Supplementary Information

High-yielding Pd$_2$(dba)$_3$·C$_6$H$_6$-based Four-fold Sonogashira Coupling for Selenophene-conjugated Magnesium Tetraethynylporphyrin for Organic Solar Cells

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Table of Contents

Experimental Section .................................................................................................................. S3

Thermal Properties of the Porphyrin Derivatives ................................................................. S6

Absorption Spectra and Electrochemical Data ................................................................. S7

Photovoltaic Data .................................................................................................................. S8

$^1$H and $^{13}$C NMR Spectra .......................................................................................... S12

MALDI-TOF HRMS Data .................................................................................................. S20
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.\(^1\) Compounds Br-DPP, Br-Se-DPP were prepared according to previous papers.\(^2\) Compounds DPP-Th, Se-DPP-Th, Br-DPP-Th, Br-Se-DPP-Th were synthesized according to previously reported procedures.\(^3\) 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/CH\(_2\)Cl\(_2\)/Petroleum ether). The NMR spectra were measured on a Bruker US400 for \(^1\)H NMR and \(^{13}\)C 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 (TBAPF\(_6\)). Current–voltage (\(J-V\)) characteristics were measured using a source meter (Keithley 2400) under sun AM 1.5G simulated sunlight irradiation (100 mW/cm\(^2\)) 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:PC\(_{71}\)BM and PC\(_{61}\)BM/MoO\(_3\)/Ag and electron-only devices with a configuration of ITO/ZnO/ 2a and 2c: PC\(_{71}\)BM and PC\(_{61}\)BM/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):

\[
J = \frac{9\varepsilon_0\varepsilon_r V^2}{8d^3}
\]

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

Where \(J\) is the current, \(\varepsilon_0\) is the permittivity of free space, \(\varepsilon_r\) 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 (1.16 g, 3.60 mmol), Br-DPP (0.72 g, 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 (0.14 g, 0.12 mmol) were added. The mixture was stirred at 100 °C for 12 h 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, NCH2), 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), 8.80 (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,
2,5-bis(2-ethylhexyl)-3,6-di(selenophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (Sc-DPP). Potassium carbonate (2.60 g, 18.8 mmol) and 18-crown-6 (~10 mg) 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-colored 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, N-CH2), 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): calcld for C30H30BrN2O2Se2 (M+): 698.0525, found 698.0532.

2,5-bis(2-ethylhexyl)-3-(5-(5-(2-ethylhexyl)thieno-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 12 h 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, thienophene), 6.70 (d, J = 3.6 Hz, 1H, thienophene), 4.04–3.87 (m, 4H, N-CH2), 2.74 (d, J = 6.8 Hz, 2H, thienophene-CH), 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)thieno-2-yl)selenophen-2-yl)-2,5 dihydropyrrolo[3,4-c]pyrrole-1,4-dione (Br-Se-DPP-Th). Se-DPP-Th

S5
(1.22 g, 1.50 mmol) and N-bromosuccinimide (0.27 g, 1.50 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), washed with water (30 mL × 2) and brine (30 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 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, CDCl₃): 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-CH₂), 2.75 (s, 2H, thiophene-CH₂), 1.95–1.82 (m, 2H, CH), 1.60 (m, 1H, CH), 1.41–1.18 (m, 24H, CH₂), 0.95–0.77 (m, 18H, CH₃). 13C NMR (101 MHz, CDCl₃): 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 C₄₂H₅₇BrN₂O₂SSe₂ (M⁺): 892.1655, found 892.1653.

2. Thermal Properties of the Porphyrin Derivatives

**Figure S1.** TGA data for 2b under a N₂ gas flow with temperature ramp rate of 10 °C/min until 600 °C. Temperature with 5% weight loss is 327.89 °C.

**Figure S2.** TGA data for 2c under a N₂ gas flow with temperature ramp rate of 10 °C/min until 600 °C. Temperature with 5% weight loss is 359.30 °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 $2a$:PC$_71$BM and $2c$:PC$_71$BM devices without and with SVA treatment in inverted configuration.

**Figure S7.** The EQE of optimized devices using as-cast and SVA-treated $2a$ and $2c$:PC$_71$BM in inverted configuration.

**Figure S8.** The hole mobilities and electron mobilities of $2a$:PC$_71$BM and $2c$:PC$_71$BM 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:PC$_{71}$BM devices. (c) $J_{ph}$ versus $V_{eff}$ under the optimized as-cast and SVA-treated devices based on 2c:PC$_{71}$BM in inverted configuration.

**Figure S10.** The hole mobilities and electron mobilities of 2a:PC$_{61}$BM and 2c:PC$_{61}$BM 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:PC$_{61}$BM and 2c:PC$_{61}$BM before and after SVA at the optimized device condition.

<table>
<thead>
<tr>
<th></th>
<th>$\mu_e$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_h$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_h/\mu_e$</th>
<th>$\mu_e$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_h$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_h/\mu_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a:PC$_{61}$BM</td>
<td>as cast</td>
<td>5.3×10$^{-4}$</td>
<td>1.3×10$^{-4}$</td>
<td>0.25</td>
<td>as cast</td>
<td>6.4×10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>SVA</td>
<td>3.4×10$^{-4}$</td>
<td>1.5×10$^{-4}$</td>
<td>0.45</td>
<td>SVA</td>
<td>8.2×10$^{-4}$</td>
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**Table S2.** Photovoltaic performance of the devices under 100 mW/cm$^2$ simulated solar irradiation.
### Table S3. Photovoltaic performance of 2a in BHJ devices with different D/A ratio.

<table>
<thead>
<tr>
<th>donor</th>
<th>acceptor</th>
<th>conc</th>
<th>SVA [s]</th>
<th>$V_{OC}$ [V]</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2b</td>
<td>PC$_{61}$BM</td>
<td>30 mg/mL</td>
<td>–</td>
<td>0.73</td>
<td>4.15</td>
<td>46.30</td>
</tr>
<tr>
<td>2</td>
<td>2b</td>
<td>PC$_{61}$BM</td>
<td>30 mg/mL</td>
<td>THF 30</td>
<td>0.73</td>
<td>4.29</td>
<td>49.20</td>
</tr>
<tr>
<td>5</td>
<td>2c</td>
<td>PC$_{71}$BM</td>
<td>30 mg/mL</td>
<td>–</td>
<td>0.58</td>
<td>6.30</td>
<td>51.50</td>
</tr>
<tr>
<td>6</td>
<td>2c</td>
<td>PC$_{71}$BM</td>
<td>30 mg/mL</td>
<td>THF 30</td>
<td>0.59</td>
<td>4.65</td>
<td>45.00</td>
</tr>
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</table>

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

<table>
<thead>
<tr>
<th>SVA</th>
<th>$V_{OC}$ [V]</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-cast</td>
<td>0.75</td>
<td>13.84</td>
<td>46.30</td>
<td>4.77</td>
</tr>
<tr>
<td>THF 10s</td>
<td>0.724</td>
<td>15.31</td>
<td>0.420</td>
<td>4.79</td>
</tr>
<tr>
<td>THF 20s</td>
<td>0.74</td>
<td>16.70</td>
<td>0.49</td>
<td>6.09</td>
</tr>
<tr>
<td>THF 40s</td>
<td>0.74</td>
<td>13.98</td>
<td>0.44</td>
<td>4.59</td>
</tr>
<tr>
<td>THF 60s</td>
<td>0.74</td>
<td>16.33</td>
<td>0.50</td>
<td>5.96</td>
</tr>
<tr>
<td>THF 80s</td>
<td>0.75</td>
<td>14.69</td>
<td>0.48</td>
<td>5.27</td>
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</table>
Table S5. Photovoltaic performance of the 2a in the BHJ devices with different SVA time.

<table>
<thead>
<tr>
<th>SVA</th>
<th>$V_{OC}$ [V]</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-cast</td>
<td>0.65</td>
<td>9.46</td>
<td>43.47</td>
<td>2.69</td>
</tr>
<tr>
<td>CS$_2$ 20s</td>
<td>0.65</td>
<td>10.83</td>
<td>44.79</td>
<td>3.14</td>
</tr>
<tr>
<td>CS$_2$ 30s</td>
<td>0.63</td>
<td>10.34</td>
<td>58.62</td>
<td>3.82</td>
</tr>
<tr>
<td>CS$_2$ 40s</td>
<td>0.63</td>
<td>9.24</td>
<td>58.67</td>
<td>3.39</td>
</tr>
<tr>
<td>CS$_2$ 60s</td>
<td>0.60</td>
<td>3.33</td>
<td>43.78</td>
<td>0.88</td>
</tr>
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</table>

Table S6. Photovoltaic performance of the devices under 100 mW/cm$^2$ simulated solar irradiation.

<table>
<thead>
<tr>
<th>2a:PC$_{71}$BM</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>$J_{SC,cal}$ [mA cm$^{-2}$]</th>
<th>error</th>
<th>$J_{SAT}$ [mA cm$^{-2}$]</th>
<th>P(E,T)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>as cast</td>
<td>9.46</td>
<td>9.16</td>
<td>–3.17%</td>
<td>12.08</td>
<td>78.3%</td>
</tr>
<tr>
<td>SVA</td>
<td>10.34</td>
<td>9.86</td>
<td>–4.46%</td>
<td>10.99</td>
<td>94.1%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2c:PC$_{71}$BM</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>$J_{SC,cal}$ [mA cm$^{-2}$]</th>
<th>error</th>
<th>$J_{SAT}$ [mA cm$^{-2}$]</th>
<th>P(E,T)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>as cast</td>
<td>5.23</td>
<td>4.44</td>
<td>–15.1%</td>
<td>6.14</td>
<td>85.0%</td>
</tr>
<tr>
<td>SVA</td>
<td>4.88</td>
<td>3.79</td>
<td>–22.3%</td>
<td>5.74</td>
<td>85.1%</td>
</tr>
</tbody>
</table>

$^a$ Exciton dissociation probability under short-circuit condition.

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

<table>
<thead>
<tr>
<th>Thickness [nm]</th>
<th>$V_{OC}$ [V]</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
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<td>5.87</td>
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7. $^1$H and $^{13}$C NMR Spectra

Figure S11. $^1$H NMR spectrum for 2a.

$^1$H NMR (400 MHz, tetrachloroethane-$d_2$ with 1% pyridine-$d_5^*$, 100 °C): $\delta$ 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, NCH$_2$), 4.05 (d, $J = 7.8$ Hz, 8H, NCH$_2$), 2.11 (s, 4H, CH), 1.97 (s, 4H, CH), 1.52–1.34 (m, 64H, CH$_2$), 1.10–0.91 (m, 48H, CH$_3$).
**Figure S12.** $^1$H NMR spectrum for 2b.

$^1$H NMR (400 MHz, tetrachloroethane-$d_2$ with 1% pyridine-$d_5^*$, 100 °C): $\delta$ 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.** $^1$H NMR spectrum for 2c.

$^1$H NMR (400 MHz, tetrachloroethane-$d_2$ with 1% pyridine-$d_5^*$, 100 °C): $\delta$ 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. $^1$H NMR spectrum for Br-Se-DPP.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$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. $^1$H NMR spectrum for Br-DPP-Th.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$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. $^1$H NMR spectrum for Br-Se-DPP-Th.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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. $^1$H NMR spectrum for S-DPP-Th.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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. $^1$H NMR spectrum for Se-DPP-Th.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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. $^1$H NMR spectrum for Se-DPP.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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. $^1$H NMR spectrum for Th-Bpin.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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, 108.52, 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, 26.66, 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$_3$): $\delta$ 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$_3$): $\delta$ 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$_3$): $\delta$ 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$_3$): $\delta$ 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$_3$): $\delta$ 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): calcld for C$_{148}$H$_{164}$MgN$_{12}$O$_8$Se$_8$ (M$^+$): 2894.6070, found 2894.6050.
Figure S28. HRMS spectrum for 2b. MALDI-TOF-HRMS (+) (m/z): calcd for C\textsubscript{196}H\textsubscript{236}MgN\textsubscript{12}O\textsubscript{8}S\textsubscript{12} (M\textsuperscript{+}): 3296.4972, found 3296.4956.

Figure S29. HRMS spectrum for 2c. MALDI-TOF-HRMS (+) (m/z): calcd for C\textsubscript{196}H\textsubscript{236}MgN\textsubscript{12}O\textsubscript{8}S\textsubscript{4}Se\textsubscript{8} (M\textsuperscript{+}): 3677.0484, found 3677.5509.

Figure S30. HRMS spectrum for Br-Se-DPP. MALDI-TOF-HRMS (+) (m/z): calcd for C\textsubscript{50}H\textsubscript{58}BrN\textsubscript{2}O\textsubscript{2}Se\textsubscript{2} (M\textsuperscript{+}): 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_{2}O_{2}SSe_{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_{2}O_{2}S_{3} (M⁺): 796.2766, found 796.2800.

**References**