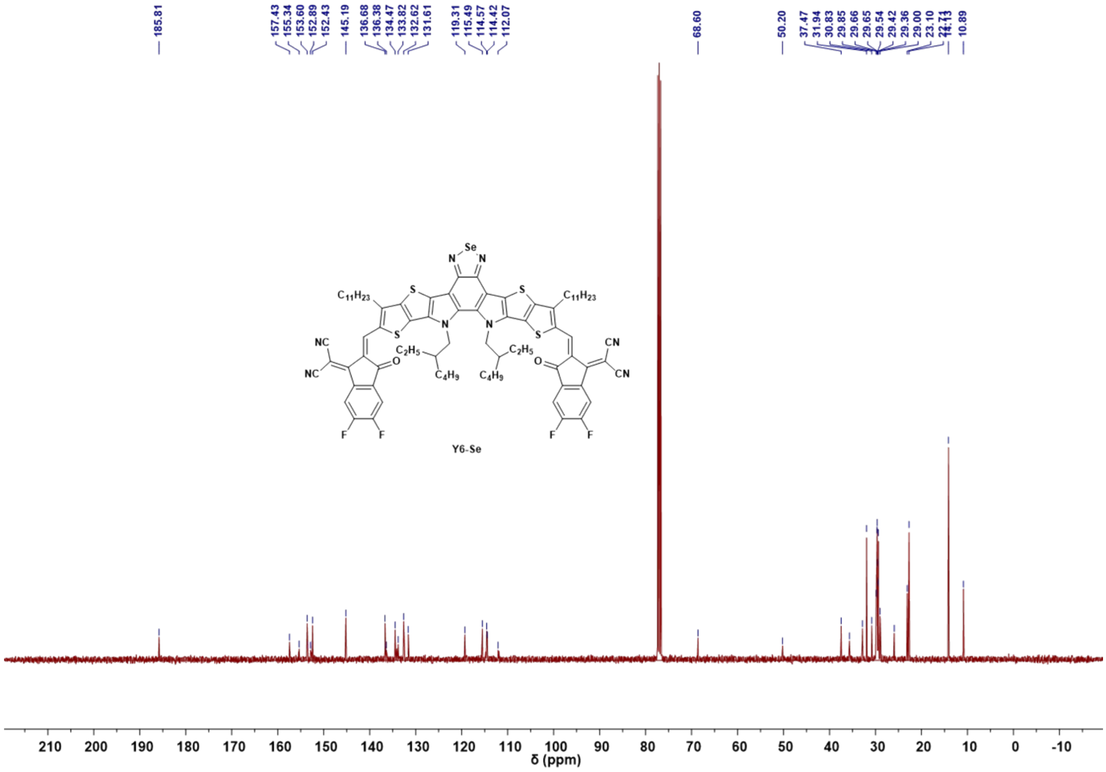


Figure S19. ^{13}CNMR spectrum of **Y6-Se** (100 MHz, $CDCl_3$).

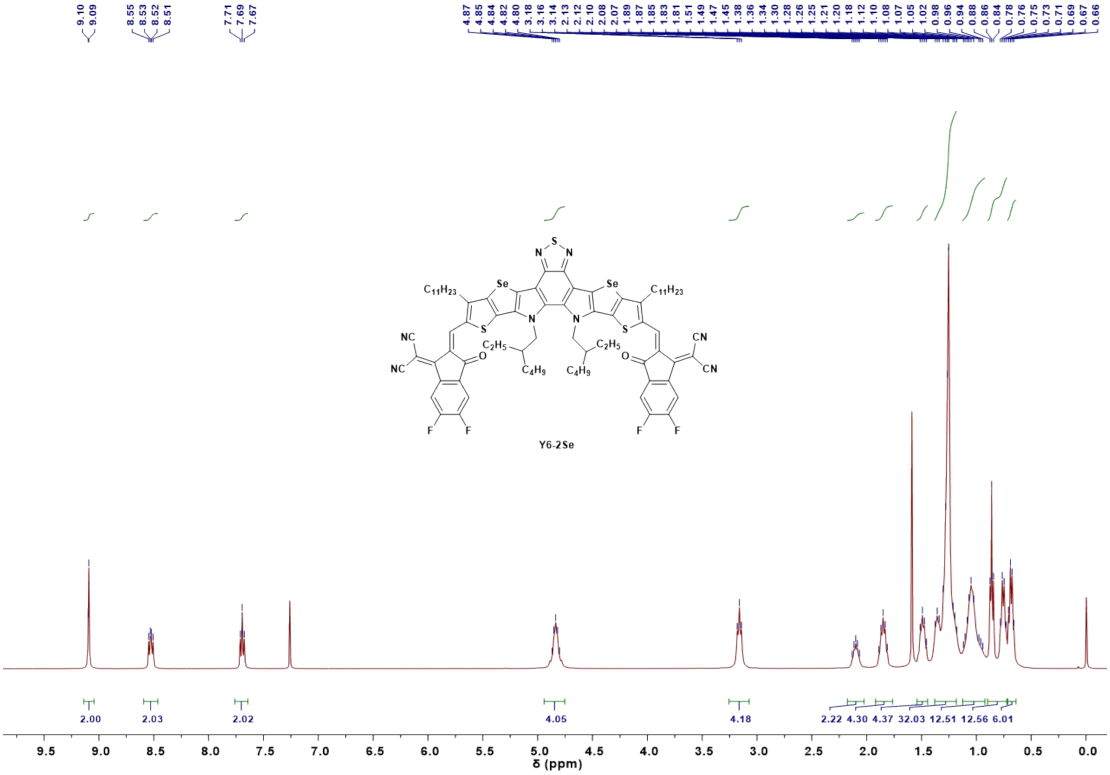


Figure S20. ^{1}HNMR spectrum of **Y6-2Se** (400 MHz, $CDCl_3$).

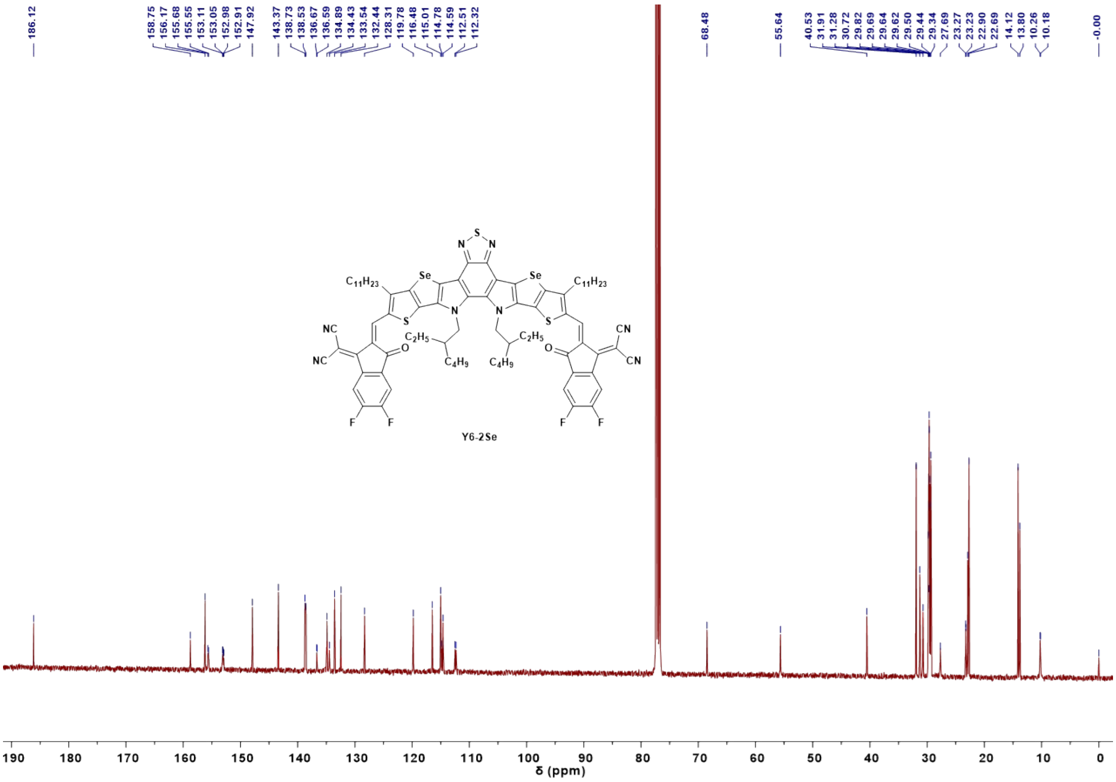


Figure S21. ^{13}CNMR spectrum of **Y6-2Se** (100 MHz, $CDCl_3$).

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