

Supporting Information

Facile One-Pot Preparation of Thermally and Photochemically Convertible Soluble Precursors of Copper Phthalocyanine and Naphthalocyanine

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General. Mass spectra were obtained by using an AB SCIEX QSTAR Elite Hybrid LC/MS/MS System mass spectrometer using methanol as a solvent. Crystal structural analyses were performed at 173 K on a Rigaku Saturn 70-CCD. The structures were solved by direct method. X-ray powder diffraction analyses were performed using Cu-K α radiation on a Rigaku Rint2000. Thermogravimetry analyses were made with a Perkin ELMER STA6000. Electronic absorption measurements were made with Perkin ELMER Lambda 19 spectrophotometers. Photo-irradiation was performed by using Mikropack DH-2000-BAL.

4: Phthalonitrile (0.50 g, 3.9 mmol) was added to methanol (20 mL) in which lithium metal (0.20 g, 25 mmol) was dissolved at room temperature under a nitrogen atmosphere. The mixture was heated at 70 °C with stirring for 10 min, followed by the addition of anhydrous copper(II) chloride (0.15 g, 1.1 mmol). The color of the mixture turned to red brown during the reaction. After 30 min, the solvent was evaporated *in vacuo*. The residue was dissolved in CH₂Cl₂, and filtered in order to remove insoluble CuPc. The filtrate was purified by alumina column chromatography using CH₂Cl₂ as the eluent. After the first red fraction was collected, the solution was concentrated *in vacuo* at below 40 °C. The resulting solution was added to hexane, to precipitate **4** as a dark red powder in 33% yield (0.21 g). Spectral data: UV-vis (TCB): λ_{\max} nm, (log ϵ) 500 (2.53) 408 (3.84) 390 (3.89). MS (ESI): m/z = 638 [$M+H$]⁺. Anal. Found: C, 63.69; H, 3.71; N, 17.18. Calcd for C₃₄H₂₂N₈O₂Cu: C, 63.99; H, 3.47; N, 17.56.

9: 2,3-Naphthalenedicarbonitrile (0.31 g, 1.7 mmol) was added to methanol (9.0 mL) in which lithium metal (90 mg, 11 mmol) was dissolved at room temperature under a nitrogen atmosphere. The mixture was heated at 70 °C with stirring for 10 min, followed by the addition of anhydrous copper(II) chloride (67 mg, 0.50 mmol). The color of the mixture turned to red brown during the reaction. After 30 min, the solvent was evaporated *in vacuo*. The residue was purified by short alumina column chromatography (activity IV) using CH₂Cl₂ as the eluent to remove insoluble CuNc. The mixture was chromatographed (ULTRON VX-ODS, Shinwa Chemical Industries, Ltd., CH₂Cl₂ : methanol = 1 : 2 (v/v)), and the eluent concentrated *in vacuo* at below 40 °C. The resulting solution was added to hexane, to precipitate **9** as an orange powder in 6.2% yield (22 mg). Spectral data: UV-vis (TCB): λ_{max} nm, (log ϵ) 405 (4.83) 396 (4.84) 386 (4.84). MS (ESI): m/z = 838 [M+H]⁺. Anal. Found: C, 70.37; H, 3.81; N, 12.95. Calcd for C₅₀H₃₀N₈O₂Cu·CH₃OH: C, 70.37; H, 3.94; N, 12.87.

Crystallographic data

4: C₃₅H₂₆CuN₈O₃, M_w = 670.19, monoclinic, space group $P2_1/c$ (#14), a = 14.038(4), b = 13.225(4), c = 17.039(6) Å, β = 112.242(3)°, V = 2928.0(16) Å³, Z = 4, ρ_{calcd} = 1.520 g cm⁻³, T = -100 °C, R = 0.0446, R_w = 0.1188 (all data), GOF = 1.060.

9: C₅₀H₃₄CuN₈O₄, M_w = 874.42, triclinic, space group $P\bar{1}$ (#2), a = 7.6409(2), b = 15.4848(4), c = 16.7357(4) Å, α = 92.401(7), β = 96.431(7), γ = 99.712(7), V = 1935.7(1) Å³, Z = 2, ρ_{calcd} = 1.500 g cm⁻³, T = -73 °C, R = 0.0506, R_w = 0.1172 (all data), GOF = 1.112.

Observed electron densities corresponding to disordered solvated methanol molecules were all assigned as oxygen atoms for reasons of expediency. CCDC 818577 and 818578, respectively.

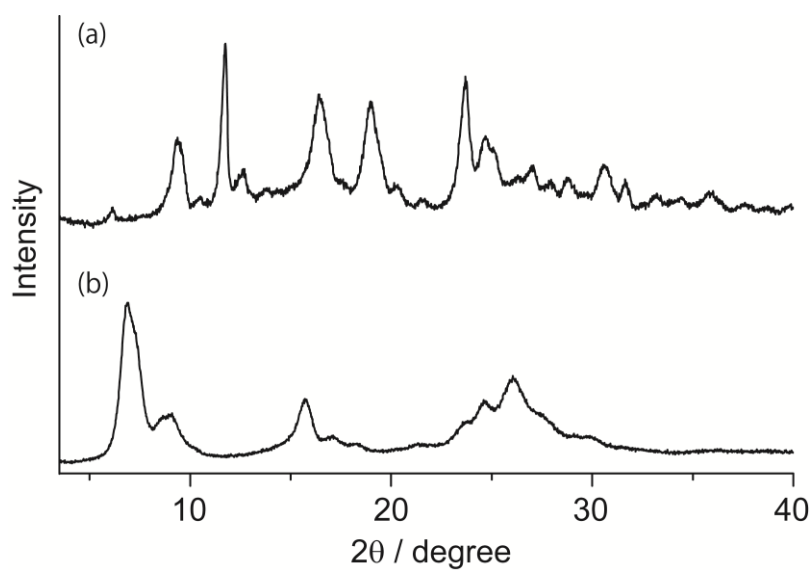


Fig. S-1 X-ray powder diffraction patterns of (a) **4** and (b) the thermally generated CuPc from **4** by the solid-to-solid conversion. Estimated crystallite diameters are 68.3 and 67.9 Å for (a) and (b), respectively, indicating that the grain sizes are maintained during the thermal process.

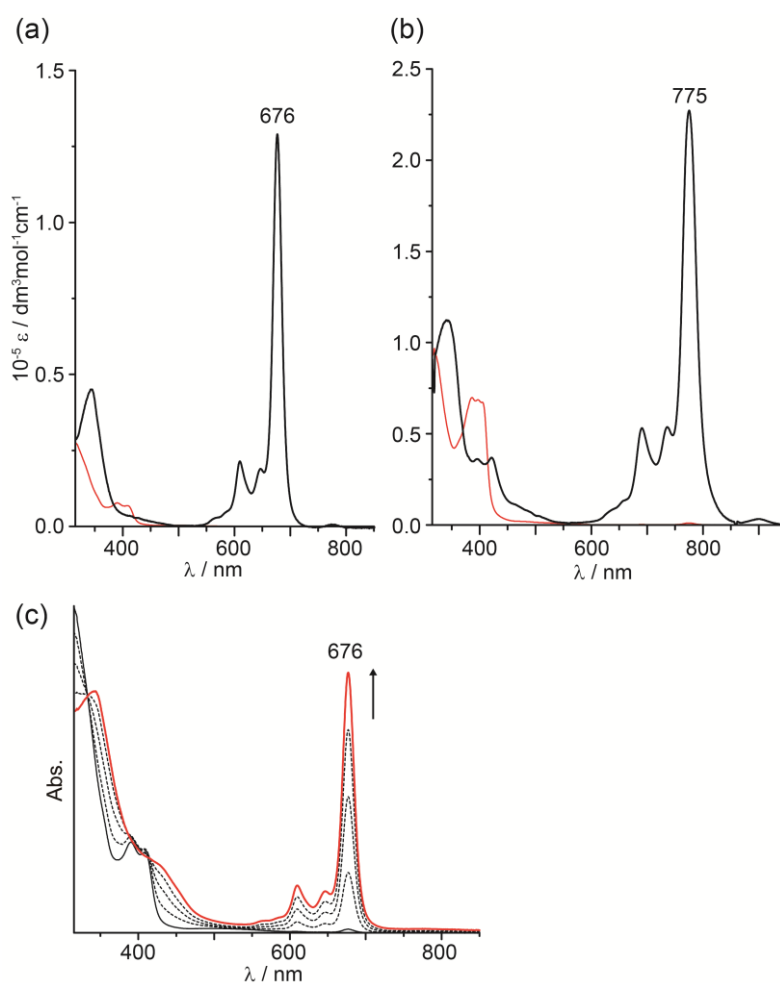


Fig. S-2 Absorption spectra of **4** and **9** in TCB (red lines in (a) and (b), respectively), and those of CuPc (a) and CuNc (b) obtained by solution-phase thermal conversion (black lines). Cell path lengths were 1 and 10 cm for (a) and (b), respectively. (c) Development of the absorption spectrum of **4** in TCB during photo-irradiation.

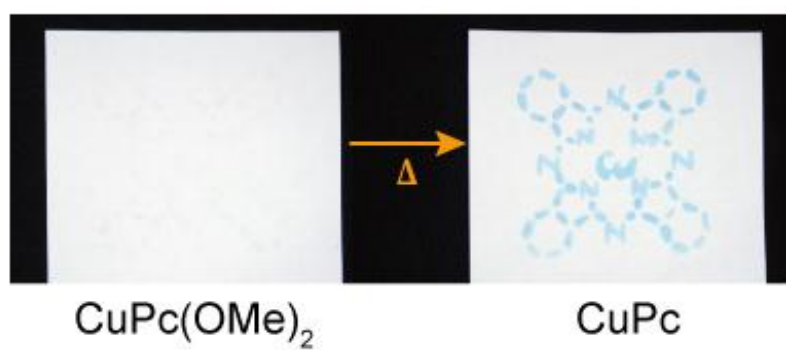
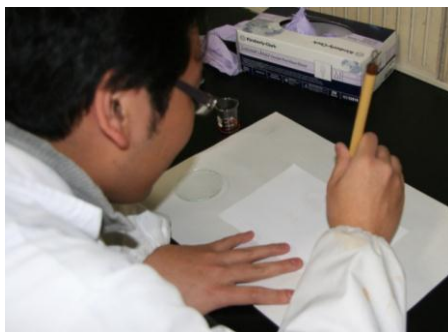


Fig. S-3 (top) Drawing of the CuPc structure using **4** dissolved in acetone. (bottom) Thermal transformation of **4** (left) to CuPc (right).

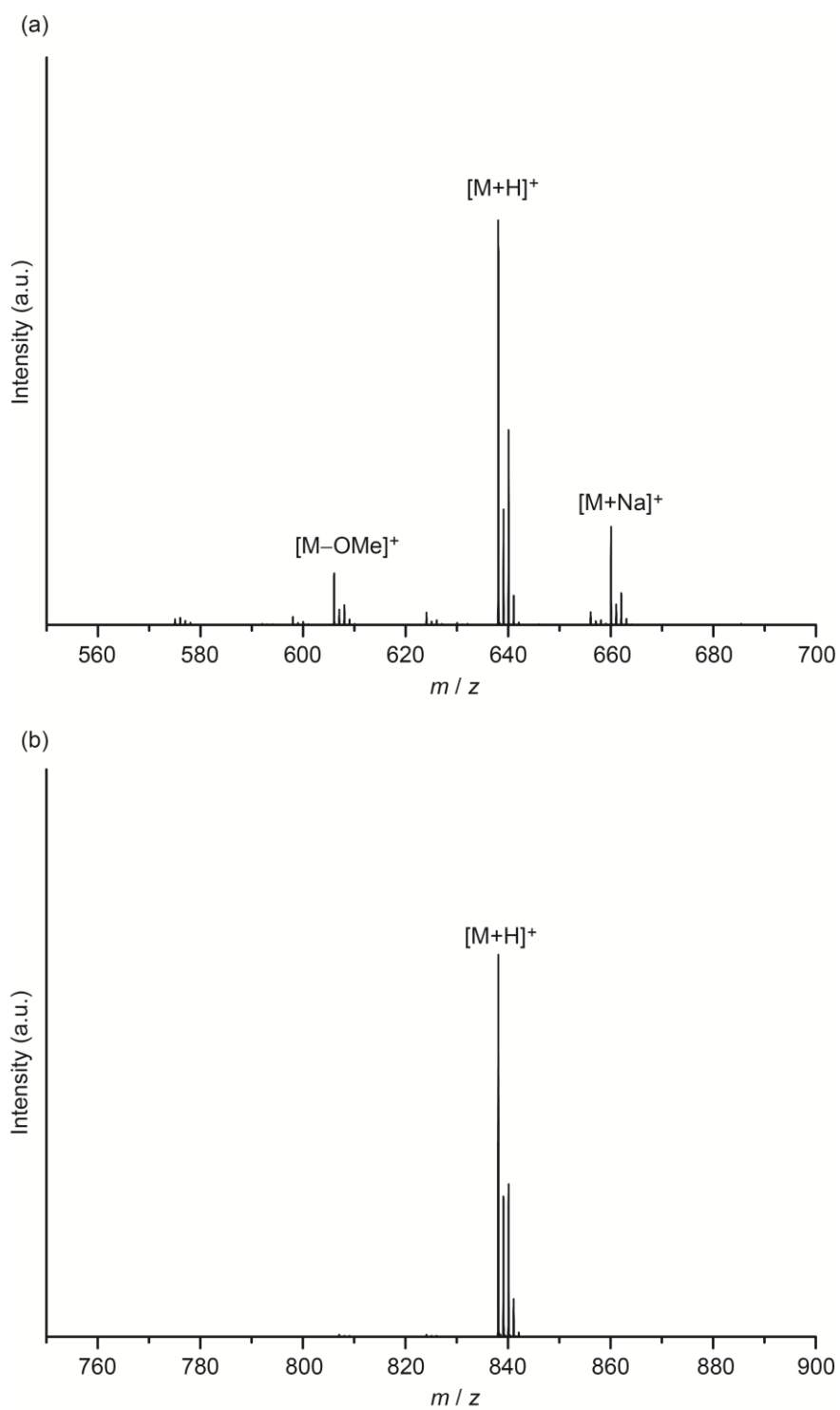


Fig. S-4. ESI-mass spectra of **4** (a) and **9** (b). **4**: $m/z = 660 [M+Na]^+$, $638 [M+H]^+$, $606 [M-OMe]^+$, **9**: $m/z = 838 [M+H]^+$.