

**Supplementary Information for**

**Programmable Arrangement of Metal Ions  
in a Cofacially Stacked Assembly of Porphyrinoids toward  
Molecular Tags**

Nozomi Mihara,<sup>1</sup> Yasuyuki Yamada,<sup>1,2,3</sup> Tatsuhisa Kato,<sup>4</sup> and Kentaro Tanaka<sup>1\*</sup>

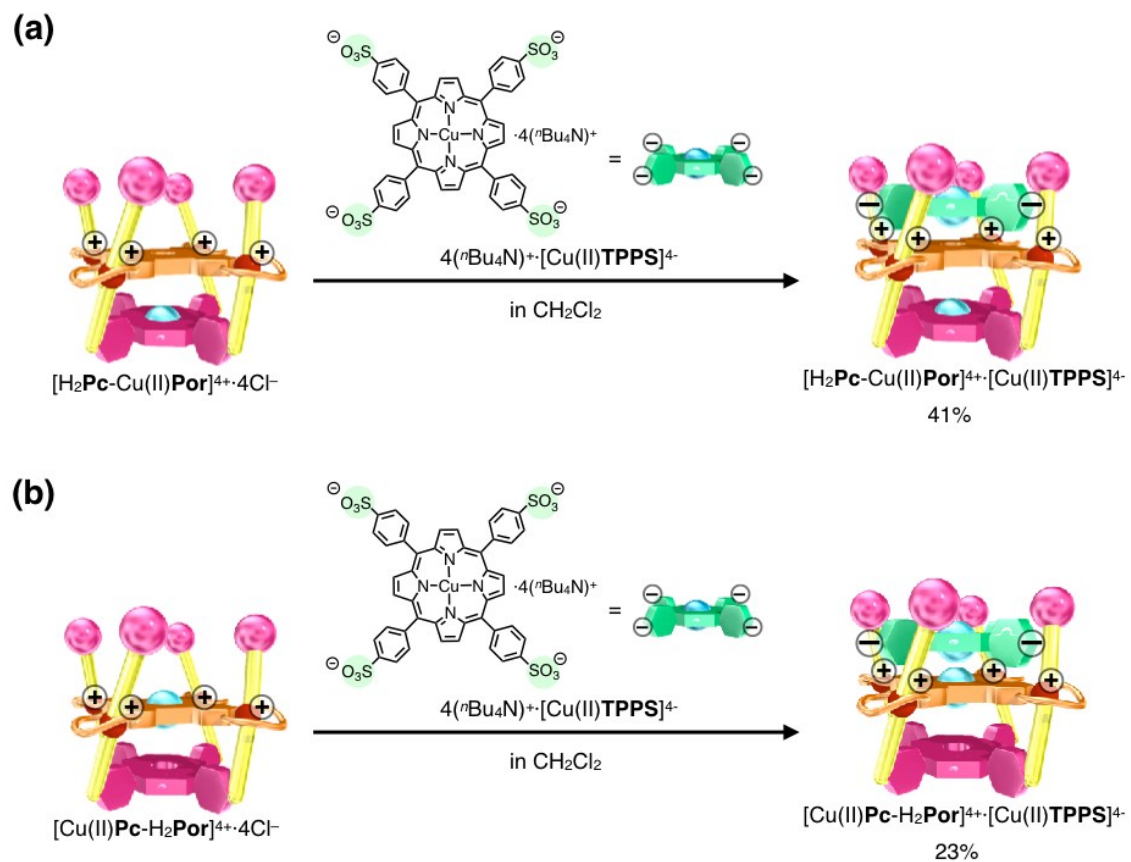
<sup>1</sup>*Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku,  
Nagoya 464-8602, Japan*

<sup>2</sup>*Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602,  
Japan*

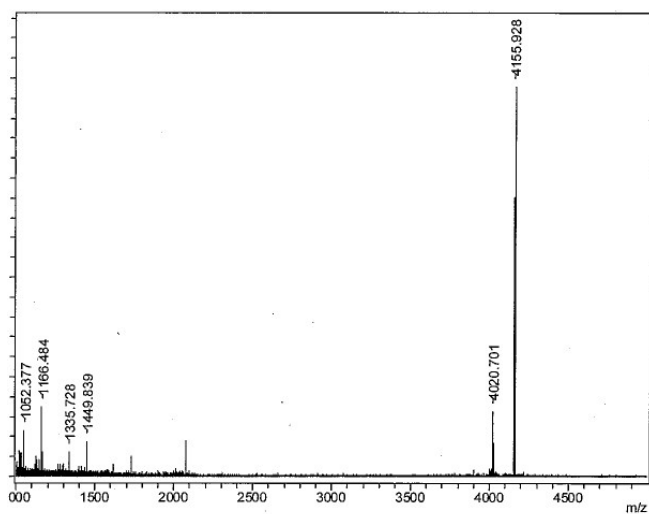
<sup>3</sup>*JST, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan*

<sup>4</sup>*Institute for the Promotion of Excellence in Higher Education, Kyoto University, Yoshidanihonmatsu-  
cho, Sakyo-ku, Kyoto, 606-8501, Japan*

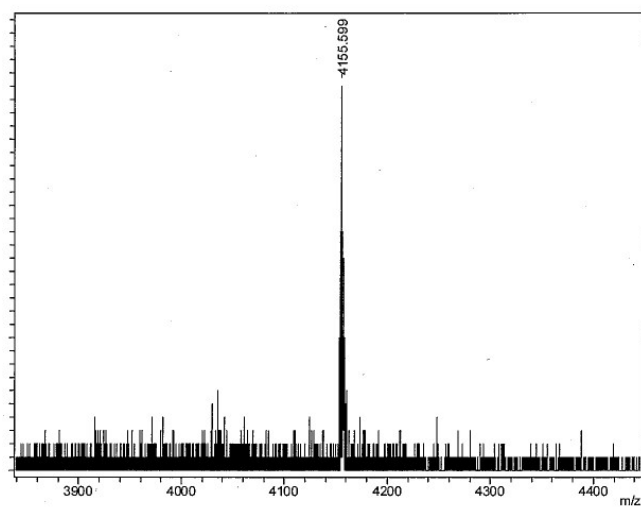
\*E-mail: kentaro@chem.nagoya-u.ac.jp



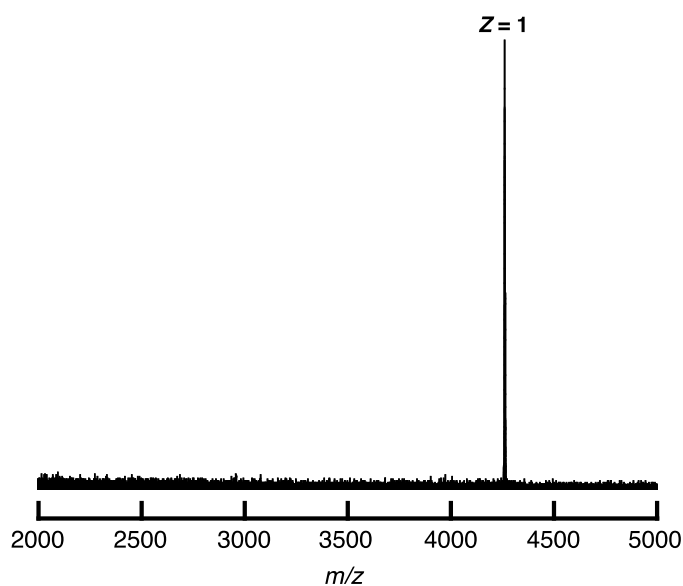
**Scheme S1.** Ionic complexation to obtain (a)  $[H_2Pc-Cu(II)Por]^{4+} \cdot [Cu(II)TPPS]^{4-}$  and (a)  $[Cu(II)Pc-H_2Por]^{4+} \cdot [Cu(II)TPPS]^{4-}$ .



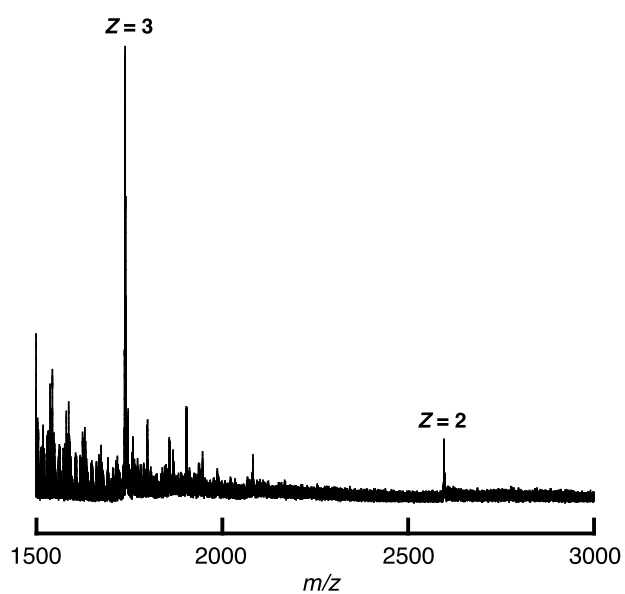
**Figure S1.** MALDI-TOF mass spectra of  $[\text{H}_2\text{Pc-Cu(II)Por}]^{4+} \cdot 4\text{Cl}^-$  (M for  $[[\text{H}_2\text{Pc-Cu(II)Por}]^{4+} - 3\text{H}]^+ = \text{C}_{220}\text{H}_{275}\text{N}_{20}\text{O}_{48}\text{P}_4\text{Cu}$ ).



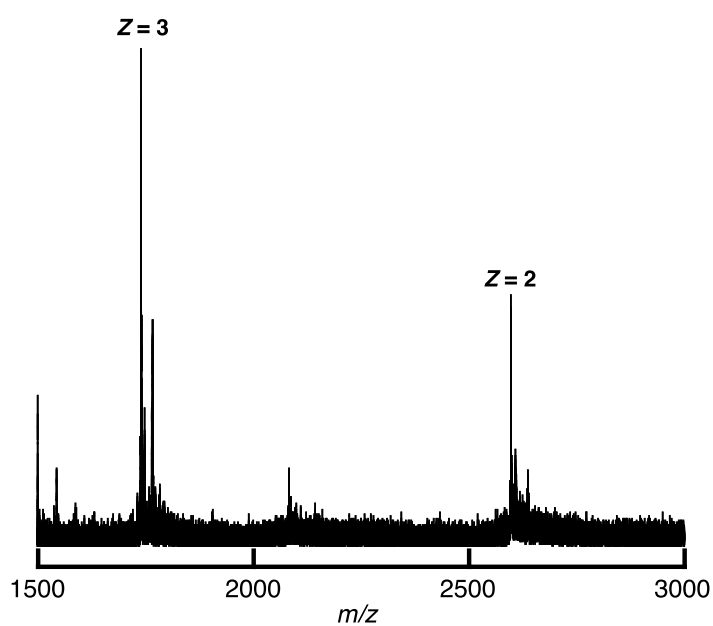
**Figure S2.** MALDI-TOF mass spectra of  $[\text{Cu(II)Pc-H}_2\text{Por}]^{4+} \cdot 4\text{Cl}^-$  (M for  $[[\text{Cu(II)Pc-H}_2\text{Por}]^{4+} - 3\text{H}]^+ = \text{C}_{220}\text{H}_{275}\text{N}_{20}\text{O}_{48}\text{P}_4\text{Cu}$ ).



**Figure S3.** MALDI-TOF mass spectra of  $[\text{Cu(II)Pc-Ag(II)Por}]^{4+} \cdot 4\text{Cl}^-$  (M for  $[[\text{Cu(II)Pc-Ag(II)Por}]^{4+} - 3\text{H}^+]^+ = \text{C}_{220}\text{H}_{273}\text{AgCuN}_{20}\text{O}_{48}\text{P}_4$ ).



**Figure S4.** ESI-TOF mass spectra of  $[\text{H}_2\text{Pc-Cu(II)Por}]^{4+} \cdot [\text{Cu(II)TPPS}]^{4-}$  (M for  $[[\text{H}_2\text{Pc-Cu(II)Por}]^{4+} \cdot [\text{Cu(II)TPPS}]^{4-} + 3\text{Na}]^{3+} = \text{C}_{264}\text{H}_{302}\text{N}_{24}\text{O}_{60}\text{P}_4\text{S}_4\text{Cu}_2\text{Na}_3$ ).



**Figure S5.** ESI-TOF mass spectra of  $[\text{Cu(II)Pc-H}_2\text{Por}]^{4+} \cdot [\text{Cu(II)TPPS}]^{4-}$  (M for  $[[\text{Cu(II)Pc-H}_2\text{Por}]^{4+} \cdot [\text{Cu(II)TPPS}]^{4-} + 3\text{Na}]^{3+} = \text{C}_{264}\text{H}_{302}\text{N}_{24}\text{O}_{60}\text{P}_4\text{S}_4\text{Cu}_2\text{Na}_3$ ).

Parameters for the simulations in **Figure 3**.

(a)

$$S=1/2$$

$$g=[2.025, 2.025, 2.171]$$

$$ACu=[3.5, 3.5, 21.0] \text{ / mT}$$

$$AN=[1.74, 1.74, 1.74], AN=[1.74, 1.74, 1.74], AN=[1.74, 1.74, 1.74], AN=[1.74, 1.74, 1.74] \text{ / mT}$$

(b)

$$S=1$$

$$g=[2.050, 2.050, 2.098]$$

$$D=42.8 \text{ / mT}, E=0.0 \text{ / mT}$$

$$ACu=[1.25, 1.25, 10.8] \text{ / mT}$$

(c)

$$S=1$$

$$g=[2.050, 2.050, 2.098]$$

$$D=44.8 \text{ / mT}, E=0.0 \text{ / mT}$$

$$ACu=[1.25, 1.25, 10.8], ACu=[1.25, 1.25, 10.8] \text{ / mT}$$

+

$$S=1/2$$

$$g=[2.035, 2.045, 2.195]$$

$$ACu=[3.5, 3.5, 21.0] \text{ / mT}$$

$$AN=[1.74, 1.74, 1.74], AN=[1.74, 1.74, 1.74], AN=[1.74, 1.74, 1.74], AN=[1.74, 1.74, 1.74] \text{ / mT}$$

(d)

$$S=1/2$$

$$g=[2.059, 2.059, 2.157], g=[2.047, 2.047, 2.186]$$

$$ACu=[1.7, 1.7, 20.0], ACu=[3.0, 3.0, 21.0] \text{ / mT}$$

$$AN=[1.86, 1.86, 1.86], AN=[1.86, 1.86, 1.86], AN=[1.86, 1.86, 1.86], AN=[1.86, 1.86, 1.86] \text{ / mT}$$

AN=[2.00, 2.00, 2.00], AN=[2.00, 2.00, 2.00], AN=[2.00, 2.00, 2.00], AN=[2.00, 2.00,  
2.00] / mT