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Metal-Templated Synthesis of Rigid and Conformationally Restricted Cyclic Bisporphyrins: Specific Retention Times on Cyanopropyl-Modified Silica Gel Column

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Figure S1. ¹H NMR spectrum (400 MHz) of 4Zn in CDCl₃.



Figure S2. ¹³C NMR spectrum (75 MHz) of 4Zn in CDCl₃.



Figure S3. ¹H NMR spectrum (400 MHz) of 5Fb₂ in CDCl₃.



Figure S4. ¹³C NMR spectrum (75 MHz) of 5Fb₂ in CDCl₃.



Figure S5. ¹H-¹H COSY spectrum (400 MHz) of 5Fb₂ in CDCl₃.



Figure S6. ¹H NMR spectrum (300 MHz) of 6Fb₂ in CDCl₃.



Figure S7. ¹H NMR spectrum (400 MHz) of 7Fb in CDCl₃.



Figure S8. ¹H NMR spectrum (400 MHz) of 8Fb₂ in CDCl₃.



Figure S9. MALDI-TOF mass spectrum (matrix: dithranol, mode: spiral) of a crude mixture after reaction of $6Zn_2$ with isophthaloyl dichloride in the presence of silver ion. Zn_2 -CP2_m.: m/z 1681. On the mass spectrum, the relative intensities do not reflect their yields. In general, cyclic compounds such as Zn_2 -CP2_m. and Zn_4 -CP4_m tend to appear significantly compared with linear porphyrin derivatives in MALDI-TOF mass spectra.



Figure S10. Molecular structures and weights estimated from the MALDI-TOF mass spectrum in Figure S9.



Figure S11. HPLC charts of crude mixtures after reaction of $6Zn_2$ (0.5 mM) with isophthaloyl dichloride in the absence and presence of metal ions (1 eq. of $6Zn_2$ except for (8)). Column: Cosmosil 5CN-MS (7.5 mm I.D. ×5 cm). Eluent: 100% pyridine. Flow rate: 0.5 mL/min. Monitored at 563 nm. Cyclic diamide Zn_2 -CP2_m was eluted around RT 3.7 min under the conditions. All the other components were eluted up to RT 3.2 min. Since the amounts as well as the concentrations of injected samples were almost constant, the areas of corresponding peaks can be directly compared in the chromatograms of (1)~(8).



Figure S12. UV-Vis spectral change of $5Zn_2$ (7.5×10⁻⁶ M) during titration with Zn(OTf)₂ in CHCl₃. Inset) The relationship between the change of absorption at 450 nm and equivalents of added Zn(OTf)₂.



Figure S13. UV-Vis spectral change of $5Zn_2$ (7.5×10⁻⁶ M) during titration with Cu(OTf)₂ in CHCl₃. (Inset) The relationship between the change of absorption at 440 nm and equivalents of added Cu(OTf)₂.



Figure S14. UV–vis spectra (in CHCl₃) of (A) 4Zn, (B) $5Zn_2$, (C) $5Zn_2$ with lequiv of Zn(OTf)₂, (D) $5Zn_2$ with lequiv of Ag(OTf), and (E) normalized overlaid spectra of (A)–(D) between 400 and 450 nm. The colors in (E) correspond to those in (A)–(D).



Figure S15. HPLC chart of a crude mixture after coupling reaction of $8Zn_2$ (0.1 mM) with Ni(cod)₂. Column: Cosmosil CN-MS (7.5 mm I.D. ×5 cm). Eluent: toluene/pyridine (15/85). Flow rate: 1.0 mL/min. Monitored at 563 nm. Cyclic diamide Zn_2 -CP2_m was eluted at *RT* 2.9 min (HPLC yield: 3%). All the other components were eluted up to *RT* 1.5 min without retention.



Zn₂-CP2_o

Figure S16. Structures of 9 and Zn₂-CP2₀



Figure S17. MALDI-TOF mass spectrum (matrix: dithranol, mode: spiral) of a crude mixture after reaction of $6Zn_2$ with phthaloyl dichloride. Zn_2 -CP2₀.: m/z 1681 [M+H]⁺, 9: m/z 1815 [M+H]⁺, and unidentified signal at 1875. On the mass spectrum, the relative intensities do not reflect their yields. Cyclic compound Zn_2 -CP2_m tends to appear significantly compared with linear porphyrin derivatives.



Figure S18. ¹H NMR of Zn_2 -CP2_m (15 mM) in pyridine- d_5 , 500 MHz.



Figure S19. ¹³C NMR (a) and DEPT-135 (b) spectra of Zn_2 -CP2_m (15 mM) in pyridine- d_5 , 125 MHz.



Figure S19 continued. ¹³C NMR (a) and DEPT-135 (b) spectra of Zn_2 -CP2_m (15 mM) in pyridine- d_5 , 125 MHz.



Figure S20. ¹H-¹H COSY of Zn_2 -CP2_m (15 mM) in pyridine- d_5 .



Figure S21. HSQC of Zn_2 -CP2_m (15 mM) in pyridine- d_5 .



Figure S22. HMBC of Zn_2 -CP2_m (15 mM) in pyridine- d_5 .



Figure S23. NOESY of Zn_2 -CP2_m (6 mM) in pyridine- d_5 .



Figure S24. (a) ¹H and ¹³C NMR assignments of 15 mM Zn_2 -CP2_m in pyridine-d₅. (b) Correlations observed in the NOESY of Zn_2 -CP2_m (~6 mM) in pyridine-d₅.

Zn ₂ -CP _{2m}	15 mM	6 mM	$\Delta \delta$ /ppm (15 mM – 6 mM)
bpy-1	8.72	8.70	0.02
bpy-2	8.31	8.28	0.03
bpy-3	8.63	8.62	0.01
β-4	8.94	8.92	0.02
β-5	8.69	8.66	0.03
β-6	8.36	8.34	0.02
β-7	8.46	8.44	0.02
Mes-8	1.67	1.65	0.02
Mes-9	7.34	7.32	0.02
Mes-10	2.48	2.47	0.01
Mes-11	7.09	7.08	0.01
Mes-12	1.50	1.51	0.01
Ar-13	8.19	8.18	0.01
Ar-14	7.69	7.68	0.01
Ar-15	8.89	8.79	0.10
Ar-16	8.27	8.26	0.01
NH-17	11.14	11.15	0.01
Ar(<i>m</i>)-18	7.52	7.47	0.05
Ar(<i>m</i>)-19	8.51	8.47	0.04
Ar(<i>m</i>)-20	9.12	9.05	0.07

Table S1	. Chemical	shifts of two	NMR samples	(15 and 6 mM)
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Figure S25. ¹H NMR (500 MHz) spectrum of $Zn-CP2_p$ in pyridine- d_5



Figure S26. ¹H NMR (500 MHz) spectrum of **Zn-CP2**_{*p*} in pyridine- d_5 (3~ –1.2 ppm). The y-range is adjusted for signals of (a) the major isomer and (b) the minor isomer. Asterisks indicate impurities. Open circles, open triangles, and filled squares are chemically exchanged, respectively.



Figure S26 continued. ¹H NMR (500 MHz) spectra of **Zn-CP2**_{*p*} in pyridine- d_5 (12~6 ppm). The y-range is adjusted for the signals of (a) the major isomer and (b) the minor isomer. Asterisks correspond signals of pyridines.



Figure S27. ¹³C NMR (a) and DEPT-135 (b) spectra of $\mathbb{Z}n_2$ -CP2_p in pyridine- d_5 , 125 MHz.



Figure S27 continued. ¹³C NMR (a) and DEPT-135 (b) spectra continued. Expanded for $170 \sim 110$ ppm.



Figure S28. ¹H-¹H COSY of $\mathbb{Z}n_2$ -CP2_{*p*} in pyridine- d_5 .



Figure S29. HSQC of Zn_2 -CP2_p in pyridine- d_5 .



Figure S30. NOESY (12 ~ 10 ppm) of **Zn-CP2**_{*p*} in pyridine- d_5 .



Figure S31. NOESY (3 ~ -1 ppm) of **Zn-CP2**_p in pyridine- d_5 .



Figure S32. NOESY ($10 \sim 7 \text{ ppm}$) of Zn-CP2_p in pyridine- d_5 .



Figure S33. (left) Assignments of ¹H (500 MHz) and ¹³C (125 MHz) NMR signals of major *syn* form of Zn-MsCP2_{*p*} in pyridine- d_5 . (right).

Zn ₂ -CP ₂ _p	major (ppm)	minor (ppm)	delta (ppm) major-minor		
Amide NH	10.44	11.67	-1.23		
		11.30	-0.86		
beta-1	8.84	9.60	-0.76		
		9.02	-0.18		
beta-2	8.65	9.35	-0.70		
		8.73	-0.08		
beta-3	8.59	8.96	-0.37		
		8.77	-0.18		
beta-4	8.45	9.00	-0.55		
		8.34	0.11		
Mes-4	2.51	2.63	-0.12		
		2.60	-0.09		
		2.45	0.06		
		2.30	0.21		
Mes-2-out	1.65	1.76	-0.11		
		1.74	-0.09		
		1.25	0.40		
		1.05	0.60		
Mes-2-in	1.47	2.56	-1.09		
		1.98	-0.51		
		0.61	0.86		
		-1.04	2.51		

Table S	2	Corelated	l siona	ls hv	chemical	exchanges	between th	he sv	mmetric ma	ior a	nd the asy	ummetric	minor	conformers
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Figure S34. ¹H NMR (500 MHz) spectrum of Zn-CP2₀ in pyridine-d₅



Figure S35. Molecular structures of *syn*-2 and *syn*-1 conformers of Zn_2 -CP2_m optimized with DFT calculations (B3LYP/6-31G(d) in vacuo), and the energy difference.



Figure S36. Molecular structures of *anti* and *syn* conformers of $\mathbb{Z}n_2$ - $\mathbb{C}P2_p$ optimized with DFT calculations (B3LPY/6-31G(d) in vacuo), and the energy difference.

Without dispersion interaction (B3LYP/6-31G(d) in vacuo)



With dispersion interaction (B3LYP-D3/6-31G(d) in vacuo)

Figure S37. DFT-optimized geometries of Zn_2 -CP2_o (*anti*), Zn_2 -CP2_m (*syn*-1), and Zn_2 -CP2_p (*syn*). Geometries were optimized and the distances between the two zinc atoms were calculated using the (a) B3LYP/6-31G(d) level of theory in vacuo (contributions from dispersion interactions were not considered) and (b) B3LYP-D3/6-31G(d) level of theory in vacuo (contributions from dispersion interactions were considered). The calculated distances between the two zinc ions have been presented.