Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Conducting metallophthalocyanine 2D covalent organic frameworks: The role of central metals in controlling π-electronic functions

Xuesong Ding, Xiao Feng, Akinori Saeki, Shu Seki, Atsushi Nagai and Donglin Jiang*

Corresponding Author:

Professor Donglin Jiang

Department of Materials Molecular Science, Institute for Molecular Science, National Institutes of Natural Sciences, 5-1 Higashiyama, Myodaiji, Okazaki 444-8787, Japan.

Tel./Fax: +81-564-59-5520. E-mail: jiang@ims.ac.jp

Section A. Materials and methods

Anhydrous *N*, *N*-dimethylacetamide (DMAc, 99.0%), *o*-dichlorobenzene, *N*,*N*-dimethyl-2-aminoethanol (DMAE), $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, and $Zn(OAc)_2 \cdot 2H_2O$ were purchased from Kanto Chemicals. Methanol, anhydrous acetone (99.5%), pyridine, toluene, urea, and anhydrous dichloromethane (99.0%) were purchased from Wako Chemicals. Mesitylene and boron tribromide were purchased from TCI. 1,4-Benzene diboronic acid, $(NH_4)_2MoO_4$, and anhydrous *N*,*N*-dimethylformamide (DMF, 99.8%) were purchased from Aldrich. CuCN was purchased from Nacalai Tesuque.

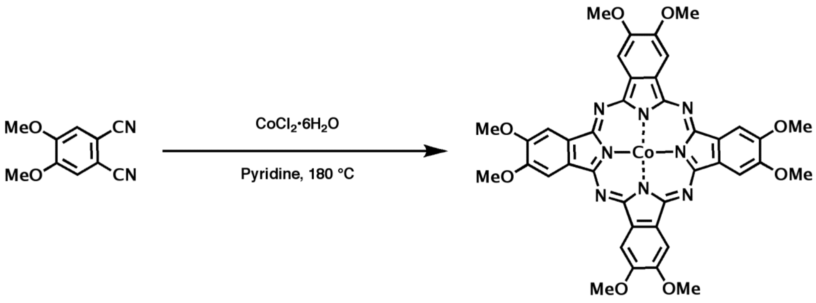
^{1}H NMR spectra were recorded on JEOL models JNM-LA400 or JNM-LA500 NMR spectrometers, where chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard. Fourier transform Infrared (FT-IR) spectra were recorded on a JASCO model FT-IR-6100 infrared spectrometer. UV-Vis-IR diffuse reflectance spectrum (Kubelka-Munk spectrum) was recorded on a JASCO model V-670 spectrometer equipped with integration sphere model IJN-727. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF MS) spectra were recorded on an Applied Biosystems BioSpectrometry model Voyager-DE-STR spectrometer in reflector or linear mode. Field-emission scanning electron microscopy (FE-SEM) was performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. The sample was prepared by drop-casting an acetone suspension onto mica substrate and then coated with gold. High-resolution transmission electron microscopy (HR-TEM) images were obtained on a JEOL model JEM-3200 microscopy. The sample was prepared by drop-casting an acetone suspension of MPc-COFs onto a copper grid. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5°$ up to 60° with 0.02° increment. Nitrogen sorption isotherms were measured at 77 K with a Bel Japan Inc. model BELSORP-mini II analyzer. Before measurement, the samples were degassed in vacuum at 200 °C for more than 10

h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the non-local density functional theory (NLDFT) model, the pore volume was derived from the sorption curve.

Molecular modeling and Pawley refinement were carried out using Reflex, a software package for crystal determination from PXRD pattern, implemented in MS modeling ver 4.4 (Accelrys Inc.).[S1] Unit cell dimension was first manually determined from the observed PXRD peak positions using the coordinates. We performed Pawley refinement to optimize the lattice parameters iteratively until the R_{WP} value converges. The refinement indicates a hexagonal crystal system with a unit cell of $a = b = 23.12$ Å and $c = 6.72$ Å. The pseudo-Voigt profile function was used for whole profile fitting and Berrar-Baldinozzi function was used for asymmetry correction during the refinement processes. The final R_{WP} and R_{P} values were 4.36 and 10.55% for CoPc-COF, 3.94 and 9.82% for CuPc-COF, and 3.68 and 10.22% for ZnPc-COF, respectively. Simulated PXRD patterns were calculated for (1) a 0.8 Å-slipped AA-stacking of $P1$ space group, and (2) a staggered stacking of $I4$ space group. The simulated XRD patterns from $P1$ show a good agreement with the observed PXRD patterns.

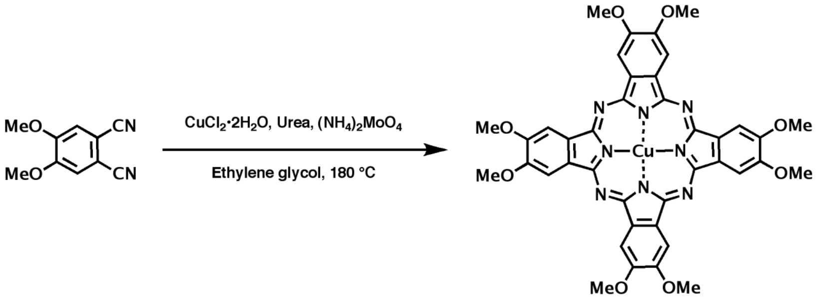
Section B. Synthetic procedures

4,5-dimethoxyphthalodinitrile was prepared from veratrole using a literature procedure.[S2]



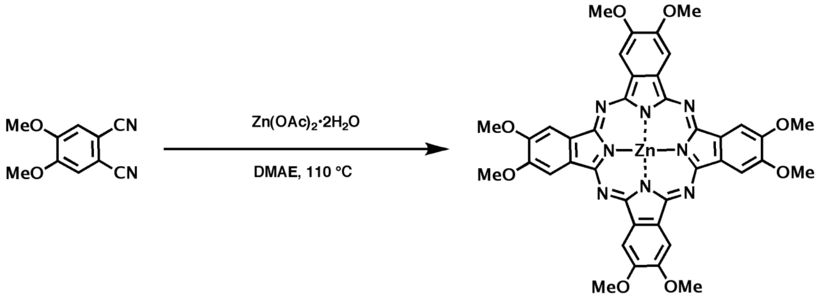
(2,3,9,10,16,17,23,24-Octamethoxyphthalocyaninato)cobalt(II) ([MeO]$_8$PcCo).

4,5-Dimethoxyphthalodinitrile (1.0 g, 5.32 mmol), and cobalt(II) chloride hexahydrate (0.32 g, 1.33 mmol) in pyridine (15 mL) were stirred at 180 °C under argon for 3 days. After cooling to room temperature, the reaction mixture was treated with water (25 mL), and the resulting solid was washed with methanol and acetone, and vacuum-dried to give [Me0]$_8$PcCo as a green solid in 40% yield. MALDI-TOF MS for $C_{40}H_{32}N_8O_8Co$ (Calc. 811.17), found *m*/*z* = 811.11 ($[M]^+$).

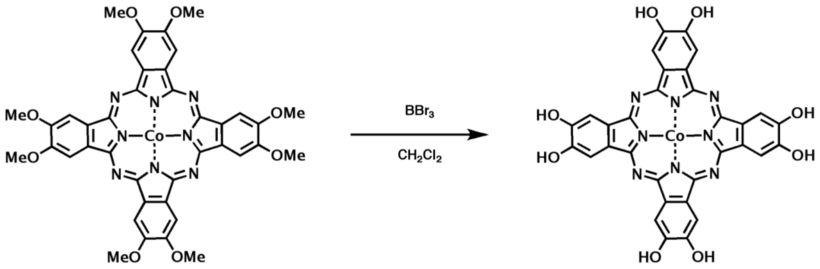


(2,3,9,10,16,17,23,24-Octamethoxyphthalocyaninato)copper(II) ([MeO]$_8$PcCu).

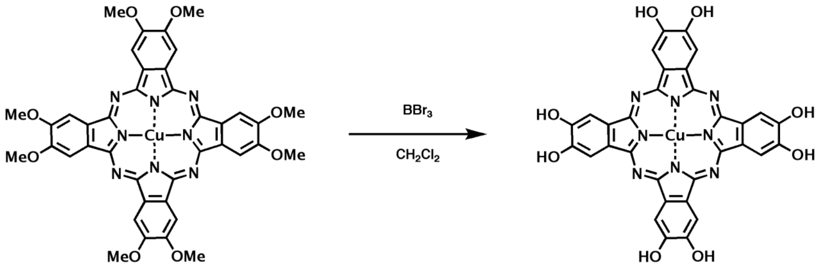
4,5-Dimethoxyphthalodinitrile (1.0 g, 5.32 mmol), urea (0.32 g, 5.32 mmol), copper(II) chloride dihydrate (0.23 g, 1.33 mmol) and ammonium molybdate (60 mg, 0.05 mmol) in ethylene glycol (15 mL) were stirred at 180 °C under argon atmosphere for 3 days. After cooling to room temperature, the reaction mixture was treated with water (25 mL), and the resulting solid was washed with methanol and acetone, and dried under vacuum to give [MeO]$_8$PcCu as a green solid in 15% yield. MALDI-TOF MS for $C_{40}H_{32}N_8O_8Cu$ (Calc. 815.16), found *m*/*z* = 814.82 ($[M]^+$).



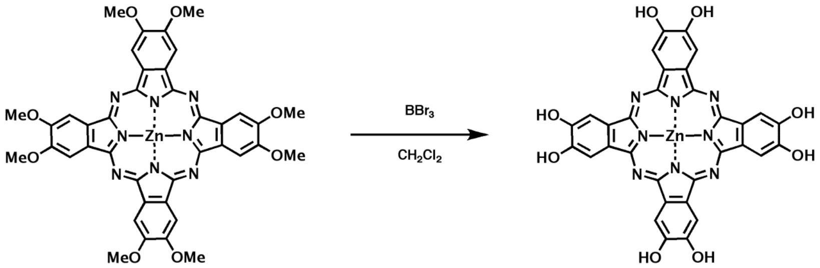
(2,3,9,10,16,17,23,24-Octamethoxyphthalocyaninato)zinc(II) ($[MeO]_8$PcZn). 4,5-Dimethoxyphthalodinitrile (1.0 g, 5.32 mmol) and zinc(II) chloride dihydrate (0.29 g, 1.33 mmol) in DMAE (10 mL) were stirred at 110 °C under argon for 16 h. After cooling to room temperature, the reaction mixture was treated with a mixture of methanol and water (3/1in vol.; 20 mL), and the resulting solid obtained was filtered, washed with methanol and acetone, and dried under vacuum to give $[MeO]_8$PcZn as a green solid in 25% yield. MALDI-TOF MS for $C_{40}H_{32}N_8O_8Zn$ (Calc. 816.65), found *m*/*z* = 815.90 ($[M]^+$).



(2,3,9,10,16,17,23,24-Octahydroxyphthalocyaninato)cobalt(II) ($[OH]_8$PcCo). $[MeO]_8$PcCo (202.6 mg, 0.25 mmol) was suspended in 10 mL of dichloromethane, and boron tribromide (0.97 mL, 10 mmol) was added under N_2 atmosphere. The mixture was stirred for 3 days and 15 mL of methanol was added slowly. After filtration, the solid residue was repetitive washed with methanol and centrifuged more than 3 times, and dried under vacuum to give $[OH]_8$PcCo as a dark green solid in 67% yield. MALDI-TOF MS for $C_{32}H_{16}N_8O_8Co$ (Calc. 699.04), found *m*/*z* = 698.75 ($[M]^+$).



(2,3,9,10,16,17,23,24-Octahydroxyphthalocyaninato)copper(II) ($[OH]_8$PcCu). $[MeO]_8$PcCu (390.0 mg, 0.48 mmol) was suspended in 10 mL of dichloromethane, and boron tribromide (1.85 mL, 19.12 mmol) was added under N_2 atmosphere. The mixture was stirred for 3 days, and 10 mL of methanol was added slowly. After filtration, the solid residue was repetitive washed with methanol and centrifuged more than 3 times, and dried under vacuum to give $[OH]_8$PcCu as a dark green solid in 70% yield. MALDI-TOF MS for $C_{32}H_{16}N_8O_8Cu$ (Calc. 703.04), found *m*/*z* = 703.86 ($[M]^+$).



(2,3,9,10,16,17,23,24-Octahydroxyphthalocyaninato)zinc(II) ($[OH]_8$PcZn). $[MeO]_8$PcZn (220.0 mg, 0.27 mmol) was suspended in 10 mL of dichloromethane, and boron tribromide (1.05 mL, 10.8 mmol) was added under N_2 atmosphere. The mixture was stirred for 3 days, and 10 mL of methanol was added slowly. After filtration, the solid residue was repetitive washed with methanol and centrifuged more than 3 times, and dried under vacuum to give $[OH]_8$PcZn as a dark green solid in 63% yield. MALDI-TOF MS for $C_{32}H_{16}N_8O_8Zn$ (Calc. 704.04), found *m*/*z* = 703.96 ($[M]^+$).

CoPc-COF. A mixture of $[OH]_8$PcCo (21 mg, 0.03 mmol) and 1,4-benzene diboronic acid (BDBA, 9.9 mg, 0.06 mmol) in a mixture of DMAC/*o*-dichlorobenzene (2/1 in vol.; 2 mL) were degassed in Pyrex tube (10 mL) by three freeze-pump-thaw cycles. The tube was sealed off and heated at 120 °C for 7 days. The precipitate was collected by centrifugation, washed with anhydrous acetone for 5 times, extracted by Soxhlet with anhydrous acetone for 3 days, and dried at 150 °C under vacuum for 24 h, to give a dark green powder in 83% isolation yield from a 2/1 stoichiometric ratio of BDBA and $[OH]_8$PcCo. Elemental analysis (%) calcd. for $(C_{44}H_{16}B_4N_8O_8Co)_n$ (theoretical formula for an infinite 2D COF) C (59.59), H (1.82), N (12.64), found C (52.90), H (2.95), N (11.62).

CuPc-COF. A mixture of $[OH]_8$PcCu (21 mg, 0.03 mmol) and 1,4-benzene diboronic acid (BDBA, 9.9 mg, 0.06 mmol) in DMAC/*o*-dichlorobenzene (2/1 in vol.; 2 mL) were degassed in Pyrex tube (10 mL) by three freeze-pump-thaw cycles. The tube was sealed off and heated at 120 °C for 7 days. The precipitate was collected by centrifugation, washed with anhydrous acetone for 5 times, extracted by Soxhlet with anhydrous acetone for 3 days, and dried at 150 °C under vacuum for 24 h, to give a dark blue powder in 90% isolation yield from a 2/1 stoichiometric ratio of BDBA and $[OH]_8$PcCu. Elemental analysis (%) calcd. for $(C_{44}H_{16}B_4N_8O_8Cu)_n$ (theoretical formula for an infinite 2D COF) C (59.28), H (1.81), N (12.57), found C (54.82), H (2.62), N (12.47).

ZnPc-COF. A mixture of $[OH]_8$PcZn (21 mg, 0.03 mmol) and 1,4-benzene diboronic acid (BDBA, 9.9 mg, 0.06 mmol) in DMAC/*o*-dichlorobenzene (2 mL, 1/1 in vol.) were degassed in

Pyrex tube (10 mL) by three freeze-pump-thaw cycles. The tube was sealed off and heated at 120 °C for 7 days. The precipitate was collected by centrifugation, washed with anhydrous acetone for 5 times, extracted by Soxhlet with anhydrous acetone for 3 days, and dried at 150 °C under vacuum for 24 h, to give a dark green powder in 85% isolation yield from a 2/1 stoichiometric ratio of BDBA and $[OH]_8PcZn$. Elemental analysis (%) calcd. for $(C_{44}H_{16}B_4N_8O_8Zn)_n$ (theoretical formula for an infinite 2D COF) C (59.16), H (1.81), N (12.54), Ni (6.62), found C (53.70), H (2.74), N (12.22).

Section C. FT-IR spectral profiles

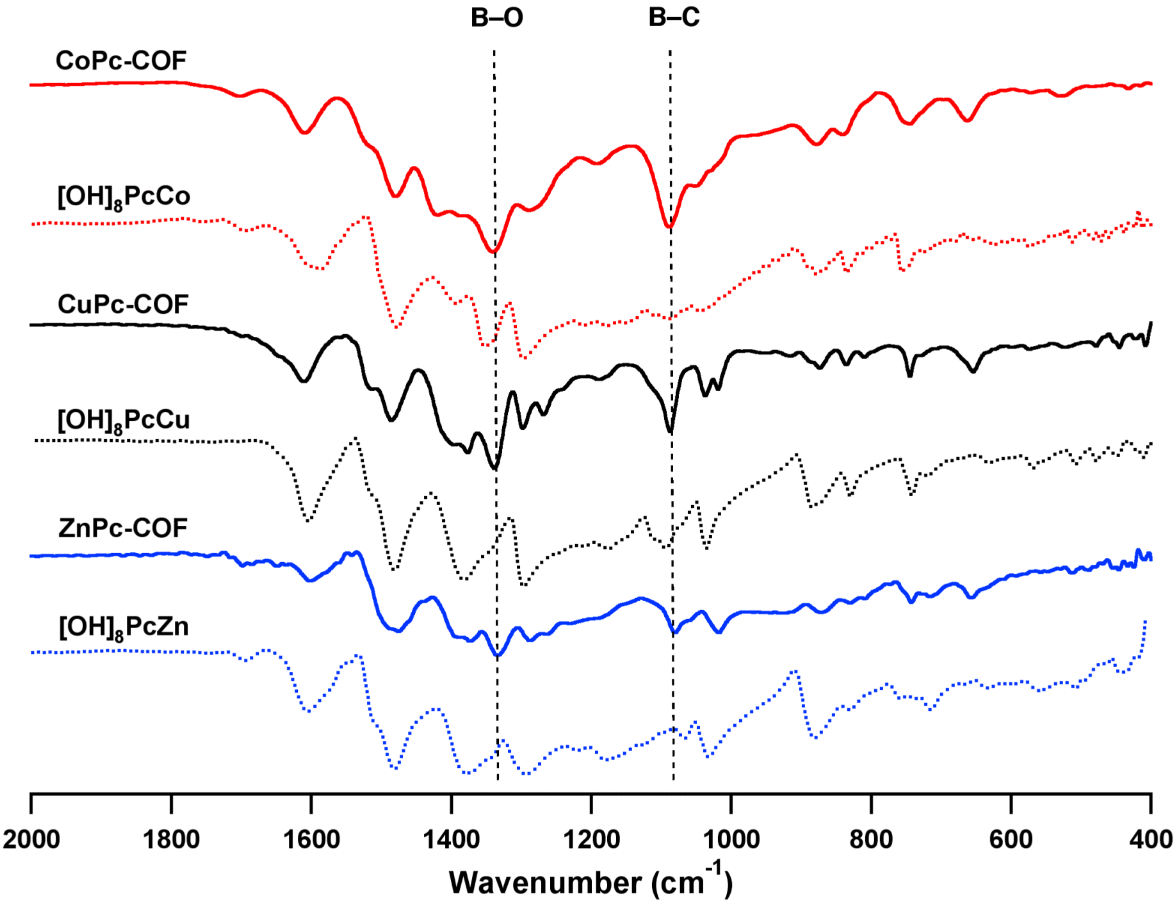


Figure *S*1. FT-IR spectra of CoPc-COF, [OH]$_8$PcCo, CuPc-COF, [OH]$_8$PcCu, ZnPc-COF, and [OH]$_8$PcZn.

Section D. Supporting references

S1. Accelrys, Material Studio Release Notes, Release 4.4, Accelrys Software, San Diego 2008.

S2. Metz, J.; Schneider, O. & Hanack, M. *Inorg. Chem.* **23**, 1065-1071 (1984).