Electronic Supplementary Information

Chirality induction on cation-driven assembly using a crowned metalloporphyrin

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General
NMR spectra were taken Bruker DRX-400 or DPX-400 (1H: 400 MHz; 13C 100.7 MHz) spectrometers. Chemical shifts (δ) are reported downfield from the initial standard Me₄Si. Cold spray ionization mass spectra were obtained on a JEOL JMS-T100CS spectrometer where CF₃COONa 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 ThermoFinigan Flash EA1112.

5-[3,4-(1,4,7,10,13-pentaoxacyclotridecano)phenyl]-10,15,20-triphenylporphynato]zinc(II) (1-Zn)
5-[3,4-(1,4,7,10,13-pentaoxacyclotridecano)phenyl]-10,15,20-triphenyl-21H,23H-porphyrin (1)
(143 mg, 0.18 mmol) was dissolved in CH₂Cl₂ (300 mL). Zn(OAc)₂·2H₂O (1.020 g, 4.47 mmol), being dissolved in MeOH (10 mL), was added to the CH₂Cl₂ 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.

1H NMR (400 MHz, CDCl₃, 25 ºC) δ 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); 13C NMR (100.7 MHz, CDCl₃, 24 ºC) δ 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 (M⁺); Anal. calcd. for C₅₂H₄₀N₄O₅Zn·H₂O: 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-triphenylporphynato]magnesium(II)
Compound (1) (140.9 mg, 0.174 mmol) was dissolved in CH₂Cl₂ (100 mL) under a N₂ condition. NEt₃ (0.5 mL, 3.6 mmol) and MgBr₂·OEt₂ (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. NaHCO₃ 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 CH₂Cl₂ 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.

1H NMR (400 MHz, 5 % (v/v) CD₃OD in CD₂Cl₂, 23 ºC) δ 8.90 (d, J = 4.5 Hz, 6H), 8.86 – 8.84 (m, 6H), 8.22 (d, J = 4 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), 3.34 (br s, 2H); 13C NMR (100.7 MHz, 5 % (v/v) CD₃OD in CD₂Cl₂, 23 ºC) 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⁺); Anal. calcd. for C₅₂H₄₂N₄O₅Mg·2H₂O: C 72.35; H 5.37; N 6.49 %, Found: C 72.43; H 5.18; N 6.45 %.


**Changes in UV–Vis spectra**

(a) K⁺: off

(b) K⁺: on (0.5 equiv.)

![UV–Vis spectra of 1-Zn](image)

**Fig. S1** UV–Vis spectra of 1-Zn upon addition of incremental amounts of DABCO in the absence or presence of K⁺ (0.5 equiv.) in CH₂Cl₂-MeCN (9:1 v/v) at 25 ºC, [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:

\[ 1-Zn + DABCO \overset{K_{11}}{\rightarrow} 1-Zn \cdot DABCO \]

\[ K_{11} = \frac{\alpha}{(1-\alpha)([DABCO]_{\text{guest}} - \alpha[1-Zn]_{\text{total}})} \quad \alpha = \frac{A - A_0}{A_{\text{lim}} - A_0} \quad \ldots \text{equ.(1)} \]

\[ [DABCO]_{\text{guest}} = \frac{\alpha}{K_{11}(1-\alpha)} + \alpha[1-Zn]_{\text{total}} \]

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

The \( K_{11} \) can be analyzed using the nonlinear curve fitting based on the Levenberg-Marquardt algorithm in KaleidaGraph, being \( 4.31 \times 10^5 \) 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:

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

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

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

![Graph](image)

**Fig. S3** The non-linear curve fitting plot of \((A - A_0) / (A_{lim} - A_0)\) of 1-Zn (4 μM) as a function of [DABCO]guest in the presence of K⁺ (2 μM) in CH₂Cl₂-MeCN (9:1 v/v) at 25 °C.

The \(K_{21}\) can be analyzed using the nonlinear curve fitting based on the Levenberg-Marquardt algorithm in KaleidaGraph, being \(6.46 \times 10^{10} \text{ M}^{-2}\) (R² = 0.982).
\(^1\)H NMR spectra

The spectra depicted in Fig. S4(c) was measured after the solid [KClO\(_4\)]–liquid [1-Zn (8 mM) and DABCO (4 mM) in CDCl\(_3\)-CD\(_3\)CN (4:1 v/v) solution] two-phase solvent extraction. We also note that slightly broad 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.** \(^1\)H NMR spectra of (a) DABCO, (b) DABCO with 1-Zn and (c) DABCO with 1-Zn in the presence of K\(^+\) in CDCl\(_3\)-CD\(_3\)CN (4:1 v/v) at 23 °C. [DABCO] = 4 mM, [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⁺ in CH₂Cl₂-MeCN (9:1 v/v) at the spray temperature of −30 °C. [1-Zn] = 0.4 mM, [DABCO] = 0.2 mM, [KClO₄] = 0.2 mM.