

Supplementary Information

High-yielding Pd₂(dba)₃·C₆H₆-based Four-fold Sonogashira Coupling for Selenophene-conjugated Magnesium Tetraethynylporphyrin for Organic Solar Cells

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1. Experimental Section

1.1. General

Materials were purchased from Tokyo Kasei (TCI) Co., Sigma-Aldrich Inc., and other commercial suppliers and used after appropriate purification. Anhydrous solvents (stabilizer-free) were purchased from Sigma-Aldrich Chemical and J&K Chemical. Compound **3** and **4** were synthesized as according to previous literature.¹⁻² Compounds **Br-DPP**, **Br-Se-DPP** were prepared according to previous papers.²⁻³ Compounds **DPP-Th**, **Se-DPP-Th**, **Br-DPP-Th**, **Br-Se-DPP-Th** were synthesized according to previously reported procedures.⁴ All reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under nitrogen or argon. All reactions were monitored by thin layer chromatography (TLC, eluent, ethyl acetate/CH₂Cl₂/ Petroleum ether). The NMR spectra were measured on a Bruker US400 for ¹H NMR and ¹³C NMR, respectively, reported in parts per million from tetramethylsilane. High-resolution mass spectra were acquired by MALDI using a time-of-flight mass analyzer on Bruker Ultra exTOF/TOF spectrometer. UV-vis absorption was recorded on Shimadzu UV-3600PLUS. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed using a HOKUTO DENKO HZ-5000 voltammetric analyzer. All CV measurements were carried out in a one-compartment cell under argon gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and an Ag/Ag⁺ reference electrode. The solvent with supporting electrolyte was a 0.1 mol L⁻¹ acetonitrile solution of tetrabutylammonium hexafluorophosphate (TBAPF₆). Current–voltage (*J–V*) characteristics were measured using a source meter (Keithley 2400) under sun AM 1.5G simulated sunlight irradiation (100 mW/cm²) from a solar simulator (EMS-35AAA, Ushio Spax Inc.), which was calibrated using a silicon diode (BS-520BK, Bunkoukeiki).

Mobility Measurements:

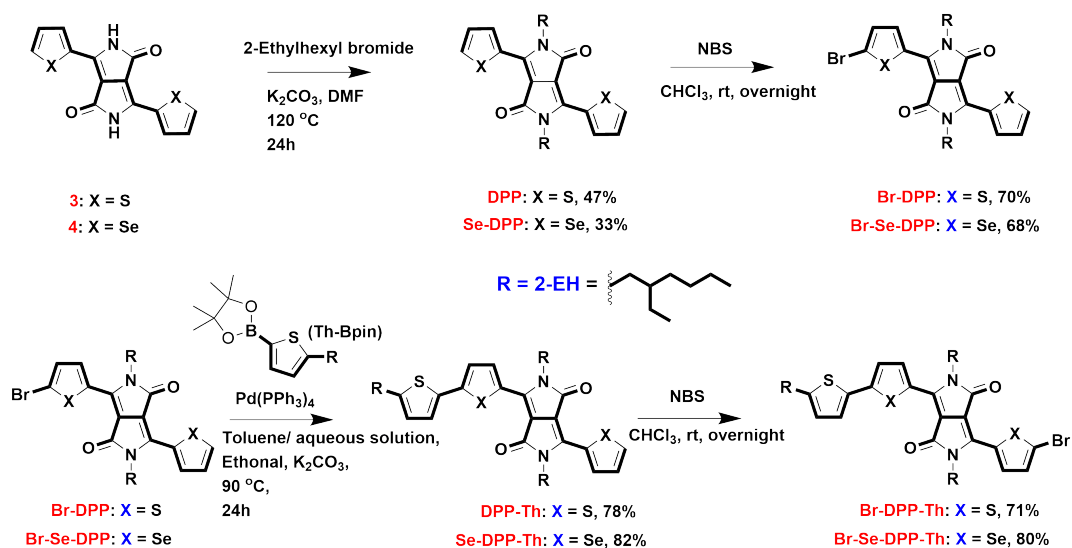
Hole-only and electron-only devices were fabricated by using hole-only devices with a configuration of ITO/PEDOT:PSS/**2a** and **2c**:PC₇₁BM and PC₆₁BM/MoO₃/Ag and electron-only devices with a configuration of ITO/ZnO/ **2a** and **2c**: PC₇₁BM and PC₆₁BM/Ca/Al, respectively. The mobilities were extracted by fitting the current density–voltage curves using space charge limited current (SCLC). The equation is as follows (Figure S11):

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

By the plots of $J^{0.5}$ vs V , hole and electron mobilities can be calculated.

Where J is the current, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, V is the effective voltage, and d is the thickness of the active layer.

1.2. Synthesis of the Starting Materials



Scheme S1. Synthetic routes of the starting materials.

1.3. Synthetic procedures

2,5-bis(2-ethylhexyl)-3-(5'-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DPP-Th). Th-Bpin (1.16g, 3.60 mmol), Br-DPP (0.72g, 1.20 mmol) were dissolved in toluene (40 mL), 2 M K₂CO₃ aqueous solution (15 mL), ethanol (5 mL) were added. The mixture was purged with argon for 30 min, then Pd(PPh₃)₄ (0.14g, 0.12 mmol) were added. The mixture was stirred at 100 °C for 12h under argon. The mixture was extracted with chloroform (30 mL × 3), washed with water (50 mL × 3) and brine (50 mL × 3), the combined organic layers were dried with anhydrous MgSO₄ and concentrated. Finally, the residue was purified with silica gel column by using ethyl acetate/petroleum ether (1/50) to afford compound **DPP-Th** as a purple solid (673 mg, 78% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.96 (d, *J* = 4.2 Hz, 2H, thiophene), 8.87 (d, *J* = 3.9 Hz, 2H, thiophene), 7.29–7.25 (m, 1H, thiophene), 7.24 (d, *J* = 4.1 Hz, 1H, thiophene), 7.15 (d, *J* = 3.6 Hz, 1H, thiophene), 6.73 (d, *J* = 3.6 Hz, 1H, thiophene), 4.04 (m, 4H, N-CH₂), 2.76 (d, *J* = 6.8 Hz, 2H, thiophene-CH₂), 2.00–1.77 (m, 1H, CH), 1.61 (m, 1H, CH), 1.40–1.24 (m, 24H, CH₂), 0.93–0.84 (m, 18H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 161.92, 161.65, 146.61, 143.78, 140.41, 139.58, 137.18, 135.10, 133.91, 130.30, 130.09, 128.49, 127.42, 126.54, 125.07, 124.09, 108.30, 107.92, 46.02, 41.60, 39.36, 39.21, 34.39, 32.50, 30.48, 30.34, 28.98, 28.68, 28.48, 25.65, 23.80, 23.68, 23.25, 23.20, 23.11, 14.25, 14.20, 14.15, 10.95, 10.68, 10.63.

3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(5'-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (Br-DPP-Th). DPP-Th (0.86 g, 1.20 mmol) and N-bromosuccinimide (0.22 g, 1.20 mmol) were dissolved in CHCl₃ (60 mL), then the solution was protected from light and stirred at room temperature for 24 h. Water (30 mL) was added and the mixture was extracted with chloroform (30 mL × 2). The organic layer was washed with brine (50 mL × 2), and dried over magnesium sulfate. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate from 80:1 to 20:1 (v/v) to afford a purple solid (0.68 g, 71% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.97 (d, *J* = 4.2 Hz, 1H, thiophene), 8.60 (d, *J* = 4.2 Hz, 1H, thiophene), 7.23 (d, *J* = 4.2 Hz, 1H, thiophene), 7.21 (d, *J* = 4.2 Hz, 1H, thiophene), 7.15 (d, *J* = 3.6 Hz, 1H, thiophene), 6.73 (d, *J* = 3.6 Hz, 1H, thiophene), 4.03–3.93 (m, 4H, NCH₂), 2.76 (d, *J* = 6.7 Hz, 2H, thiophene-CH₂), 1.88 (m, 2H, CH), 1.59 (m, 1H, CH), 1.39–1.22 (m, 24H, CH₂), 0.92–0.85 (m, 18H, CH₃). ¹³C NMR (101 MHz,

CDCl₃): δ 161.81, 161.35, 146.78, 144.16, 140.84, 138.04, 137.52, 134.90, 133.87, 131.54, 131.44, 127.30, 126.58, 125.19, 124.12, 118.34, 108.51, 107.75, 46.09, 41.61, 39.35, 39.24, 34.41, 32.51, 30.49, 30.48, 30.32, 30.31, 28.99, 28.68, 28.48, 28.46, 25.66, 23.80, 23.72, 23.70, 23.25, 23.18, 23.12, 14.26, 14.21, 14.16, 10.96, 10.68, 10.63. MALDI-TOF-HRMS (+) (*m/z*): calcd for C₄₂H₅₇BrN₂O₂S₃ (M⁺): 796.2766, found 796.2800.

2,5-bis(2-ethylhexyl)-3,6-di(selenophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (Se-DPP). Potassium carbonate (2.60 g, 18.8 mmol) and 18-crown-6 (~10mg) were added to a solution of **4** (1.66 g, 4.20 mmol) in dry DMF (60 mL), and the mixture was heated at 120 °C for 1 h. Then 2-Ethylhexyl bromide (3.25 g, 16.8 mmol) was injected in one portion and the mixture was stirred for another 24 h at the same temperature. The suspension was then filtered and the solvent removed under reduced pressure. The crude mixture was filtered and washed with methanol to give a copper-color solid, the solid was dried under vacuum and used for next step without further purification (0.86g, 33% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.84 (d, *J* = 4.1 Hz, 1H, selenophene), 8.38 (d, *J* = 5.6 Hz, 1H, selenophene), 7.49 (d, *J* = 5.6 Hz, 1H, selenophene), 3.97 (m, 2H, N-CH₂), 1.90–1.82 (m, 1H, CH), 1.38–1.20 (m, 16H, CH₂), 0.97–0.83 (m, 12H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 161.98, 137.13, 136.70, 134.14, 130.88, 108.14, 45.91, 39.13, 30.39, 30.36, 28.48, 23.72, 23.18, 14.14, 10.61.

3-(5-bromoselenophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(selenophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (Br-Se-DPP). **Se-DPP** (0.74g, 1.20 mmol) and N-bromosuccinimide (0.22 g, 1.20 mmol) were dissolved in CHCl₃ (60 mL), then the solution was protected from light and stirred at room temperature for 24 h. Water (30 mL) was added and the mixture was extracted with chloroform (60 mL × 2). Washed with water (60 mL × 2) and brine (30 mL × 2). The organic layer was separated and dried over magnesium sulfate. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography on silica gel with petroleum ether/dichloromethane/ethyl acetate from 100/5/1 to 20/5/1 (v/v/v) to afford **Br-Se-DPP** as a red powder (0.57 g, 68% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.86 (d, *J* = 3.2 Hz, 1H, selenophene), 8.40 (d, *J* = 3.0 Hz, 2H, selenophene), 7.49 (d, *J* = 4.1 Hz, 1H, selenophene), 7.40 (d, *J* = 4.4 Hz, 1H, selenophene), 3.98–3.91 (m, 4H, NCH₂), 1.85 (s, 2H, CH), 1.37–1.21 (m, 16H, CH₂), 0.90–0.83 (m, 12H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 161.91, 161.76, 142.70, 140.68, 137.52, 137.01, 136.29, 135.57, 134.33, 134.04, 130.98, 123.76, 108.58, 108.00, 46.06, 45.95, 39.12, 30.35, 30.33, 28.44, 23.72, 23.68, 23.18, 14.15, 10.61, 10.59. MALDI-TOF-HRMS (+) (*m/z*): calcd for C₃₀H₃₉BrN₂O₂Se₂ (M⁺): 698.0525, found 698.0532.

2,5-bis(2-ethylhexyl)-3-(5-(5-(2-ethylhexyl)thiophen-2-yl)selenophen-2-yl)-6-(selenophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (Se-DPP-Th). **Th-Bpin** (1.26 g, 3.90 mmol), compound **Br-Se-DPP** (0.91 g, 1.30 mmol) were dissolved in to (50 mL) toluene and 2 M aqueous K₂CO₃ solution (20 mL), ethanol (8 mL) were added. The mixture was purged with argon for 30 min. Then Pd (PPh₃)₄ (0.15 g, 0.13 mmol) were added. The mixture was stirred at 100 °C for 12h under argon. the mixture was extracted with chloroform (60 mL × 2), washed with water (60 mL × 2) and brine (30 mL × 2), the combined organic layers were dried with anhydrous MgSO₄ and concentrated. Finally, the residue was purified with silica gel column by using ethyl acetate/petroleum ether (1/60) to afford compound **Se-DPP-Th** as a purple solid (866 mg, 82% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.82 (d, *J* = 4.1 Hz, 1H, selenophene), 8.77 (d, *J* = 4.4 Hz, 1H, selenophene), 8.34 (d, *J* = 5.6 Hz, 1H, selenophene), 7.46 (d, *J* = 4.1 Hz, 1H, selenophene), 7.34 (d, *J* = 4.4 Hz, 1H, selenophene), 7.11 (d, *J* = 3.6 Hz, 1H, thiophene), 6.70 (d, *J* = 3.6 Hz, 1H, thiophene), 4.04–3.87 (m, 4H, N-CH₂), 2.74 (d, *J* = 6.8 Hz, 2H, thiophene-CH₂), 1.88 (m, 2H, CH), 1.59 (m, 1H, CH), 1.36–1.23 (m, 24H, CH₂), 0.92–0.83 (m, 18H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 162.01, 161.72, 149.78, 146.86, 141.92, 141.34, 137.92, 136.77, 136.39, 136.34, 134.24, 131.34, 130.81, 126.65, 125.99, 125.74, 108.36, 108.07, 46.01, 45.91, 41.54, 39.11, 34.43, 32.48, 30.37, 30.35, 28.96, 28.49, 28.48, 28.46, 25.64, 23.73, 23.17, 23.09, 14.24, 14.15, 14.13, 10.94, 10.62.

3-(5-bromoselenophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(5-(5-(2-ethylhexyl)thiophen-2-yl)selenophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (Br-Se-DPP-Th). **Se-DPP-Th**

(1.22 g, 1.50 mmol) and N-bromosuccinimide (0.27 g, 1.50 mmol) were dissolved in CHCl_3 (60 mL), then the solution was protected from light and stirred at room temperature for 24 h. Water (30 mL) was added and the mixture was extracted with chloroform (30 mL \times 2), washed with water (30 mL \times 2) and brine (30 mL \times 2), and dried over magnesium sulfate. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography on silica gel with dichloromethane/ethyl acetate from 100:1 to 30:1 (v/v) to afford a purple powder (1.07 g, 80% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.79 (s, 1H, selenophene), 8.37 (s, 1H, selenophene), 7.39 (d, $J = 4.3$ Hz, 1H, selenophene), 7.35 (d, $J = 4.3$ Hz, 1H, selenophene), 7.12 (s, 1H, thiophene), 6.71 (d, $J = 3.6$ Hz, 1H, thiophene), 3.92 (m, 4H, N- CH_2), 2.75 (s, 2H, thiophene- CH_2), 1.95–1.82 (m, 2H, CH), 1.60 (m, 1H, CH), 1.41–1.18 (m, 24H, CH_2), 0.95–0.77 (m, 18H, CH_3). ^{13}C NMR (101 MHz, CDCl_3): δ 161.82, 161.37, 150.17, 146.99, 142.19, 138.25, 136.29, 135.15, 134.20, 131.19, 126.67, 126.00, 125.83, 123.32, 108.76, 46.02, 41.52, 39.05, 34.42, 32.46, 30.32, 28.94, 28.45, 28.42, 28.39, 25.61, 23.73, 23.71, 23.68, 23.17, 23.15, 23.08, 14.24, 14.14, 14.12, 10.93, 10.60, 10.58. MALDI-TOF-HRMS (+) (m/z): calcd for $\text{C}_{42}\text{H}_{57}\text{BrN}_2\text{O}_2\text{SSe}_2$ (M^+): 892.1655, found 892.1653.

2. Thermal Properties of the Porphyrin Derivatives

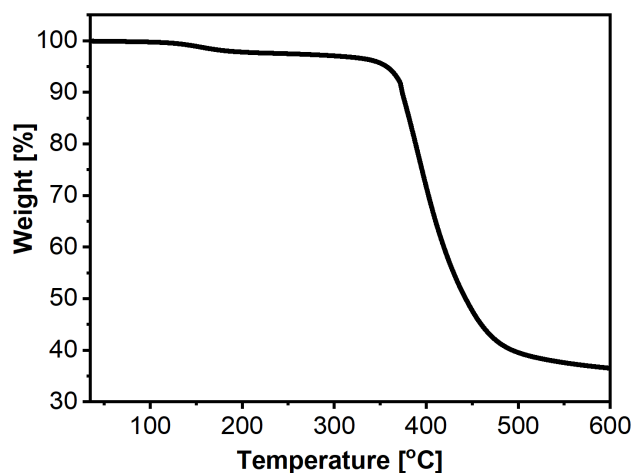


Figure S1. TGA data for **2b** under a N_2 gas flow with temperature ramp rate of 10 $^\circ\text{C}/\text{min}$ until 600 $^\circ\text{C}$. Temperature with 5% weight loss is 327.89 $^\circ\text{C}$.

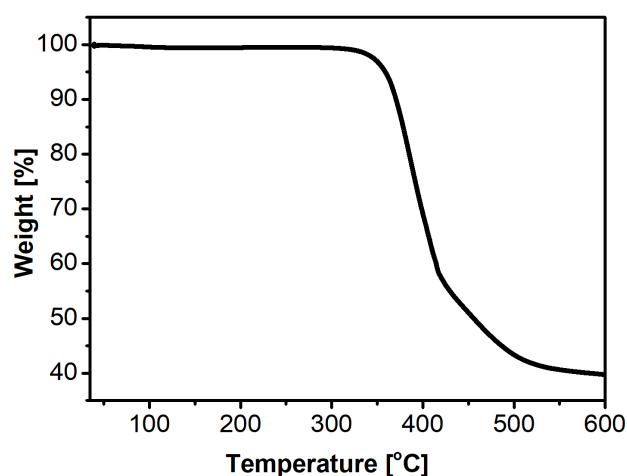


Figure S2. TGA data for **2c** under a N_2 gas flow with temperature ramp rate of 10 $^\circ\text{C}/\text{min}$ until 600 $^\circ\text{C}$. Temperature with 5% weight loss is 359.30 $^\circ\text{C}$.

3. Absorption Spectra and Electrochemical Data

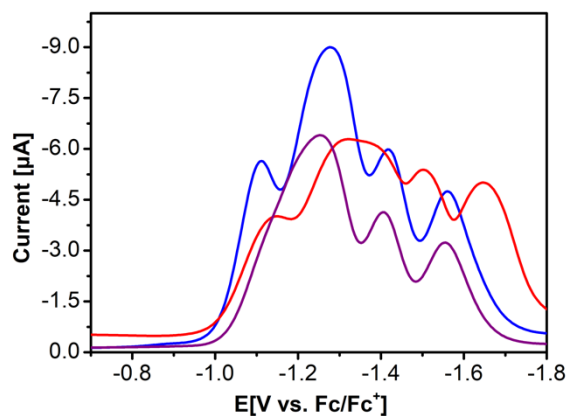


Figure S3. Differential pulse voltammetry (DPV) of the reduction range for **2a** (blue), **2b** (red) and **2c** (purple) in THF.

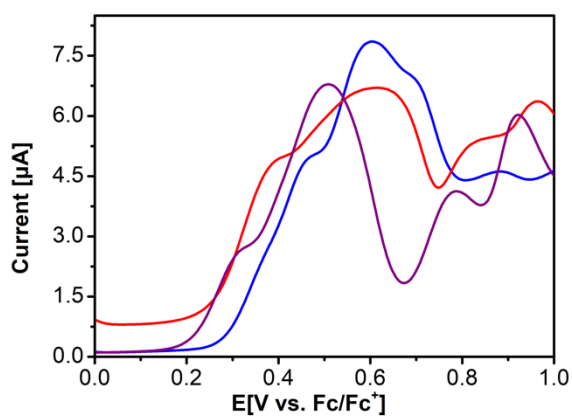


Figure S4. Differential pulse voltammetry (DPV) of the oxidation range for **2a** (blue), **2b** (red) and **2c** (purple) in THF.

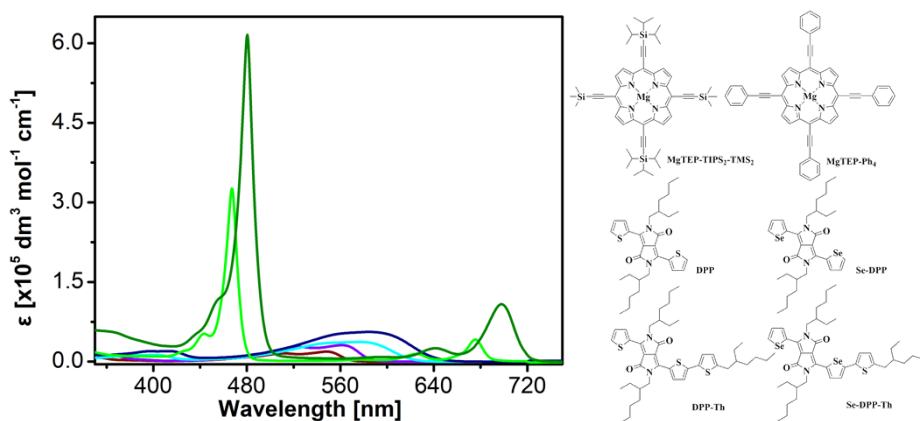


Figure S5. UV-vis absorption spectra of **Mg-TEP-TMS₂-TIPS₂** (green), **Mg-TEP-Ph₄** (olive), **DPP** (wine), **Se-DPP** (violet), **DPP-Th** (cyan) and **Se-DPP-Th** (navy) in THF.

4. Photovoltaic Data

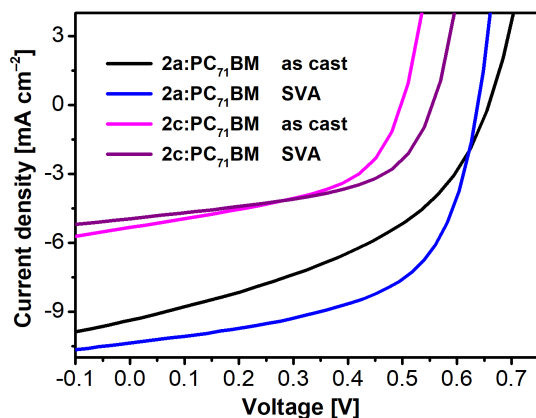


Figure S6. The J - V curves of optimized **2a:PC₇₁BM** and **2c:PC₇₁BM** devices without and with SVA treatment in inverted configuration.

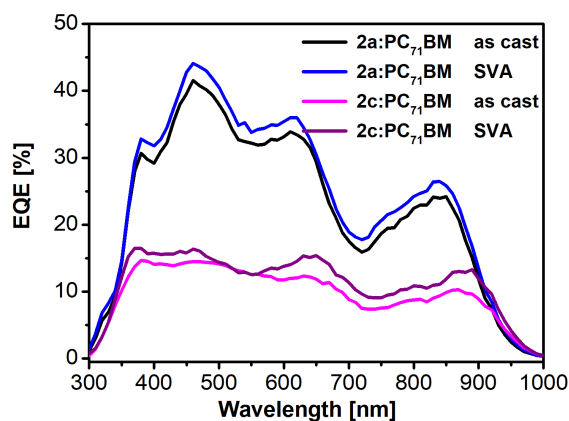


Figure S7. The EQE of optimized devices using as-cast and SVA-treated **2a** and **2c:PC₇₁BM** in inverted configuration.

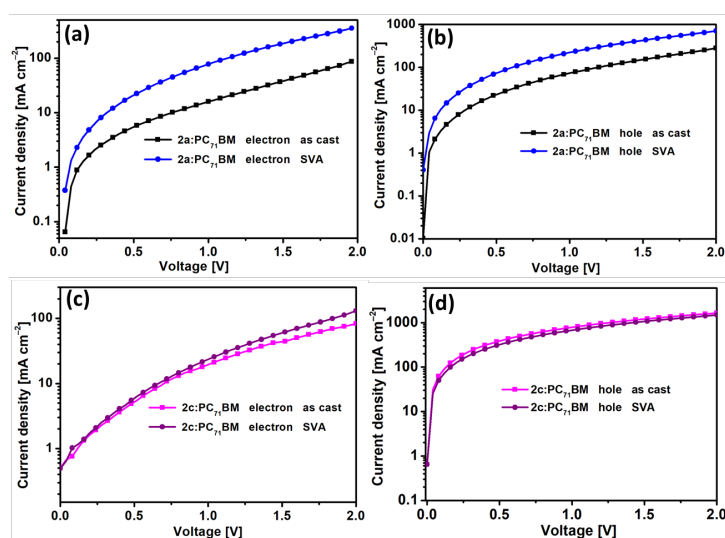


Figure S8. The hole mobilities and electron mobilities of **2a:PC₇₁BM** and **2c:PC₇₁BM** before and after SVA at the optimized device condition.

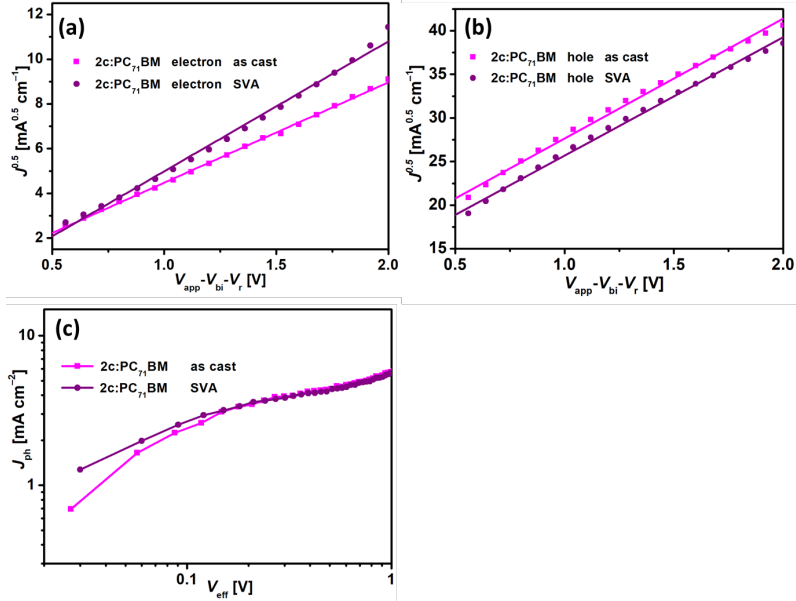


Figure S9. The $J^{0.5}$ - V curves for the (a) electron-only and (b) hole-only devices based on as-cast and SVA-treated **2c:PC₇₁BM** devices. (c) J_{ph} versus V_{eff} under the optimized as-cast and SVA-treated devices based on **2c:PC₇₁BM** in inverted configuration.

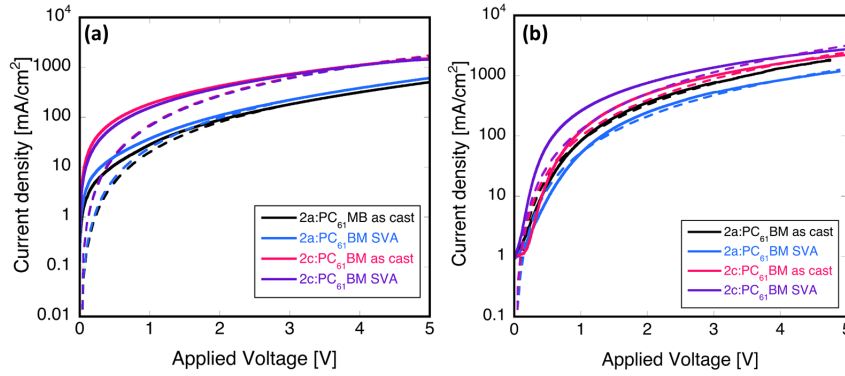


Figure S10. The hole mobilities and electron mobilities of **2a:PC₆₁BM** and **2c:PC₆₁BM** before and after SVA at the optimized device condition measured by SCLC method and the detailed parameters are summarized in **Table S1**.

Table S1. The detailed parameters of the hole mobility and electron mobility of **2a:PC₆₁BM** and **2c:PC₆₁BM** before and after SVA at the optimized device condition.

| 2a:PC₆₁BM | μ_e (cm ² V ⁻¹ s ⁻¹) | μ_h (cm ² V ⁻¹ s ⁻¹) | μ_h/μ_e | 2c:PC₆₁BM | μ_e (cm ² V ⁻¹ s ⁻¹) | μ_h (cm ² V ⁻¹ s ⁻¹) | μ_h/μ_e |
|-----------------------------|--|--|---------------|-----------------------------|--|--|---------------|
| as cast | 5.3×10^{-4} | 1.3×10^{-4} | 0.25 | as cast | 6.4×10^{-4} | 4.5×10^{-4} | 0.70 |
| SVA | 3.4×10^{-4} | 1.5×10^{-4} | 0.45 | SVA | 8.2×10^{-4} | 4.4×10^{-4} | 0.54 |

Table S2. Photovoltaic performance of the devices under 100 mW/cm² simulated solar irradiation.

| conventional device structure of ITO/PEDOT:PSS/ 2b-c :PC ₆₁ BM and PC ₇₁ BM /LiF/Al | | | | | | | | |
|--|-----------|---------------------|----------|--------------------|--------------|----------------------------------|--------|---------|
| | donor | acceptor | conc | SVA [s] | V_{oc} [V] | J_{sc} [mA cm ⁻²] | FF [%] | PCE [%] |
| 1 | 2b | PC ₆₁ BM | 30 mg/mL | – | 0.73 | 4.15 | 46.30 | 1.39 |
| 2 | 2b | PC ₆₁ BM | 30 mg/mL | THF 30 | 0.73 | 4.29 | 49.20 | 1.55 |
| 5 | 2c | PC ₇₁ BM | 30 mg/mL | – | 0.58 | 6.30 | 51.50 | 1.89 |
| 6 | 2c | PC ₇₁ BM | 30 mg/mL | THF 30 | 0.59 | 4.65 | 45.00 | 1.22 |
| inverted device structure of ITO/ZnO/ 2b :PC ₇₁ BM/MoO ₃ /Ag | | | | | | | | |
| | donor | acceptor | conc | SVA [s] | V_{oc} [V] | J_{sc} [mA cm ⁻²] | FF [%] | PCE [%] |
| 1 | 2b | PC ₇₁ BM | 30 mg/mL | – | 0.57 | 5.47 | 30.66 | 0.96 |
| 2 | 2b | PC ₇₁ BM | 30 mg/mL | CS ₂ 30 | 0.58 | 5.53 | 50.70 | 1.63 |

Table S3. Photovoltaic performance of **2a** in BHJ devices with different D/A ratio.

| conventional device structure of ITO/PEDOT:PSS/ 2a :PC ₆₁ BM/LiF/Al | | | | | |
|---|--------------|---------------------------------|--------|---------|--|
| D:A | V_{oc} [V] | J_{sc} [mA cm ⁻²] | FF [%] | PCE [%] | |
| 5:4 | 0.65 | 13.32 | 44.46 | 3.85 | |
| 1:1 | 0.72 | 15.42 | 46.83 | 5.20 | |
| 1:1.5 | 0.74 | 16.70 | 49.20 | 6.09 | |
| 1:2 | 0.76 | 15.82 | 44.91 | 5.40 | |

Table S4. Photovoltaic performance of the **2a** in the BHJ devices with different SVA time.

| conventional device structure of ITO/PEDOT:PSS/ 2a :PC ₆₁ BM/LiF/Al | | | | | |
|---|--------------|---------------------------------|--------|---------|--|
| SVA | V_{oc} [V] | J_{sc} [mA cm ⁻²] | FF [%] | PCE [%] | |
| as-cast | 0.75 | 13.84 | 46.30 | 4.77 | |
| THF 10s | 0.744 | 15.31 | 0.420 | 4.79 | |
| THF 20s | 0.74 | 16.70 | 0.49 | 6.09 | |
| THF 40s | 0.74 | 13.98 | 0.44 | 4.59 | |
| THF 60s | 0.74 | 16.33 | 0.50 | 5.96 | |
| THF 80s | 0.75 | 14.69 | 0.48 | 5.27 | |

Table S5. Photovoltaic performance of the **2a** in the BHJ devices with different SVA time.

| inverted device structure of ITO/ZnO/ 2a :PC ₇₁ BM/MoO ₃ /Ag | | | | |
|---|--------------|---------------------------------|--------|---------|
| SVA | V_{oc} [V] | J_{sc} [mA cm ⁻²] | FF [%] | PCE [%] |
| as-cast | 0.65 | 9.46 | 43.47 | 2.69 |
| CS ₂ 20s | 0.65 | 10.83 | 44.79 | 3.14 |
| CS ₂ 30s | 0.63 | 10.34 | 58.62 | 3.82 |
| CS ₂ 40s | 0.63 | 9.24 | 58.67 | 3.39 |
| CS ₂ 60s | 0.60 | 3.33 | 43.78 | 0.88 |

Table S6. Photovoltaic performance of the devices under 100 mW/cm² simulated solar irradiation.

| inverted device structure of ITO/ZnO/ 2a :PC ₇₁ BM/MoO ₃ /Ag | | | | | |
|---|---------------------------------|---------------------------------------|--------|----------------------------------|---------------------|
| 2a :PC ₇₁ BM | J_{sc} [mA cm ⁻²] | J_{sc}^{cal} [mA cm ⁻²] | error | J_{SAT} [mA cm ⁻²] | P(E,T) ^a |
| as cast | 9.46 | 9.16 | -3.17% | 12.08 | 78.3% |
| SVA | 10.34 | 9.86 | -4.46% | 10.99 | 94.1% |
| inverted device structure of ITO/ZnO/ 2c :PC ₇₁ BM/MoO ₃ /Ag | | | | | |
| 2c :PC ₇₁ BM | J_{sc} [mA cm ⁻²] | J_{sc}^{cal} [mA cm ⁻²] | error | J_{SAT} [mA cm ⁻²] | P(E,T) ^a |
| as cast | 5.23 | 4.44 | -15.1% | 6.14 | 85.0% |
| SVA | 4.88 | 3.79 | -22.3% | 5.74 | 85.1% |

^a Exciton dissociation probability under short-circuit condition.

Table S7. Thickness influence on photovoltaic performance of **2a** in BHJ devices after SVA for 20s.

| Thickness [nm] | V_{oc} [V] | J_{sc} [mA cm ⁻²] | FF [%] | PCE [%] |
|----------------|--------------|---------------------------------|--------|---------|
| 90 | 0.75 | 15.67 | 46.71 | 5.49 |
| 110 | 0.74 | 16.70 | 49.20 | 6.09 |
| 130 | 0.73 | 16.97 | 47.39 | 5.87 |

7. ¹H and ¹³C NMR Spectra

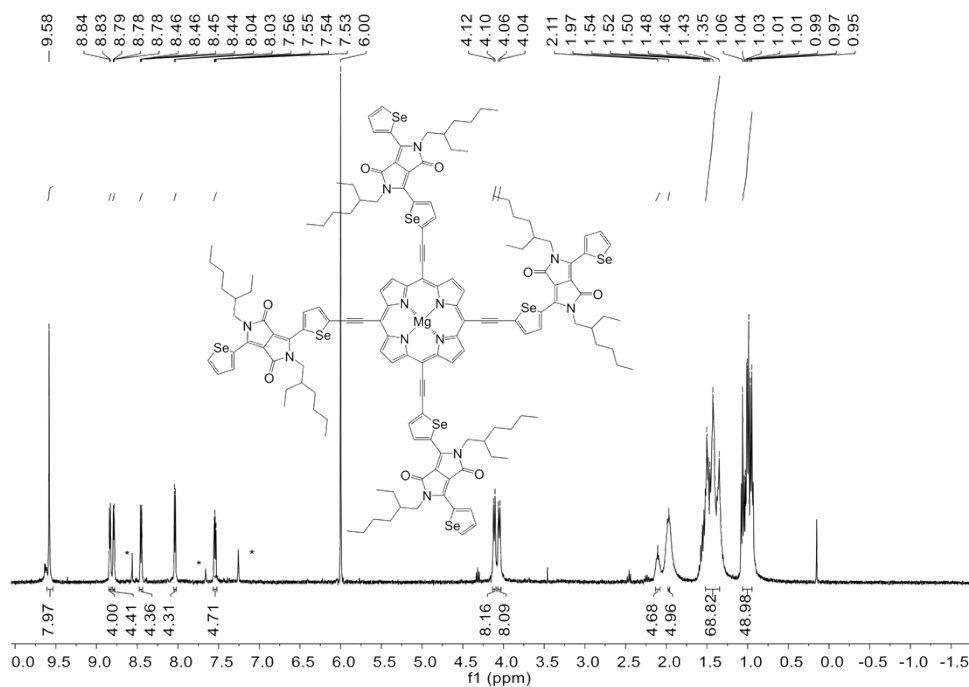


Figure S11. ¹H NMR spectrum for **2a**.

¹H NMR (400 MHz, tetrachloroethane-*d*₂ with 1% pyridine-*d*₅^{*}, 100 °C): δ 9.58 (s, 8H, porphyrin), 8.83 (d, *J* = 4.3 Hz, 4H, selenophene), 8.81–8.76 (m, 4H, selenophene), 8.45 (d, *J* = 5.5 Hz, 4H, selenophene), 8.04 (d, *J* = 4.3 Hz, 4H, selenophene), 7.54 (d, *J* = 5.6 Hz, 4H, selenophene), 4.11 (d, *J* = 7.7 Hz, 8H, NCH₂), 4.05 (d, *J* = 7.8 Hz, 8H, NCH₂), 2.11 (s, 4H, CH), 1.97 (s, 4H, CH), 1.52–1.34 (m, 64H, CH₂), 1.10–0.91 (m, 48H, CH₃).

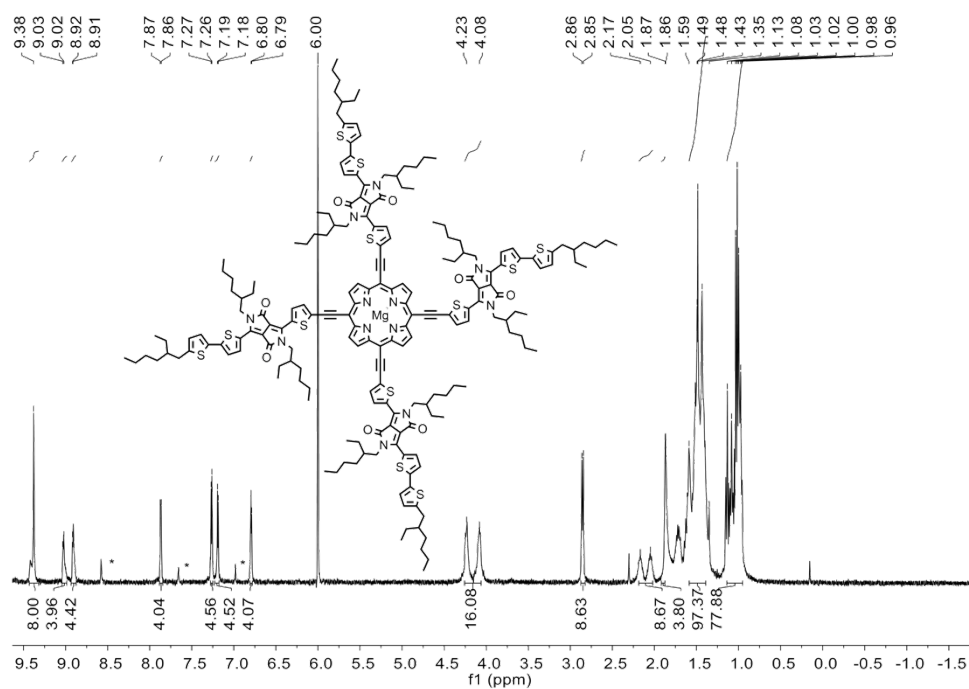


Figure S12. ^1H NMR spectrum for **2b**.

^1H NMR (400 MHz, tetrachloroethane- d_2 with 1% pyridine- d_5^* , 100 °C): δ 9.38 (s, 8H, porphyrin), 9.03 (d, $J = 5.4$ Hz, 4H, thiophene), 8.91 (d, $J = 2.5$ Hz, 4H, thiophene), 7.87 (d, $J = 4.4$ Hz, 4H, thiophene), 7.26 (d, $J = 3.8$ Hz, 4H, thiophene), 7.19 (d, $J = 3.5$ Hz, 4H, thiophene), 6.79 (d, $J = 3.2$ Hz, 4H, thiophene), 4.16 (m, 16H, NCH_2), 2.85 (d, $J = 6.6$ Hz, 8H, thiophene- CH_2), 2.11 (m, 8H, CH), 1.87 (m, 4H, CH), 1.59–1.39 (m, 96H, CH_2), 1.14–0.95 (m, 72H, CH_3).

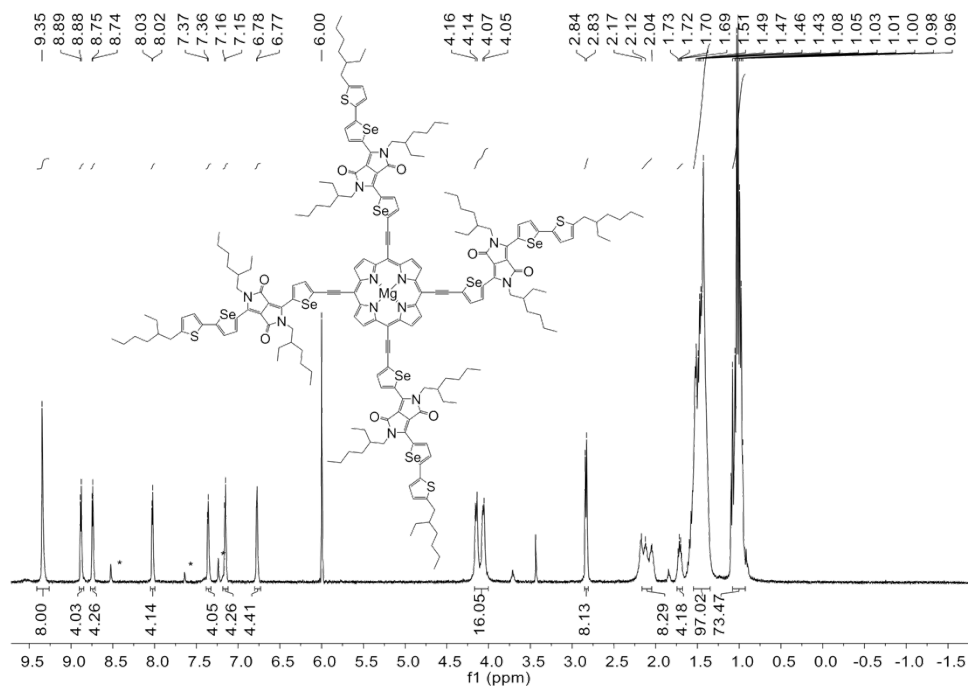


Figure S13. ^1H NMR spectrum for **2c**.

^1H NMR (400 MHz, tetrachloroethane- d_2 with 1% pyridine- d_5^* , 100 °C): δ 9.35 (s, 8H, porphyrin), 8.88 (d, $J = 4.2$ Hz, 4H, selenophene), 8.74 (d, $J = 4.0$ Hz, 4H, selenophene), 8.03 (d, $J = 4.1$ Hz, 4H, selenophene), 7.36 (d, $J = 4.0$ Hz, 4H, selenophene), 7.16 (d, $J = 3.4$ Hz, 4H, thiophene), 6.77 (d, $J = 2.6$ Hz, 4H, thiophene), 4.11 (m, 16H, NCH_2), 2.83 (d, $J = 6.7$ Hz, 8H, thiophene- CH_2), 2.15 (m, 8H, CH), 1.71 (m, 4H, CH), 1.55–1.35 (m, 96H, CH_2), 1.08–0.96 (m, 72H, CH_3).

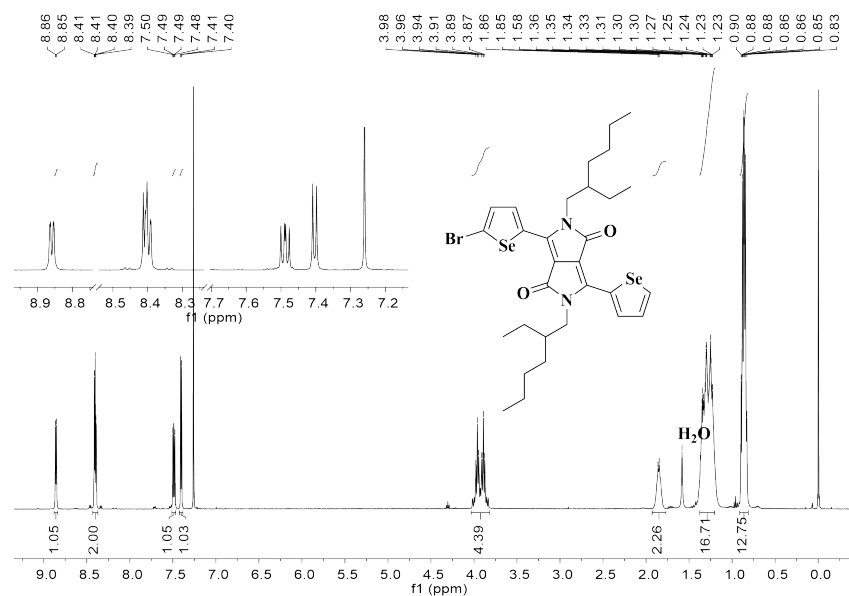


Figure S14. ^1H NMR spectrum for **Br-Se-DPP**.

^1H NMR (400 MHz, CDCl_3): δ 8.86 (d, $J = 3.2$ Hz, 1H, selenophene), 8.40 (d, $J = 3.0$ Hz, 2H, selenophene), 7.49 (d, $J = 4.1$ Hz, 1H, selenophene), 7.40 (d, $J = 4.4$ Hz, 1H, selenophene), 3.98–3.91 (m, 4H, NCH_2), 1.85 (s, 2H, CH), 1.37–1.21 (m, 16H, CH_2), 0.90–0.83 (m, 12H, CH_3).

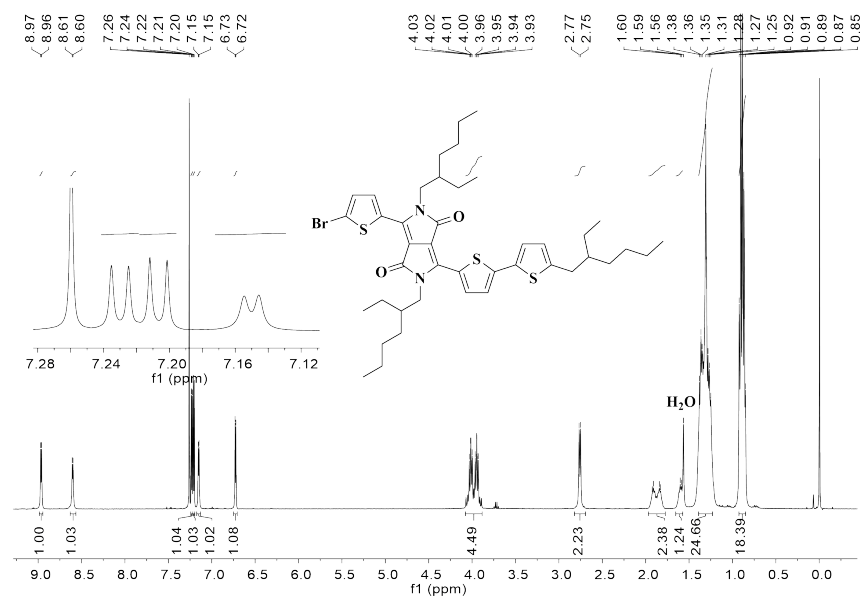


Figure S15. ^1H NMR spectrum for **Br-DPP-Th**.

^1H NMR (400 MHz, CDCl_3): δ 8.97 (d, $J = 4.2$ Hz, 1H, thiophene), 8.60 (d, $J = 4.2$ Hz, 1H, thiophene), 7.23 (d, $J = 4.2$ Hz, 1H, thiophene), 7.21 (d, $J = 4.2$ Hz, 1H, thiophene), 7.15 (d, $J = 3.6$ Hz, 1H, thiophene), 6.73 (d, $J = 3.6$ Hz, 1H, thiophene), 4.03–3.93 (m, 4H, NCH_2), 2.76 (d, $J = 6.7$ Hz, 2H, thiophene- CH_2), 1.88 (m, 2H, CH), 1.59 (m, 1H, CH), 1.39–1.22 (m, 24H, CH_2), 0.92–0.85 (m, 18H, CH_3).

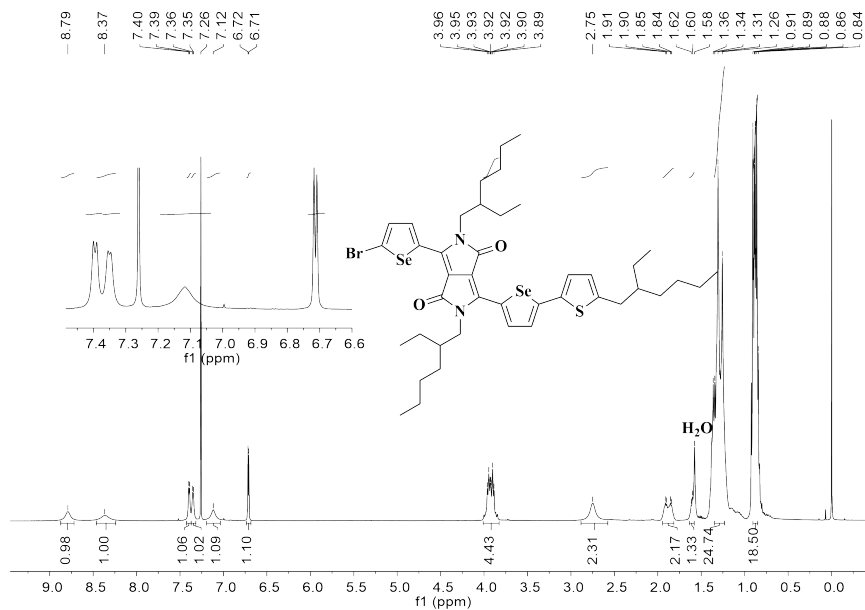


Figure S16. ^1H NMR spectrum for **Br-Se-DPP-Th**.

^1H NMR (400 MHz, CDCl_3): δ 8.79 (s, 1H, selenophene), 8.37 (s, 1H, selenophene), 7.39 (d, $J = 4.3$ Hz, 1H, selenophene), 7.35 (d, $J = 4.3$ Hz, 1H, selenophene), 7.12 (s, 1H, thiophene), 6.71 (d, $J = 3.6$ Hz, 1H, thiophene), 3.92 (m, 4H, N- CH_2), 2.75 (s, 2H, thiophene- CH_2), 1.95–1.82 (m, 2H, CH), 1.60 (m, 1H, CH), 1.41–1.18 (m, 24H, CH_2), 0.95–0.77 (m, 18H, CH_3).

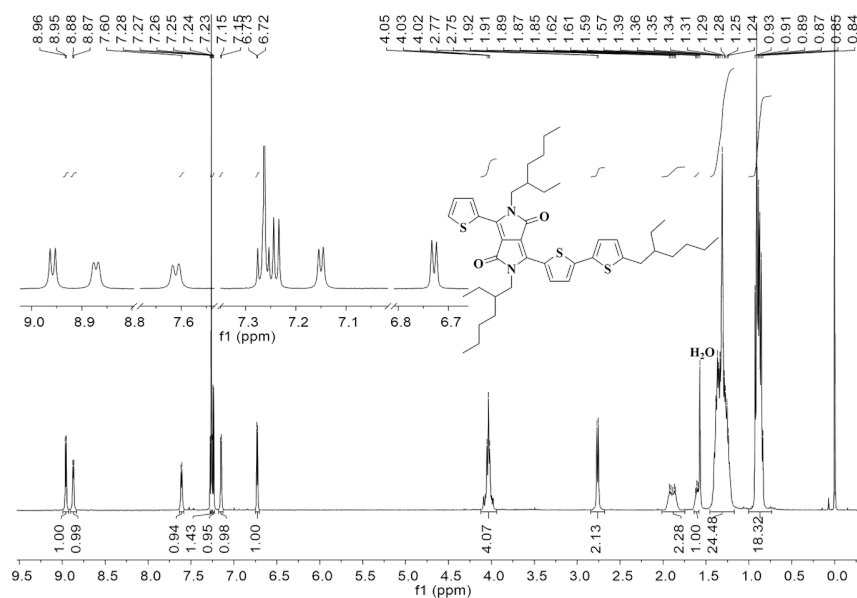


Figure S17. ^1H NMR spectrum for **S-DPP-Th**.

^1H NMR (400 MHz, CDCl_3): δ 8.96 (d, $J = 4.2$ Hz, 2H, thiophene), 8.87 (d, $J = 3.9$ Hz, 2H, thiophene), 7.29–7.25 (m, 1H, thiophene), 7.24 (d, $J = 4.1$ Hz, 1H, thiophene), 7.15 (d, $J = 3.6$ Hz, 1H, thiophene), 6.73 (d, $J = 3.6$ Hz, 1H, thiophene), 4.04 (m, 4H, N- CH_2), 2.76 (d, $J = 6.8$ Hz, 2H, thiophene- CH_2), 2.00–1.77 (m, 1H, CH), 1.61 (m, 1H, CH), 1.40–1.24 (m, 24H, CH_2), 0.93–0.84 (m, 18H, CH_3).

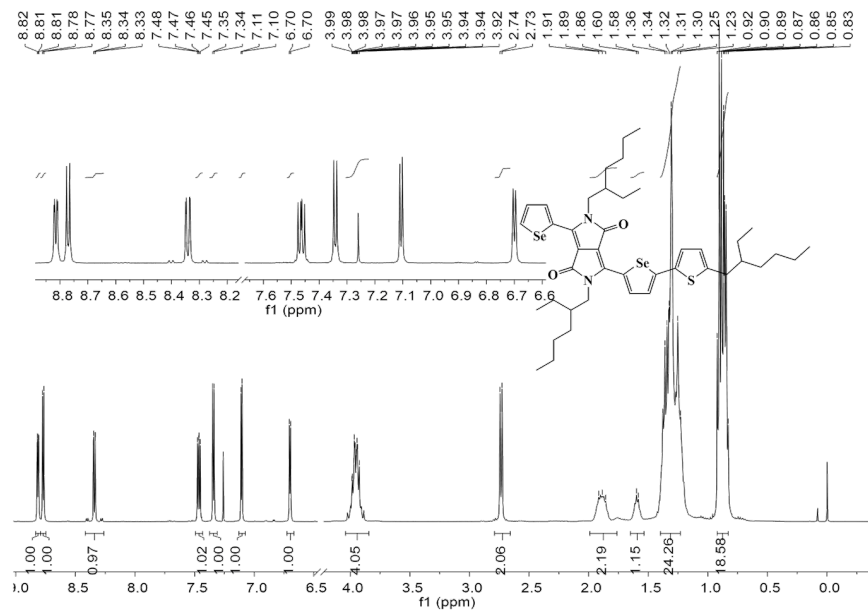


Figure S18. ^1H NMR spectrum for Se-DPP-Th.

^1H NMR (400 MHz, CDCl_3): δ 8.82 (d, $J = 4.1$ Hz, 1H, selenophene), 8.77 (d, $J = 4.4$ Hz, 1H, selenophene), 8.34 (d, $J = 5.6$ Hz, 1H, selenophene), 7.46 (d, $J = 4.1$ Hz, 1H, selenophene), 7.34 (d, $J = 4.4$ Hz, 1H, selenophene), 7.11 (d, $J = 3.6$ Hz, 1H, thiophene), 6.70 (d, $J = 3.6$ Hz, 1H, thiophene), 4.04–3.87 (m, 4H, N- CH_2), 2.74 (d, $J = 6.8$ Hz, 2H, thiophene- CH_2), 1.88 (m, 2H, CH), 1.59 (m, 1H, CH), 1.36–1.23 (m, 24H, CH_2), 0.92–0.83 (m, 18H, CH_3).

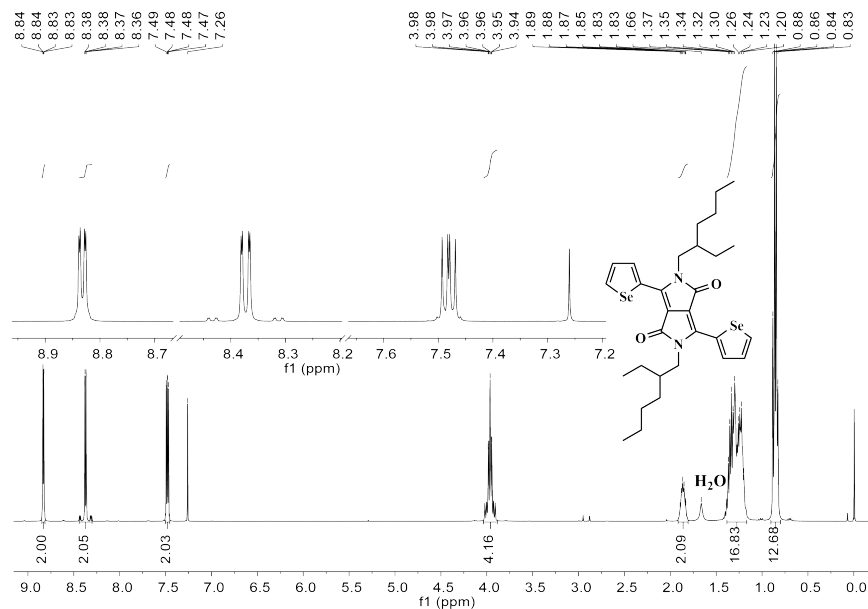


Figure S19. ^1H NMR spectrum for Se-DPP.

^1H NMR (400 MHz, CDCl_3): δ 8.84 (d, $J = 4.1$ Hz, 1H, selenophene), 8.38 (d, $J = 5.6$ Hz, 1H, selenophene), 7.49 (d, $J = 5.6$ Hz, 1H, selenophene), 3.97 (m, 2H, N- CH_2), 1.90–1.82 (m, 1H, CH), 1.38–1.20 (m, 16H, CH_2), 0.97–0.83 (m, 12H, CH_3).

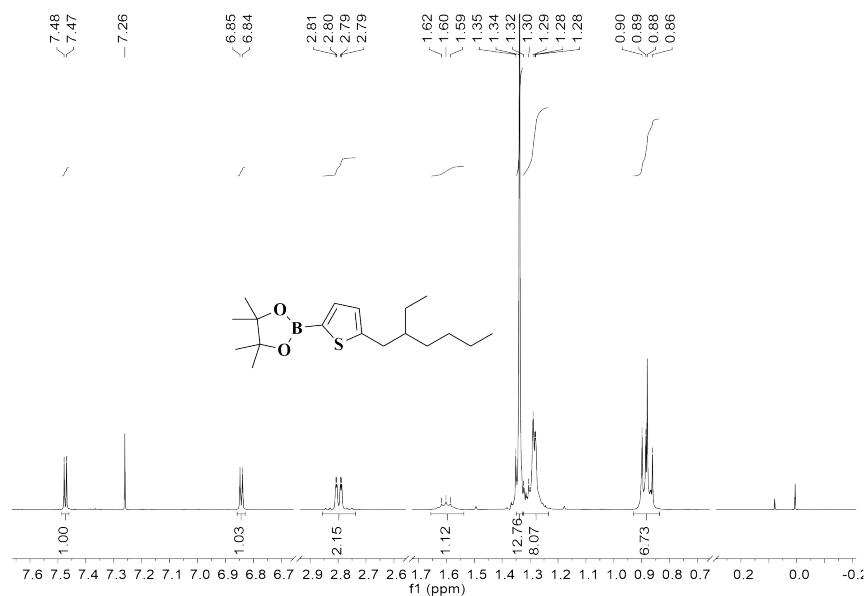


Figure S20. ^1H NMR spectrum for **Th-Bpin**.

^1H NMR (400 MHz, CDCl_3): δ 7.47 (d, $J = 3.4$ Hz, 1H, thiophene), 6.84 (d, $J = 3.4$ Hz, 1H, thiophene), 2.80 (d, $J = 6.7$ Hz, 2H), 1.63–1.53 (m, 1H, CH), 1.34 (s, 12H, Bpin), 1.29–1.28 (m, 9H, CH_2), 0.90–0.86 (m, 6H, CH_3).

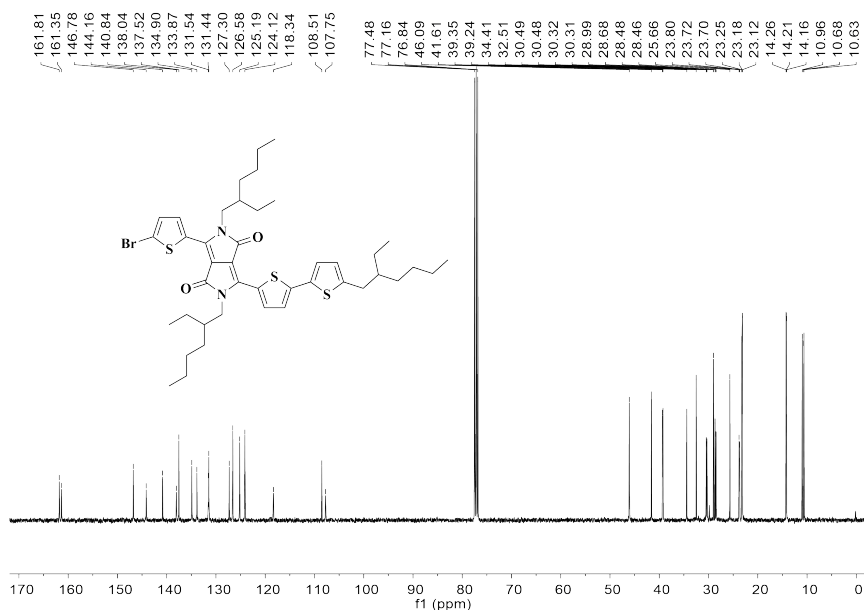


Figure S21. ^{13}C NMR spectrum for **Br-DPP-Th**.

^{13}C NMR (101 MHz, CDCl_3): δ 161.81, 161.35, 146.78, 144.16, 140.84, 138.04, 137.52, 134.90, 133.87, 131.54, 131.44, 127.30, 126.58, 125.19, 124.12, 118.34, 108.51, 107.75, 46.09, 41.61, 39.35, 39.24, 34.41, 32.51, 30.49, 30.48, 30.32, 30.31, 28.99, 28.68, 28.48, 28.46, 25.66, 23.80, 23.72, 23.70, 23.25, 23.18, 23.12, 14.26, 14.21, 14.16, 10.96, 10.68, 10.63.

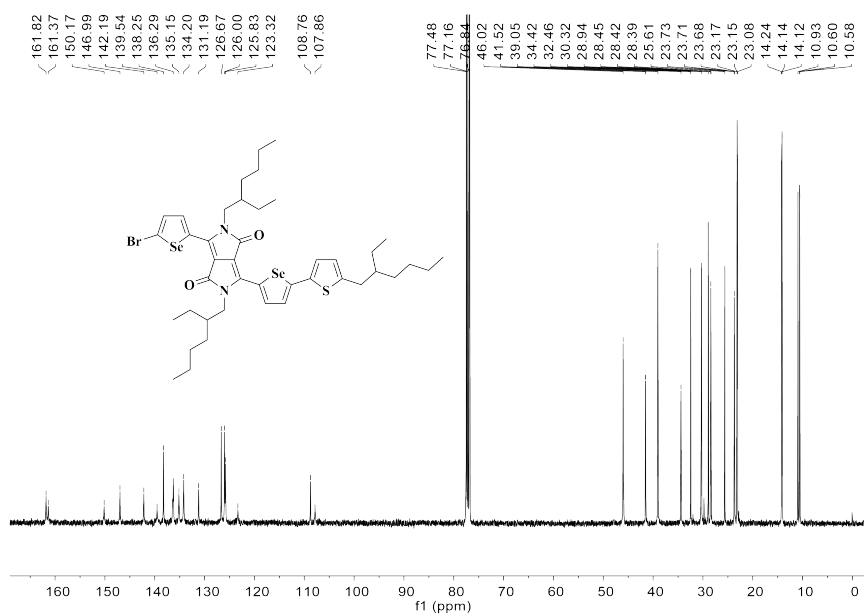


Figure S22. ^{13}C NMR spectrum for Br-Se-DPP-Th.

^{13}C NMR (101 MHz, CDCl_3): δ 161.82, 161.37, 150.17, 146.99, 142.19, 138.25, 136.29, 135.15, 134.20, 131.19, 126.67, 126.00, 125.83, 123.32, 108.76, 46.02, 41.52, 39.05, 34.42, 32.46, 30.32, 28.94, 28.45, 28.42, 28.39, 25.61, 23.73, 23.71, 23.68, 23.17, 23.15, 23.08, 14.24, 14.14, 14.12, 10.93, 10.60, 10.58.

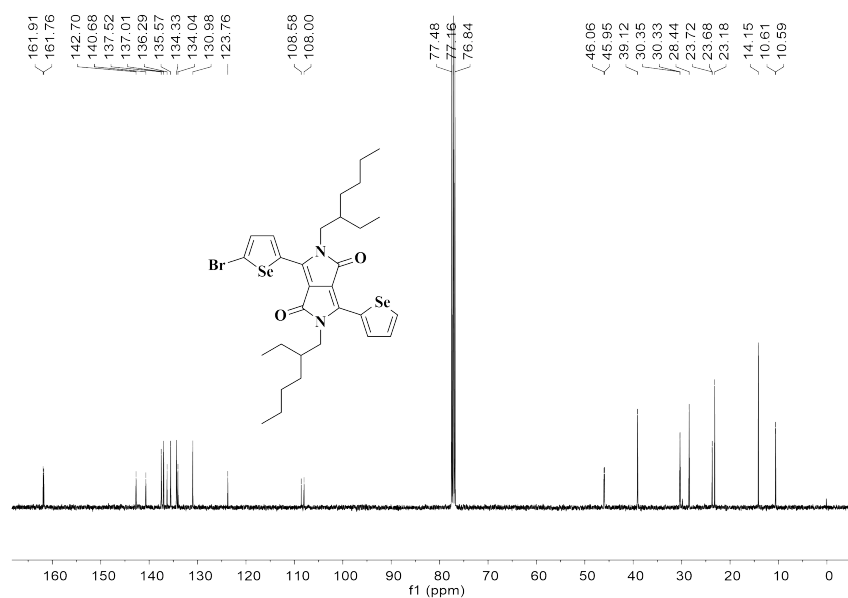


Figure S23. ^{13}C NMR spectrum for Br-Se-DPP.

^{13}C NMR (100 MHz, CDCl_3): δ 161.91, 161.76, 142.70, 140.68, 137.52, 137.01, 136.29, 135.57, 134.33, 134.04, 130.98, 123.76, 108.58, 108.00, 46.06, 45.95, 39.12, 30.35, 30.33, 28.44, 23.72, 23.68, 23.18, 14.15, 10.61, 10.59.

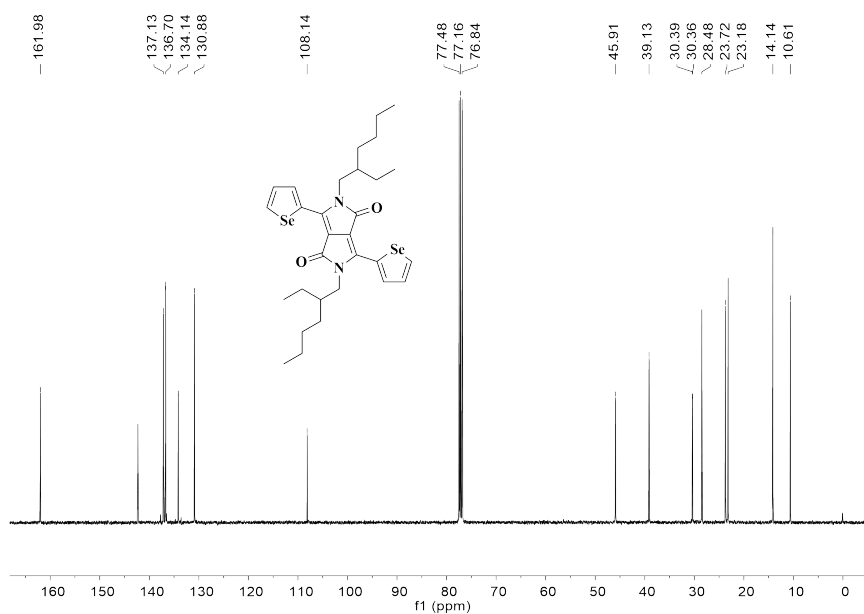


Figure S24. ^{13}C NMR spectrum for **Se-DPP**.

^{13}C NMR (100 MHz, CDCl_3): δ 161.98, 137.13, 136.70, 134.14, 130.88, 108.14, 45.91, 39.13, 30.39, 30.36, 28.48, 23.72, 23.18, 14.14, 10.61.

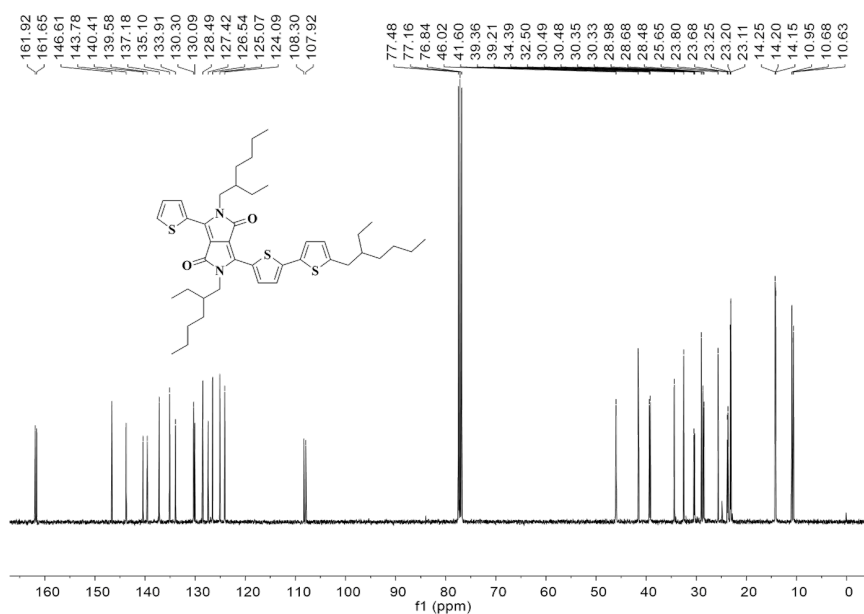


Figure S25. ^{13}C NMR spectrum for **DPP-Th**.

^{13}C NMR (100 MHz, CDCl_3): δ 161.92, 161.65, 146.61, 143.78, 140.41, 139.58, 137.18, 135.10, 133.91, 130.30, 130.09, 128.49, 127.42, 126.54, 125.07, 124.09, 108.30, 107.92, 46.02, 41.60, 39.36, 39.21, 34.39, 32.50, 30.49, 30.48, 30.35, 30.33, 28.98, 28.68, 28.48, 25.65, 23.80, 23.68, 23.25, 23.20, 23.11, 14.25, 14.20, 14.15, 10.95, 10.68, 10.63.

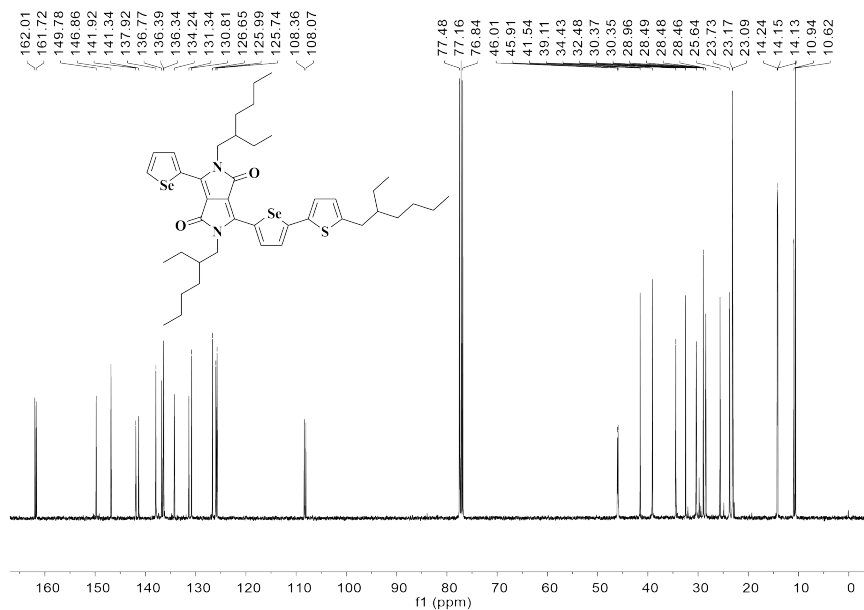


Figure S26. ^{13}C NMR spectrum for **Se-DPP-Th**.

^{13}C NMR (100 MHz, CDCl_3): δ 162.01, 161.72, 149.78, 146.86, 141.92, 141.34, 137.92, 136.77, 136.39, 136.34, 134.24, 131.34, 130.81, 126.65, 125.99, 125.74, 108.36, 108.07, 46.01, 45.91, 41.54, 39.11, 34.43, 32.48, 30.37, 30.35, 28.96, 28.49, 28.48, 28.46, 25.64, 23.73, 23.17, 23.09, 14.24, 14.15, 14.13, 10.94, 10.62.

8. MALDI-TOF HRMS Data

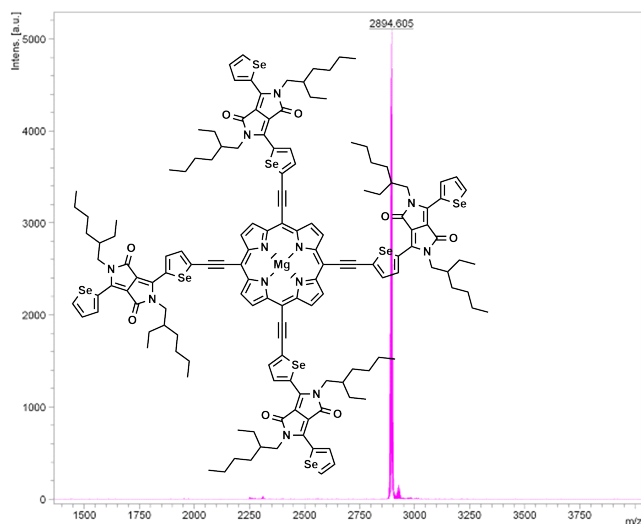


Figure S27. HRMS spectrum for **2a**. MALDI-TOF-HRMS (+) (m/z): calcd for $\text{C}_{148}\text{H}_{164}\text{MgN}_{12}\text{O}_8\text{Se}_8$ (M^+): 2894.6070, found 2894.6050.

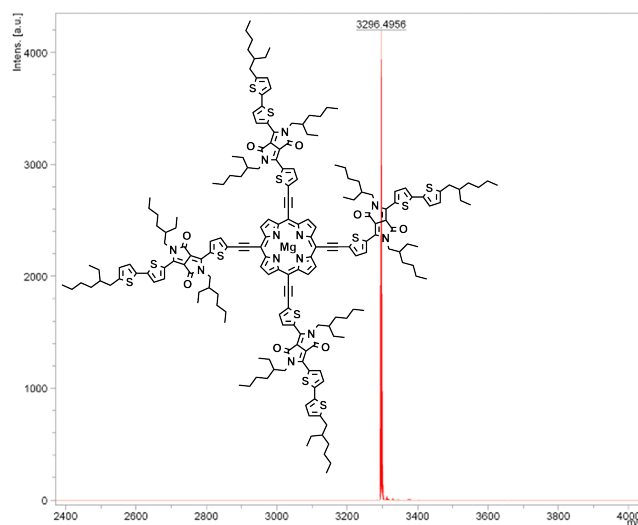


Figure S28. HRMS spectrum for **2b**. MALDI-TOF-HRMS (+) (m/z): calcd for $C_{196}H_{236}MgN_{12}O_8S_{12}$ (M^+): 3296.4972, found 3296.4956.

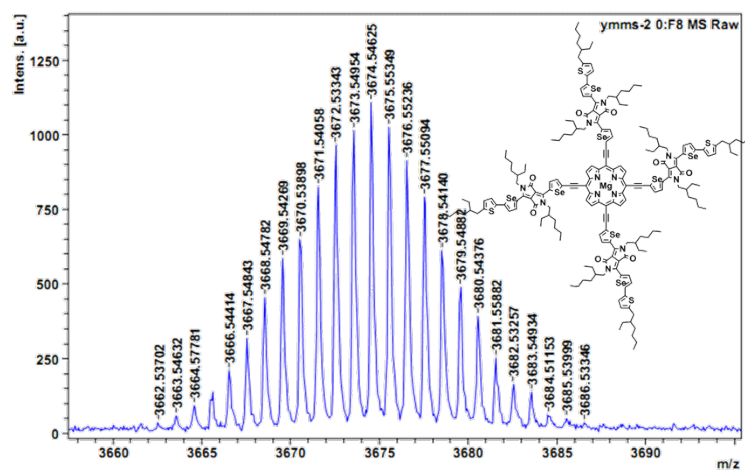


Figure S29. HRMS spectrum for **2c**. MALDI-TOF-HRMS (+) (m/z): calcd for $C_{196}H_{236}MgN_{12}O_8S_4Se_8$ (M^+): 3677.0484, found 3677.5509.

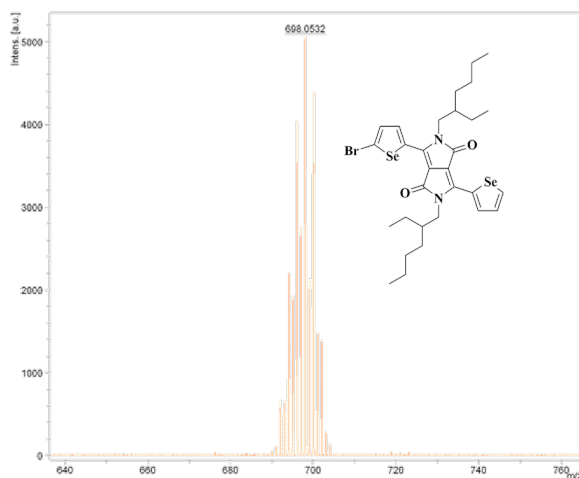


Figure S30. HRMS spectrum for **Br-Se-DPP**. MALDI-TOF-HRMS (+) (m/z): calcd for $C_{30}H_{39}BrN_2O_2Se_2$ (M^+): 698.0525, found 698.0532.

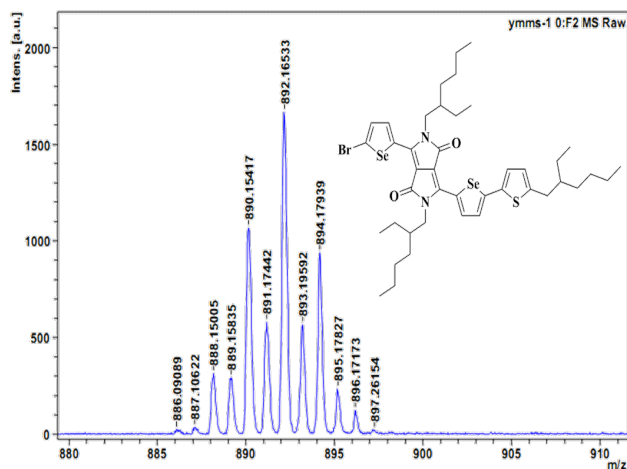


Figure S31. HRMS spectrum for **Br-Se-DPP-Th**. MALDI-TOF-HRMS (+) (m/z): calcd for $C_{42}H_{57}BrN_2O_2SSe_2$ (M^+): 892.1655, found 892.1653.

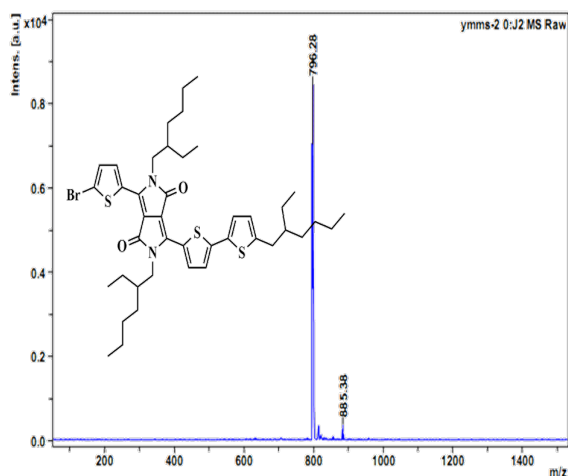


Figure S32. HRMS spectrum for **Br-DPP-Th**. MALDI-TOF-HRMS (+) (m/z): calcd for $C_{42}H_{57}BrN_2O_2S_3$ (M^+): 796.2766, found 796.2800.

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