

Supporting information

Emergence of electrical conductivity in a flexible coordination polymer by using chemical reduction

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Experimental details

General information

All reagents were used without further purification.

^1H NMR spectrum was acquired by Bruker AV-500 at room temperature.

IR spectra of samples dispersed in KBr pellets were collected on a JASCO FT/IR-4200 Fourier Transform Infrared Spectrometer.

UV-Vis-NIR diffuse reflectance spectra of samples dispersed in BaSO_4 were recorded on a Shimadzu UV-3100.

Single crystal X-ray diffraction (SXRD) measurement was carried out by using a Bruker APEX-II diffractometer with a APEX II CCD detector, graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) and JAPAN thermal Engineering Co., Ltd Cryo system DX-CS190LD. The crystal structures were solved by using direct methods (SHELXS-97),^{S1} followed by Fourier syntheses. Structure refinement was performed by using full matrix least-squares procedures using SHELXL^{S2} on F^2 in the Yadokari-XG2009 software.^{S3}

Powder X-ray diffraction (PXRD) patterns were performed by Bruker D2 PHASER with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at room temperature.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out by using Shimadzu DTG-60H under nitrogen gas flow (50 mL/min).

The ESR spectra were acquired by using a JEOL JES-FA100.

The temperature dependence of the electrical conductivity was measured in a liquid He cryostat of a Quantum Design Physical Property Measuring System (PPMS) MODEL 6000 by using the two-probe method in direct current (DC) mode with Keithley sourcemeter model 2611. The applied voltage was 1 V. The pressed pellet sample was prepared with a diameter of 2.5 mm. It was attached onto the sample puck by gold wires (15 $\mu\text{m}\phi$) and carbon paste (Dotite XC-12 in diethyl succinate). The diameter of the carbon-paste electrode was 1.72 mm and the thickness of the pellet was 250 μm .

X-ray absorption near edge structure (XANES) spectra of Cu K-edge were recorded at the BL-12C (energy: 4–23 keV, Energy resolution: $\Delta E/E \sim 2 \times 10^{-4}$, Photon flux at sample position: 9×10^{10} photons/s (8 keV), monochromator: Si(111), focusing mirror: Double Bent conical mirror (Rh coated), beam size: 0.6 mm \times 0.6 mm) beamline of the Photon Factory (Ring energy: 2.5 GeV, Max. current: 450 mA (Usually Top-up operation), Critical energy: 4 keV, Horizontal acceptance: 3 mrad), the High Energy Accelerator Research Organization (KEK). The edge position was calibrated by that of Cu foil. The samples except Cu foil were prepared as 7 mm ϕ pellets (containing the only sample) and packed into aluminum zipper bag

in the N₂ atmosphere to measure by step scan. The analysis was performed on the Demeter software platform.⁵⁴

Elemental analysis was performed by using J-Science Lab Co. Ltd. JM11 at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

Because NDI^{•-} radicals are gradually oxidized in air. Some measurements were carried out in the inert (oxygen-free) condition. IR, ESR and XANES spectroscopies were carried out in fully inert condition. Compound **2** was put into sealed glass capillary (for ESR), aluminum zipper bag (for XANES) or specially designed sealed pellet holder (for IR) in glove box filled with nitrogen gas. The sample preparations for SXRD, TGA/DTA and conductivity measurements were performed out of the glove box for a short time, but the measurements were carried out in inert conditions (under the nitrogen gas flow for SXRD and TGA/DTA, and under the helium gas atmosphere for conductivity measurement). Although PXRD measurements were performed in ambient air condition, the PXRD pattern did not change at least for 7 hours, indicating that the framework of **2** is resistant to oxidation in this time range. UV-Vis-NIR diffuse reflectance spectra were also acquired in ambient air condition within approx. 10 minutes. The appearance of radical absorption band of **2** in Fig. 3b supports that the effect of oxidation was limited in the short air-exposure time.

Syntheses

Synthesis of *N,N'*-di(2-(pyridin-4yl)ethyl)-1,4,5,8-naphthalenetetracarboxdiimide (NDI-ency)

Naphthalene-1,4,5,8-tetracarboxylic dianhydride (NDA) 1.35 g (5.04 mmol) was suspended in 20 mL *N,N*-dimethylformamide (DMF). To this suspension, 4-(2-aminoethyl)pyridine 1.96 g (16.1 mmol) was added. This brown suspension was heated up to 115 °C and stirred overnight. The suspension was cooled to room temperature and added into 100 mL water. Precipitates were collected by filtration, washed by a little amount of methanol and dried. Yield, 79%. ¹H NMR (500 MHz, CDCl₃, 300 K): 8.78(s, 4H), 8.53(d, 4H), 7.27(d, 4H), 4.46(t, 4H), 3.05(t, 4H), Calcd. For C₂₈H₂₀N₄O₄: C, 70.58; H, 4.23; N, 11.76. Found: C, 70.40; H, 4.20; N, 11.89.

[Cu(NDI-ency)₂(NO₃)₂]₂·2CHCl₃ (**1**)

DMF/chloroform (1:1, v/v) solution (0.10 mL) was layered on chloroform solution of 10 mM NDI-ency (1 mL). Then, DMF solution of 33 mM Cu(NO₃)₂·3H₂O (0.33 mL) was slowly layered. After a week, purple crystals of **1** were formed with impurities (mostly ligand crystal). The crystals of **1** were separated by decantation using methanol and chloroform. Yield 10%. Calcd. For C₅₈H₄₂N₁₀Cl₆CuO₁₄: C, 50.51; H, 3.07; N, 10.16; Cl, 15.42, Found: C, 50.27; H, 3.09; N, 10.35; Cl, 15.16.

[Cu(NDI-enpy)₂]₂·5H₂O (**2**)

16 mg (0.012 mmol) of **1** was soaked into 1 mL of H₂O, followed by the addition of hydrazine monohydrate (one drop) under nitrogen atmosphere. Black solid of **2** was collected by filtration. Calcd. For C₅₆H₅₀N₈CuO₁₃: C, 60.78; H, 4.55; N, 10.13, Found: C, 60.76; H, 4.26; N, 10.13.

Table S1. Crystallographic data for **1**.

1	
Radiation type, wave length /Å	MoK α , 0.7107
Empirical formula	C ₅₈ H ₄₂ Cl ₆ CuN ₁₀ O ₁₄
Formula weight	1379.25
Crystal system	triclinic
Space group	<i>P</i> -1
Crystal size /mm ³	0.27 × 0.09 × 0.05
<i>a</i> /Å	11.189(4)
<i>b</i> /Å	11.495(5)
<i>c</i> /Å	11.892(5)
α /°	104.709(7)
β /°	98.483(7)
γ /°	101.948(7)
<i>V</i> /Å ³	1414.6(10)
Temperature / K	296
<i>Z</i>	1
Density(calculated) / gcm ⁻³	1.619
Absorption coefficient /mm ⁻¹	0.749
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0686, 0.1942
<i>R</i> 1, <i>wR</i> 2 [all data]	0.1010, 0.2148
<i>F</i> (000)	703
Goodness of fit on <i>F</i> ²	1.051

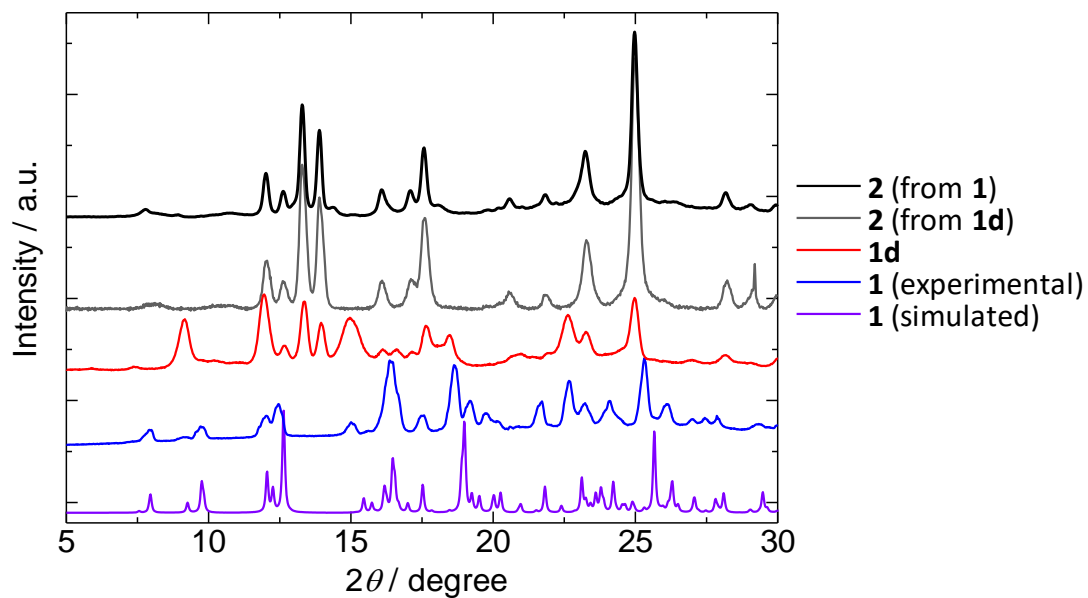


Fig. S1. PXRD patterns of **2** obtained from **1** and **1d** by chemical reduction. Those of **1** and **1d** are shown for the sake of comparison.

References

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