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Experimental and Theoretical Studies on Oligomer Formation of N-Confused Porphyrin–Zinc(II) Complexes

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Abstract: Dimer formation of the N-confused porphyrin zinc(II), cadmium(II), and mercury(II) complexes was investigated experimentally as well as theoretically. The stable dimers were formed through coordination of the peripheral nitrogen atoms owing to flexible rotation of the confused pyrrole rings. The *Z* dimers were significantly more stable than the *E* dimers likely due to π–π interaction between the two confused pyrrole rings. The possible formation of higher oligomers such as trimers was suggested in the case of *meso*-unsubstituted derivatives.

Keywords: density functional calculations • oligomerization • porphyrinoids • supramolecular chemistry • zinc

Introduction

The importance of porphyrin assemblies in photosynthetic systems has inspired considerable interest in the construction of artificial multiporphyrin arrays. Since well-organized porphyrin arrays have potential application as optical molecular devices as well as redox-active materials, a wide variety of multiporphyrin oligomers have been synthesized and their properties have investigated enthusiastically.[1] Among several synthetic strategies for the preparation of multiporphyrin systems, the self-assembling approach by metal coordination has proven to be particularly attractive, because the assembled structure can be easily controlled by the synergy of metal ion species and donor ligands.[2] In fact, metal–porphyrins with pyridyl,[3] pyrazolyl,[4] imidazolyl,[5] or hydroxyl substituents[6] were extensively studied in recent years.

N-Confused porphyrin (NCP) is an isomer of porphyrin which bears a coordination site at the peripheral position of the porphine skeleton.[7,8] Consequently, its metal complexes can form self-assembled dimers without introduction of further coordination sites as for normal porphyrins. Such dimer formation was already reported for Zn, Cd, Hg, Fe, and Mn complexes.[9–11] Some unique dimeric structures were also reported in Pd, Pt, and Ag complexes.[12–14] In the former complexes, the confused pyrrole moieties inclined typically in 40–45° relative to the porphyrin planes so as to form homodimers. Based on previous results on NCP derivatives bearing the inverted conformation[15] and the formation of N-fused porphyrin at ambient temperature,[16,17] the angles between the porphyrin planes and the confused pyrrole plane should vary.[18] Depending on the angles as well as the whole shape of the molecules, NCP–metal complexes might form a variety of assemblies in the same manner as the normal porphyrin cases. Herein we describe our investigations on the oligomer formation of NCP zinc(II) complexes by self-assembly, both experimentally as well as theoretically.

Results and Discussion

Study on *meso*-pyridyl N-confused porphyrin zinc(II) complex: To examine the efficiency of the dimer formation through peripheral coordination of NCP–zinc(II) complexes, *meso*-pyridyl NCP was synthesized and the dimer formation of its Zn^{II} complex was analyzed spectroscopically. The results were then analyzed with the aid of computational study.

The synthetic route of the *meso*-pyridyl NCPs was shown in Scheme 1. First, 2-benzoyl pyrrole (**1**) was treated with picolinoyl chloride hydrogen chloride salt in the presence of $AlCl_3$ to give 2-benzoyl-4-picolynoylpyrrole (**2**) in 25% yield. Reduction of **2** with $LiAlH_4$ afforded the correspond-

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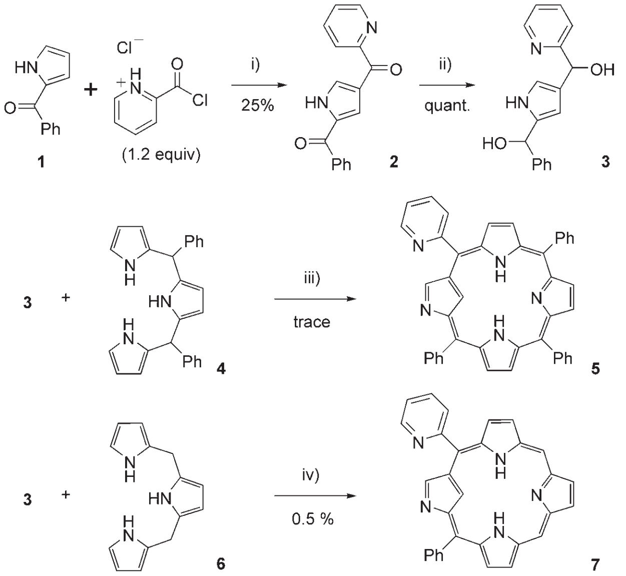
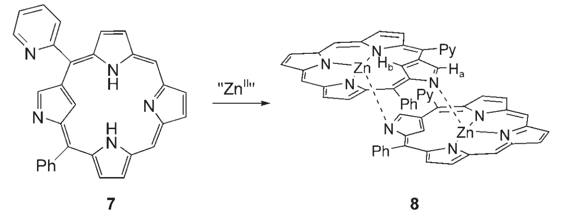
ing diol **3** in a quantitative yield. Next, the acid-catalyzed condensation reaction of **3** with diphenyltripyran (**4**) was investigated. While the formation of the desired NCP **5** was confirmed by ^{1}H NMR and UV spectroscopical analysis, isolation of sufficient amounts in a pure form was extremely difficult possibly due to side reactions. Then, acid condensation reaction of **3** with tripyran (**6**) was attempted in an effort to minimize the side reactions. As expected, 20-phenyl-5-(2′-pyridyl) N-confused porphyrin (**7**) was obtained in 0.5 % yield. The structure of **7** was elucidated by ^{1}H NMR analysis. For example, the signals due to the *meso*-hydrogen atoms were observed at δ 9.71 and 9.60 ppm. The signals due to the inner NH and inner CH were observed at δ −3.26 and −5.80 ppm, respectively, which was fully consistent with the assigned NCP structure.



Scheme 1. Syntheses of pyridyl substituted NCPs **5** and **7**. i) $AlCl_3$ (4.0 equiv), CH_2ClCH_2Cl, 84 °C, 3 d; ii) $LiAlH_4$ (5 equiv), THF, 23 °C, 1 h; iii) CH_3SO_3H (1.2 equiv), CH_2Cl_2, 23 °C, 1 h, then DDQ (3 equiv); iv) $BF_3 \cdot OEt_2$ (1.2 equiv), CH_2Cl_2, 23 °C, 90 min, then DDQ (3.0 equiv).

According to reported procedures,[9] zinc(II) was added to **7** at ambient temperature to give zinc(II) dimer (**8**, Scheme 2), which was further purified by recrystallization from CH_2Cl_2/hexane to give a single product. The ^{1}H NMR analysis on the crude product and the recrystallized product suggested that the complex coordinated through the peripheral nitrogen atoms of the confused pyrrole moieties was produced as a major product. Pyridine-coordinated oligomers were not formed at all. For example, the signal due to the α-hydrogen atoms of the confused pyrrole ring (H_a) appeared at δ 2.58 ppm. Such significant high-field shift was reasonably explained by the dimeric structure. The H_a proton was placed just above the paired porphyrin ring and, consequently, received a considerable shielding effect. The signal due to the inner CH proton (H_b) was observed at δ −4.23 ppm. The low-field shift of 1.6 ppm from the free base NCP (**7**) was in agreement with zinc(II) dimers. The signal due to the 3′-proton of the *meso*-pyridyl moiety was observed at δ 9.02 ppm, which clearly excluded the possibility of coordination by the *meso*-pyridyl moiety because a large up-field shift can be expected when it is directly involved in the dimer formation. While it was difficult to determine the stereochemistry, the ^{1}H NMR spectrum of **8** resembled that of **ZZ-Zn$_2$-Ph$_2$** (see below) and we postulated the formation of the *Z* dimer, which was supported by theoretical studies also shown below.

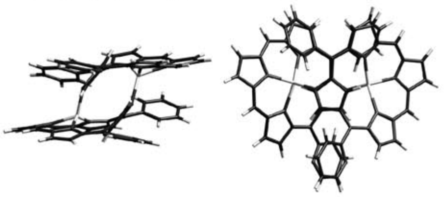


Scheme 2. Zinc(II) metallation of **7**.

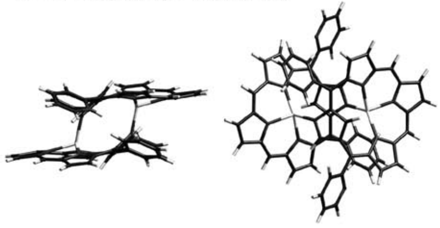
Given the asymmetric structure of **7**, the following six dimers were subjected to energy calculations (see Figure 1: the *Z* isomer (**ZZ-CP**) and *E* isomer (***EE*-CP**) of confused pyrrole coordinated dimers; the *Z* isomer (**ZZ-PY**) and the *E* isomer (***EE*-PY**) of *meso*-pyridine coordinated dimers; the *Z* isomer (**ZZ-MIX**) and the *E* isomer (***EE*-MIX**) of alternately coordinated dimers. Among the six isomers, **ZZ-CP** had the lowest energy as expected from the experimental result. The second lowest energy was obtained for ***EE*-CP**; the energy difference between **ZZ-CP** and ***EE*-CP** was 1.7 kcal mol^{-1}, which supports the preferential formation of the *Z* isomer at ambient temperature. The *meso*-pyridine coordinated dimers and the alternately coordinated dimers were far less stable than the confused pyrrole coordinated dimers, which strongly supported effectiveness of peripheral coordination on dimer formation. Surprisingly, **ZZ-MIX** was even more stable than **ZZ-PY** or ***EE*-PY**, which also implied an efficient peripheral coordination. Then, to clarify the reasons for the efficient formation of the peripheral coordinated dimers, the oligomer formation of the NCP–Group 12 metal complexes were studied theoretically.

Preferential formation of *Z* dimers in NCP–Zn^{II} complexes: Since NCP has an asymmetrical structure, formation of two diastereomers, *E* dimer and *Z* dimer, is possible during dimer formation. Experimentally, the dimers of the NCP–zinc(II) complexes were prepared at ambient temperature and the *Z* dimers were obtained exclusively.[9] Nevertheless, formation of the *E* dimers was confirmed for iron and manganese complexes.[10,11] Since the exchange reaction of the two dimers was observed at ambient temperature, the formation of the *Z* dimers should be governed not by a kinetic factor but by a thermodynamic factor. Thus, the stability of

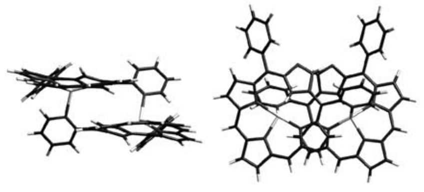
ZZ–CP (C_2 symmetry) 0.0 kcal mol^{-1}



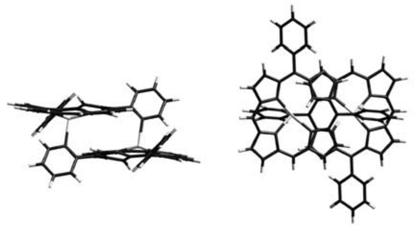
***EE*–CP** (C_i symmetry) +1.7 kcal mol^{-1}



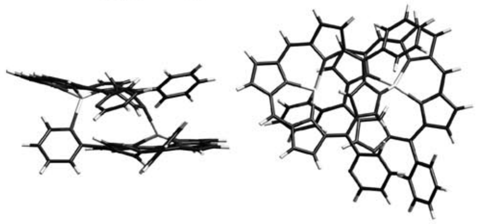
ZZ–PY (C_1 symmetry) +13.6 kcal mol^{-1}



***EE*–PY** (C_1 symmetry) +14.8 kcal mol^{-1}



ZZ–MIX (C_1 symmetry) +11.8 kcal mol^{-1}



***EE*–MIX** (C_1 symmetry) +13.8 kcal mol^{-1}

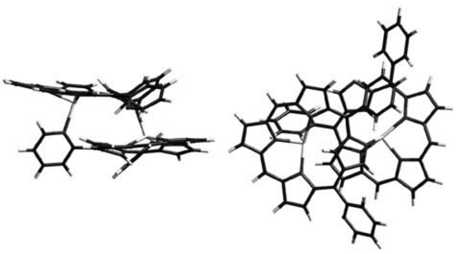
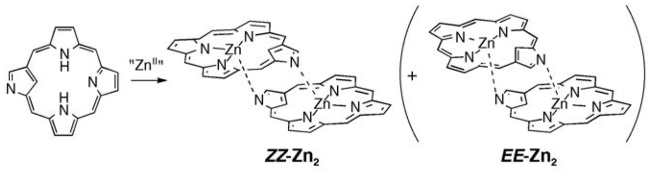


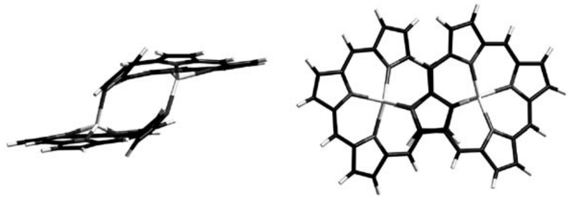
Figure 1. Structures and relative energies of the zinc(II) complex dimers of **7** calculated at B3LYP/631A//B3LYP/321A level.

the *Z* dimers and the *E* dimers of the NCP–zinc(II) complexes was investigated to determine the factors, which stabilize the *Z* dimers.

First, the zinc complexes of N-confused porphine[24] were calculated. The optimized structures and the relative energies are shown in Figure 2. The *Z* dimer (**ZZ-Zn$_2$**) was more stable in 4.0 kcal mol^{-1} than the *E* dimer (***EE*-Zn$_2$**). While no significant difference was recognized from the side views, a considerable difference in the positional relationship between the two confused pyrrole rings was observed in the top views. In **ZZ-Zn$_2$**, one confused pyrrole ring was overlapped with the paired confused pyrrole ring ("face-to-face"). On the other hand, one confused pyrrole ring was overlapped with the paired *meso*-carbon ("stacked") in ***EE*-Zn$_2$**. Since no significant steric repulsion was observed for the optimized structures of both **ZZ-Zn$_2$** and ***EE*-Zn$_2$**, π–π interaction between two parallel confused pyrrole planes would play an important role in stabilization of **ZZ-Zn$_2$**.[25] Comparison of the structural parameters supported this assumption (Table 1). The distance between the two confused pyrrole planes (denoted by CP–CP′) in **ZZ-Zn$_2$** was 3.354 Å, which was appropriate for π–π interaction of aromatic compounds.[26] No significant difference was found in the other structural parameters (Table 1). The bond length between the peripheral nitrogen atom and the paired metal center (denoted by M–N′) was slightly shorter in the **ZZ-Zn$_2$** (2.089 Å) than in the ***EE*-Zn$_2$** (2.111 Å). The distances between two porphyrin planes (denoted by Por–Por′), the angles between the two porphyrin planes (denoted by ∢Por–Por′), and the angles between the porphyrin plane and the confused pyrrole plane (denoted by ∢Por–CP)



ZZ–Zn$_2$ (C_2 symmetry) 0.0 kcal mol^{-1}



***EE*–Zn$_2$** (C_i symmetry) +4.0 kcal mol^{-1}

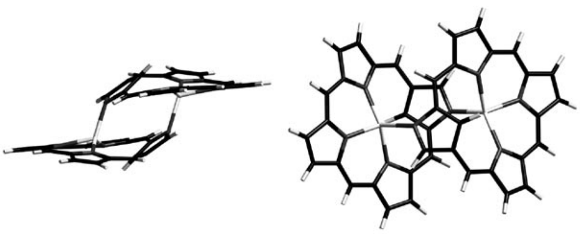


Figure 2. Structures and relative energies of **ZZ-Zn$_2$** and ***EE*-Zn$_2$** at B3LYP/631A//B3LYP/321A level.

Table 1. Structural parameters for the optimized structures of the NCP–zinc(II) dimers at B3LYP/321A level.

	CP–CP′ [Å]	M–N′ [Å]	Por–Por′ [Å]	∢Por–Por′ [°]	∢Por–CP [°]
ZZ-Zn$_2$	3.354	2.089	3.738	10.2	39.3
***EE*-Zn$_2$**	–	2.111	3.672	0.3	36.3
ZZ-Zn$_2$-Ph$_2$	3.332	2.074	4.397	4.3	46.2
ZZ-Zn$_2$-Ph$_2$[a]	3.240	2.060	4.294	10.2	43.9
***EE*-Zn$_2$-Ph$_2$**	–	2.106	4.570	4.7	45.8
ZZ-Zn$_2$-Ph$_4$	3.340	2.077	4.418	2.4	46.0
***EE*-Zn$_2$-Ph$_4$**	–	2.110	4.587	0.3	46.2
ZZ-Cd$_2$-Ph$_2$	3.439	2.285	4.504	1.9	40.5
***EE*-Cd$_2$-Ph$_2$**	–	2.304	4.624	0.2	42.1
ZZ-Hg$_2$-Ph$_2$	3.474	2.334	4.516	0.8	37.5
***EE*-Hg$_2$-Ph$_2$**	–	2.351	4.649	0.1	39.8

[a] X-ray structure (ref. [9]).

showed similar values and hence the differences of these parameters would not affect the relative energy.

Next, we performed calculations on the zinc(II) complexes of 5,20-diphenyl N-confused porphyrin (Figure 2). Similarly to the porphine case, the *Z* dimer (**ZZ-Zn$_2$-Ph$_2$**) was more stable by 4.9 kcal mol^{-1} than the *E* dimer (***EE*-Zn$_2$-Ph$_2$**) (see Figure 3. The energy difference was large enough for the exclusive formation of **ZZ-Zn$_2$-Ph$_2$** at ambient temperatures, which was confirmed experimentally by X-ray diffraction and ^{1}H NMR analysis.[9b] The Por–Por′ distances in **ZZ-Zn$_2$-Ph$_2$** (4.397 Å) and ***EE*-Zn$_2$-Ph$_2$** (4.294 Å) were significantly longer than those in **ZZ-Zn$_2$** and ***EE*-Zn$_2$** possibly due to the steric repulsion between the *meso*-phenyl group and the paired porphyrin skeleton. To compensate for the steric repulsion, the confused pyrrole rings inclined at larger degrees (*Z*: 46.2°, *E*: 45.8°) and, as a result, the Zn–N′ bond lengths remained unchanged. Consequently, the CP–CP′ distance was still sufficiently short in **ZZ-Zn$_2$-Ph$_2$** (3.332 Å) for π–π interactions, which would stabilize the *Z* conformation. The results indicated that N-confuse porphyrins could form oligomeric structures flexibly through alignment of ∢Por–CP angles. Note that the structural parameters for the optimized structure of **ZZ-Zn$_2$-Ph$_2$** showed good agreement with those of its X-ray structure.

Finally, the zinc(II) complexes of 5,10,15,20-tetraphenyl N-confused porphyrins were studied (Figure 4), where the preferential formation of the *Z* dimer was illustrated experimentally. In the theoretical studies, the *Z* dimer (**ZZ-Zn$_2$-Ph$_4$**) was more stable in 2.7 kcal mol^{-1} than the *E* dimer (***EE*-Zn$_2$-Ph$_4$**) as was expected. In spite of the presence of additional phenyl groups, the structural parameters for **ZZ-Zn$_2$-Ph$_4$** or ***EE*-Zn$_2$-Ph$_4$** were almost same as those for **ZZ-Zn$_2$-Ph$_2$** or ***EE*-Zn$_2$-Ph$_2$**. Nevertheless, steric repulsion imposed by the 15-phenyl group and the 20′-phenyl group in **ZZ-Zn$_2$-Ph$_4$** would cause slight destabilization, which would lead to a decrease in the difference of the relative energy. No significant steric repulsion imposed by the phenyl groups was observed in ***EE*-Zn$_2$-Ph$_4$**.

The results obtained here lead us to the conclusion that the important factor to stabilize *Z* dimers in NCP–Zn^{II} complexes should be interaction between the two confused pyrrole rings by the aid of flexible rotation of the confused pyrrole rings. Steric effect would be secondary cause. Thus, 5,20-diphenyl NCP seemed appropriate for a selective preparation of *Z* dimers.

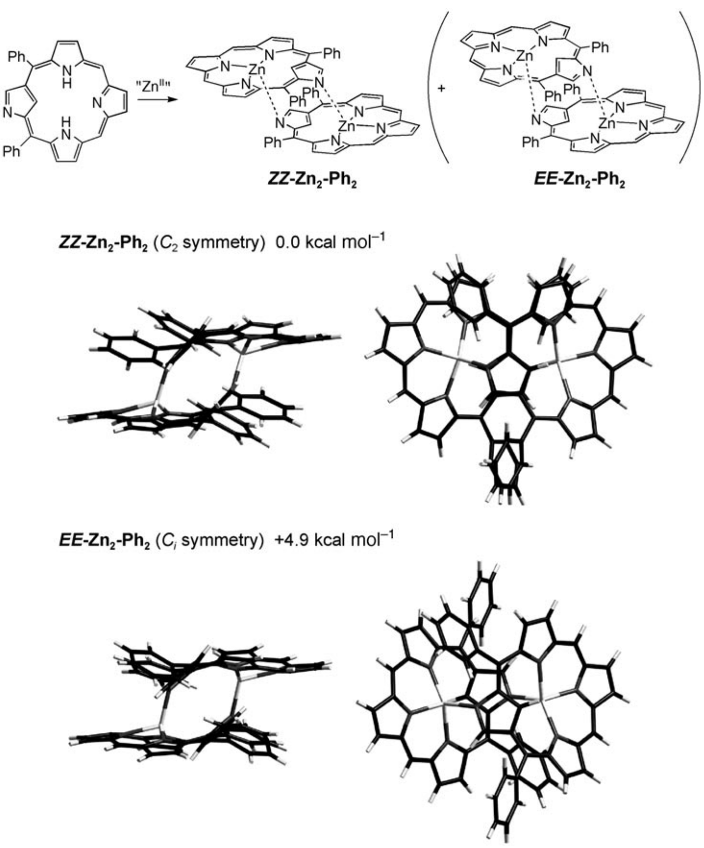


Figure 3. Structures and relative energies of **ZZ-Zn$_2$-Ph$_2$** and ***EE*-Zn$_2$-Ph$_2$** at B3LYP/631A//B3LYP/321A level.

Comparison of NCP with *meso*-pyridyl porphyrin: To verify efficient formation of homodimers in the NCP–Zn^{II} complexes, it was compared with a 5-(2′-pyridyl)-porphyrin–Zn^{II} complex. Ligand exchange reactions with pyridine were utilized as a probe (Scheme 3). In the case of the NCP–Zn^{II} complex, the pyridine-coordinated monomer (**Zn-Py**) was less stable than the corresponding *Z* dimer (**ZZ-Zn$_2$**) by 2.1 kcal mol^{-1}. Meanwhile, the pyridine-coordinated monomer of the normal porphyrin (**Zn-Por-Py**) was more stable than the corresponding dimer (**Zn$_2$-Por$_2$**) by 3.4 kcal mol^{-1}. These results clearly show enhanced dimer formation of NCP compared with *meso*-pyridyl porphyrin. Interestingly, even in the case of the NCP–Zn^{II} complex, the *E* dimer (***EE*-Zn$_2$**) was less stable than the monomer (**Zn-Py**) by 1.9 kcal mol^{-1}. Therefore, π–π interactions between two confused pyrrole rings would be important not only for exclusive formation of the *Z* dimers compared with the *E* dimers but also efficient formation of the dimers compared with monomers.

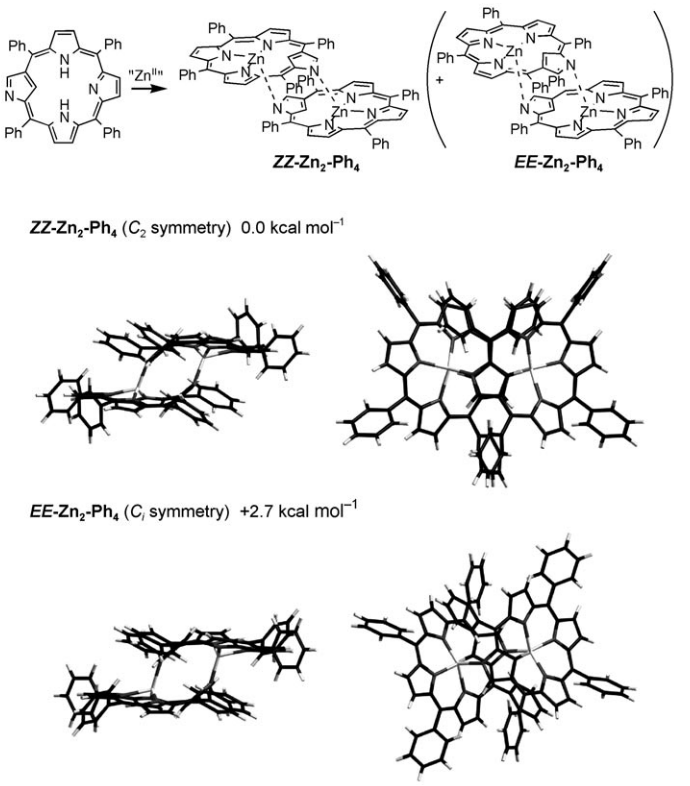


Figure 4. Structures and relative energies of ***ZZ*-Zn$_2$-Ph$_4$** and ***EE*-Zn$_2$-Ph$_4$** at B3LYP/631A//B3LYP/321A level.

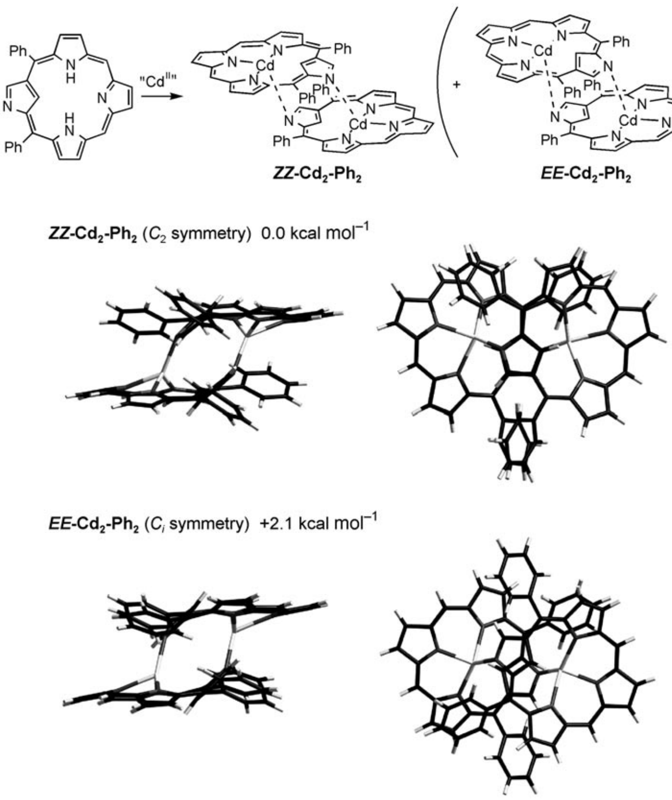
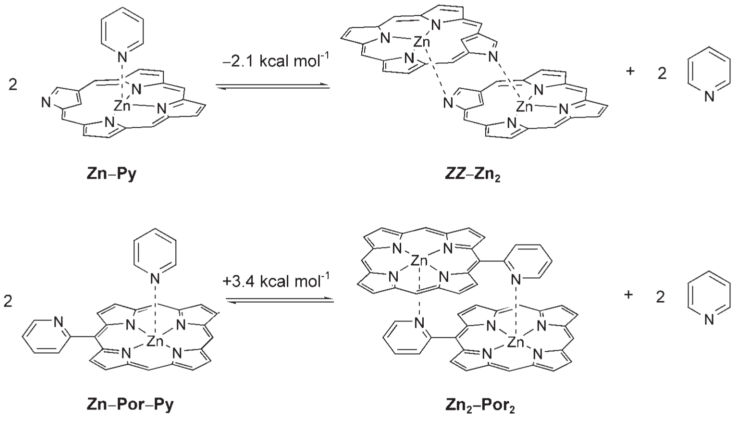


Figure 5. Structures and relative energies of **ZZ-Cd$_2$-Ph$_2$** and ***EE*-Cd$_2$-Ph$_2$** at B3LYP/631L//B3LYP/321L level.



Scheme 3. Formation of the homodimers through ligand exchange.

Dimer formation of cadmium(II) and mercury(II) complexes: The Cd^{II} and Hg^{II} complexes of 5,20-diphenyl NCP were subjected to theoretical calculations similar to the Zn^{II} complexes, for which comparable results were obtained. The optimized structures for the *Z* dimer (**ZZ-Cd$_2$-Ph$_2$**) and *E* dimer (***EE*-Cd$_2$-Ph$_2$**) of NCP–Cd^{II} complexes are shown in Figure 5. The M–N′ lengths of the NCP–Cd^{II} complexes (*Z*: 2.285 Å, *E*: 2.304 Å) were significantly longer than those of the Zn^{II} complexes (av. 2.095 Å) and subsequently the ∢Por–CP angles became smaller (*Z*: 40.5°, *E*: 42.1°) and the CP–CP′ distance became longer (3.439 Å). Thus, π–π interaction between the two confused pyrrole rings should be weaker than that of the Zn^{II} complex, which could explain small energy difference between **ZZ-Cd$_2$-Ph$_2$** and ***EE*-Cd$_2$-Ph$_2$**. Then, the *Z* dimer (**ZZ-Hg$_2$-Ph$_2$**) and *E* dimer (***EE*-Hg$_2$-Ph$_2$**) of NCP–Hg^{II} complexes were calculated (Figure 6). The M–N′ lengths (*Z*: 2.334 Å, *E*: 2.351 Å) become even longer than those of the Cd^{II} complex dimers (av. 2.295 Å). Accordingly, the ∢Por–CP angles was much smaller (*Z*: 37.5°, *E*: 39.8°) and the CP–CP′ distance was much longer (3.474 Å). The smallest energy difference among the homodimers calculated here would be result from such structural features.

Heterodimers of NCP–metal complexes: The heterodimers were also observed experimentally through exchange reactions between two homodimers; the heterodimers would be slightly more stable than the corresponding homodimers. Enthalpy changes in the exchange reactions between two homodimers were examined (Scheme 4) and the structural parameters are listed in Table 2. While the heterodimers were less stable than the homodimers, the energy differences were rather small or even negligible. Such a small energy loss in spite of mismatching could be explained by flexible rotation of the confused pyrrole rings. The mismatching M–N′ bond lengths in the heterodimers should be countered by adjustment of the ∢Por–CP angles.

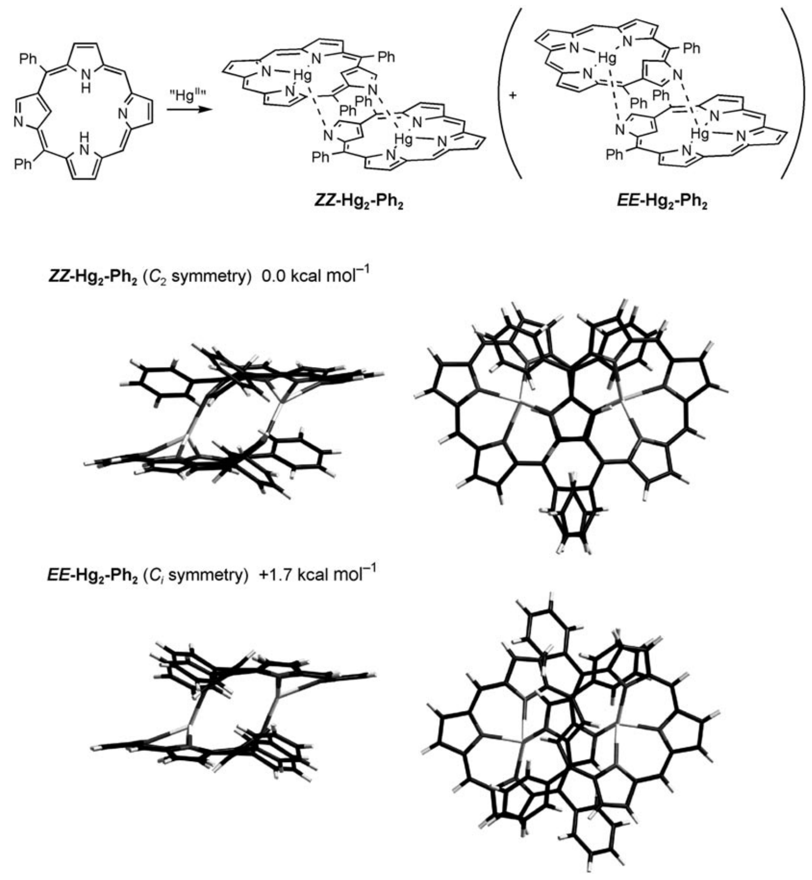


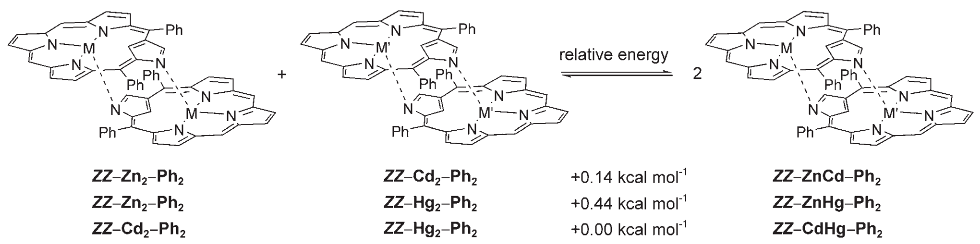
Figure 6. Structures and relative energies of ***ZZ*-Hg$_2$-Ph$_2$** and ***EE*-Hg$_2$-Ph$_2$** at B3LYP/631L//B3LYP/321L level.

Oligomers of NCP–Zn^{II} complex: A possible oligomer formation by the NCP–zinc(II) complexes was also examined. In the case of normal porphyrins, oligomer formation was often observed by use of *meso*-substituents.[2] Meanwhile, we have postulated that NCP–zinc(II) complexes could form oligomeric assemblies simply by rotation of the confused pyrrole rings without sophisticated chemical functionalization. Therefore the relative energies per one NCP–zinc(II) complex were calculated for the trimers (Figure 7), the tetramers (Figure 8) and the pentamers (Figure 9). According to their structures, two isomers were calculated for trimers, four isomeric tetramers and four isomeric pentamers.

The relative energies per one NCP molecule for the oligomers of NCP–zinc(II) complex are summarized in Table 3. The dimers were significantly less stable than the larger oligomers, indicating that NCP–zinc(II) complexes would form higher oligomers intrinsically. In the case of 5,20-Ph$_2$-NCP or 5,10,15,20-Ph$_4$-NCP, steric repulsion imposed by the 20-Ph groups severely disturbs the formation of higher oligomers and thus they reluctantly form the dimers. Among the higher oligomers discussed here, the trimers (***ZZZ*-Zn$_3$** and ***ZEE*-Zn$_3$**) gave the lowest energies, although no π–π interaction between two confused pyrrole was expected in higher oligomers in the same manner as the dimers. This contradiction might be explained by the ∢Por–CP angles. In the monomer (**Zn-PY**), the ∢Por–CP angle was 25.4°, wherein the conformational strain should be negligible. The ∢Por–CP angles of the trimers were quite similar to that of **Zn-PY** and hence the NCP moieties took relaxed conformation. This was also true for the tetramers and the pentamers. On the other hand, in the dimers, the ∢Por–CP angles were significantly larger and hence they were destabilized by skeletal strain.

Table 2. Structural parameters for the optimized structures of the heterodimers at B3LYP/321AL level.

	CP–CP′ [Å]	M–N′ [Å]	Por–Por′ [Å]	∢Por–Por′ [°]	∢Por–CP [°]
ZZ-ZnCd-Ph$_2$	3.338	Zn 2.077 Cd 2.283	4.032	8.7	Zn 44.1 Cd 42.5
ZZ-ZnHg-Ph$_2$	3.513	Zn 2.074 Hg 2.334	3.843	11.8	Zn 43.4 Hg 39.9
ZZ-CdHg-Ph$_2$	3.483	Cd 2.283 Hg 2.336	4.305	3.9	Cd 39.9 Hg 37.9



Scheme 4. Exchange reactions between the two homodimers. The heterodimers were calculated at B3LYP631AL//B3LYP321AL level.

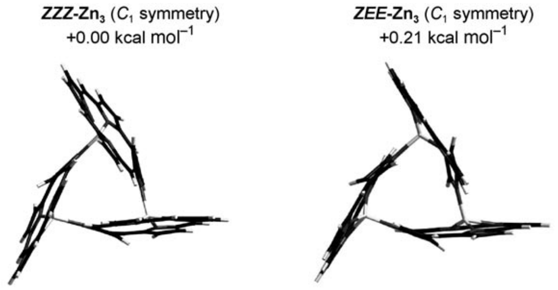


Figure 7. Structures and relative energies of the trimers of the NCP–zinc(II) complexes at B3LYP/631A//B3LYP/321A level.

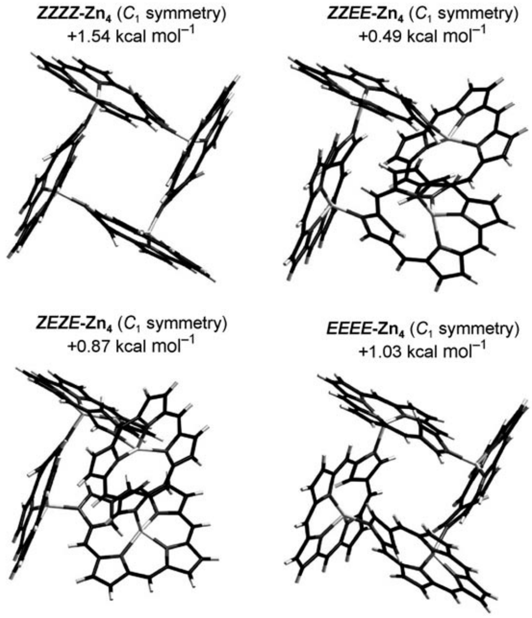


Figure 8. Structures and relative energies of the tetramers of the NCP–zinc(II) complexes at B3LYP/631A//B3LYP/321A level.

Conclusion

The NCP–zinc(II) complexes could form the stable dimers owing to flexible rotation of the confused pyrrole rings. The *Z* dimers were significantly more stable than the *E* dimers likely due to π–π interaction between the two confused pyrrole rings. Besides, the possibility of the formation of the higher oligomers was suggested through theoretical studies. Since the relative energy differences between one oligomer and the others were sufficiently small, construction of cyclic porphyrin array system that can be switched from one ordered assembly to another would be possible by using NCP–metal complexes.[27] Based on the information obtained here, preparation of unique metal complex oligomers bearing NCP ligands is now undergoing.

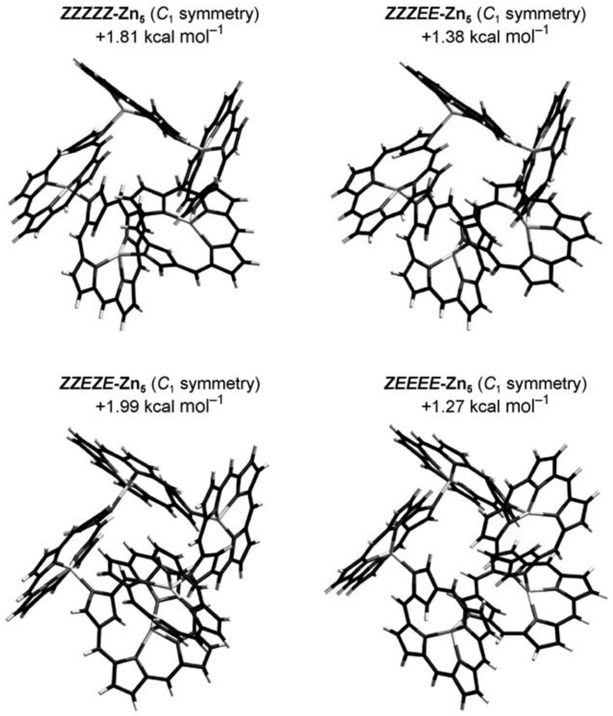


Figure 9. Structures and relative energies of the pentamers of the NCP–zinc(II) complexes at B3LYP/631A//B3LYP/321A level.

Table 3. Relative energy per unit and structural parameters for the optimized structures of NCP–zinc(II) oligomers at B3LYP/321A level.

	Relative energy [kcal mol^{-1}]	M−N′ [av, Å]	∢Por–CP [av, °]
Zn-PY	–	2.121	25.4
***ZZ*-Zn$_2$**	+7.25	2.089	39.3
***EE*-Zn$_2$**	+9.25	2.111	36.3
***ZZZ*-Zn$_3$**	0.00	2.056	23.6
***ZEE*-Zn$_3$**	+0.21	2.057	25.2
***ZZZZ*-Zn$_4$**	+1.54	2.061	18.3
***ZZEE*-Zn$_4$**	+0.49	2.060	22.7
***ZEZE*-Zn$_4$**	+0.87	2.063	21.6
***EEEE*-Zn$_4$**	+1.03	2.059	19.7
***ZZZZZ*-Zn$_5$**	+1.81	2.070	20.1
***ZZZEE*-Zn$_5$**	+1.38	2.066	20.7
***ZZEZE*-Zn$_5$**	+1.99	2.070	19.7
***ZEEEE*-Zn$_5$**	+1.27	2.063	20.3

Experimental Section

General: Commercially available solvents and reagents were used without further purification unless otherwise mentioned. 2-Benzoylpyrrole,[19] 5,10-diphenyltripyrran and tripyrran[20] were prepared as reported. THF was distilled over sodium/benzophenone. CH_2Cl_2 was distilled over CaH_2. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 (Merck 5554). Preparative purifications were performed by flash column chromatography (Kanto Silica Gel 60 N, spherical, neutral, 40–50 μm), and gravity column chromatography (Kanto Silica Gel 60 N, spherical, neutral, 63–210 μm). The ^{1}H NMR was recorded on a JNM-AI Series FT-NMR spectrometer (JEOL) at 300 MHz. Proton chemical shifts were reported relative to residual proton of deuterated solvent (δ 7.26 ppm for $CHCl_3$). UV/Vis absorption spectra were recorded on UV-3150PC spectrometer (Shimadzu).

2-Benzoyl-4-*o*-picolinoylpyrrole (2): A solution of *o*-picolinoyl chloride hydrocholoride (1.8 g, 10 mmol, 1.2 equiv) in $ClCH_2CH_2Cl$ (75 mL) was added dropwise over 15 min at ambient temperature under Ar to a stirred suspension of anhydrous $AlCl_3$ (4.6 g, 35 mmol, 4 equiv) in $ClCH_2CH_2Cl$ (20 mL) and the mixture was stirred at room temperature for 10 min. Then a solution of 2-benzoylpyrrole (**1**, 1.5 g, 8.6 mmol, 1.0 equiv) in $ClCH_2CH_2Cl$ was added dropwise at ambient temperature over 15 min, and the resulting slurry was heated under reflux for 3 d. The reaction mixture was quenched with ice and water. The organic phase was separated and aqueous phase was extracted with CH_2Cl_2 (2×). The combined organic layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to dryness. The residue was separated by silica gel chromatography with 1% MeOH/CH_2Cl_2 to give **2** (0.59 g, 2.1 mmol, 25%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 10.14 (brs, 1H), 8.72 (dd, J=0.9, 4.5 Hz, 1H), 8.55–8.53 (m, 1H), 8.15 (d, J= 8.1 Hz, 1H), 7.99–7.95 (m, 2H), 7.88 (dt, J=1.2, 2.4 Hz, 1H), 7.72–7.69 (m, 1H), 7.64–7.45 ppm (m, 4H).

2-(Hydroxyphenylmethyl)-4-(hydroxy-(2′-pyridyl)methyl)pyrrole (3): A solution of **2** (0.10 g, 0.18 mmol, 1.0 equiv) in THF (1 mL) was added dropwise over 10 min at ambient temperature under Ar to a stirred suspension of $LiAlH_4$ (35 mg, 0.90 mmol, 5.0 equiv) in THF (4 mL) and the mixture was stirred for 1 h. After quenching with ice and water, the organic phase was separated and the remaining aqueous phase was extracted with CH_2Cl_2 (2×). The combined organic layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to dryness to give **3**, which was used in the next step without further purification.

5-(2′-Pyridyl)-10,15,20-triphenyl N-confused porphyrin (5): CH_3SO_3H (28 µL, 0.22 mmol, 1.2 equiv) was added at ambient temperature under Ar to a stirred mixture of **3** (≈0.18 mmol, 1.0 equiv) and 5,10-diphenyltripyrrane (**4**, 0.68 g, 0.18 mmol, 1.0 equiv) in dry CH_2Cl_2 (35 mL). After stirring for 1 h, the reaction mixture was treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.12 g, 0.50 mmol, 2.8 equiv) and subsequently with Et_3N. The resulting slurry was evaporated to dryness and the residue was subjected to silica gel column chromatography with 1% MeOH/CH_2Cl_2 to give **3** (>0.2 mg, >0.32 µmol, >0.2%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 9.23 (d, J=4.9 Hz, 1H), 9.18 (d, J=4.9 Hz, 1H), 8.91 (d, J=4.9 Hz, 1H), 8.84 (s, 1H), 8.66 (d, J=4.9 Hz, 1H), 8.60–8.52 (m, 3H), 8.45 (d, J=7.3 Hz, 1H), 8.38 (d, J=7.3 Hz, 2H), 8.24–8.13 (m, 4H), 7.87–7.66 (m, 11H), −2.41 (brs, 2H), −4.99 ppm (s, 1H); UV (CH_2Cl_2): λ_{max} = 440, 539, 582, 725 nm.

20-Phenyl-5-(2′-pyridyl) N-confused porphyrin (7): $BF_3{\cdot}OEt_2$ (275 µL, 2.2 mmol, 1.2 equiv) was added at ambient temperature under Ar to a stirred solution of **3** (≈1.8 mmol, 1.0 equiv) and tripyrrane (**6**, 0.41 g, 1.8 mmol, 1.0 equiv) in dry CH_2Cl_2 (350 mL). After stirring for 90 min, the reaction mixture was treated with DDQ (0.82 g, 3.6 mmol, 2.0 equiv) and subsequently with Et_3N. The resulting slurry was filtered with a pad of Celite and the filtrate was concentrated to dryness under reduced pressure. The residue was purified by an alumina column with 2% MeOH/CH_2Cl_2 and then by a silica gel column with 1% MeOH/CH_2Cl_2 to give **7** (3.7 mg, 8.0 µmol, 0.5%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 9.71 (brs, 1H), 9.60 (brs, 1H), 9.31–9.01 (m, 7H), 8.76 (s, 1H), 8.40 (d, J=7.8 Hz, 1H), 8.30 (d, J=7.5 Hz, 2H), 8.24 (dt, J=1.8, 7.8 Hz, 1H), 7.76–7.60 (m, 4H), −3.26 (brs, 2H), −5.80 ppm (s, 1H); MS (MALDI, positive): m/z: 464.2 $[M+H]^+$; UV (CH_2Cl_2): λ_{max} = 431, 528, 568, 704 nm.

Zn^{II} complex of 20-phenyl-5-(2′-pyridyl) N-confused porphyrin (8): A solution of **7** (3.7 mg, 8.0 µmol) in CH_2Cl_2 was treated with $Zn(OAc)_2{\cdot}2H_2O$ at ambient temperature. After stirring for 2.5 h, the reaction mixture was treated with 1% Et_4NOH aqueous solution and then washed with water (2×). The organic phase was concentrated under reduced pressure to give **8**, which was further purified by recrystallization from CH_2Cl_2/hexane. ^{1}H NMR (CD_2Cl_2): δ = 9.01 (dd, J=0.9, 4.5 Hz, 1H), 8.88 (d, J=4.8 Hz, 1H), 8.79 (s, 1H), 8.67 (d, J=4.2 Hz, 1H), 8.52 (d, J=4.5 Hz, 1H), 8.47 (d, J=4.8 Hz, 1H), 8.38 (s, 1H), 8.32 (d, J= 4.2 Hz, 1H), 8.10 (d, J=4.5 Hz, 1H), 8.04 (dt, J=1.8, 7.8 Hz, 1H), 7.57 (ddd, J=1.2, 4.8, 7.5 Hz, 1H), 7.53–7.47 (m, 2H), 7.26 (brs, 2H), 6.58 (brs, 2H), 2.58 (d, J=1.2 Hz, 1H), −4.23 ppm (d, J=0.9 Hz, 1H); MS (MALDI, positive): m/z: 526.2 $[M+H]^+$; UV (CH_2Cl_2): λ_{max} = 452, 739 nm.

Computational methods: All the calculations were performed with B3LYP methods using a Gaussian03 program package.[21] The initial structures for the dimers were constructed on the basis of the reported X-ray structures.[9] The initial structures for the trimers, tetramers and pentamers were arbitrarily constructed. For structural optimization, all electron SVP basis set by Horn and Ahlrichs[22] was used for Zn and 3-21G* for C, H, and N (denoted as 321 A). All the stationary points except for those of the pentamers were verified by calculating the vibrational frequencies that resulted in absence of imaginary eigenvalues. The calculations of vibrational frequencies for the pentamers could not be achieved due to limitation of the computer. For the single point energy calculations, SVP was used for Zn and 6-31G** for C, H, and N (denoted as 631 A). For the unsubstituted and diphenyl NCP–zinc(II) dimers, structural optimization was also performed at B3LYP/631A level and no significant change was observed either for structures and relative energies. For Cd and Hg, LANL2DZ basis set[23] was used in place of SVP basis set and denoted as 321L, 321AL, 631L or 631AL in a similar manner as above.

Definition of structural parameters and stereochemistry: Porphyrin plane (plane A) was defined with nineteen heavy atoms composing the porphyrin substructure (The five heavy atoms composing the confused pyrrole ring was excluded). Confused pyrrole plane (plane B) was defined with the five heavy atoms. Rotation angle of the confused pyrrole ring (angle X) was calculated from plane A and plane B. When the peripheral nitrogen atom and a metal center were placed on the same side of porphyrin plane, positive values were used for angle X. Negative values were used in inverse situation.

When the nitrogen atom of the confused pyrrole moiety of an NCP lies on the same side with that of an adjacent NCP, relationship between these two NCPs is called "*E*". In the case of the opposite side, it is called "*Z*". The *Z* dimers were optimized under C_2 symmetry and the *E* dimers were optimized under C_i symmetry. The other oligomers and the heterodimers were optimized under C_1 symmetry.

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