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 ellipsometry 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.

Porphyrin 1 was synthesized via Sonogashira–Hagihara coupling reaction of porphyrin 2 and 9,10-bis(ethynyl)anthracene 3 using a Schlenk technique. A solution of 2 (0.30 g, 0.19 mmol) in i-Pr₂NH (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(PPh₃)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 thaw cycles, was added. The mixture was stirred at 70 °C 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 the product 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 peeled off with the addition of methanol. Then, a “porphyrin foil” of 1 was determined to be 35.5 and 0.40 mN·m⁻¹ (CH₂Cl₂), and therefore γ was found to be 35.9 mN·m⁻¹.

3. Static contact angle measurements

The static contact angle (θ) of H₂O and CH₃I₂ was observed. Based on the Young equation, the surface free energy (γ) is the sum of a dispersion force component (γd) and a hydrogen bonding (dipole–dipole interaction) component (γh), i.e., γ = γd + γh. Then, simultaneous Owens equations of θ for H₂O and CH₃I₂ give γd and γh, and therefore γ. The Owens equation defines the surface free energy of liquid (γliq) as

\[ \gamma_{liq} = \gamma_{solid} \cdot \cos \theta = 2(\gamma_{solid} \cdot \gamma_{liq})^{1/2} \]

wherein γliq is 21.8 (H₂O) and 49.5 mN·m⁻¹ (CH₃I₂), and \( \gamma_{liq} = 51 \) (H₂O) and 1.3 mN·m⁻¹ (CH₃I₂). Accordingly, γd and γh of the porphyrin foil were estimated to be 35.5 and 0.40 mN·m⁻¹, respectively. Therefore, the γ value was determined to be 35.9 mN·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 experiments 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 (~10⁻¹³ 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.

![Scheme 1. Synthesis of polymer 1.](image-url)
on surface-oxidized Si substrates as the source and drain contacts.

The hole mobility, $\mu$, was determined in the linear region based on the following equation.

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

wherein $I_D$ is the drain current, $L \ (= 1.0 \times 10^{-3} \text{ cm})$ and $W \ (= 0.2 \text{ cm})$ are the channel length and width, respectively, $C_i$ is the insulator capacitance per unit area ($C_i = \varepsilon_i \varepsilon_0 / D$, where $\varepsilon_0$ is the permittivity of vacuum $= 8.854 \times 10^{-12} \text{ F cm}^{-1}$, $\varepsilon_i$ is the relative permittivity of SiO$_2$ $= 3.9$, $D$ is the thickness of SiO$_2$ layer $= 300 \text{ nm}$), $V_G$, $V_{th}$, and $V_D$ are the gate voltage, threshold voltage, and drain voltage, respectively. The average hole mobility was roughly estimated as $\mu = (4.0 \pm 1.4) \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under the conditions, where gate voltage was applied from $-10$ to $-50 \text{ V}$ (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.

![Graph](image)

**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 \text{ $\mu m}$ and $W = 2 \text{ mm}$).

**References**


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.