

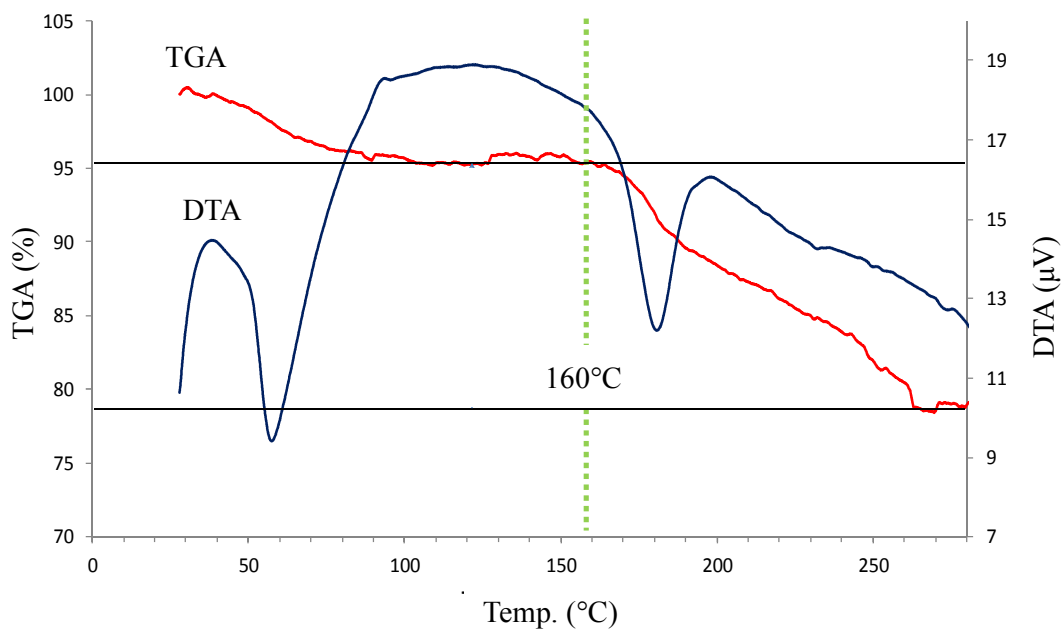
**Solid-State Polycondensation via Ionic-to-Covalent Bond Transformation to  
Control Polymer Structure: Preparation of Porphyrin-Based Ladder Polymer**

Masato Suzuki,<sup>\*,†</sup> Kohei Yokota,<sup>†</sup> Hiroe Tsuchida,<sup>†</sup> Kazuhisa Yamoto,<sup>†</sup> Masayuki  
Nagata,<sup>†</sup> Shin-ichi Matsuoka,<sup>†</sup> Koji Takagi,<sup>†</sup> Kohei Johmoto,<sup>‡</sup> and Hidehiro Uekusa<sup>‡</sup>

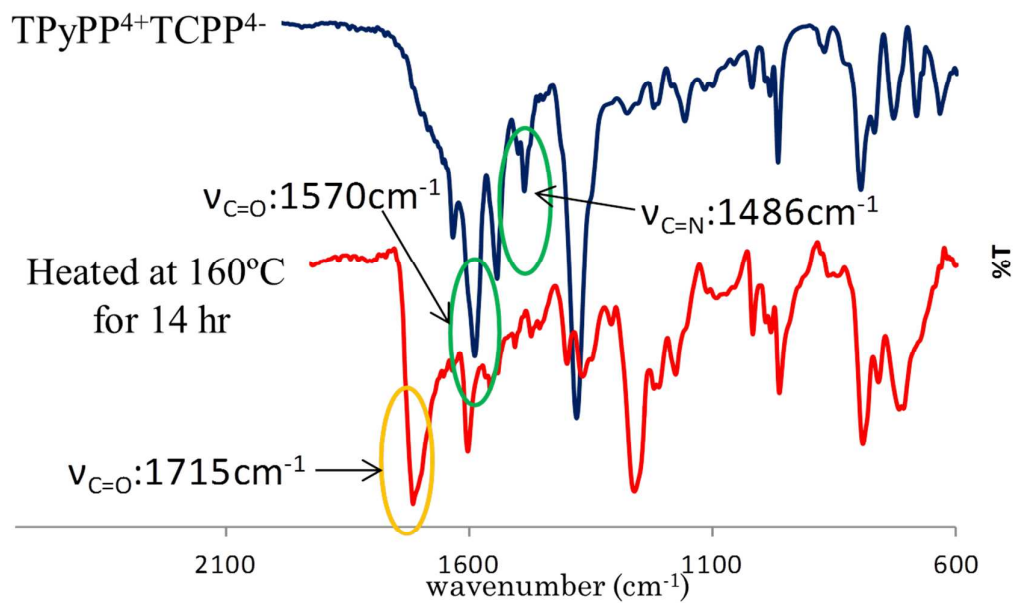
<sup>†</sup>Department of Materials Science and Engineering, Nagoya Institute of Technology,  
Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

<sup>‡</sup>Department of Chemistry and Materials Science, Tokyo Institute of Technology,  
O-okayama 2-12-1, Meguro-ku, Tokyo 152-8551, Japan

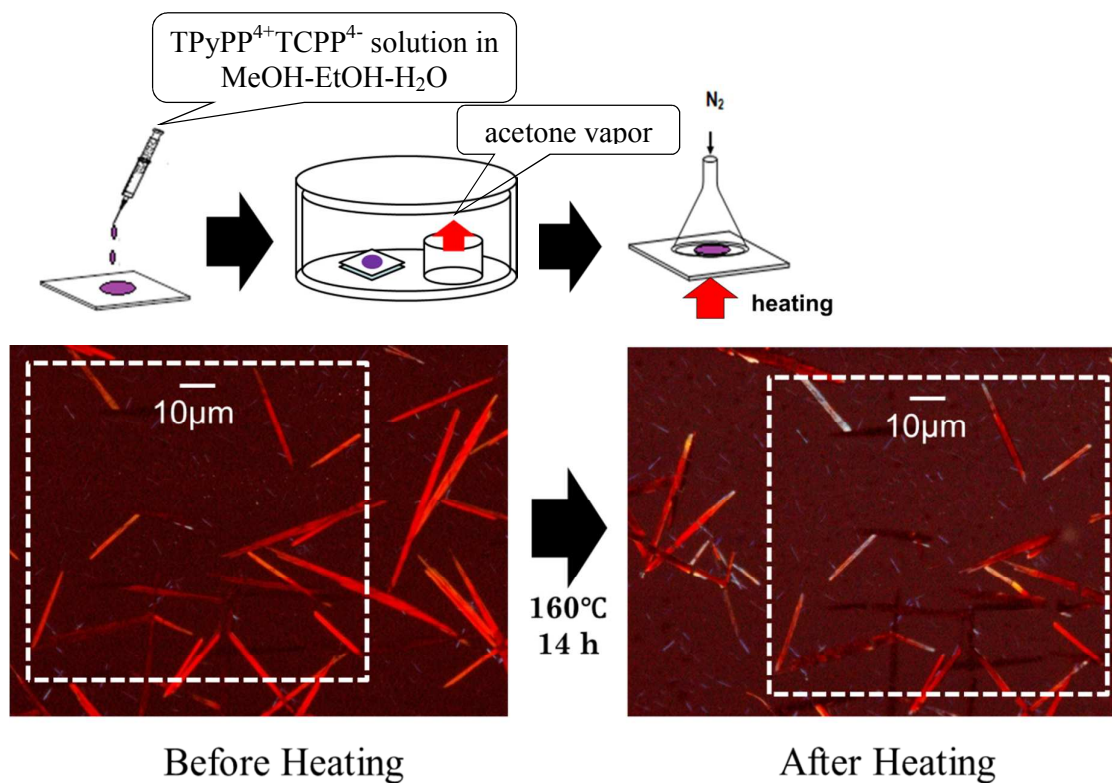
## Supporting Information



**Figure S1.** TG-TDA analyses of TPyPP<sup>4+</sup>TCPP<sup>4-</sup> increasing the temperature at the rate of 10°C/min under N<sub>2</sub>.



**Figure S2.** IR spectra (ATR) of TPyPP<sup>4+</sup>TCPP<sup>4-</sup> and the product heated at 160°C for 14 hr.



**Figure S3.** Preparation of small crystals on the glass plate and cross-polarized optical microscopic pictures of them before and after heating; the dot-line squares show the same part of the sample.

## Experimental Section

**Measurements.** The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AVANCE-200FT-NMR spectrometer in  $\text{CDCl}_3$  (0.03 v/v% TMS as the internal standard),  $\text{DMSO-d}_6$  (the signals due to the residual protons were used for the standards), and  $\text{CD}_3\text{OD}$  (the signals due to the residual protons were used for the standards). The IR spectra were recorded on JASCO FT/IR-460 plus or JASCO FT/IR-6300 with IRT-5000 spectrometer systems. Thermogravimetry and differential thermal analyses (TG-DTA) were performed with a Simadzu DTG-60 apparatus (heating rate:  $10^\circ\text{C}/\text{min}$ , under a  $\text{N}_2$  flow). Powder X-ray diffraction was measured on a glass plate or in a rotating glass capillary at r.t. by a Rigaku SmartLab system equipped with a  $\text{CuK}\alpha$  X-ray source and a D/teX Ultra detector. Single crystal X-ray diffraction was measured by a Rigaku VariMax RAPID-II system.

**Materials.** meso-Tetrakis(4-carboxyphenyl)porphyrin<sup>8</sup> and meso-tetrakis[(4-bromomethyl)phenyl]porphyrin<sup>9</sup> were prepared according to the literatures.

### meso-Tetrakis[4-(pyridiniummethyl)phenyl]porphyrin tetrabromide

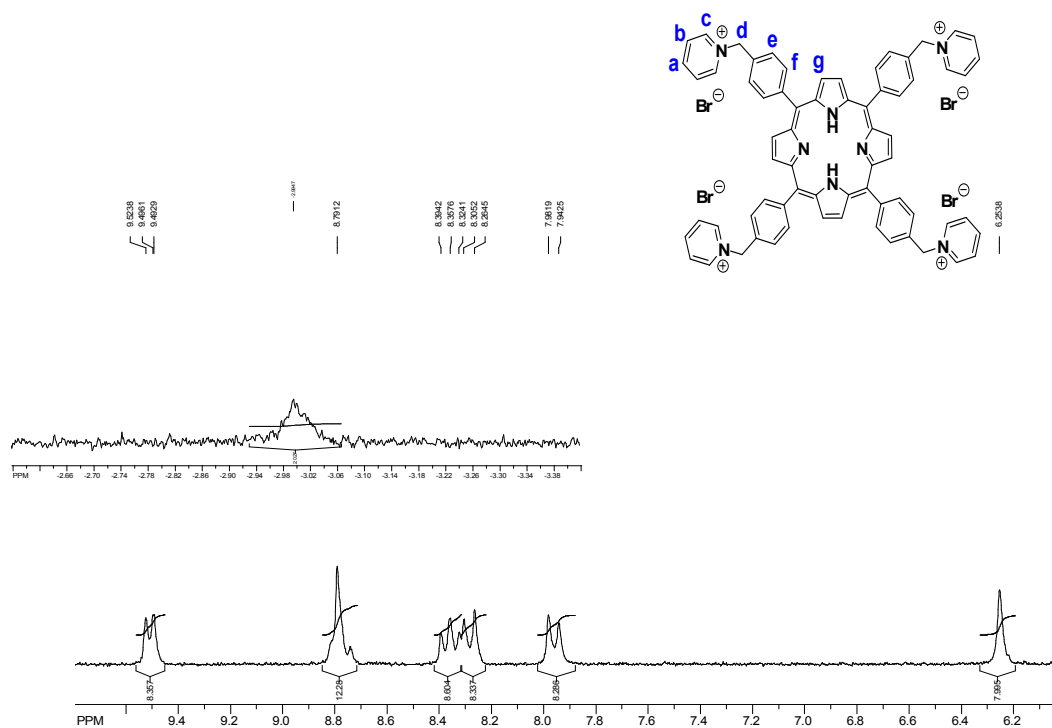
**(TPyPP<sup>4+</sup>Br<sub>4</sub>)** Tetrakis[(4-bromomethyl)phenyl]porphyrin (424 mg, 0.42 mmol) was dissolved into pyridine (9 mL) and stirred overnight at r.t. Diethyl ether was added to form precipitate, which was collected by filtration and washed with diethyl ether. The obtained precipitate was purified by reprecipitation into diethyl ether from the methanol solution. When there is observed a methanol-insoluble part, it is excluded by filtration before the reprecipitation. Vacuum drying the obtained solid gave tetrakis[4-(pyridiniummethyl)phenyl]porphyrin tetrabromide (410 mg, 74% yield).

$^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  (ppm) 9.51 (d,  $J=6.2$  Hz, 8H), 8.80 (s, 8H), 8.74 (m, 4H), 8.36 (t-like,  $J=7.7$  Hz, 8H), 8.28 (d,  $J=7.8$  Hz, 8H), 7.96 (d,  $J=7.8$  Hz, 8H), 6.25 (s, 8H), -2.99 (br, 2H).  $^{13}\text{C}$ -NMR ( $\text{D}_2\text{O}/\text{DMSO}-d_6$ ):  $\delta$  (ppm) 148.0, 146.5, 146.3, 141.6, 140.9, 136.6, 131.3, 130.5, 130.3, 123.5, 65.8.

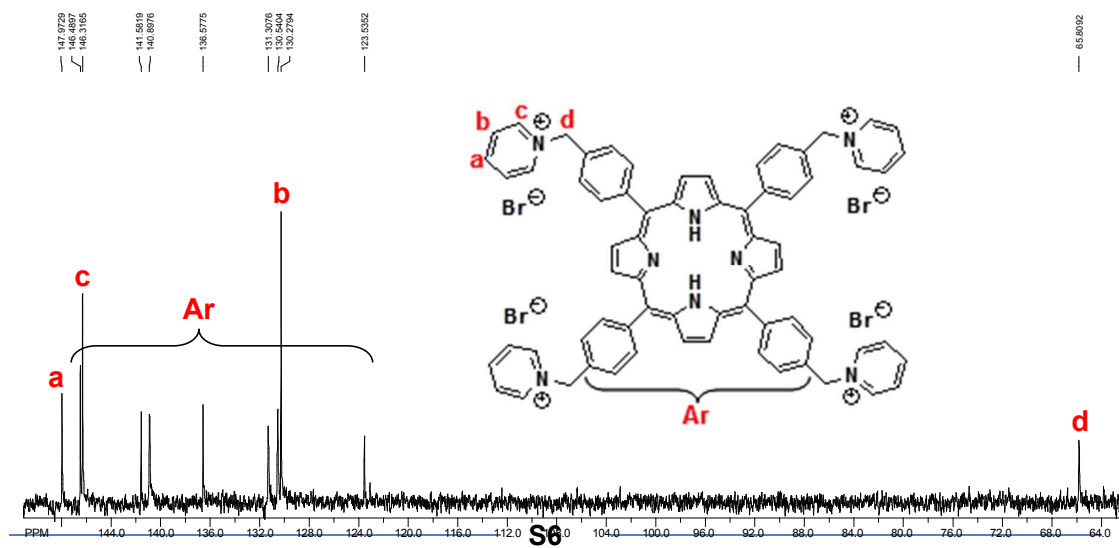
**meso-tetrakis[4-(pyridiniummethyl)phenyl]porphyrin**

**meso-tetrakis(4-carboxylatephenyl)porphyrin salt ( $\text{TPyPP}^{4+}\text{TCPP}^{4-}$ )** To meso-tetrakis(4-carboxyphenyl)porphyrin (200 mg, 0.25 mmol) suspended in MeOH (4 mL) was added 40% aqueous solution of tetrabutylammonium hydroxide (670  $\mu\text{L}$ , 1.03 mmol). To the resultant homogenous solution was added the methanol (4 mL) solution of  $\text{TPyPP}^{4+}\text{Br}^{-}_4$  (408 mg, 0.25 mmol). This solution was added dropwise into  $\text{CH}_2\text{Cl}_2$ . The generated precipitate was collected by filtration and washed with  $\text{CH}_2\text{Cl}_2$ . Vacuum drying gave crude  $\text{TCPP}^{4-}\text{TPyPP}^{4+}$  (408 mg, 89%yield), which was recrystallized by vapor diffusion of acetone into the MeOH/EtOH/ $\text{H}_2\text{O}$  solution, giving dark purple needle-like crystals.  $^1\text{H}$ -NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  (ppm) 9.23 (d,  $J=5.6$  Hz, 8H), 8.74 (t-like,  $J=7.8$  Hz, 4H), 8.27 (t-like,  $J=6.7$  Hz, 8H) 7.86 (d,  $J=7.5$  Hz, 8H), 7.74 (br, 16H), 7.21 (d,  $J=7.5$  Hz, 8H), 7.1-7.0 (brm, 16H), 5.99 (s, 8H).

$^1\text{H}$  NMR spectrum (DMSO- $d_6$ ) of TPyPP $^{4+}\text{Br}^-_4$



$^{13}\text{C}$ -NMR spectrum (D $_2$ O/DMSO- $d_6$ ) of TPyPP $^{4+}\text{Br}^-_4$



$^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{OD}$ ) of  $\text{TPyPP}^{4+}\text{TCPP}^{4-}$

