

## Electronic Supplementary Information

### Chirality induction on cation-driven assembly using a crowned metalloporphyrin

Yusuke Ishii, Yoshiei Soeda and Yuji Kubo\*

Department of Applied Chemistry, Graduate School of Science and Technology, Saitama University,  
255 Shimo-ohkubo, Sakura-ku, Saitama 338-8570, Japan

E-mail; yuji@apc.saitama-u.ac.jp

Fax: +81-48-858-3514

#### General

NMR spectra were taken Bruker DRX-400 or DPX-400 ( $^1\text{H}$ : 400 MHz;  $^{13}\text{C}$  100.7 MHz) spectrometers. Chemical shifts ( $\delta$ ) are reported downfield from the initial standard  $\text{Me}_4\text{Si}$ . Cold spray ionization mass spectra were obtained on a JEOL JMS-T100CS spectrometer where  $\text{CF}_3\text{COONa}$  was employed for the calibration. Fast atom bombardment (FAB) mass spectra were obtained on a JEOL JMS-DX 303 double focusing spectrometer where *m*-nitrobenzyl alcohol was used as a matrix. Absorption spectra were measured using a Shimadzu UV-3100PC spectrophotometer and circular dichroism spectra were measured using a JASCO J-720W circular dichroism spectropolarimeter. Elemental analyses were obtained on ThermoFinnigan Flash EA1112.

5-[3,4-(1,4,7,10,13-pentaoxacyclotridecano)phenyl]-10,15,20-triphenylporphyrinato]zinc(II) (**1-Zn**)

5-[3,4-(1,4,7,10,13-pentaoxacyclotridecano)phenyl]-10,15,20-triphenyl-21*H*,23*H*-porphyrin (**1**)<sup>1</sup> (143 mg, 0.18 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (300 mL).  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (1.020 g, 4.47 mmol), being dissolved in MeOH (10 mL), was added to the  $\text{CH}_2\text{Cl}_2$  solution of **1**. After the mixture was stirred overnight at room temperature, the resulting solution was treated with water. The organic phase was evaporated *in vacuo*, and then washed with *n*-hexane. In this way, 152 mg of **1-Zn** was obtained in 98 % yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  8.92 (s, 8H), 8.20 (d,  $J = 7.3$  Hz, 6H), 7.76 – 7.69 (m, 9H), 7.61 (dd,  $J = 8.0, 1.7$  Hz, 1H), 7.56 (d,  $J = 1.6$  Hz, 1H), 6.92 (d,  $J = 8.1$  Hz, 1H), 3.91 (br s, 2H), 3.66 (br s, 2H), 3.36 (br s, 2H), 3.15 (br s, 2H), 3.13 (br s, 2H), 3.07 (br s, 2H), 3.02 (t,  $J = 4.6$  Hz, 2H); 2.85 (br s, 2H);  $^{13}\text{C}$  NMR (100.7 MHz,  $\text{CDCl}_3$ , 24 °C)  $\delta$  150.48, 150.28, 150.23, 148.14, 146.39, 143.27, 135.99, 134.66, 132.07, 131.94, 127.78, 127.49, 126.64, 121.03, 120.94, 120.75, 120.27, 111.09, 70.31, 70.13, 70.07, 69.93, 69.03, 68.85, 68.36, 68.26;  $m/z$  (FAB MS) 866 ( $\text{M}^+$ ); Anal. calcd. for  $\text{C}_{52}\text{H}_{42}\text{N}_4\text{O}_5\text{Zn} \cdot \text{H}_2\text{O}$ : C 70.47; H 5.00; N 6.32%, Found: C 70.67; H 4.84; N 6.22%.

5-[3,4-(1,4,7,10,13-pentaoxacyclotridecano)phenyl]-10,15,20-triphenylporphyrinato]magnesium(II)

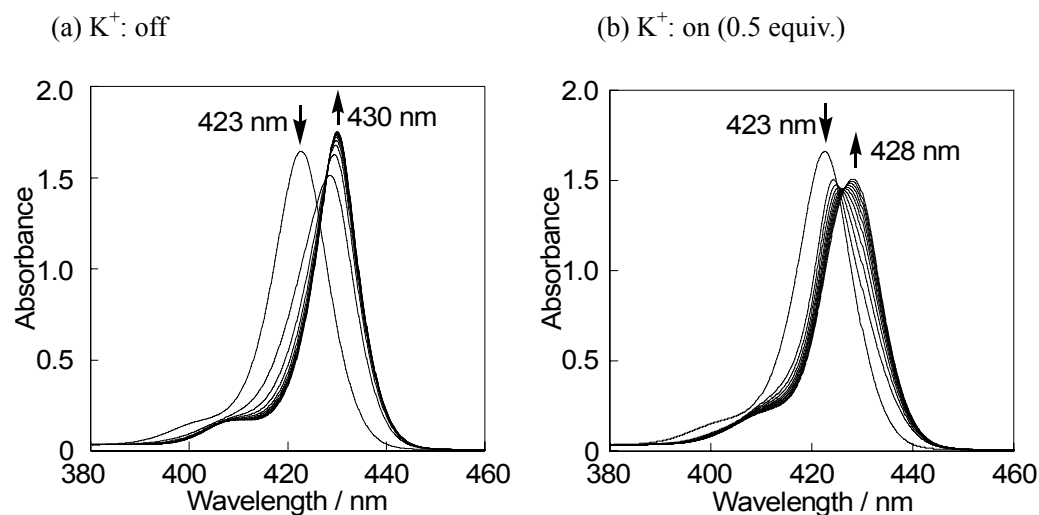
**(1-Mg)**

Compound **(1)** (140.9 mg, 0.174 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) under a N<sub>2</sub> condition. NEt<sub>3</sub> (0.5 mL, 3.6 mmol) and MgBr<sub>2</sub>·OEt<sub>2</sub> (459.7 mg, 1.78 mmol) were added to the solution and the resulting mixture was stirred overnight at room temperature. The resulting solution was washed with sat. NaHCO<sub>3</sub> aqueous solution (100 mL × 2) and then washed water (100 mL). The organic phase was evaporated *in vacuo* and chromatographed on activated alumina (Wako) using a gradient MeOH (0 – 5 % (v/v)) in CH<sub>2</sub>Cl<sub>2</sub> as an eluent. The desired product was collected and washed with *n*-hexane. In this way, 67.7 mg of **1-Mg** was obtained in 47 % yield.

<sup>1</sup>H NMR (400 MHz, 5 % (v/v) CD<sub>3</sub>OD in CD<sub>2</sub>Cl<sub>2</sub>, 23 °C) δ 8.90 (d, J = 4.5 Hz, 6H), 8.86 – 8.84 (m, 6H), 8.22 (d, J = 4.8 Hz, 6H), 7.77 – 7.71 (m, 9H), 7.69 – 7.67 (m, 2H), 7.08 (d, J = 8.6 Hz, 1H), 4.11 (t, J = 4.0 Hz, 2H), 4.01 (t, J = 4.0 Hz, 2H), 3.61 (br s, 2H), 3.55 (t, J = 4.3 Hz, 2H), 3.51 (t, J = 4.4 Hz, 2H), 3.47 (br s, 4H), 3.38 (br s, 2H); <sup>13</sup>C NMR (100.7 MHz, 5 % (v/v) CD<sub>3</sub>OD in CD<sub>2</sub>Cl<sub>2</sub>, 23 °C) δ 150.64, 150.40, 150.36, 150.33, 148.69, 147.03, 144.31, 137.25, 135.15, 132.24, 132.09, 128.29, 127.50, 126.75, 122.02, 121.97, 121.81, 121.04, 111.74, 70.90, 70.85, 70.54, 70.51, 69.67, 69.54, 69.17, 69.06; m/z (FAB MS) 826 (M<sup>+</sup>); Anal. calcd. for C<sub>52</sub>H<sub>42</sub>N<sub>4</sub>O<sub>5</sub>Mg·2H<sub>2</sub>O: C 72.35; H 5.37; N 6.49 %, Found: C 72.43; H 5.18; N 6.45 %.

1. V. Thanabai and V. Krishnan, *J. Am. Chem. Soc.*, 1982, **104**, 3643.

**Changes in UV–Vis spectra**

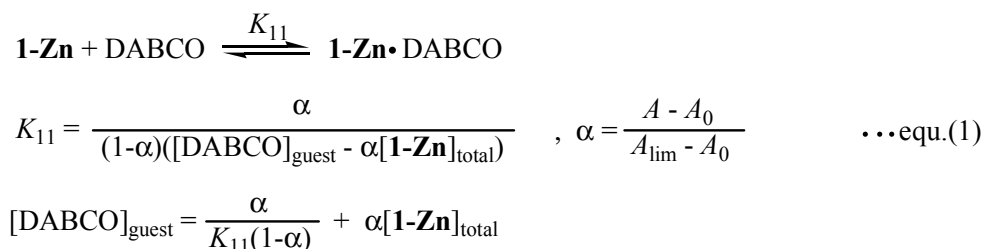


**Fig. S1** UV–Vis spectra of **1-Zn** upon addition of incremental amounts of DABCO in the absence or presence of K<sup>+</sup> (0.5 equiv.) in CH<sub>2</sub>Cl<sub>2</sub>-MeCN (9:1 v/v) at 25 °C, [1-Zn] = 4 μM, [DABCO] = 0, 8, 16, 24, 32, 40, 48, 56, 64, 72, 80 μM.

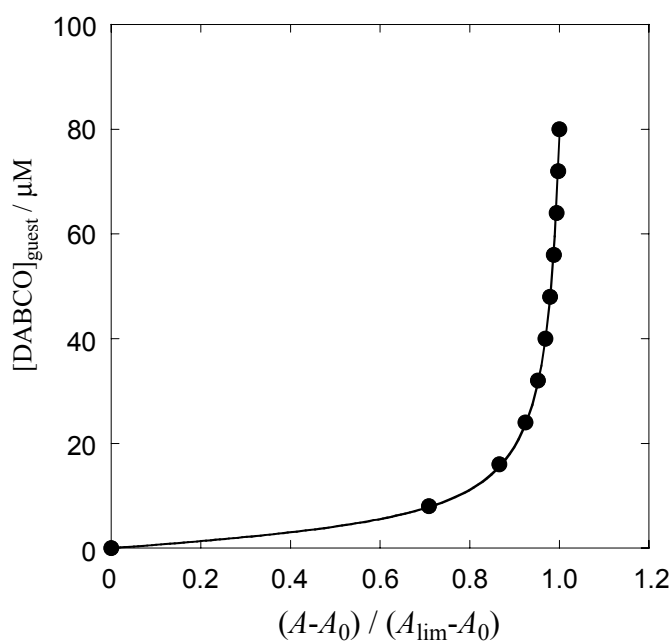
### UV-Vis titrations of **1-Zn** upon the addition of DABCO in the absence or presence of $K^+$

1)  $K^+$ -free conditions

Fig. S2 shows the curve fit to determine the association constant of **1-Zn** with DABCO. The experimental curve could be reproduced in terms of equ. (1) assuming the following equation:



where  $A$  is the DABCO concentration-dependent absorption intensity at 603 nm, with  $A_0$  and  $A_{\text{lim}}$  denoting intensity at zero and infinite DABCO concentrations, respectively.



**Fig. S2** The non-linear curve fitting plot of  $(A - A_0) / (A_{\text{lim}} - A_0)$  of **1-Zn** (4  $\mu\text{M}$ ) as a function of  $[\text{DABCO}]_{\text{guest}}$  in the absence of  $K^+$  in  $\text{CH}_2\text{Cl}_2$ -MeCN (9:1 v/v) at 25  $^\circ\text{C}$ .

The  $K_{11}$  can be analyzed using the nonlinear curve fitting based on the Levenberg-Marquardt algorithm in KaleidaGraph, being  $4.31 \times 10^5 \text{ M}^{-1}$  ( $R^2 = 0.999$ ).

2) In the presence of  $K^+$ .

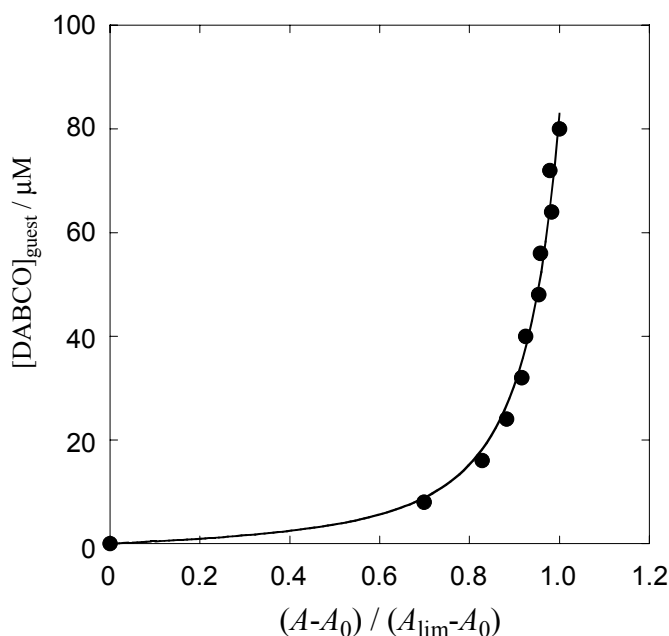
The experimental curve of Fig. S3 could be reproduced in terms of equ. (2) assuming the following equation:

$$2(\mathbf{1-Zn}) + \text{DABCO} \xrightleftharpoons{K_{21}} (\mathbf{1-Zn})_2 \cdot \text{DABCO}$$

$$K_{21} = \frac{\alpha}{2[\mathbf{1-Zn}]_{\text{total}}(1-\alpha)^2([\text{DABCO}]_{\text{guest}} - \frac{\alpha}{2}[\mathbf{1-Zn}]_{\text{total}})}, \quad \alpha = \frac{A - A_0}{A_{\text{lim}} - A_0} \quad \dots \text{equ.}(2)$$

$$[\text{DABCO}]_{\text{guest}} = \frac{\alpha}{2K_{21}(1-\alpha)^2[\mathbf{1-Zn}]_{\text{total}}} + \frac{\alpha}{2}[\mathbf{1-Zn}]_{\text{total}}$$

where  $A$  is the DABCO concentration-dependent absorption intensity at 603 nm, with  $A_0$  and  $A_{\text{lim}}$  denoting intensity at zero and infinite DABCO concentrations, respectively.

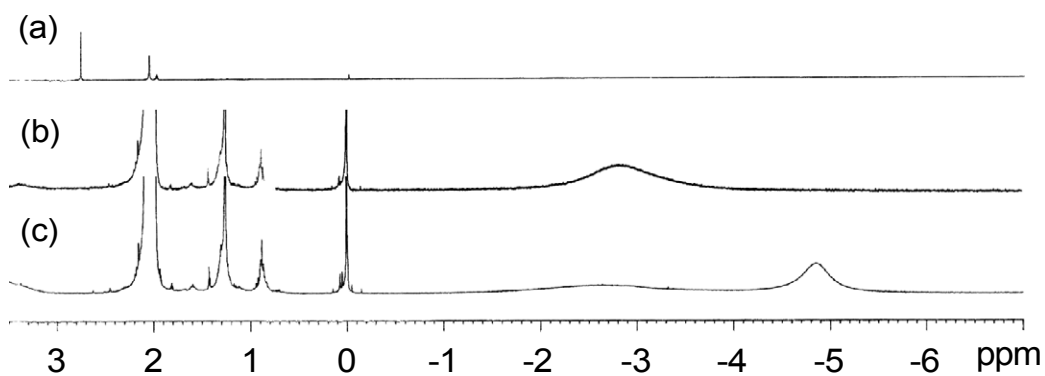


**Fig. S3** The non-linear curve fitting plot of  $(A - A_0) / (A_{\text{lim}} - A_0)$  of  $\mathbf{1-Zn}$  ( $4 \mu\text{M}$ ) as a function of  $[\text{DABCO}]_{\text{guest}}$  in the presence of  $K^+$  ( $2 \mu\text{M}$ ) in  $\text{CH}_2\text{Cl}_2\text{-MeCN}$  (9:1 v/v) at  $25^\circ\text{C}$ .

The  $K_{21}$  can be analyzed using the nonlinear curve fitting based on the Levenberg-Marquardt algorithm in KaleidaGraph, being  $6.46 \times 10^{10} \text{ M}^{-2}$  ( $R^2 = 0.982$ ).

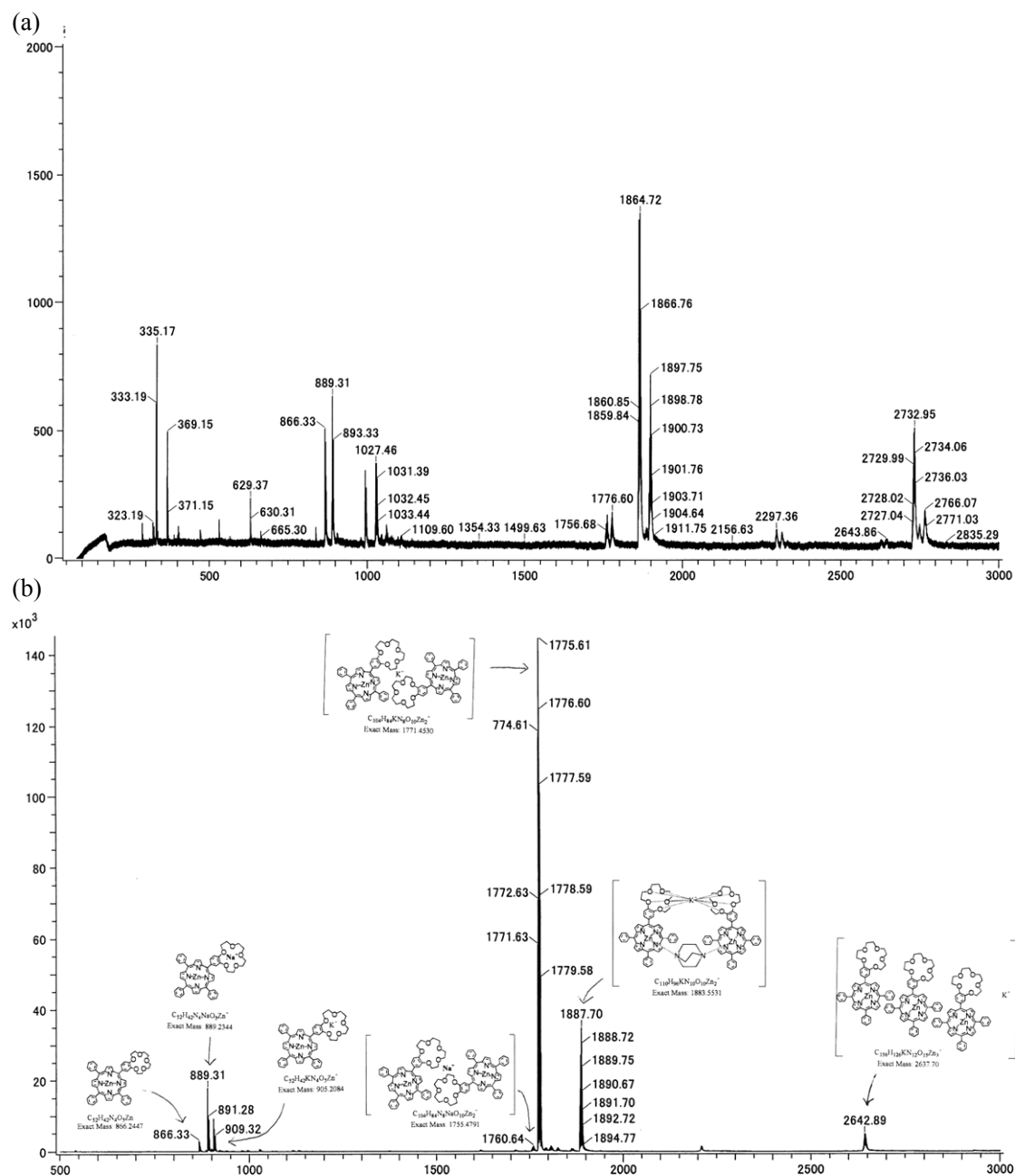
### $^1\text{H}$ NMR spectra

The spectra depicted in Fig. S4(c) was measured after the solid  $[\text{KClO}_4]$ –liquid [**1-Zn** (8 mM) and DABCO (4 mM) in  $\text{CDCl}_3$ – $\text{CD}_3\text{CN}$  (4:1 v/v) solution] two-phase solvent extraction. We also note that slightly board signal was observed at ca.  $-2.6$  ppm, possibly due to monotopic binding of DABCO to **1-Zn**. However, the intensity is too small to assign the complex mode.



**Fig. S4.**  $^1\text{H}$  NMR spectra of (a) DABCO, (b) DABCO with **1-Zn** and (c) DABCO with **1-Zn** in the presence of  $\text{K}^+$  in  $\text{CDCl}_3$ – $\text{CD}_3\text{CN}$  (4:1 v/v) at 23 °C.  $[\text{DABCO}] = 4$  mM,  $[\mathbf{1-Zn}] = 8$  mM.

### CSI MS spectra



**Fig. S5** CSI-MS spectra of (a) **1-Zn** with DABCO and (b) **1-Zn** with DABCO in the presence of K<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub>-MeCN (9:1 v/v) at the spray temperature of -30 °C. [**1-Zn**] = 0.4 mM, [DABCO] = 0.2 mM, [KClO<sub>4</sub>] = 0.2 mM.