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Programmed asymmetrical trimer formation of β-alkyl N-confused porphyrin zinc(II) complex

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Self-coordination of β-alkyl N-confused porphyrin (NCP) zinc(II) complexes has been studied to reveal that asymmetrical trimers formed exclusively. A key factor to control the configuration of the trimers (symmetric or asymmetric) has been studied theoretically, and revealed that the steric environment around the peripheral nitrogen atoms as well as rotational angles of the confused pyrrole rings play a crucial role in trimer formation of β-alkyl NCP zinc(II) complexes.

Keywords: N-confused porphyrin; zinc complex; trimer; DFT calculation

Introduction

Control of molecular assemblies is one of the most important areas of research for the development of supramolecular architectures. Especially, study on porphyrin assemblies is of great importance to obtain deep insight into photosynthetic systems (*1–4*). Among several strategies for the preparation of porphyrin arrays, self-assembling approach through metal coordination has proven to be particularly attractive, because the supramolecular structures can be controlled effectively by donor ligand moieties such as pyridyl (*5–10*), pyrazolyl (*11*, *12*), imidazolyl (*13–15*) or hydroxyl (*16–20*) groups.

N-confused porphyrin (NCP) is an isomer of porphyrin, which has a coordinative nitrogen atom at the periphery of the macrocycle (Figure 1) (*21*, *22*). Consequently, unlike regular porphyrins, NCP metal complexes can form self-assembled oligomers without additional donor ligand moieties. In most cases, 5,10,15,20-tetraaryl NCP metal complexes are investigated and formation of self-dimers is reported in Zn (*23–26*), Cd (*25*), Hg (*25*), Fe (*27*) and Mn (*28*, *29*) complexes (Figure 2). Furthermore, the unique dimeric structures with extra ligands and/or metal centres are observed in Zn (*23*), Ag (*30*), Pd (*31*), Pt (*32*, *33*), Rh (*34*) and Fe (*27*, *35*) complexes. Meanwhile, the study on β-alkyl substituted NCP metal complexes is quite limited possibly due to relatively uneasy access to the free-base ligands. Although the formation of anion-recognising dimers is studied in detail (*36*), self-assembly of β-alkyl NCP through metal coordination has not been reported yet.

In the case of 5,10,15,20-tetraaryl or 5,20-diaryl NCP metal complexes, the self-coordinated dimers are formed preferentially to the other oligomeric structures and the configurations depend on the metal centres (*23–29*). The Zn, Cd and Hg complexes give *Z*-dimers, while the Mn and Fe complexes are reported to afford *E*-dimers (Figure 2). Contrastingly, the Zn(II) complex of unsubstituted NCP forms a mixture of *S*- and *A*-trimers (Figure 3) (*37*, *38*). Formation of dimers is not recognised in this case. Furthermore, selective formation of *S*-trimer is accomplished with 5-phenyl NCP, which would be triggered by the interaction among the three phenyl groups. Favourable arrangement of three phenyl groups in the *S*-trimer is unambiguously confirmed by X-ray crystallographic analysis (*38*).

Herein, we have synthesised the β-alkyl NCP zinc(II) complexes and their oligomer formation have been studied to reveal that the configuration of the self-coordinated trimers can be controlled by the steric environment around the peripheral coordinative nitrogen atoms. When 3-alkyl NCP is utilised, exclusive formation of an *A*-trimer is observed. Besides, NCP zinc(II) complex trimers are theoretically studied to obtain an insight into difference between *A*- and *S*-trimers, from which importance of pyrrole ring rotation is suggested.

Experimental

Materials and methods

Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Precursors of NCP (tripyrrane diester and 2,4-diformylpyrrole derivatives) were prepared according to the reported procedures (*39*, *40*). THF was distilled over benzophenone ketyl. CH_2Cl_2 was distilled over CaH_2. Thin-layer chromatography (TLC) was carried out on aluminium sheets coated with silica gel 60 (Merck 5554). Preparative purifications were performed by flash column chromatography (KANTO Silica Gel 60 N,

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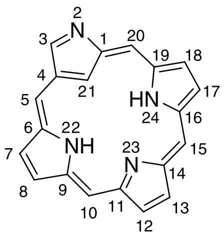


Figure 1. Structure and numbering system of NCP.

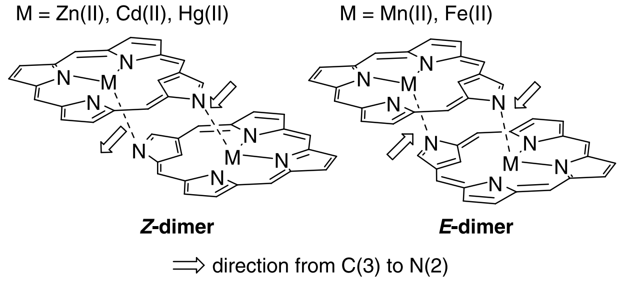


Figure 2. Structures of NCP metal complex dimers.

spherical, neutral, 40–50 μm) or 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 $CHCl_3$).

Typical procedures of [3 + 1] condensation reactions

To a solution of tripyrrane diester in THF, 10% Pd/C was added under N_2. After adding a drop of Et_3N, N_2 gas was replaced by H_2 gas and stirred at ambient temperature for 4 h. The resulting slurry was filtered through a pad of celite and the filtrate was concentrated under reduced pressure. The residue was dissolved in 5% NH_4OH aqueous solution and neutralised with acetic acid at 0°C. The resulting mixture was left for 1 h at 0°C and the precipitates were collected by suction and thoroughly washed with water to give tripyrrane dicarboxylic acid in a quantitative yield. The tripyrrane was treated with CF_3COOH (1 ml) for 2 min at ambient temperature under N_2 and diluted with CH_2Cl_2 (100 ml). Then 2,4-diformylpyrrole was added and the resulting solution was stirred for 16 h at ambient temperature followed by treatment with 0.1% $FeCl_3$ aqueous solution. The organic layer was separated, washed with aqueous $NaHCO_3$ solution and water, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography ($MeOH/CH_2Cl_2 = 7/93$ (v/v)) to give an NCP derivative. The product was further purified by recrystallisation from CH_2Cl_2/MeOH or CH_2Cl_2/hexane.

8,17-Diethyl-7,18-dimethyl-2-aza-21-carbaporphyrin (1)

15% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ −6.53 (s, 1H), −4.08 (br s, 1H), −4.00 (br s, 1H), 1.81 (t, $J = 7.3$ Hz, 3H), 1.83 (t, $J = 7.3$ Hz, 1H), 3.52 (s, 3H), 3.58 (s, 3H), 3.95 (q, $J = 7.3$ Hz, 2H), 4.00 (q, $J = 7.3$ Hz, 2H), 9.11 (d, $J = 4.3$ Hz, 1H), 9.14 (d, $J = 4.3$ Hz, 1H), 9.63 (s, 1H), 9.71 (s, 1H), 9.83 (s, 1H), 10.21 (s, 1H); MALDI-TOF-MS: $m/z = 395.1$ ($[M + H]^+$); UV/vis (CH_2Cl_2, λ_{max}/nm): 682, 550, 513, 417.

8,17-Diethyl-3,7,18-trimethyl-12,13-diphenyl-2-aza-21-carbaporphyrin (2)

50% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ −6.27 (s, 1H), −3.80 (br s, 1H), −3.68 (br s, 1H), 1.73 (t, $J = 7.6$ Hz, 6H), 3.537 (s, 3H), 3.543 (s, 3H), 3.63 (s, 3H), 3.84 (q, $J = 7.6$ Hz, 2H), 3.87 (q, $J = 7.6$ Hz, 2H), 7.59 (t, $J = 7.3$ Hz, 2H), 7.67 (t, $J = 7.3$ Hz, 4H), 7.92 (d, $J = 7.3$ Hz, 4H); MALDI-TOF-MS: $m/z = 561.0$ ($[M + H]^+$); UV/vis (CH_2Cl_2, λ_{max}/nm): 681, 553, 515, 420.

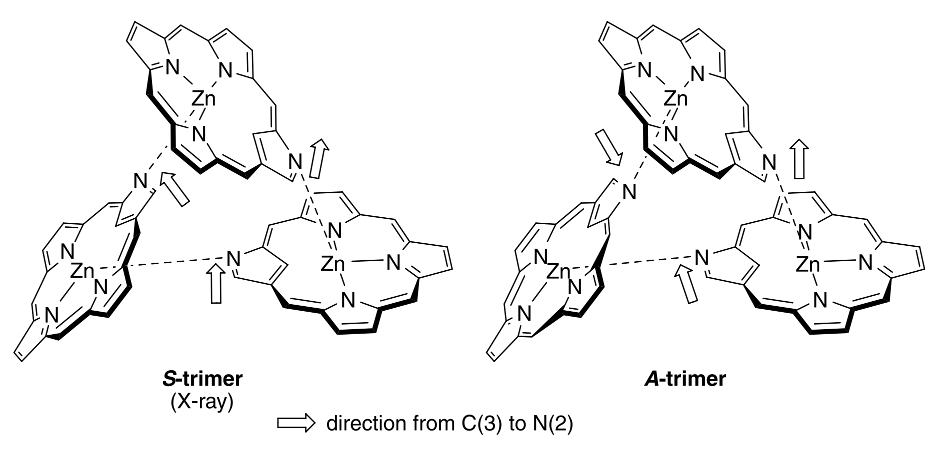


Figure 3. Structures of NCP zinc(II) complex trimers.

3,8,12,13,17-Pentaethyl-7,18-dimethyl-2-aza-21-carbaporphyrin (3)

20% yield. ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): δ − 6.14 (s, 1H), − 3.59 (br s, 2H), 1.77–1.86 (m, 12H), 1.93 (t, $J = 7.3$ Hz, 3H), 3.53 (s, 6H), 3.83–4.10 (m, 10H), 9.59 (s, 1H), 9.66 (s, 1H), 9.75 (s, 1H), 10.09 (s, 1H); UV/vis (CH$_2$Cl$_2$, λ_{max}/nm): 678, 553, 512, 421.

Asymmetric zinc(II) complex trimer of 2 (A-[(2-Zn)$_3$])

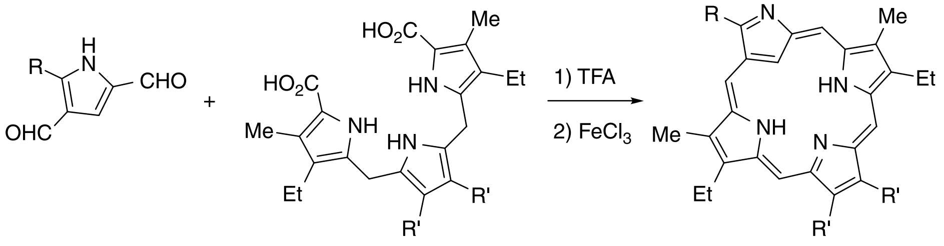
^{1}H NMR (CDCl$_3$, 300 MHz, ppm): δ − 5.85 (s, 1H), − 5.68 (s, 1H), − 5.40 (s, 1H), − 1.70 (s, 3H), − 0.25 (s, 3H), − 0.22 (s, 3H), 1.50–1.65 (m, 18H), 3.036 (s, 3H), 3.048 (s, 3H), 3.054 (s, 3H), 3.15 (s, 3H), 3.29 (s, 3H), 3.37 (s, 3H), 3.58–3.66 (m, 12H), 3.66 (s, 1H), 3.91 (s, 1H), 4.86 (s, 1H), 7.41–7.79 (m, 18H), 7.94–8.04 (m, 12H), 8.60 (s, 1H), 8.78 (s, 1H), 9.16 (s, 1H), 9.21 (s, 1H), 9.31 (s, 1H), 9.32 (s, 1H), 9.37 (s, 1H), 9.46 (s, 1H), 9.76 (s, 1H); UV/vis (CH$_2$Cl$_2$, λ_{max}/nm): 698, 631, 445, 357.

Calculation details

All the calculations were performed with B3LYP methods using a Gaussian03 program package (*41*). For structural optimisation, all electron SVP basis set by Horn and Ahlrichs (*42*) was used for Zn and 6-31G** for C, H and N (denoted as 631A). All the stationary points were verified by calculating the vibrational frequencies that resulted in the absence of imaginary eigenvalues.

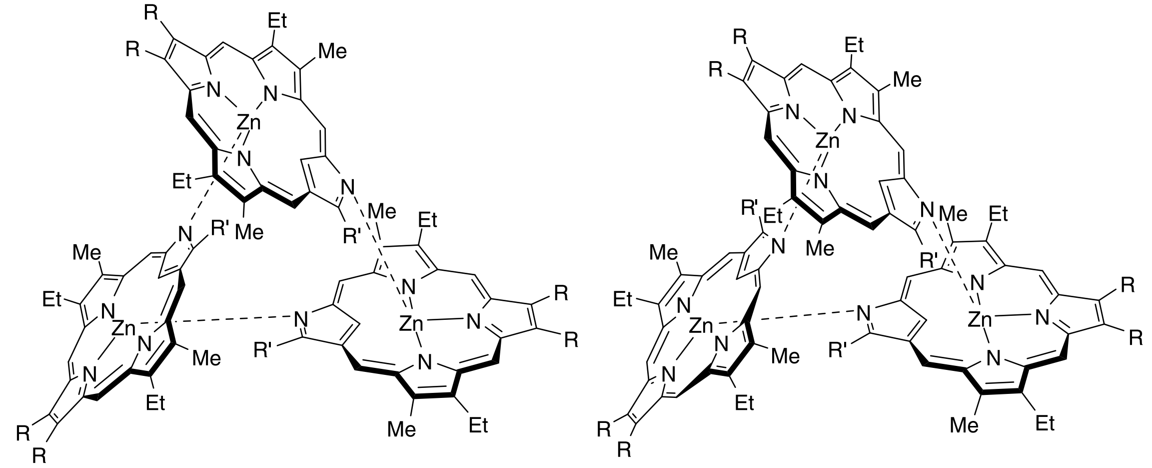
Results and discussion

β-Alkyl NCPs can be synthesised by the [3+1] condensation reactions developed by Lash et al. (*40*). This



1: R = H, R' = H
1-Et: R = H, R' = Et
2: R = Me, R' = Ph
2-Et: R = Me, R' = Et
3: R = Et, R' = Et

Scheme 1. Synthesis of 5,10,15,20-unsubstituted NCPs by the [3+1] condensation reactions.



R = H, R' = H	***S*-[(1-Zn)$_3$]**	39:61	***A*-[(1-Zn)$_3$]**
R = Ph, R' = Me	***S*-[(2-Zn)$_3$]**	0:100	***A*-[(2-Zn)$_3$]**
R = Et, R' = Et	***S*-[(3-Zn)$_3$]**	0:100	***A*-[(3-Zn)$_3$]**

Figure 4. Product ratio of NCP zinc(II) complex trimers.

time, 3-unsubstituted NCP (**1**), 3-methyl NCP (**2**) and 3-ethyl NCP (**3**) were synthesised from the corresponding precursors (Scheme 1). In the early stage of this study, **1-Et**, **2-Et** and **3**, where R′ is ethyl group, were examined. While **1-Et** was stable enough for silica gel column separation, recrystallisation did not work well and isolation in a crystalline form was so far inefficient. Then an unsubstituted derivative (**1**) was utilised in place of **1-Et**, which can be recrystallised more easily. In the case of **2-Et**, gradual decomposition was observed during silica gel column separation. Consequently, the phenyl derivative (**2**) was adopted since it showed considerably better stability than **2-Et**. Although a similar trend was also observed in **3**, it was used for further study without modification.

Preparation of the zinc(II) complexes corresponding to **1**–**3** was achieved in the reported manner (Figure 4) (*23*). The ^{1}H NMR spectrum for the zinc(II) complex of **1** in $CDCl_3$ is shown in Figure 5. The four singlet signals assignable to the protons on the 21-positions were observed in a high-field region around $\delta -5.6$ ppm. This resembles those of unsubstituted NCP zinc(II) complex, in which a mixture of the *A*- and *Z*-trimers was observed (*38*). Thus, the three singlet signals at $\delta -5.71$, -5.69 and -5.59 ppm, which have the same intensities, are assignable to those of ***A*-[(1-Zn)$_3$]** and the remaining singlet signal at $\delta -5.63$ ppm is assignable to that of ***S*-[(1-Zn)$_3$]**. Based on the integrated area ratio of those signals, the product ratio of ***A*-[(1-Zn)$_3$]** to ***S*-[(1-Zn)$_3$]** at 25°C in $CDCl_3$ is estimated to be 61:39. Interestingly, in the case of the zinc(II) complex of **2**, only three singlet signals are observed at $\delta -5.85$, -5.68 and -5.40 ppm in an integrated area ratio of 1:1:1 (Figure 6). This indicates selective formation of ***A*-[(2-Zn)$_3$]**. The other signals are fully consistent with the asymmetric trimeric structure. For example, the NCP macrocycles exercise the shielding effect on the neighbouring 3-Me and 20-H protons and then the sets of signals corresponding to the 3-Me protons ($\delta -1.70$, -0.25 and -0.22 ppm) and 20-H protons (δ 3.66, 3.91 and 4.86 ppm) are observed in a high-field region. The signals corresponding to ***S*-[(2-Zn)$_3$]** was not

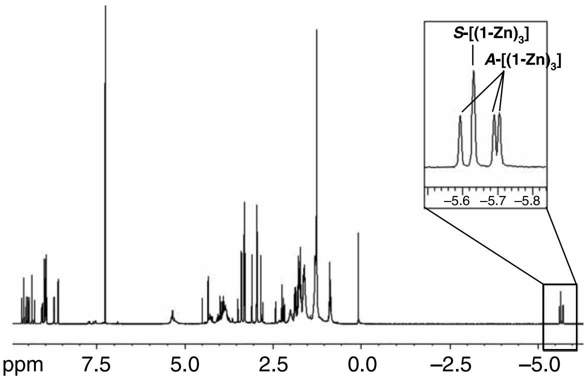
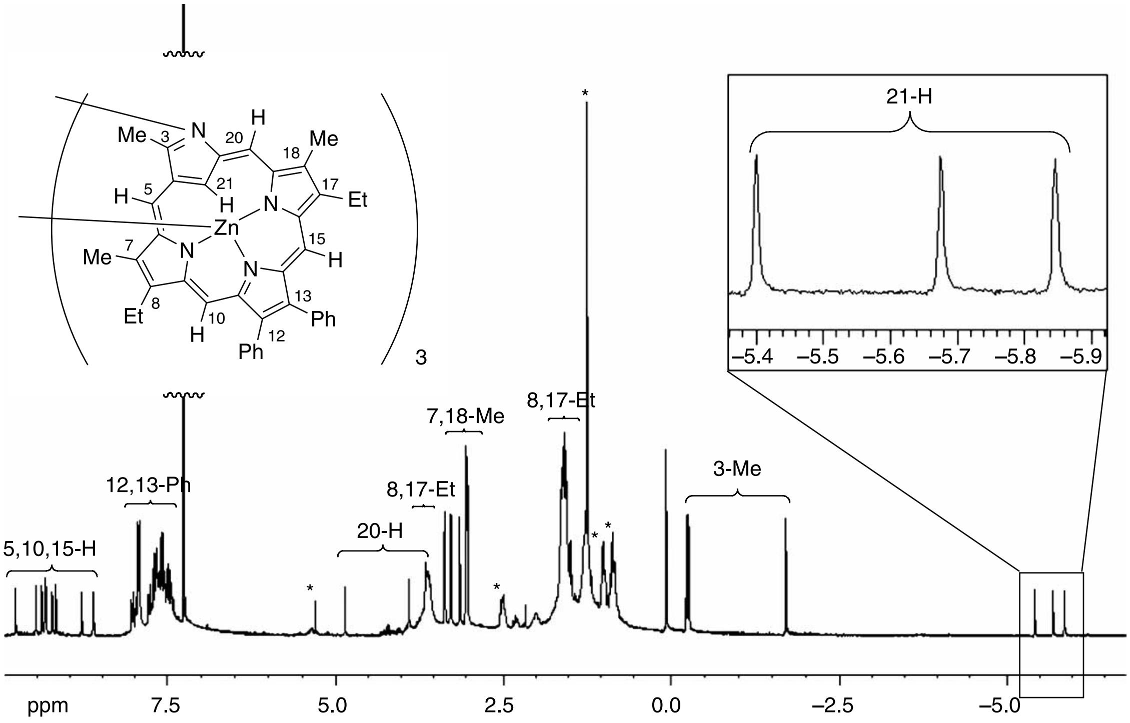


Figure 5. ^{1}H NMR spectrum of a mixture of ***S*-[(1-Zn)$_3$]** and ***A*-[(1-Zn)$_3$]** in $CDCl_3$.

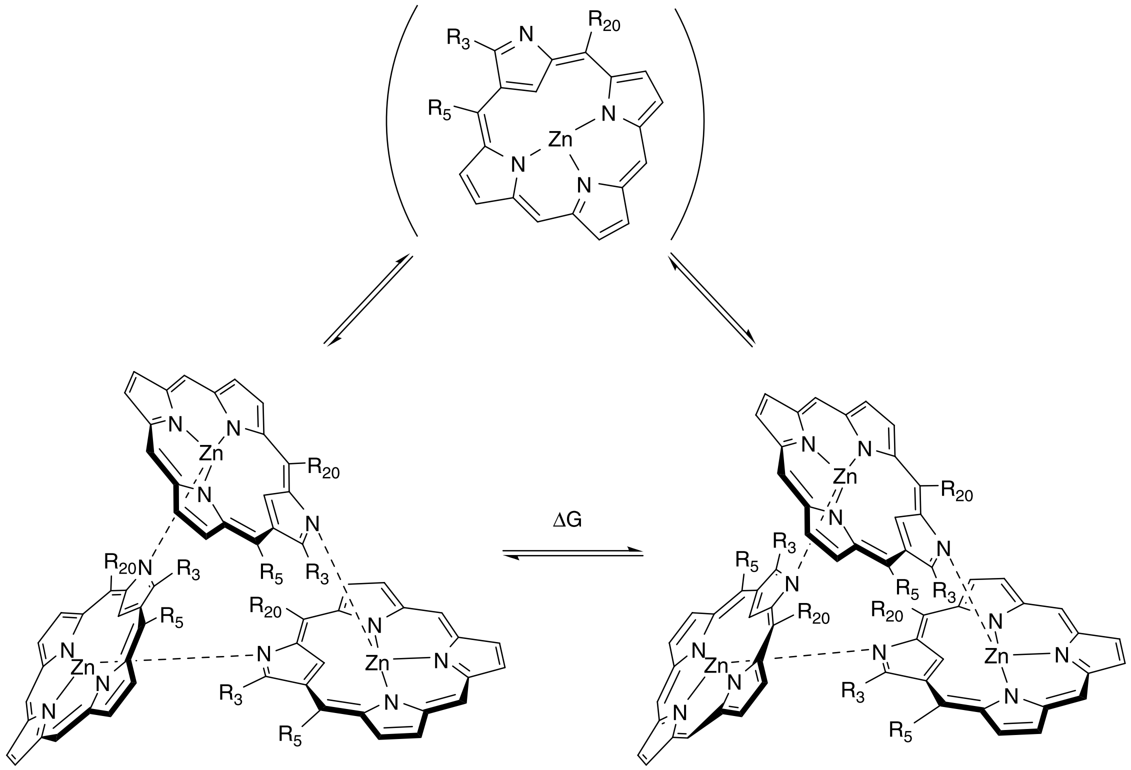


*Impurities (CH_2Cl_2, hexane, Et_3N)

Figure 6. ^{1}H NMR spectrum of ***A*-[(2-Zn)$_3$]** in $CDCl_3$.

detected by ^{1}H NMR analysis. Similar result was obtained for the zinc(II) complex of **3**. Again, only three singlet signals are observed in a high-field region at δ -5.71, -5.58 and -5.24 ppm with the same intensities, suggesting selective formation of ***A*-[(3-Zn)$_3$]**.

Configuration of NCP zinc(II) complex trimers was studied by DFT calculations. Because *A*- and *S*-trimers are expected to be under equilibrium (*25*, *37*), regioselectivity in trimer formation would be governed by thermodynamic stability of *A*- and *S*-trimers. On the assumption that the substituents around the coordinative nitrogen atoms would play an important role in regioselectivity, unsubstituted NCP (**4**), 3-Me-NCP (**5**), 3-Et-NCP (**6**), 5-Me-NCP (**7**) and 20-Me-NCP (**8**) were subjected to calculations (Figure 7). All the structures were fully optimised at a B3LYP/631A level. The optimised structures of ***A*-[(5-Zn)$_3$]** and ***S*-[(5-Zn)$_3$]** are shown in Figure 8. Relative enthalpies (not corrected) and Gibbs free energies at 298.15 K under 1.0 atom (corrected by the zero-point vibration energies) of NCP zinc(II) complex trimers (that is, energy difference between *S*- and *A*-isomers) are listed in Table 1. In the case of unsubstituted NCP (**4**), the *S*-trimer is slightly more stable than the *A*-trimer (entry 1). The small energy difference in **4** is not against the production of a mixture of *A*- and *S*-trimers in **1**. When methyl groups are introduced into the 3-positions, relative stability is inverted. The *A*-trimer is more stable than the *S*-trimer in **5** (entry 2), which is consistent with the preferential production of ***A*-[(2-Zn)$_3$]** mentioned above. The energy difference becomes larger in the case of 3-Et-NCP (**6**, entry 3). This is also in good agreement with the experimental result on **3**. Preference of *A*-trimer is only observed for the 3-alkyl derivatives. Almost no energy difference is found in 5-Me-NCP (**7**, entry 4) and the *S*-trimer is more stable than the *A*-trimer in 20-Me-NCP (**8**, entry 5).



***S*-[(4-Zn)$_3$]**	$R_3 = R_5 = R_{20} = H$	***A*-[(4-Zn)$_3$]**
***S*-[(5-Zn)$_3$]**	$R_3 = Me, R_5 = R_{20} = H$	***A*-[(5-Zn)$_3$]**
***S*-[(6-Zn)$_3$]**	$R_3 = Et, R_5 = R_{20} = H$	***A*-[(6-Zn)$_3$]**
***S*-[(7-Zn)$_3$]**	$R_5 = Me, R_3 = R_{20} = H$	***A*-[(7-Zn)$_3$]**
***S*-[(8-Zn)$_3$]**	$R_{20} = Me, R_3 = R_5 = H$	***A*-[(8-Zn)$_3$]**

Figure 7. Structures of the model compounds for DFT study.

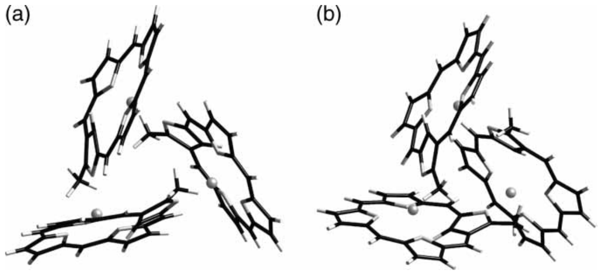


Figure 8. Optimised structures of (a) ***A*-[(5-Zn)$_3$]** and (b) ***S*-[(5-Zn)$_3$]**.

Table 1. Relative enthalpies and Gibbs free energies calculated for the model compounds.

Entry	Compound	Δ*H* (kcal/mol)	Δ*G* (kcal/mol)	Compound	Δ*H* (kcal/mol)	Δ*G* (kcal/mol)
1	***S*-[(4-Zn)$_3$]**	0.00	0.00	***A*-[(4-Zn)$_3$]**	+0.80	+0.59
2	***S*-[(5-Zn)$_3$]**	+1.25	+0.91	***A*-[(5-Zn)$_3$]**	0.00	0.00
3	***S*-[(6-Zn)$_3$]**	+2.05	+2.39	***A*-[(6-Zn)$_3$]**	0.00	0.00
4	***S*-[(7-Zn)$_3$]**	0.00	+0.06	***A*-[(7-Zn)$_3$]**	+0.48	0.00
5	***S*-[(8-Zn)$_3$]**	0.00	0.00	***A*-[(8-Zn)$_3$]**	+2.42	+1.67

Table 2. Structural parameters for the optimised structures at B3LYP/631A level.

Compound	Zn–N length (Å)			Av (Å)	Rotational angle (°)			Av (°)	C–NCP length (Å)			Av (Å)
***S*-[(4-Zn)$_3$]**	2.087	2.087	2.087	2.087	23.1	23.4	23.8	23.4	–	–	–	–
***A*-[(4-Zn)$_3$]**	2.083	2.092	2.092	2.089	23.7	24.3	24.5	24.2	–	–	–	–
***S*-[(5-Zn)$_3$]**	2.135	2.138	2.140	2.138	23.6	23.6	23.7	23.6	3.246	3.249	3.252	3.249
***A*-[(5-Zn)$_3$]**	2.120	2.125	2.134	2.126	**17.7**	22.9	25.1	21.9	3.243	3.243	3.247	3.244
***S*-[(6-Zn)$_3$]**	2.153	2.153	2.153	2.153	22.8	22.9	23.0	22.9	3.399	3.404	3.408	3.404
***A*-[(6-Zn)$_3$]**	2.126	2.127	2.149	2.134	**17.7**	23.5	25.4	22.2	3.327	3.394	3.368	3.363
***S*-[(7-Zn)$_3$]**	2.086	2.087	2.087	2.087	25.0	25.0	25.1	25.0	5.197	5.202	5.206	5.202
***A*-[(7-Zn)$_3$]**	2.082	2.092	2.093	2.089	24.9	25.4	26.8	25.7	5.071	5.187	5.336	5.198
***S*-[(8-Zn)$_3$]**	2.144	2.145	2.145	2.145	24.3	24.6	24.6	24.5	3.267	3.270	3.280	3.272
***A*-[(8-Zn)$_3$]**	2.149	2.164	2.164	2.159	25.0	25.6	25.9	25.5	3.262	3.279	3.306	3.282

To obtain further insight into regioselectivity in trimer formation, difference between *S*- and *A*-trimers was carefully verified. The structural parameters of the optimised structures are summarised in Table 2. ‘Zn–N length’ is a distance between the peripheral nitrogen atom and the neighbouring zinc metal of adjacent NCP. ‘Rotational angle’ is a dihedral angle between the confused pyrrole plane composing of 5 heavy atoms and the NCP plane composing of 19 heavy atoms (confused pyrrole is not included). ‘C–NCP length’ is a distance from the adjacent NCP plane to the methyl carbon atom (for **5**, **7** and **8**) or the methylene carbon atom (for **6**). Generally, no significant differences are observed between the *S*- and *A*-isomers in the averaged structural parameters. Nevertheless, one of the three rotational angles is exceptionally small (17.7°) only in ***A*-[(5-Zn)$_3$]** and ***A*-[(6-Zn)$_3$]**, while all the other rotational angles are around 24°. The smaller rotational angles would mean less skeletal strain in NCP macrocycles and then formation of ***A*-[(5-Zn)$_3$]** and ***A*-[(6-Zn)$_3$]** seems more favourable than the formation of corresponding *S*-trimers. Note that the importance of pyrrole rotation is often pointed out in the metal coordination of NCP (*26*, *43*, *44*). In the other trimers, *S*-trimers are intrinsically more stable than *A*-trimers. While clear explanation is so far difficult, it can be rationalised by fine difference in the rotational angles. The *S*-trimers commonly have the smaller rotational angles than the *A*-trimers in **4**, **7** and **8**, implying less skeletal strain in the NCP macrocycles.

Conclusion

In conclusion, we have synthesised β-alkyl NCP zinc(II) complexes and their configurations have been investigated. When 3-Me or 3-Et NCPs are utilised, selective formation of *A*-trimers is observed, while *S*-trimers are intrinsically more stable than *A*-trimers in the other substrates. Theoretical study reveals that the small difference around the coordinative nitrogen atom of NCP would give a decisive effect on regioselectivity in oligomer formation. Further study on controlling porphyrin arrays as well as their applications are now underway.

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References

(1) Wasielewski, M.R. *Chem. Rev.* **1992**, *92*, 435–461.
(2) Ward, M.D. *Chem. Soc. Rev.* **1997**, *26*, 365–375.
(3) Hayashi, T.; Ogoshi, H. *Chem. Soc. Rev.* **1997**, *26*, 355–364.
(4) Blanc, M.-J.; Jiménez, M.C.; Chambron, J.-C.; Heitz, V.; Linke, M.; Sauvage, J.-P. *Chem. Soc. Rev.* **1999**, *28*, 293–305.
(5) Fleischer, E.B.; Shachter, A.M. *Inorg. Chem.* **1991**, *30*, 3763–3769.
(6) Stibrany, R.T.; Vasudevan, J.; Knapp, S.; Potenza, J.A.; Emge, T.; Schugar, H.J. *J. Am. Chem. Soc.* **1996**, *118*, 3980–3981.
(7) Funatsu, K.; Imamura, T.; Ichimura, A.; Sasaki, Y. *Inorg. Chem.* **1998**, *37*, 4986–4995.
(8) Gerasimchuk, N.N.; Mokhir, A.A.; Rodgers, K.R. *Inorg. Chem.* **1998**, *37*, 5641–5650.
(9) Vinodu, M.; Stein, Z.; Goldberg, I. *Inorg. Chem.* **2004**, *43*, 7582–7584.
(10) Iengo, E.; Zangrando, E.; Bellini, M.; Alessop, E.; Prodi, A.; Chiorboil, C.; Scandola, F. *Inorg. Chem.* **2005**, *44*, 9752 – 9762.
(11) Ikeda, C.; Nagahara, N.; Yoshioka, N.; Inoue, H.; *New J. Chem.* **2000**, *24*, 897–902.
(12) Ikeda, C.; Tanaka, Y.; Fujihara, T.; Ishii, Y.; Ushiyama, T.; Yamamoto, K.; Yoshioka, N.; Inoue, H. *Inorg. Chem.* **2001**, *40*, 3395–3405.
(13) Kobuke, Y.; Miyaji, H. *J. Am. Chem. Soc.* **1994**, *116*, 4111–4112.
(14) Kobuke, Y.; Miyaji, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3563–3569.
(15) Kobuke, Y. *J. Porphyrins Phthalocyanines* **2004**, *8*, 156–174.
(16) Goff, H.M.; Shimomura, E.T.; Lee, Y.J.; Scheidt, W.R. *Inorg. Chem.* **1984**, *23*, 315–321.
(17) Godziela, G.M.; Tilotta, D.; Goff, H.M. *Inorg. Chem.* **1986**, *25*, 2142–2146.
(18) Balch, A.L.; Latos-Grażyński, L.; Noll, B.C.; Olmstead, M.M.; Zovinka, E.P. *Inorg. Chem.* **1992**, *31*, 2248–2255.
(19) Wojaczynski, J.; Latos-Grażyński, L. *Inorg. Chem.* **1995**, *34*, 1044–1053.
(20) Wojaczynski, J.; Latos-Grażyński, L. *Inorg. Chem.* **1995**, *34*, 1054–1062.
(21) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767–768.
(22) Chmielewski, P.J.; Latos-Grażyński, L.; Rachlewicz, K.; Głowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779–781.
(23) Furuta, H.; Ishizuka, T.; Osuka, A. *J. Am. Chem. Soc.* **2002**, *124*, 5622–5623.
(24) Furuta, H.; Morimoto, T.; Osuka, A. *Org. Lett.* **2003**, *5*, 1427–1430.
(25) Furuta, H.; Morimoto, T.; Osuka, A. *Inorg. Chem.* **2004**, *43*, 1618–1624.
(26) Toganoh, M.; Harada, N.; Morimoto, T.; Furuta, H. *Chem. Eur. J.* **2007**, *13*, 2257–2265.
(27) Hung, C.-H.; Chen, W.-C.; Lee, G.-H.; Peng, S.-M. *Chem. Commun.* **2002**, 1516–1517.
(28) Harvey, J.D.; Ziegler, C.J. *Chem. Commun.* **2002**, 1942–1943.
(29) Harvey, J.D.; Ziegler, C.J. *Chem. Commun.* **2003**, 2890 – 2891.
(30) Chmielewski, P.J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6417–6420.
(31) Furuta, H.; Kubo, N.; Maeda, H.; Ishizuka, T.; Osuka, A.; Nanami, H.; Ogawa, T. *Inorg. Chem.* **2000**, *39*, 5424–5425.
(32) Furuta, H.; Youfu, K.; Maeda, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 2186–2188.
(33) Chmielewski, P.J.; Schmidt, I. *Inorg. Chem.* **2004**, *43*, 1885–1894.
(34) Toganoh, M.; Niino, T.; Maeda, H.; Andrioletti, B.; Furuta, H. *Inorg. Chem.* **2006**, *45*, 10428–10430.
(35) Hung, C.H.; Chang, C.H.; Ching, W.M.; Chuang, C.H. *Chem. Commun.* **2006**, 1866–1868.
(36) Furuta, H.; Nanami, H.; Morimoto, T.; Ogawa, T.; Kral, V.; Sessler, J.L.; Lynch, V. *Chem. Asian J.* **2008**, *3*, 592–599.
(37) Morimoto, T.; Uno, H.; Furuta, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 3672–3675.
(38) Morimoto, T.; Taniguchi, S.; Osuka, A.; Furuta, H.; *Eur. J. Org. Chem.* **2005**, 3887–3890.
(39) Nguyen, L.T.; Senge, M.O.; Smith, K.M. *J. Org. Chem.* **1996**, *61*, 998–1003.
(40) Lash, T.D.; Richter, D.T.; Shiner, C.M. *J. Org. Chem.* **1999**, *64*, 7973–7982.
(41) Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, J.A., Jr.; Vreven, T.; Kudin, K.N.; Burant, J.C.; Millam, J.M.; Iyengar, S.S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G.A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J.E.; Hratchian, H.P.; Cross, J.B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Ayala, P.Y.; Morokuma, K.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Zakrzewski, V.G.; Dapprich, S.; Daniels, A.D.; Strain, M.C.; Farkas, O.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Ortiz, J.V.; Cui, Q.; Baboul, A.G.; Clifford, S.; Cioslowski, J.; Stefanov, B.B.; Liu, G.; Liashenko, A,; Piskorz, P.; Komaromi, I.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Challacombe, M.; Gill, P.M.W.; Johnson, B.; Chen, W.; Wong, M.W.; Gonzalez, C.; Pople, J.A. *Gaussian 03, Revision C.02*; Gaussian: Wallingford, CT, 2004.
(42) Schafer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571–2577.
(43) Toganoh, M.; Konagawa, J.; Furuta, H. *Inorg. Chem.* **2006**, *45*, 3852–3854.
(44) Toganoh, M.; Ikeda, S.; Furuta, H. *Inorg. Chem.* **2007**, *46*, 10003–10015.