Electric Supplementary Information

Soluble Porphyrin Donors for Small Molecule Bulk Heterojunction Solar Cells

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1. NMR Spectra

* = solvents and impurities

Figure S1. $^1$H NMR spectrum of 2 in CDCl$_3$.

Figure S2. $^{13}$C NMR spectrum of 2 in CDCl$_3$. 
Figure S3. $^1$H NMR spectrum of 3 in CDCl$_3$.

Figure S4. $^{13}$C NMR spectrum of 3 in CDCl$_3$. 
Figure S5. $^1$H NMR spectrum of 4 in THF-$d_8$.

Figure S6. $^{13}$C NMR spectrum of 4 in THF-$d_8$. 
2. X-ray Crystallographic Studies

Single crystals of 2 suitable for X-ray analysis were obtained by slow diffusion of methanol into a solution of 2 in CHCl₃.

![X-ray Crystallographic Structure of 2](image)

**Figure S7.** X-ray crystal structure of compound 2 coordinated by methanol. C₆₀H₆₈Mg₆N₆O₆Si₂, \(M_W = 957.67\), triclinic, \(P\bar{1}\) (#2), \(a = 10.7018(2)\), \(b = 16.4164(3)\), \(c = 16.4397(3)\) Å, \(\alpha = 102.6540(10)^\circ\), \(\beta = 98.9910(10)^\circ\), \(\gamma = 95.3040(10)^\circ\), \(V = 2759.28(9)\) Å³, \(Z = 2\), \(T = 123\) K, \(R_1 = 0.1206\) \([I > 2\sigma(I)]\) \(wR_2 = 0.3153\) [All data], \(GOF [I > 2\sigma(I)] = 1.202\).

Single crystals of 4 suitable for X-ray analysis were obtained by slow diffusion of methanol into a solution of 4 in THF.

![X-ray Crystallographic Structure of 4](image)

**Figure S8.** X-ray crystal structure of compound 4 coordinated by THF. C₆₆H₇₄Mg₆N₆O₆Si₂, \(M_W = 1127.80\), monoclinic, \(P2_1/n\) (#14), \(a = 15.3573(3)\), \(b = 7.48620(10)\), \(c = 27.0680(5)\) Å, \(\beta = 103.4350(10)^\circ\), \(V = 3026.79(9)\) Å³, \(Z = 2\), \(T = 123\) K, \(R_1 = 0.0775\) \([I > 2\sigma(I)]\) \(wR_2 = 0.2465\) [All data], \(GOF [I > 2\sigma(I)] = 1.033\).
3. Thermogravimetric-Differential Thermal Analysis (TG-DTA)

*Figure S9.* TG-DTA curves of compounds 2, 3 and 4. About 5% mass reduction of compounds 2 and 3 around 100 ºC are attributed the removal of methanol that coordinated to the magnesium in reprecipitation.
4. Cyclic Voltammetry (CV)

Figure S10. Cyclic voltammograms of compounds 2 (black), 3 (red) and 4 (blue). Measurements were performed in CH$_2$Cl$_2$ (THF for compound 4) solution containing TBAPF$_6$ (0.1 M) as a supporting electrolyte at 25 °C with a scan rate of 100 mV/s. Glassy-carbon, platinum wire, and Ag/AgClO$_4$ electrodes were used as working, counter, and reference electrodes, respectively. The potential was corrected against Fc/Fc$^+$. The HOMO and LUMO levels were estimated by the following equation; HOMO = -(4.8 + E$_{1/2}$(ox)), LUMO = -(4.8 + E$_{1/2}$(red)).
5. Hole-only and Electron-only Device Fabrication and Data
The hole mobilities of the porphyrin film was evaluated by the SCLC model using hole-only devices. The hole mobilities and the electron mobilities of the blend films composed of porphyrins and PC_{60}BM in a mixture of 1:4 weight ratio were also evaluated by the SCLC model using hole-only and electron-only devices, respectively. For fabrication of hole-only device using each porphyrin as p-type semiconducting material, a 145-nm-thick, patterned indium-tin oxide (ITO) glass with a sheet resistance of 8 Ω/square was used as the substrate. A conducting poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Clevios AI4083) layer was formed on the glass/ITO substrate to obtain a 30-nm-thick thin film. For fabricating blend film, compound 2 or 3:PC_{60}BM in a 1:4 mixture was dissolved in chlorobenzene to obtain each solution (total concentration, 3.0 wt%). Compound 4:PC_{60}BM in a 1:4 mixture was dissolved in THF/toluene (1/1 wt ratio) to obtain a solution (total concentration, 1.5 wt%). For fabricating porphyrin film, compounds 2 and 3 were dissolved in chloroform, and compound 4 was dissolved in THF to obtain each porphyrin solution (1.0 wt%). Each blend film, porphyrin film was formed by spin-coating method at 4500 rpm, 30 s for compound 2 or 3, or 3000 rpm, 30 s for compound 4 on the ITO/PEDOT:PSS substrate. MoO_{3} (10 nm) was deposited in vacuum (3 x 10^{-4} Pa) on top of the porphyrin layer to reduce energy barrier for hole injection, followed by deposition of an aluminum electrode (Al, 110 nm) in vacuum. For fabrication of electron-only device using each compound as n-type semiconducting material, a 110-nm-thick, patterned aluminum vacuum-deposited (3 x 10^{-4} Pa) on the glass was used as the substrate. Compound 2 or 3:PC_{60}BM in a 1:4 mixture was dissolved in chlorobenzene to obtain each solution (total concentration, 3.0 wt%). Compound 4:PC_{60}BM in a 1:4 mixture was dissolved in THF/toluene (1/1 wt ratio) to obtain a solution (total concentration, 1.5 wt%). Each blend film was formed by spin-coating method at 4500 rpm, 30 s for compound 2 or 3, or 3000 rpm, 30 s for compound 4 on the ITO/Al substrate. We consider that the difference of the blend film thickness between ITO/PEDOT:PSS substrate and ITO/Al substrate is attributed to wettability of each solution on each substrate surface. LiF (0.6 nm) was deposited in vacuum (3 x 10^{-4} Pa) on top of blend film to reduce the energy barrier for electron injection, followed by the deposition of an aluminum electrode (Al, 110 nm) in vacuum. All devices were encapsulated in a glove box in nitrogen atmosphere. The current of the fabricated hole-only and electron-only devices was measured with a sweeping voltage using a Keithley 2400 source measurement unit controlled by a computer. A film thickness is obtained by using a Dektak 6M stylus profiler.

Figure S11. J-V curves of the devices. (a) hole mobility and (b) electron mobility of blend films were evaluated by space-charge current limited (SCLC) model. Dash lines show $J \sim V^2$. 

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Table S1. Summary of hole mobilities ($\mu_h$) and electron mobilities ($\mu_e$) of the blend films using porphyrins and PC$_{60}$BM in a mixture of 1:4 weight ratio.

<table>
<thead>
<tr>
<th>Blend films Compound:PC$_{60}$BM (1:4)</th>
<th>Hole-only device</th>
<th>Electron-only device</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\mu_h$ [cm$^2$/Vs]</td>
<td>Thickness [nm]</td>
</tr>
<tr>
<td>2 (R = H)</td>
<td>$2.3 \times 10^{-5}$</td>
<td>175.5</td>
</tr>
<tr>
<td>3 (R = NMe$_2$)</td>
<td>$3.7 \times 10^{-5}$</td>
<td>174.5</td>
</tr>
<tr>
<td>4 (R = NO$_2$)</td>
<td>no data</td>
<td>139.5</td>
</tr>
</tbody>
</table>

Hole-only device configuration: glass/ITO/PEDOT:PSS/blend film/MoO$_3$/Al, electron-only device configuration: glass/Al/blend film/LiF/Al.

Table S2. Summary of hole mobilities ($\mu_h$) of compounds 2, 3 and 4 evaluated by SCLC model.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Thickness [nm]</th>
<th>Hole mobility [cm$^2$/Vs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (R = H)</td>
<td>CF</td>
<td>144.4</td>
<td>$4.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>3 (R = NMe$_2$)</td>
<td>CF</td>
<td>141.6</td>
<td>$8.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>4 (R = NO$_2$)</td>
<td>THF</td>
<td>139.8</td>
<td>$5.7 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Hole-only device configuration: glass/ITO/PEDOT:PSS/porphyrin film/MoO$_3$/Al.
6. OFET Device Fabrication and Data

In order to estimate the field-effect hole mobility of porphyrin derivatives, we fabricated and characterized OFETs that have a top-contact geometry. A substrate of glass/Au gate electrode / Parylene-C insulator was prepared using methods given in previous papers. Organic semiconductors were spin-coated onto the Parylene-C layer. The substrate was transferred to an N₂ glovebox and then dried at 80°C for 10 min on a hot plate. Source and drain electrodes of Au (40 nm) were thermally evaporated through shadow masks. The channel length and width were fixed at 75 µm and 5 mm, respectively. OFET measurement was conducted under air using a Keithley 2636A source measurement unit.

Table S3. Summary of top-contact OFET performances of compounds 2, 3 and 4. (CB = chlorobenzene, CF = chloroform)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Thickness [nm]</th>
<th>Field-effect hole mobility [cm²/Vs]</th>
<th>Threshold voltage [V]</th>
<th>On/off ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (R = H)</td>
<td>CB</td>
<td>40</td>
<td>1.0 × 10⁻⁶</td>
<td>-6.0</td>
<td>3.2 × 10²</td>
</tr>
<tr>
<td>3 (R = NMe₂)</td>
<td>CF:CB = 1:1</td>
<td>30</td>
<td>3.0 × 10⁻³</td>
<td>-4.5</td>
<td>7.5 × 10²</td>
</tr>
<tr>
<td>4 (R = NO₂)</td>
<td>THF:Toluene =1:1</td>
<td>26</td>
<td>3.2 × 10⁻⁴</td>
<td>-36.1</td>
<td>6.2 × 10³</td>
</tr>
</tbody>
</table>

Device structure: Glass/gate-Au/Parylene-C/Porphyrin/Source-drain electrodes

2 (R = H): 0.6 wt% in CB. Spin-coating conditions: 600 rpm, 60 s.
3 (R = NMe₂): 0.5 wt% in CF/CB (1/1 wt ratio). Spin-coating conditions: 600 rpm, 60 s.
4 (R = NO₂): 0.5 wt% THF/Toluene (1/1 wt ratio). Spin-coating conditions 600 rpm, 60 s.
7. Atomic Force Microscopy
Morphology of the active layer composed of each porphyrin and PC₆₀BM was investigated by atomic force microscopy (AFM) in a tapping mode.

Figure S12. Surface topographies of the active layers composed of each porphyrin and PC₆₀BM in a 1:4 weight ratio coated on glass/ITO/PEDOT:PSS observed by AFM. (a) Compound 2 (surface roughness, Ra = 0.74 nm), (b) compound 3 (Ra = 0.57 nm), and (c) compound 4 (Ra = 2.5 nm). Scale bars indicate 500 nm.

8. Reference