Supporting Information

For
Structures and Ligand Exchange of N-Confused Porphyrin Dimer Complexes of Group 12 Metals

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(A) $^1$H NMR spectra of 7 – 9.

(B) ORTEP drawings of 7 and 8.

(C) van’t Hoff plot for the exchange reaction of 7 and 8.

(D) $^1$H NMR spectra of mixture solutions of 7-8, 8-9, 9-7, and 10-7.

(E) NOE difference $^1$H NMR spectrum of a mixture solution of 7-8.

(F) Identification of the hetero dimer complex formed from 8 and 11.
(A) $^1$H NMR spectra of 7 – 9

(1) Zn(II) dimer complex of 2-aza-5,20-diphenyl-21-carbaporphyrin (7)

Supporting Figure S1. $^1$H NMR spectra of 7 (300 MHz, CDCl$_3$). *: hexane, **: H$_2$O, ***: CH$_2$Cl$_2$, ****: CHCl$_3$. The signals at 2.57 and –3.99 ppm are assigned to the outer CH and inner CH, respectively (see Figure 3).
(2) Cd(II) dimer complex of 2-aza-5,20-diphenyl-21-carbaporphyrin (8)

Supporting Figure S2. $^1$H NMR (300 MHz, CDCl$_3$) and $^{13}$C NMR (75.5 MHz, CD$_2$Cl$_2$) spectra of 8. *: hexane, **: H$_2$O, ***: CH$_2$Cl$_2$, ****: CHCl$_3$. The signals at 3.44 and -4.17 ppm in the $^1$H NMR are assigned to the outer CH and inner CH, respectively (see Figure 3).
(3) Hg(II) dimer complex of 2-aza-5,20-diphenyl-21-carbaporphyrin (9)

Supporting Figure S3. $^1$H NMR (300 MHz, CDCl$_3$) and $^{13}$C NMR (75.5 MHz, CD$_2$Cl$_2$) spectra of 9. A in the $^1$H NMR spectrum represents the signals assigned to the free base NCDPP (1). *: hexane, **: H$_2$O, ***: CH$_2$Cl$_2$, ****: CHCl$_3$. The signals at 3.60 and –3.27 ppm in the $^1$H NMR are assigned to the outer CH and inner CH, respectively (see Figure 3).
Supporting Figure S4. ORTEP drawings of Zn-dimer (7, (a)) and Cd-dimer (8, (b)).
van’t Hoff plots for the exchange reaction of 7 and 8

\[ \Delta G = \Delta H - T(298 \text{ K})\Delta S \]
\[ = 0.68 - 3.0 \text{ J/Kmol} = -2.3 \text{ kJ/mol} < 0 \]

\[ \Delta H = 0.68 \text{ kJ/mol} > 0 \]
\[ \Delta S = 10 \text{ J/Kmol} \]

Supporting Figure S5. van’t Hoff plots for the exchange reaction of 7 and 8. The negative slope indicates the positive \( \Delta H \), and the negative \( \Delta G \) results from the larger mixing entropy term (\( T\Delta S > \Delta H \)).
(D) $^1$H NMR spectra of the mixture solutions of 7-8, 8-9, 9-7, and 10-7

(1) Mixture solution of 7 (Zn(II) Dimer) and 8 (Cd(II) Dimer).

Supporting Figure S6. $^1$H NMR spectrum of a mixture solution of 7-8 (300 MHz, CDCl$_3$). *: hexane, **: H$_2$O, ***: CH$_2$Cl$_2$, ****: CHCl$_3$. The signals of the inner and outer CH are shown in Figure 4.
(2) Mixture solution of 8 (Cd(II) Dimer) and 9 (Hg(II) Dimer).

Supporting Figure S7. $^1$H NMR spectrum of a mixture solution of 8-9 (300 MHz, 50 °C, CDCl$_3$). *: hexane, **: H$_2$O, ***: CH$_2$Cl$_2$, ****: CHCl$_3$. A and B represent the outer CH signals of 9 and 8, respectively, and C and D the inner CH signals of 9 and 8, respectively.
(3) Mixture solution of 9 (Hg(II) Dimer) and 7 (Zn(II) Dimer).

Supporting Figure S8. $^1$H NMR spectrum of a mixture solution of 9-7 (300 MHz, 50 °C, CDCl$_3$). *: hexane, **: H$_2$O, ***: CH$_2$Cl$_2$, ****: CHCl$_3$. A and B represent the outer CH signals of 9 and 7, respectively, and C and D the inner CH signals of 9 and 7, respectively.
(4) Mixture solution of 10 (Zn(II) dimer complex of NCTPP) and 7 (Zn(II) dimer complex of NCDPP).

**Supporting Figure S9.** $^1$H NMR spectrum of a mixture solution of 10-7 (300 MHz, CDCl$_3$). *: hexane, **: H$_2$O, ***: CH$_2$Cl$_2$, ****: CHCl$_3$. A and B represent the outer CH signals of 10 and 7, respectively, and C and D the inner CH signals of 10 and 7, respectively.
E) NOE difference $^1$H NMR spectrum of a mixture solution of 7-8

Supporting Figure S10. NOE difference $^1$H NMR spectrum obtained after irradiation of the resonance at 2.50 ppm (outer CH proton (H$^2$) of the Cd-I). The enhancement of the resonance at 3.46 ppm (outer CH proton (H$^4$) of the Zn-I) was observed. In the case of homo-dimers, the closest outer CH carbons are separated by less than 4 Å in the solids.
Identification of the hetero dimer complex formed from 8 and 11.

Supporting Figure S11. $^1$H NMR spectra of the hetero dimer complex formed from 8 ((Cd—1)$_2$) and 11 ((Zn—2)$_2$), (Zn—1)(Cd—1), and (Zn—2)(Cd—2). For the three hetero dimer complexes, H$^1$ represents the signal of inner CH close to Cd, and H$^3$ represents that close to Zn. By comparing the chemical shifts, it is suggested that the hetero dimer complex from 8 ((Cd—1)$_2$) and 11 ((Zn—2)$_2$) is composed of (Cd—1) and (Zn—2), which supports the mechanism shown in scheme 3(c).