*Electric Supplementary Information*

# Soluble Porphyrin Donors for Small Molecule Bulk Heterojunction Solar Cells

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## 1. NMR Spectra

* = solvents and impurities

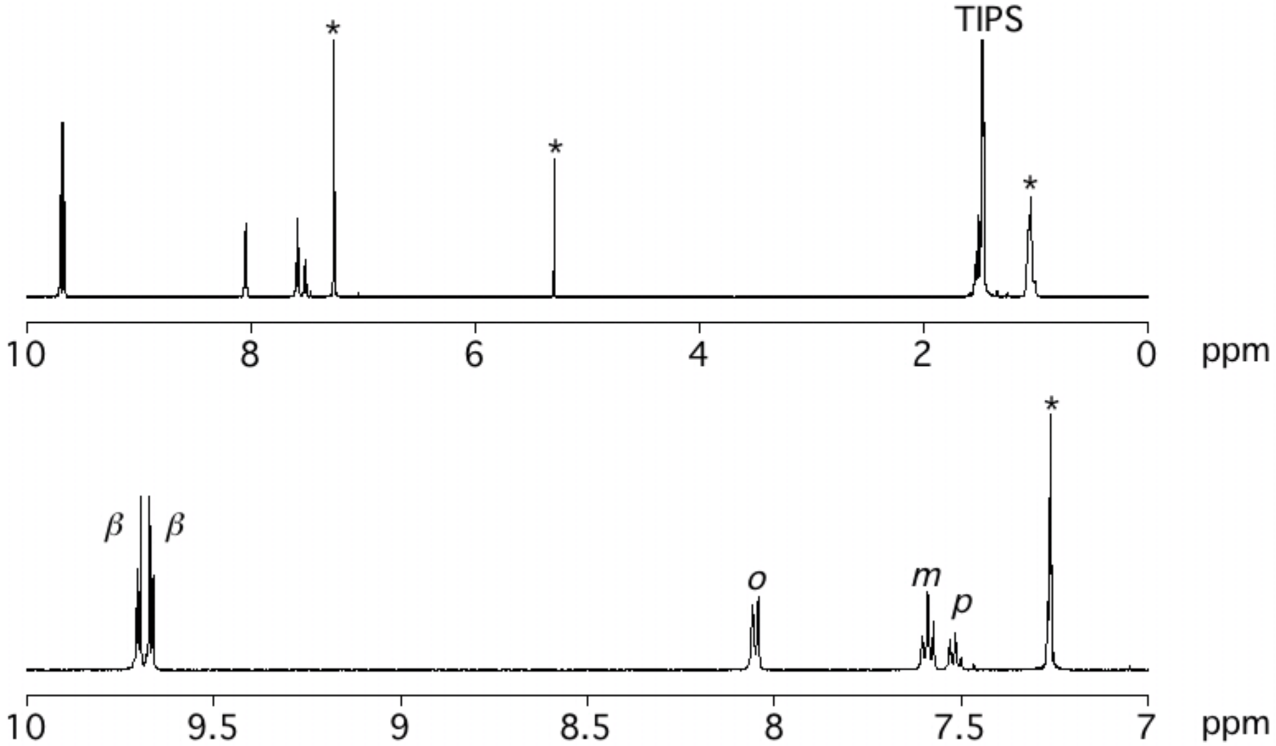

**Figure S1.** $^1$H NMR spectrum of **2** in $CDCl_3$.

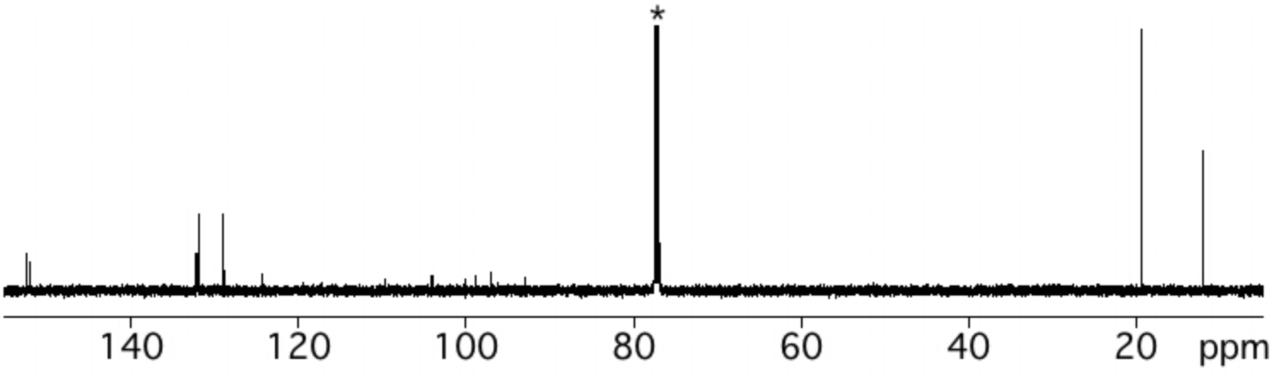

**Figure S2.** $^{13}$C NMR spectrum of **2** in $CDCl_3$.

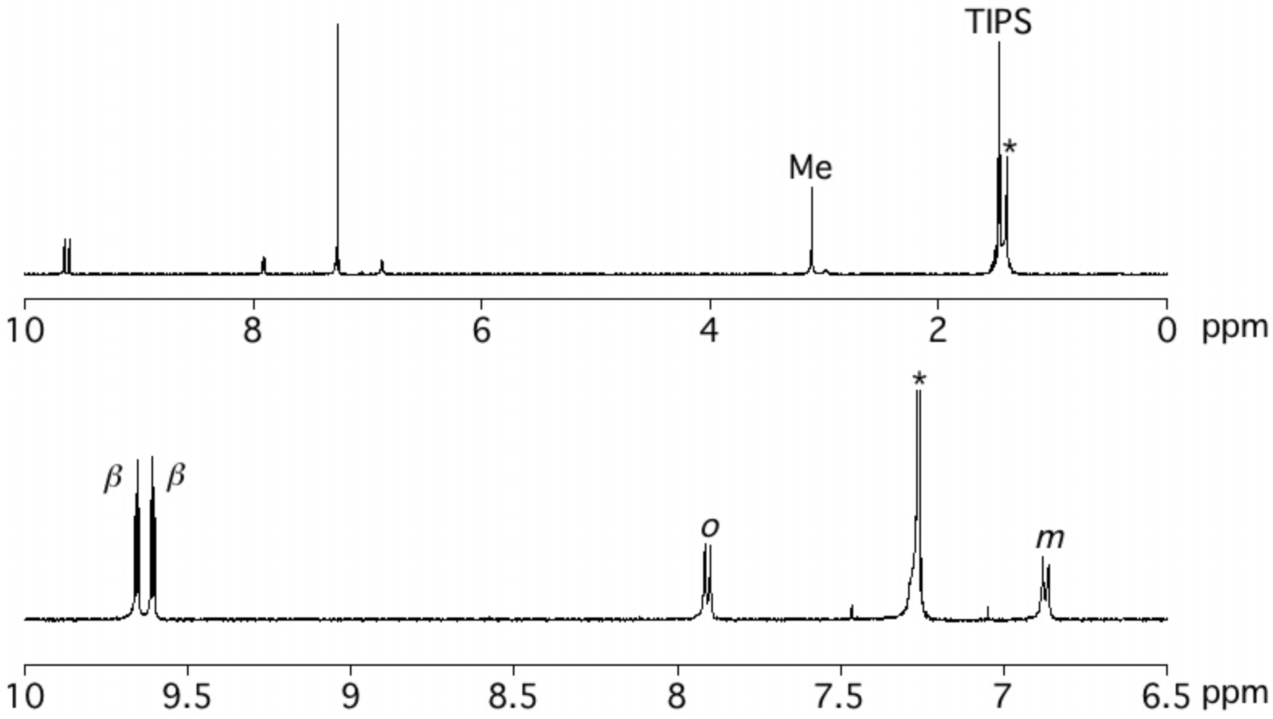

**Figure S3.** $^1$H NMR spectrum of **3** in $CDCl_3$.

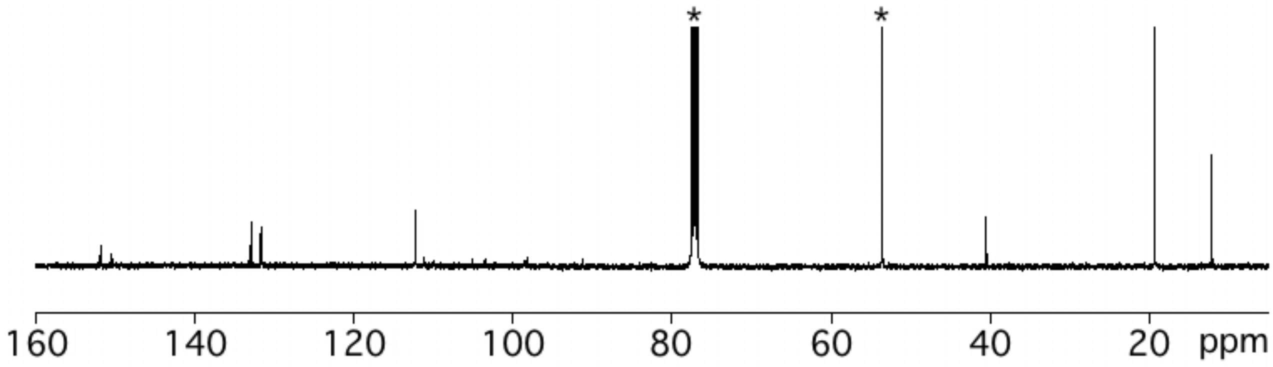

**Figure S4.** $^{13}$C NMR spectrum of **3** in $CDCl_3$.

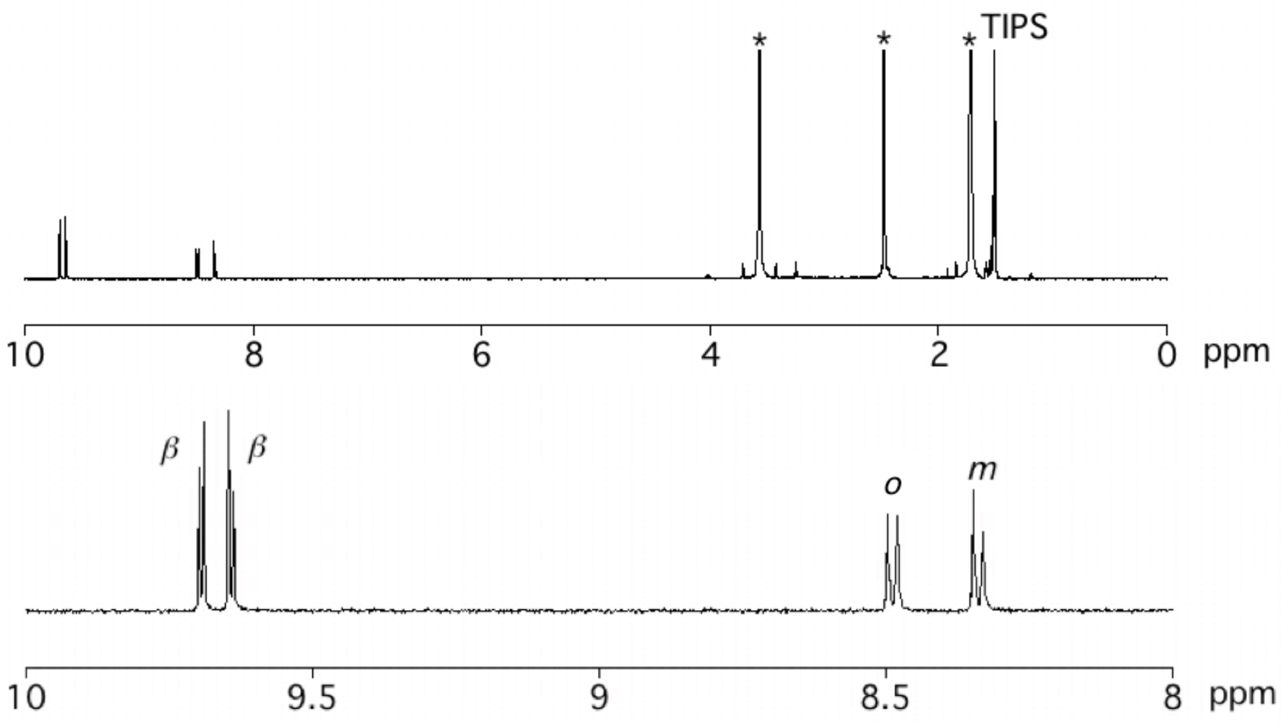

**Figure S5.** $^{1}$H NMR spectrum of **4** in THF-$d_8$.

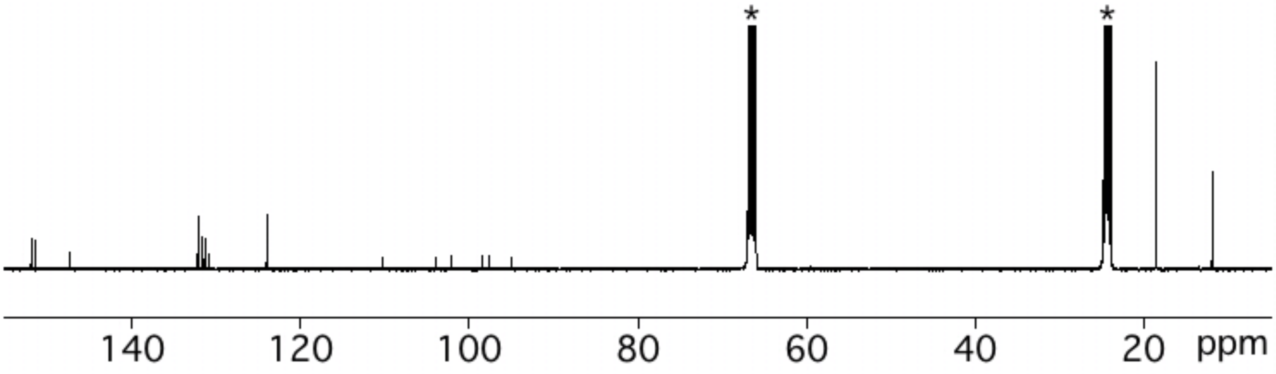

**Figure S6.** $^{13}$C NMR spectrum of **4** in THF-$d_8$.

## 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 $CHCl_3$.

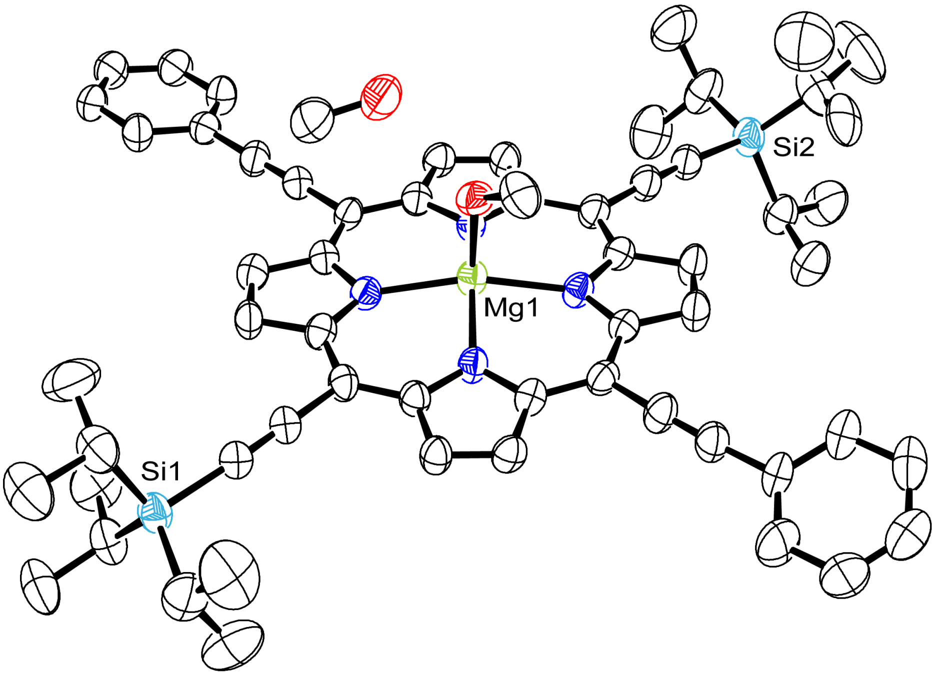

**Figure S7.** X-ray crystal structure of compound **2** coordinated by methanol. $C_{60}H_{68}MgN_4O_2Si_2$, *Mw* = 957.67, triclinic, *P–1* (#2), *a* = 10.7018(2), *b* = 16.4164(3), *c* = 16.4397(3) Å, *α* = 102.6540(10)°, *β* = 98.9910(10)°, *γ* = 95.3040(10)°, *V* = 2759.28(9) Å$^3$, *Z* = 2, *T* = 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.

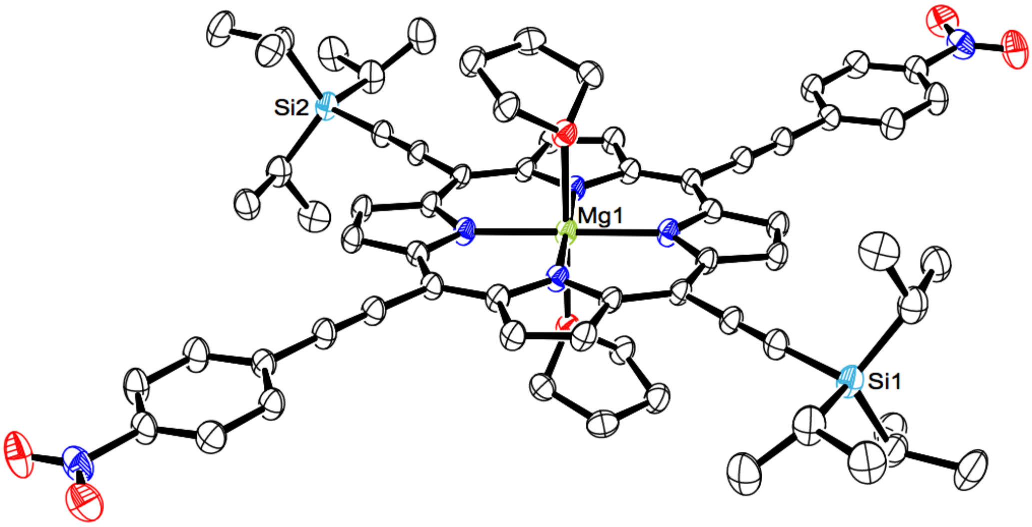

**Figure S8.** X-ray crystal structure of compound **4** coordinated by THF. $C_{66}H_{74}MgN_6O_6Si_2$, *Mw* = 1127.80, monoclinic, $P2_1/n$ (#14), *a* = 15.3573(3), *b* = 7.48620(10), *c* = 27.0680(5) Å, *β* = 103.4350(10)°, *V* = 3026.79(9) Å$^3$, *Z* = 2, *T* = 123 K, $R_1 = 0.0775$ [$I > 2\sigma(I)$] $wR_2 = 0.2465$ [All data], GOF [$I > 2\sigma(I)$] = 1.033.

## 3. Thermogravimetric-Differential Thermal Analysis (TG-DTA)

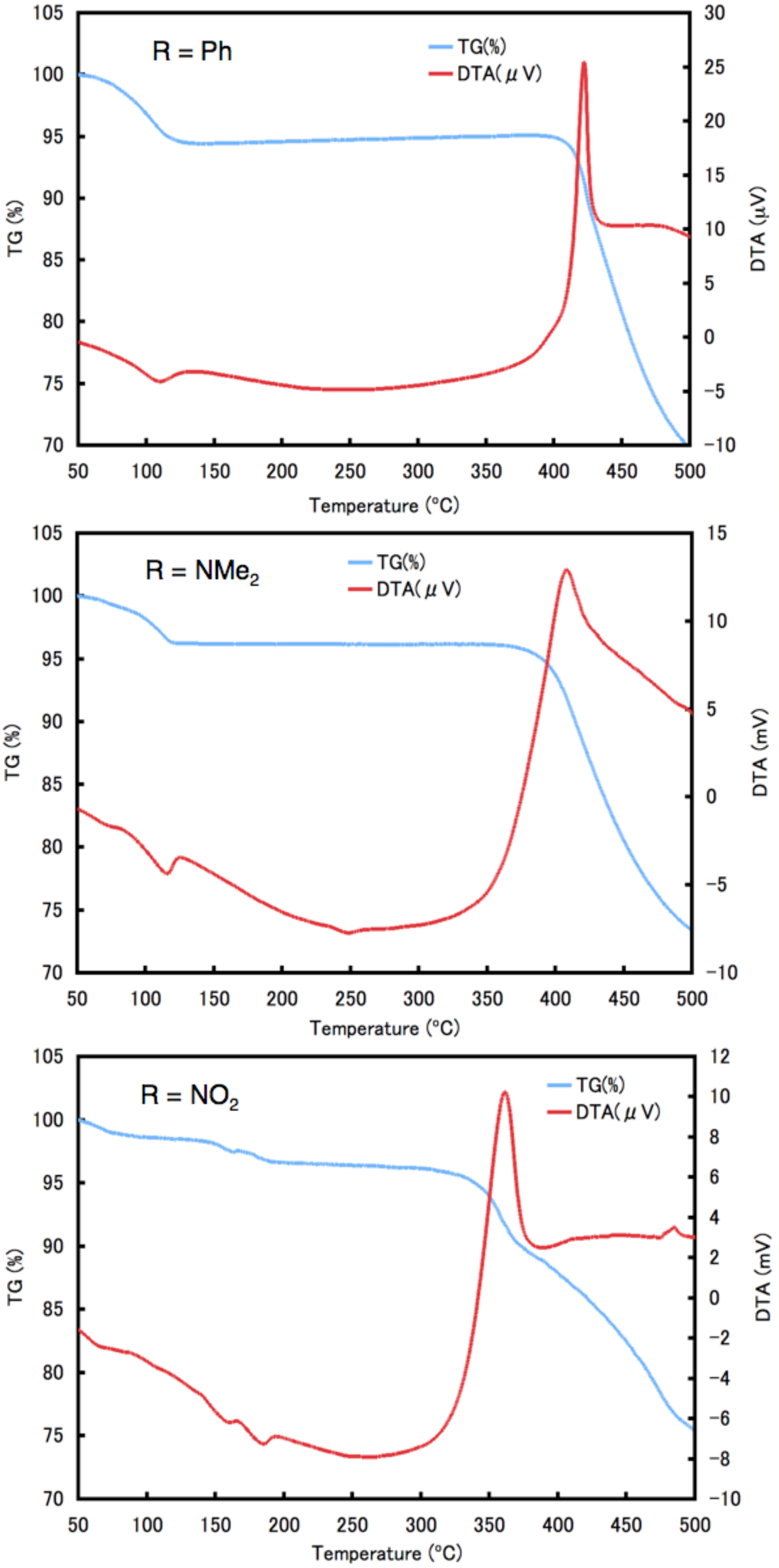

**Figure S9.** TG-DTA curves of compounds **2**, **3** and **4**. About 5% mass reduction of compounds **2** and **3** around 100 ºC are attributed the removal of methanol that coordinated to the magnesium in reprecipitation.

## 4. Cyclic Voltammetry (CV)

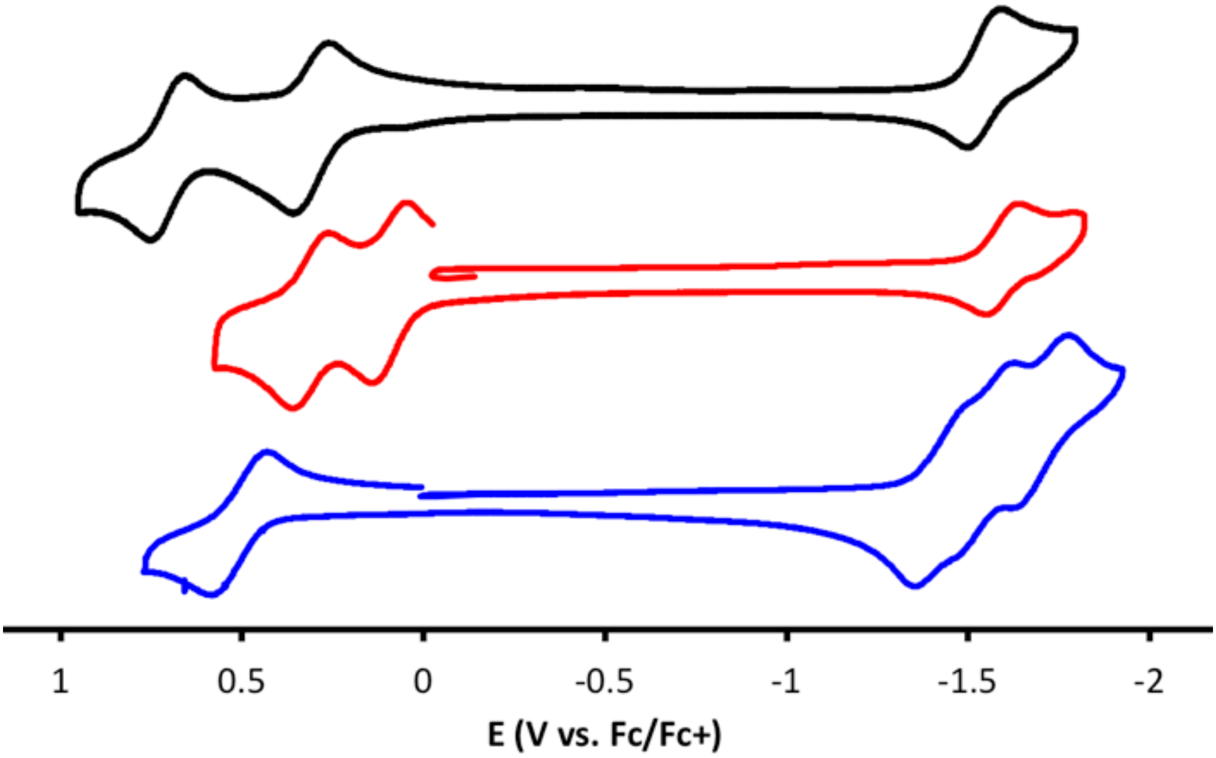

**Figure S10.** Cyclic voltammograms of compounds **2** (black), **3** (red) and **4** (blue). Measurements were performed in $CH_2Cl_2$ (THF for compound **4**) solution containing $TBAPF_6$ (0.1 M) as a supporting electrolyte at 25 ºC with a scan rate of 100 mV/s. Glassy-carbon, platinum wire, and $Ag/AgClO_4$ 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.[1] The hole mobilities and the elecron 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 ($3 \times 10^{-4}$ 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 ($3 \times 10^{-4}$ 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 ($3 \times 10^{-4}$ 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.

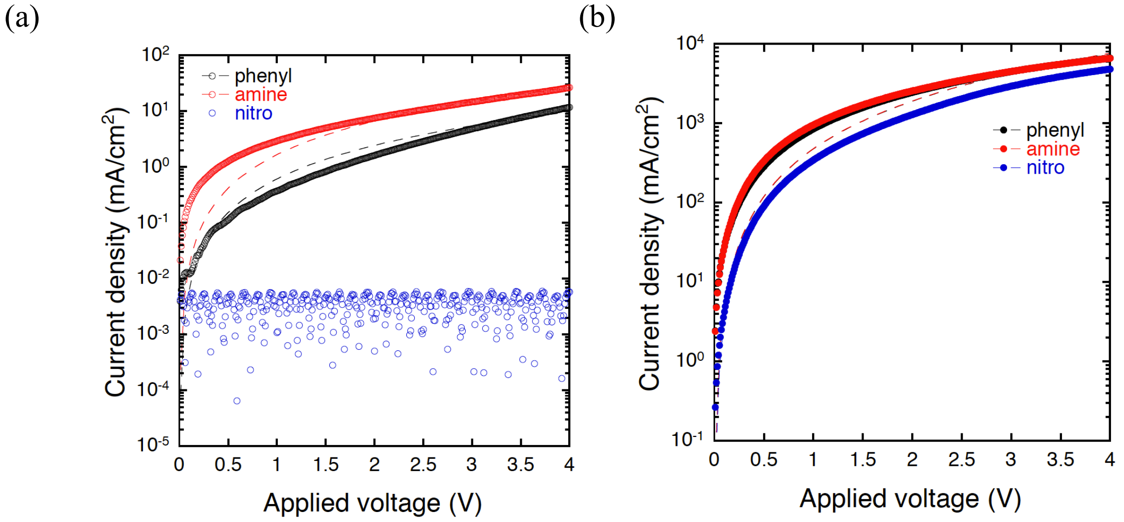

**Figure S11.** *J-V* curves of the devices. (a) hole mobility and (b) electron mobility of blend films were evaluated by space-charge current limited (SCLC) model. Dash lines show $J \sim V^2$.

**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.

| Blend films Compound:$PC_{60}BM$ (1:4) | Hole-only device | | Electron-only device | |
|---|---|---|---|---|
| | $\mu_h$ [cm$^2$/Vs] | Thickness [nm] | $\mu_e$ (cm$^2$/Vs) | Thickness [nm] |
| **2** (R = H) | $2.3 \times 10^{-5}$ | 175.5 | $9.1 \times 10^{-4}$ | 76.7 |
| **3** (R = $NMe_2$) | $3.7 \times 10^{-5}$ | 174.5 | $5.9 \times 10^{-4}$ | 66.5 |
| **4** (R = $NO_2$) | no data | 139.5 | $1.2 \times 10^{-3}$ | 96.6 |

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.

| Compound | Solvent | Thickness [nm] | Hole mobility [cm$^2$/Vs] |
|---|---|---|---|
| **2** (R = H) | CF | 144.4 | $4.6 \times 10^{-5}$ |
| **3** (R = $NMe_2$) | CF | 141.6 | $8.0 \times 10^{-4}$ |
| **4** (R = $NO_2$) | THF | 139.8 | $5.7 \times 10^{-4}$ |

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.[2] Organic semiconductors were spin-coated onto the Parylene-C layer. The substrate was transferred to an $N_2$ 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)

| Compound | Solvent | Thickness [nm] | Field-effect hole mobility [$cm^2/Vs$] | Threshold voltage [V] | On/off ratio |
|---|---|---|---|---|---|
| **2** (R = H) | CB | 40 | $1.0 \times 10^{-6}$ | -6.0 | $3.2 \times 10$ |
| **3** (R = $NMe_2$) | CF:CB = 1:1 | 30 | $3.0 \times 10^{-3}$ | -4.5 | $7.5 \times 10^{2}$ |
| **4** (R = $NO_2$) | THF:Toluene =1:1 | 26 | $3.2 \times 10^{-4}$ | -36.1 | $6.2 \times 10^{3}$ |

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 = $NMe_2$): 0.5 wt% in CF/CB (1/1 wt ratio). Spin-coating conditions: 600 rpm, 60 s.
**4** (R = $NO_2$): 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 $PC_{60}BM$ was investigated by atomic force microscopy (AFM) in a tapping mode.

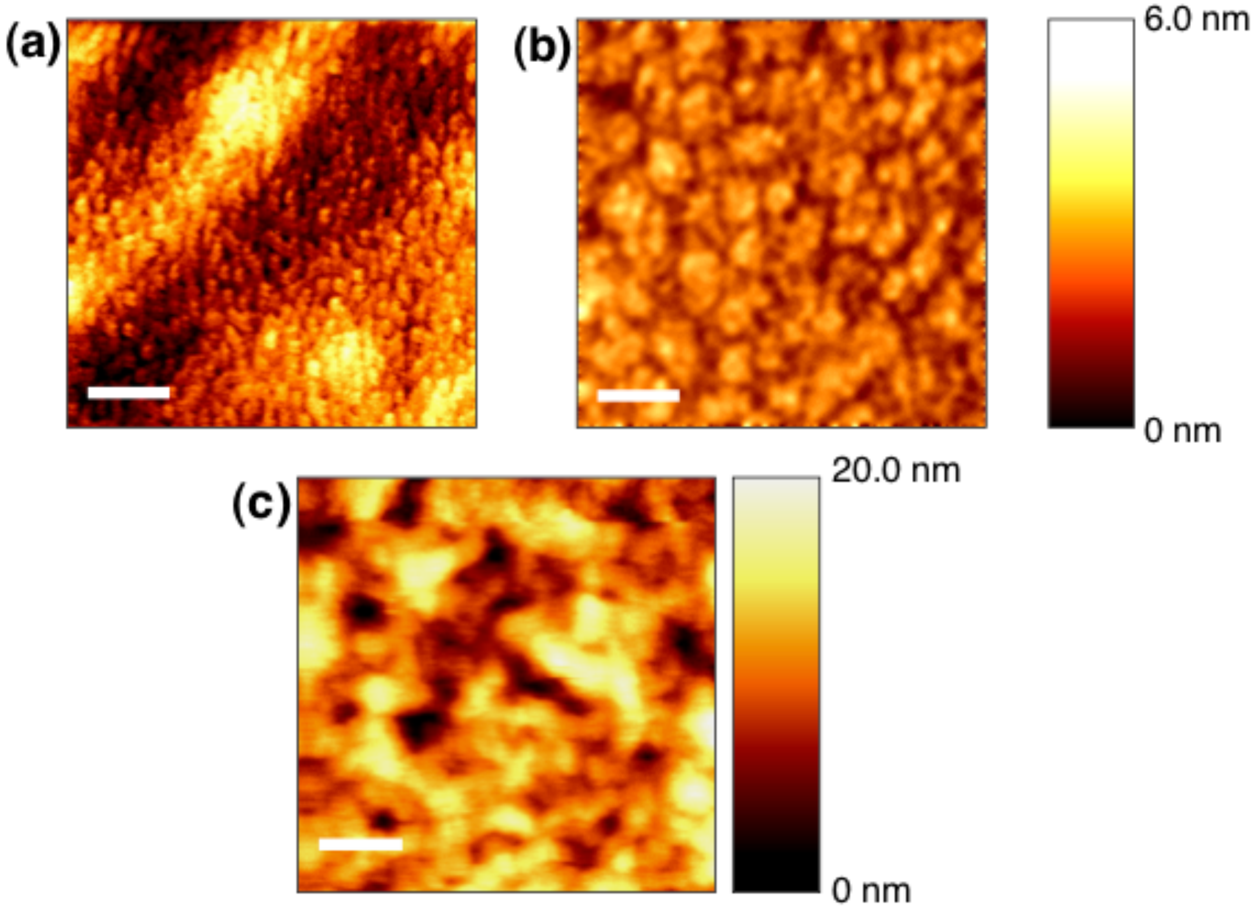

**Figure S12.** Surface topographies of the active layers composed of each porphyrin and $PC_{60}BM$ in a 1:4 weight ratio coated on glass/ITO/PEDOT:PSS observed by AFM. (a) Compound **2** (surface roughness, Ra = 0.74 nm), (b) compound **3** (Ra = 0.57 nm), and (c) compound **4** (Ra = 2.5 nm). Scale bars indicate 500 nm.

## 8. Reference

[1] *a*) M. A. Lampert and P. Mark, *Current Injection in Solids*, 1970; *b*) P. W. M. Blom, M. J. M. de Jong, J. J. M. Vleggaar, *Appl. Phys. Lett*. **1996**, *68*, 3308.

[2] T. Yasuda, K. Fujita, H. Nakashima, T. Tsutsui, *Jpn. J. Appl. Phys*. **2001**, *42*, 6614.