Supporting Information for

A metal-lustrous porphyrin foil

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1. General Method

NMR spectra were recorded on Bruker AV-300. Matrix-assisted laser-dissociation ionization time-of-flight (MALDI–TOF) mass spectra were recorded on mass spectrometer (Bruker, Autoflex Speed). UV/vis absorption spectra were recorded on a spectrophotometer (Shimadzu, UV-1800) equipped with a Peltier thermoelectric temperature controlling unit (Shimadzu, TCC-240A). The thickness of porphyrin foil was measured by a thickness gauge. Absolute reflection spectrum was performed by JASCO MSV-370 (0° of incident and reflection angles for Fig 2A), and reflection angle-dependence was conducted by JASCO ARSV-732 equipped with V-650/B13861150 (5° of incident angle (θ) and varying reflection angles ϕ for Fig S1). X-ray fluorescence (XRF) was performed by Rigaku ZSX primus II. Spectrometric ellipsometory was recorded by Otsuka Electronics FE-5000S. The glass transition temperature (T_g) was observed under nitrogen stream by differential scanning calorimeter (Shimadzu, DSC-60Plus). Analytical size-exclusion chromatography was performed by a PU-2086 Plus (JASCO) equipped with columns of Shodex GPC LF-804 × 2 in a column oven (JASCO, 860-CO) with THF as the eluent, monitored by a UV detector (JASCO, UV-1570) and a RI detector (Shodex, RI-101).

Fig. S1. Schematic representation of the colour wheel.

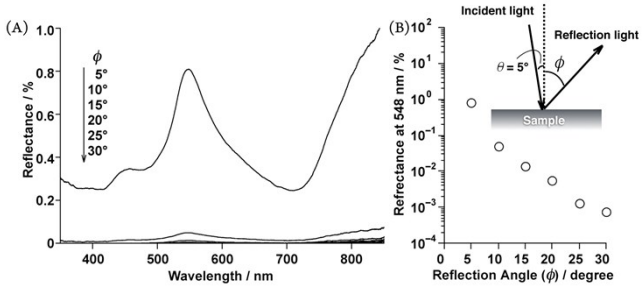
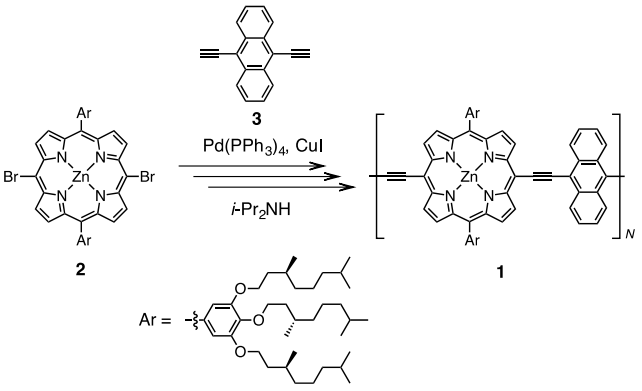


Fig. S2. Reflection angle-dependence in reflection spectra of the porphyrin foil, observed at a constant incident angle of 5° (A), and the plot of reflectance at 548 nm (B). Inset shows the configuration of experimental set-up.

2. Synthesis of 1.

Porphyrin **1** was synthesized via Sonogashira–Hagihara coupling reaction of porphyrin **2** and 9,10-bis(ethynyl)anthracene **3** using a Schlenk technique.[S1,S2] A solution of **2** (0.30 g, 0.19 mmol) in *i*-Pr_2NH (5 mL) in a Schlenk tube was degassed by freeze-pump-thaw cycles. To the solution, a solution of **3** (42 mg, 0.19 mmol) in THF (5 mL), $Pd(PPh_3)_4$ (10 mg, 8.6 μmol), and CuI (3 mg, 16 μmol), which was separately degassed by freeze-pump-thaw cycles, was added. The mixture was stirred at 70 °C for 4 days. The reaction mixture was diluted with chloroform/pyridine mixture, and then successively washed with water and brine. The organic layer was dried over anhydrous sodium sulfate. The residue dissolved in chloroform with 10% pyridine was repetitively reprecipitated from methanol and *n*-hexane. The solution of the product **1** in chloroform with 10% pyridine placed in a round-bottom flask was dried using a rotary evaporator, and then the product on the wall of the flask pealed off with the addition of methanol. Then, a "porphyrin foil" of **1** (0.3 g) was obtained in a 96% yield. An alternating porphyrin–anthracene sequence was identified based on 1:1 content of porphyrin–anthracene as well as no multiplied signals of them in pyridine-d_5 in ^1H and ^{13}C NMR spectra. The Sonogashira–Hagihara coupling reaction exclusively proceeded to provide **1**. ^1H NMR (300 MHz, $CDCl_3$ with 5% pyridine-d_5): δ 10.11 (brs, 4H; porphyrin-β), 9.56 (brs, 4H; anthracene), 9.18 (brs, 4H; porphyrin-β), 8.00 (brs, 4H, 4H; anthracene), 7.54 (s, 4H; Ar), 4.41–4.24 (brm, 12H, -O-CH_2-), 2.35–0.84 ppm (m, 114H; alkyl). ^{13}C NMR (75 MHz, $CDCl_3$ with 5% pyridine-d_5): δ 152.4, 151.3, 150.3, 138.1, 133.3, 127.4, 123.7, 114.5, 101.6, 72.1, 67.8, 39.5, 39.3, 37.7, 37.5, 36.7, 30.0, 28.1, 28.0, 24.9, 24.8, 22.8, 22.7, 22.6, 19.9, 19.8, 19.2 ppm. Molecular weight of **1** was determined to be M_n = 54,000 and M_w/M_n = 4.2 using polystyrene as the standard (Fig. S3). The XRF measurement found no bromine terminal.



Scheme 1. Synthesis of polymer **1**.

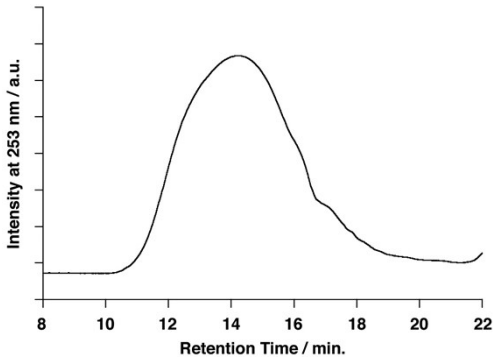


Fig. S3. SEC profile of **1** with THF as the eluent.

3. Static contact angle measurements.[S3]

The static contact angle (θ) of H_2O and CH_2I_2 was observed. Based on the Young equation, the surface free energy (γ) is the sum of a dispersion force component (γ^d) and a hydrogen bonding (dipole–dipole interaction) component (γ^h), *i.e.*, $\gamma = \gamma^d + \gamma^h$. Then, simultaneous Owens equations of θ for H_2O and CH_2I_2 give γ^d and γ^h, and therefore γ. The Owens equation defines the surface free energy of liquid (γ_{lq}) as; $\gamma_{lq}(1 + \cos\theta) = 2(\gamma_{solid}{}^d\gamma_{lq}{}^d)^{1/2} + 2(\gamma_{solid}{}^h\gamma_{lq}{}^h)^{1/2}$, wherein $\gamma_{lq}{}^d$ = 21.8 (H_2O) and 49.5 $mN{\cdot}m^{-1}$ (CH_2I_2), and $\gamma_L{}^h$ = 51 (H_2O) and 1.3 $mN{\cdot}m^{-1}$ (CH_2I_2). Accordingly, γ^d and γ^h of the porphyrin foil were estimated to be 35.5 and 0.40 $mN{\cdot}m^{-1}$, respectively. Therefore, the γ value was determined to be 35.9 $mN{\cdot}m^{-1}$.

4. Synchrotron X-ray scattering measurements.

The wide-angle X-ray scattering (WAXS) and ultra-small angle X-ray scattering (USAXS) experiments of the porphyrin foil were performed using synchrotron radiation at the BL45XU and BL19B2 beamline, respectively, in SPring-8 (RIKEN SPring-8 Centre Hyogo, Japan). The WAXS experiment were carried out using the combination of an image intensifier and a CMOS camera (Hamamatsu Photonics K. K.) or a PILATUS 300K-W (Dectris Ltd.) at 308.6 mm of the sample-to-detector distance. The USAXS experiment were carried out using the combination of an image intensifier and a CMOS camera (Hamamatsu Photonics K. K.) or a PILATUS 300K-W (Dectris Ltd.) at 40 m of the sample-to-detector distance.

5. Field-effect transistor experiments

Field-effect transistor experiments were performed in vacuum (~10^{-3} Pa) using two source meters (Keithley 2400). A toluene solution of **1** was cast on a microgap Au electrodes (channel length: 10 μm, channel width: 2 mm, height: 100 nm), wherein the Au electrodes were fabricated

on surface-oxidized Si substrates as the source and drain contacts.

The hole mobility, μ, was determined in the linear region based on the following equation.

$$I_D = (W/L)\mu C_i(V_G - V_{th})V_D$$

wherein I_D is the drain current, L (= 1.0×10^{-3} cm) and W (= 0.2 cm) are the channel length and width, respectively, C_i is the insulator capacitance per unit area ($C_i = \varepsilon_i \varepsilon_0/D$, where ε_0 is the permittivity of vacuum = 8.854×10^{-12} F cm^{-1}, ε_i is the relative permittivity of SiO_2 = 3.9, D is the thickness of SiO_2 layer = 300 nm), V_G, V_{th}, and V_D are the gate voltage, threshold voltage, and drain voltage, respectively. The average hole mobility was roughly estimated as $\mu = (4.0 \pm 1.4) \times 10^{-6}$ cm^2 V^{-1} s^{-1} under the conditions, where gate voltage was applied from –10 to –50 V (Fig. S4). The result was moderate, comparing with the reported values,[S4] considering the fact that we did not optimize the experimental conditions at this moment.

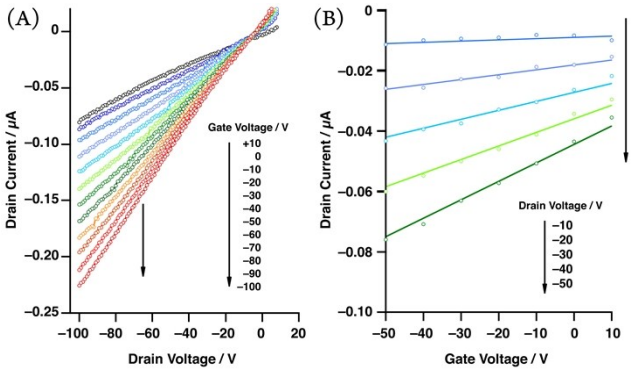


Fig. S4. (A) Drain current–drain voltage (I_D–V_D) characteristics of **1** as a function of the gate voltage (V_G). (B) Drain current–gate voltage (I_D–V_G) characteristics of **1** as a function of the drain voltage (V_D) in the linear region. (Electrode: L = 10 μm and W = 2 mm).

References

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[S2] Y.-P. Ou, C. Jiang, D. Wu, J. Xia, J. Yin, S. Jin, G.-A. Yu, S. H. Liu, *Organometallics* 2011, **30**, 5763–5770.

[S3] D. K. Owens, *J. App. Polym. Sci.* 1969, **13**, 1741–1747.

[S4] X. Huang, C. Zhu, S. Zhang, W. Li, Y. Guo, X. Zhang, Y. Liu, Z. Bo, *Macromolecules* 2008, **41**, 6895–6902.

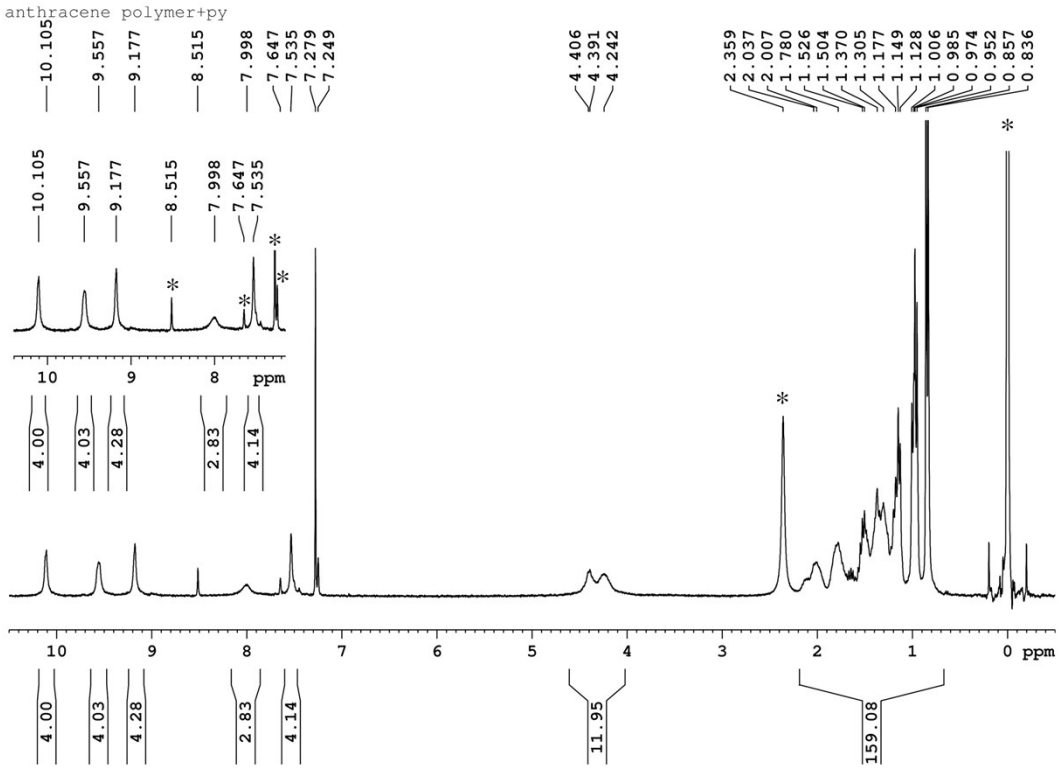

Fig. S6. ^{1}H NMR (300 MHz, $CDCl_3$ with 5% pyridine-d_5) of **1**. Asterisk indicates residual solvent and water.

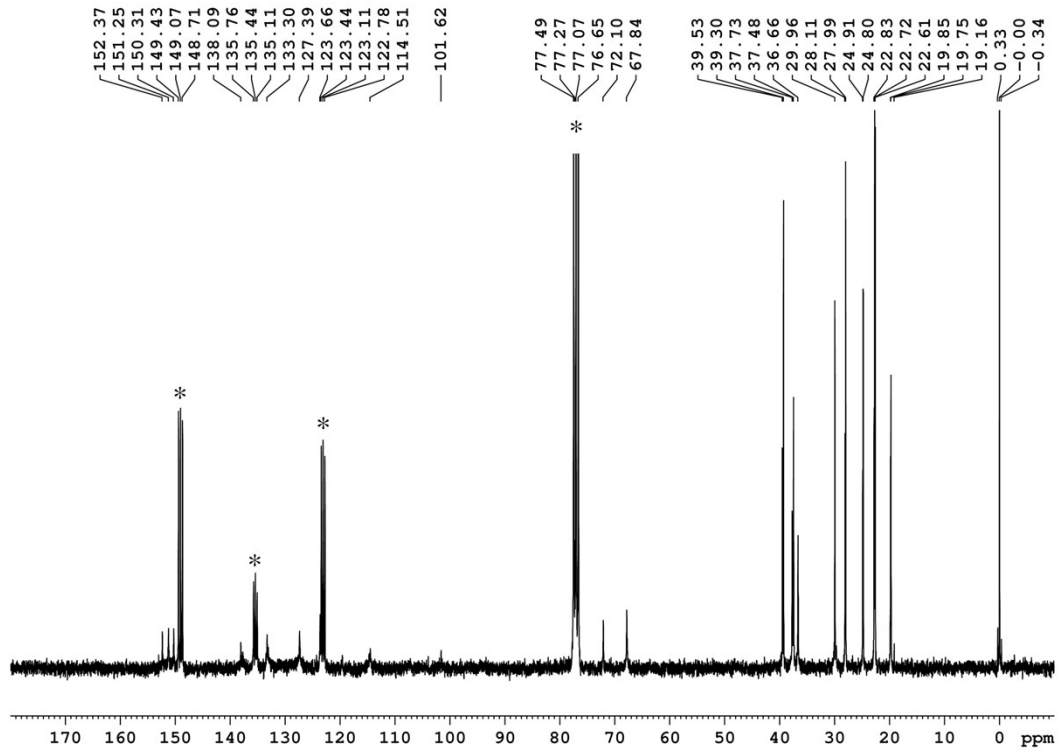

Fig. S7. ^{13}C NMR (75 MHz, $CDCl_3$ with 5% pyridine-d_5) of **1**. Asterisk indicates solvent.