# Supporting Information

# Chemical Control of Supramolecular Organizations in Tetrapyridylporphyrin Thin Films

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# Experimental

## **Film Preparation**

Silicon wafers were purchased from Valqua FFT Inc. (Tokyo, Japan). The wafers were cut into a rectangular shape of  $40 \times 20 \text{ mm}^2$ , and cleaned by sonication in pure water, ethanol, acetone, and 1,2-dichloroethane, sequentially. Physical vapor-deposition was performed to obtain metallated tetrapyridylporphyrin (MTPyP) films under a base pressure of  $2.0 \times 10^{-3}$  Pa using a Sanyu Electron (Tokyo, Japan) SVC-700TM vacuum deposition system. The film thickness and the average deposition rate were determined to be 50 nm and 2.0 nm min<sup>-1</sup>, respectively, by a quartz crystal microbalance. During the deposition, the substrate temperature was maintained at 200 °C.

# **2D-GIXD** Measurements

Two-dimensional grazing incidence X-ray diffraction (2D-GIXD) measurements were performed by using a Rigaku (Tokyo, Japan) SmartLab diffractometer equipped with a two-dimensional image detector, HyPix-3000. 3 kW sealed X-ray tube, was operated at 40 kV and 50 mA (2 kW) generating Cu K $\alpha$  ( $\lambda = 0.15418$  nm) radiation. The incident angle to the sample was set to be 0.20°. The diffraction spots were indexed by comparing with simulated patterns of uniaxially oriented crystallites (Fig. S1), which were calculated from the lattice parameters of the known bulk structures (Table S1).<sup>1–3</sup> Diffraction intensities were not simulated.



Fig. S1 Simulated 2D-GIXD patterns of the (a) form I, (b) II, and (c) III structures and schematics of their orientation. The simulated patterns are obtained by assuming that the (200), (40-2), and (010) planes of the form I, II, and III structures are parallel to the substrate, respectively.

|                                      | Form I              | Form II           | Form III    |
|--------------------------------------|---------------------|-------------------|-------------|
| Reference No.                        | [1]                 | [2]               | [3]         |
| CCDC No.                             | 179299              | 749711            | 1275315     |
| Empirical Formula                    | $C_{40}H_{24}N_8Fe$ | $C_{40}H_{26}N_8$ | C44H30N4    |
| Formula Weight / g mol <sup>-1</sup> | 672.52              | 618.69            | 614.73      |
| Space Group                          | Cmca                | Сс                | <i>P</i> -1 |
| Polymorph                            | Orthorhombic        | Monoclinic        | Triclinic   |
| Lattice Constant / nm                | 1.818               | 1.360             | 0.644       |
|                                      | 1.378               | 2.087             | 1.042       |
|                                      | 1.376               | 1.145             | 1.241       |
|                                      | 90                  | 90                | 96.05       |
| Lattice Constant / °                 | 90                  | 116.27            | 99.14       |
|                                      | 90                  | 90                | 101.12      |
| Lattice Volume / nm <sup>3</sup>     | 3.447               | 2.914             | 0.7988      |
| Ζ                                    | 4                   | 4                 | 1           |
| Density / g cm <sup>-3</sup>         | 1.296               | 1.410             | 1.278       |

Table S1 The crystal parameters of the Form I, II and III structures.

#### **IR pMAIRS Measurements**

Infrared p-polarized multiple-angle incidence resolution spectrometry (IR pMAIRS) measurements were performed by using a Thermo Fischer Scientific Co., Ltd. (Madison, WI, USA) Magna 550 spectrometer. The substrate was set on a MAIRS automatic analysis accessory (TN 10-1500). The incident light was p-polarized thorough a germanium wire-grid linear polarizer (090-1500) provided by PIKE Technologies (Madison, WI, USA). The transmitted light was detected by using a mercury cadmium telluride (MCT) detector cooled by liquid nitrogen. The incidence angle was varied in 5° intervals from 9° to 44°, which is the optimum condition when using a silicon substrate.<sup>4</sup> The signal accumulation was 500 times for each angle. The resulting single beam spectra were used for generating the pMAIRS in-plane (IP) and out-of-plane (OP) spectra, corresponding to the spectra obtained by normal-incidence transmission and reflection–absorption measurements, respectively.<sup>5</sup>

# **Atomic Force Microscopy Measurements**

Atomic force microscopy (AFM) images were obtained in the dynamic force mode by using a Seiko Instruments (Chiba, Japan) Nanocute-NanoNavi IIs system attached on an antivibration stage. The force constant and resonance frequency of the silicon cantilever were 14 Nm<sup>-1</sup> and 118 kHz, respectively.



Fig. S2 AFM topographic images of (a) FeTPyP, (b) CoTPyP, (c) NiTPyP, and (d) CuTPyP films. The values of root means square (RMS) roughness are noted below the images.

#### **Density Functionalized Theory Calculation**

Geometry optimization was carried out for CuTPyP. All calculations were performed without any symmetry constraints using B3LYP level of density functional theory.<sup>7</sup> The 6-31G\* basis set was used for all atoms.<sup>8</sup> Gaussian 16 program package was used for all calculations.<sup>9</sup> The optimized geometry of CuTPyP exhibited no imaginary frequency. The calculated vibrational frequencies were scaled by 0.9613, which is customary for the B3LYP method.<sup>10–14</sup> Calculated vibrational wavenumbers were summarized in Table S2. The calculated data were consistent with the experimental values (Fig. S3 and Table S2).



Fig. S3 IR ATR spectra of powder (a) FeTPyP, (b) CoTPyP, (c) NiTPyP, and (d) CuTPyP, and a calculated IR spectrum (B3LYP/6-31G\*) of (e) CuTPyP.

| Vibration Frequency / cm <sup>-1</sup> |                              |                          |        |                      |                                                              |  |  |
|----------------------------------------|------------------------------|--------------------------|--------|----------------------|--------------------------------------------------------------|--|--|
| FeTPyP                                 | СоТРуР                       | NiTPyP                   | CuTPyP | CuTPyP<br>Calculated | Vibration Mode                                               |  |  |
| 718                                    | 710                          | 716                      | 718    | 717                  | γ(С−H) <sub>рог</sub> , γ(С−H) <sub>ру</sub>                 |  |  |
| 795                                    | 797                          | 704                      | 795    | 800                  | ү(С-Н)ру                                                     |  |  |
| 810                                    | 808                          | /94                      |        |                      |                                                              |  |  |
| 787                                    | 791                          | 801                      | 801    | 806                  | γ(С−H) <sub>рог</sub> , γ(С−H) <sub>ру</sub>                 |  |  |
| 992                                    | 993                          | 1006                     | 1004   | 986                  | ν(ring) <sub>por</sub> , γ(C-H) <sub>py</sub>                |  |  |
| 1073                                   | 1067                         | 1070                     | 1072   | 1066                 | ү(С-Н) <sub>ру</sub>                                         |  |  |
| 1082                                   | 1081                         | 1085                     | 1082   | 1092                 | δ(C-H) <sub>por</sub>                                        |  |  |
| 1209                                   | 1207                         | 1215                     | 1210   | 1196                 | δ(C-H) <sub>por</sub>                                        |  |  |
| 1352                                   | 1351                         | 1355                     | 1349   | 1337                 | $\delta$ (C-H) <sub>por</sub> , $\delta$ (C-H) <sub>py</sub> |  |  |
| 1408                                   | 1409                         | 1405                     | 1403   | 1397                 | δ(C-H) <sub>py</sub>                                         |  |  |
| 1543                                   | 1544                         | 1547                     | 1545   | 1527                 | δ(C-H) <sub>py</sub> , ν(ring) <sub>por</sub>                |  |  |
| 1595                                   | 1596                         | 1505                     | 1594   | 1573                 | v(ring) <sub>py</sub>                                        |  |  |
| 1612                                   | 1604                         | 1393                     |        |                      |                                                              |  |  |
| γ(С-Н);                                | C-H out-of-plane deformation |                          |        |                      |                                                              |  |  |
| δ(С-Н);                                | (                            | C–H in-plane deformation |        |                      |                                                              |  |  |
| ν(С-Н);                                | (                            | C-H stretching           |        |                      |                                                              |  |  |
| v(C=C);                                | (                            | C=C stretching           |        |                      |                                                              |  |  |
| v(ring);                               | 2                            | aromatic ring stretching |        |                      |                                                              |  |  |
| por;                                   | I                            | porphyrin                |        |                      |                                                              |  |  |
| ру;                                    | I                            | oyridyl group            |        |                      |                                                              |  |  |

Table S2 Band assignment of IR ATR spectra of powder MTPyPs.

#### **High-Resolution Mass Spectroscopy Measurements**

High-resolution mass (HRMS) spectra were recorded on a Bruker (Billerica, MA, USA) solariX Fourier transform ion-cyclotron resonance mass spectrometer in the matrix-assisted laser desorption/ionization (MALDI) mode.

# **IR ATR measurements**

IR attenuated total reflection (ATR) spectra of MTPyP powder samples were obtained by using a Thermo Fischer Scientific Co., Ltd. Nicolet 6700 spectrometer equipped with a Spectra-Tech Foundation Thunder Dome attachment with a Ge prism. The signals were detected by a deuterated triglycine sulfate (DTGS) detector and accumulated 500 times.

# **UV-Vis Spectroscopy Measurements**

UV-Vis absorption spectra were recorded on a Jasco (Tokyo, Japan) V-630 spectrometer using a 1 cm cell. Saturated solutions of MTPyP ( $< \sim 10^{-6}$  M) in chloroform were prepared and used for the measurements.



Fig. S4 UV-Vis spectra of MTPyPs (M = Fe, Co, Ni, Cu) in CHCl<sub>3</sub>.

Preparation of Tetra(4-pyridyl)porphyrin-M(II) (MTPyP; M = Fe, Co, Ni, Cu).



Scheme S1. Preparation of MTPyP (M = Fe, Co, Ni, Cu)

MTPyP were prepared according to the literature<sup>6</sup> with some modifications (Scheme S1). A typical procedure is as follows. Tetra(4-pyridyl)porphyrin (H<sub>2</sub>TPyP; 248 mg, 0.40 mmol) and Fe(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> (176 mg, 1.0 mmol, 2.5 equiv/H<sub>2</sub>TPyP) were added to a mixed solvent of dimethylformamide (DMF) (20 mL) and AcOH (20 mL). The resulting suspension was stirred under reflux overnight, giving a homogeneous solution. The solution was cooled to room temperature to precipitate a dark purple crystalline solid. The solid was collected by filtration, washed with water, and dried at 150 °C under vacuum to give FeTPyP (265 mg, 95% yield).

CoTPyP, NiTPyP, and CuTPyP were similarly prepared using Co(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O (2.5 equiv/H<sub>2</sub>TPyP), Ni(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O (3.8 equiv/H<sub>2</sub>TPyP), and Cu(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O (2.5 equiv/H<sub>2</sub>TPyP), respectively, in place of Fe(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>. The products were characterized by elemental analysis, high-resolution mass spectrometry (HRMS), IR ATR spectroscopy (Fig. S3), and UV-Vis spectroscopy (Fig. S4). The IR ATR spectra showed that the products contained no raw materials and no organic solvents such as DMF and acetic acid. The characterization data for MTPyP are as follows.

FeTPyP: HRMS (MALDI, *m/z*) Calcd for C<sub>40</sub>H<sub>24</sub>N<sub>8</sub>Fe: 672.14678 ([M]<sup>+</sup>). Found: 672.14593. Anal. Calcd for C<sub>40</sub>H<sub>24</sub>N<sub>8</sub>Fe·H<sub>2</sub>O: C, 69.57; H, 3.80; N, 16.23%. Found: C, 69.10; H, 3.59; N, 16.13%. IR (ATR):  $\nu$  = 1612, 1595, 1543, 1408, 1352, 1209, 1082, 1073, 992, 810, 801, 795, 718 cm<sup>-1</sup>. UV-vis (CHCl<sub>3</sub>):  $\lambda$ <sub>max</sub> = 414 nm (Soret-band).

CoTPyP: dark red crystalline solid (83% yield). HRMS (MALDI, m/z) Calcd for C<sub>40</sub>H<sub>24</sub>N<sub>8</sub>Co: 675.14504 ([M]<sup>+</sup>). Found: 675.14506. Anal. Calcd for C<sub>40</sub>H<sub>24</sub>N<sub>8</sub>Co·4H<sub>2</sub>O: C, 64.25; H, 4.31; N, 14.99%. Found: C, 63.56; H, 4.18; N, 14.04%. IR (ATR):  $\nu$ = 1604, 1596, 1544, 1409, 1351, 1207, 1081, 1067, 993, 808, 791, 797, 710 cm<sup>-1</sup>. UV-vis (CHCl<sub>3</sub>):  $\lambda_{max}$  = 408 nm (Soret-band).

NiTPyP: dark red crystalline solid (74% yield). HRMS (MALDI, m/z) Calcd for C<sub>40</sub>H<sub>24</sub>N<sub>8</sub>Ni: 674.14719 ([M]<sup>+</sup>). Found: 674.14611. Anal. Calcd for C<sub>40</sub>H<sub>24</sub>N<sub>8</sub>Ni·3H<sub>2</sub>O: C, 65.86; H, 4.15; N, 15.37%. Found: C, 65.83; H, 3.58; N, 15.24%. IR (ATR):  $\nu$ = 1595, 1547, 1405, 1355, 1215, 1085, 1070, 1006, 801, 794, 716 cm<sup>-1</sup>. UV-vis (CHCl<sub>3</sub>):  $\lambda_{max}$  = 415 nm (Soret-band).

CuTPyP: dark purple crystalline solid (>99% yield). HRMS (MALDI, m/z) Calcd for C<sub>40</sub>H<sub>24</sub>N<sub>8</sub>Cu: 679.14144 ([M]<sup>+</sup>). Found: 679.14039. Anal. Calcd for C<sub>40</sub>H<sub>24</sub>N<sub>8</sub>Cu·H<sub>2</sub>O: C, 68.80; H 3.75; N, 16.05%. Found: C, 68.35; H, 3.64; N, 15.57%. IR (ATR):  $\nu$ = 1594, 1545, 1403, 1349, 1210, 1082, 1072, 1004, 801, 795, 718 cm<sup>-1</sup>. UV-vis (CHCl<sub>3</sub>):  $\lambda_{max}$  = 414 nm (Soret-band).

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