Formation of cyclic trimers and tetramers of zinc(II) pyrazolylporphyrins by mutual coordination

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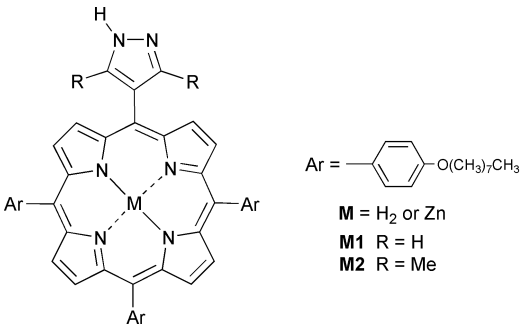
The self-assembly of zinc(II) porphyrins bearing a pyrazole substituent are reported. ^{1}H NMR, UV/Vis and VPO measurements indicate the formation of a cyclic trimer of zinc(II) pyrazol-4-ylporphyrin and a tetramer of zinc(II) 3,5-dimethypyrazol-4-ylporphyrin by mutual coordination.

In recent years, numerous attempts have been made to design porphyrin assemblies with a particular geometry because they have the potential capability to act as artificial photosynthetic systems and optical molecular devices.[1] Self-assembling strategies based on reversible, non-covalent interactions such as metal coordination[2] and hydrogen bonding[3] have been widely used to construct porphyrin assemblies since their spontaneous assembly can lead to large-scale ordered arrays, which can hardly be achieved by covalent bonding only. In particular, the metal coordination approach to porphyrin architecture in which a peripheral ligand substituent coordinates to the porphyrin central metal ion has been extensively studied using pyridyl, hydroxyl, imidazolyl and aminophenyl metalloporphyrins because the assembled structure can be easily controlled by the combination of metal ion species and donor ligands.[4–7] Recently, we have reported the synthesis of novel pyrazolylporphyrins and their self-assembly by intermolecular hydrogen bonding between peripheral pyrazole groups.[8] Here we sought to extend our investigation and focused on the coordination properties of pyrazolylporphyrins because pyrazoles are known to be excellent ligands and to form intermolecular hydrogen bonds. The spectroscopic characterization of self-assembled zinc(II) pyrazolylporphyrins has revealed the formation of mutually coordinated cyclic trimers and tetramers in solution, dependent on the substituent on the pyrazolyl ring.



Results and discussion

The monopyrazolylporphyrins $\mathbf{H_21}$ and $\mathbf{H_22}$ were synthesized *via* precursor porphyrins having a *p*-methoxybenzyl substituent as a protecting group on the pyrazole NH group. The desired zinc(II) complexes **Zn1** and **Zn2** were obtained by the conventional insertion of zinc(II) ions. Both **Zn1** and **Zn2** showed good solubility in most non-polar solvents such as chloroform and toluene. The ability of **Zn1** and **Zn2** to associate in solution was examined by UV/Vis absorption, ^{1}H NMR spectroscopy and vapor pressure osmometry (VPO). Both zinc(II) porphyrins exhibited concentration-dependent ^{1}H NMR and UV/Vis spectra in chloroform and toluene but not in solvents with coordinating properties such as pyridine, suggesting the formation of coordination assemblies. Hydrogen bonding between pyrazole units was negligible in **Zn1** and **Zn2** because the stability constant for axial coordination of pyrazole and 3,5-dimethylpyrazole is much larger than that for hydrogen bonding between pyrazoles.[9]

Self-assembly of Zn1

Fig. 1 shows a typical ^{1}H NMR spectrum of **Zn1** in CD_2Cl_2,[10] together with that of the free-base porphyrin $\mathbf{H_21}$. Although the spectral pattern of $\mathbf{H_21}$ is characteristic of monomeric porphyrin, the spectrum of **Zn1** is completely different from that of $\mathbf{H_21}$. The spectral assignment based on variable temperature measurements and COSY experiments revealed that the pyrazole ring protons and pyrrole-β_1 protons experience large upfield shifts. The degree of these upfield shifts, $\Delta\delta$,[11] for pyrazole-$H_{3,5}$ and pyrrole-β_1 is 3.7 and 1.7 ppm, respectively, in 10 mM CD_2Cl_2 at 295 K; these values became smaller upon dilution or increasing temperature. The upfield shifts observed for the pyrazole ring protons indicate that the pyrazole nitrogens coordinate to the central zinc(II) ions and come into the shielding region of the coordinated porphyrin ring to afford the self-assembly of **Zn1** by coordination. The proton signals assignable to the oxyphenyl ring were split into two peaks with an integrated ratio 2 : 1, showing that the aryl protons of the 10 and 20 positions are not equivalent to those of the 15 position in the assembly. At ambient temperature, the signals of the pyrazole ring protons were nearly coalesced around 4.5 ppm but no coalescence of pyrazole protons was observed in the mixture of pyrazole and zinc(II) tetraphenylporphyirn (ZnTPP) or in that of $\mathbf{H_21}$ and ZnTPP. This observation indicates that the exchange lifetime for self-assembly of **Zn1** becomes longer than that for simple axial coordination, probably due to cooperative formation of the assembly (*vide infra*).

The UV/Vis spectra of **Zn1** recorded in $CDCl_3$[12] also exhibited a concentration dependence. In dilute solution below 0.01 mM, **Zn1** showed an intense B band and two weak Q bands, which are typical of the zinc(II) porphyrin[13] and whose absorbance obeyed the Beer–Lambert law, indicating that **Zn1** exists as a monomer in these dilute conditions.

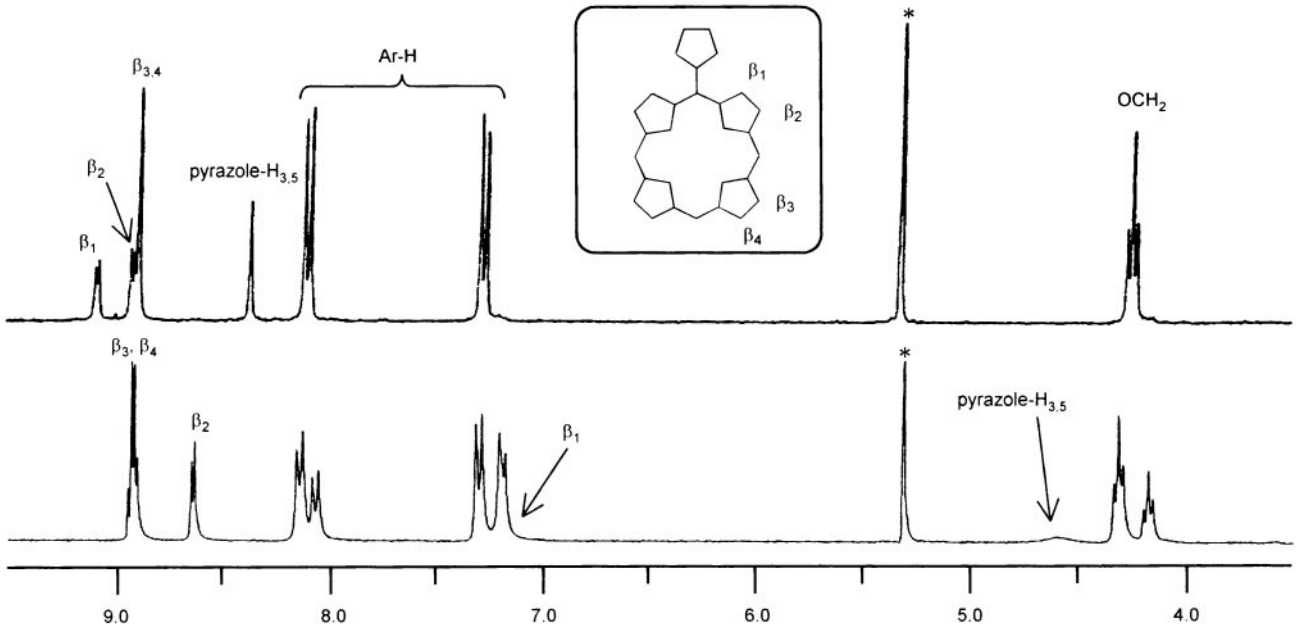


Fig. 1 Typical ^{1}H NMR spectra of $\mathbf{H_2 1}$ (6 mM, top) and **Zn1** (10 mM, bottom) in CD_2Cl_2 at 295 K. Pyrrole-β_1 protons of **Zn1** are overlapped with aryl protons. See insert for the labeling of pyrrole-β protons. Asterisks denote the residual solvent peaks.

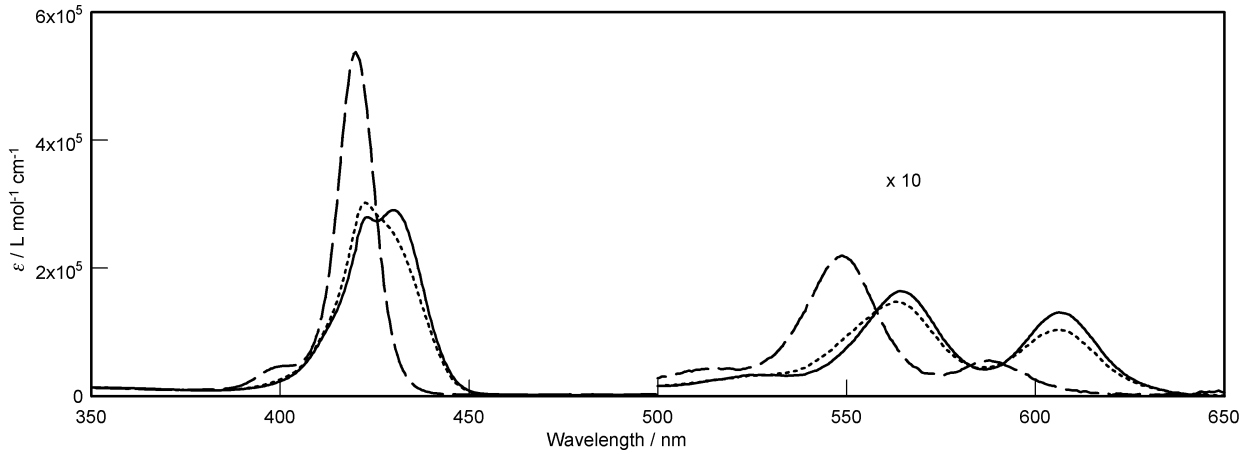


Fig. 2 Absorption spectra of **Zn1** recorded at 0.004 mM in $CDCl_3$ at 295 K (– – –), 2 mM at 295 K (· · ·) and 2 mM at 273 K (——). Quartz cells of 10 and 0.025 mm path length were used for the measurements.

However, the B band became broader upon increasing concentration to 2 mM and was split into two bands at 422 and 430 nm at 273 K (Fig. 2).[14] Compared with the NMR spectral data, these spectral changes may be ascribed to the formation of a self-assembly by coordination. It is well known that the B band of zinc(II) porphyrins is red-shifted upon coordination of an axial ligand such as pyridine or pyrazole[13b] but it does not split in that process. Therefore, the spectral change observed in the B band of **Zn1** may be attributed to the excitonic interaction[15] between the large transition dipoles of the constituent porphyrin chromophores in the assembly. The Q(1,0) band was also red-shifted from 552 to 564 nm upon increasing the concentration but did not split, which is very similar to the spectral change caused by coordination of axial ligands to zinc(II) porphyrins.

In order to confirm the nature of the self-assembly structure, a curve-fitting analysis was carried out for the change of observed molar absorption coefficient at 552 nm where monomeric **Zn1** shows its Q(1,0) band. The dilution curves observed at 295 K in $CDCl_3$ were fitted to the model for a cooperative *n*-merization process (association number $n = 2$, 3, 4) by

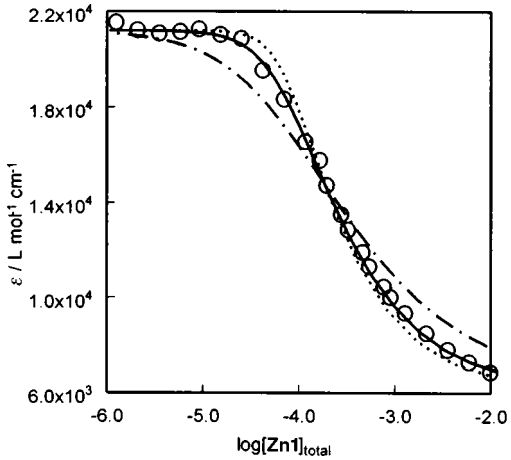


Fig. 3 Curve fitting analysis of the concentration dependence of the molar absorption coefficient of **Zn1** at 552 nm recorded in 0.1 and 1.0 mm path length quartz cells in $CDCl_3$: (○) experimental data, (– · –) dimer model, (——) trimer model, (· · ·) tetramer model.

Saunders–Hyne analysis (Fig. 3).[16] The dilution curve fits well with the optimized trimer model throughout the concentration range, but the best-fit dimer or tetramer models deviate substantially from the experimental data. This analysis indicates that **Zn1** forms a trimer and the equilibrium in the self-assembly process is nearly complete above *ca.* 10 mM.

In this context, a series of VPO measurements were carried out between 5 and 20 mM using the same solvent as that for the UV/Vis spectra ($CDCl_3$, 25 °C, benzil and TPP as standards). The average molecular weight obtained was 3260 ± 110, corresponding to a trimer of **Zn1** (FW = 3161 g mol^{-1}). The combined VPO, UV/Vis and ^1H NMR spectral results demonstrate that **Zn1** forms a self-assembled trimer by coordination of the pyrazole nitrogen to the central zinc(II) ion. The binding constant for the trimer, K_3, was estimated to be $3.5 \pm 0.5 \times 10^7$ M^{-2} from the fitting. If we assume a linear trimer (oligomer), the binding constant for chain extension ($K_{1,2} = K_{2,3} = K_{n,n+1}$) can be estimated to be 5.5×10^3 M^{-1} from K_3. However, this value is apparently larger than the binding constant of 630 M^{-1} for the axial coordination of pyrazole to zinc(II) tetratolylporphyrin,[17] suggesting the cooperative formation of a mutually coordinated cyclic trimer. Moreover, the possibility of the open polymeric structure was ruled out because the dilution curve did not fit the non-cooperative linear polymerization isotherm.[7a] These results indicate that **Zn1** self-assembles into a mutually coordinated cyclic trimer structure at higher concentrations owing to three coordination bonds between central zinc(II) ions and pyrazolyl nitrogen atoms (Fig. 4).

Self-assembly of Zn2

The ^1H NMR and UV/Vis spectra of **Zn2**, possessing a 3,5-dimethylpyrazole ring, also showed concentration and/or temperature dependencies, but the spectral behavior was quite different from that of **Zn1**. The most striking feature was observed in ^1H NMR spectra of **Zn2**. Though the upfield shifts of proton signals due to the pyrrole-β and pyrazole ring were observed as in **Zn1**, all the signals of **Zn2** were broad above *ca.* 1 mM in $CDCl_3$, CD_2Cl_2, or toluene-d_5 (Fig. 5) and no sharp spectra could be obtained, even upon lowering the temperature to 220 K. These spectral features suggest the formation of coordination polymers or oligomers that have a flexible conformation,[18] although a chemical exchange process may be an alternative explanation.

At higher concentrations, **Zn2** showed a split B band and a red shift of the Q band, similar to **Zn1**. The λ_{max} of the split B band and the red-shifted Q band of **Zn2** were quite similar to those of **Zn1**, though these spectral changes occurred at lower concentrations. The red shift of the Q band of **Zn2** was complete above *ca.* 1 mM, while that of **Zn1** was complete above

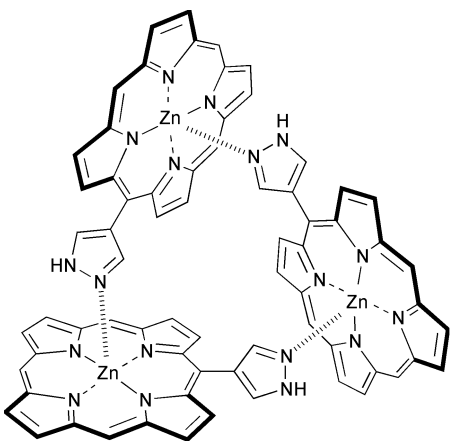


Fig. 4 Proposed structure of the self-assembled cyclic trimer of **Zn1**. The *meso p*-octyloxyphenyl group is omitted for clarity.

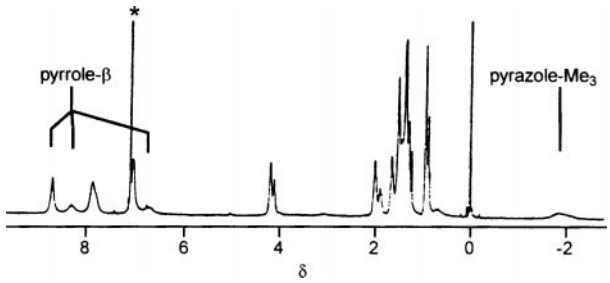


Fig. 5 ^1H NMR spectra of **Zn2** (10 mM) in $CDCl_3$ at 295 K. A broad peak around −2 ppm was assigned to pyrazole-Me_3.

ca. 10 mM. The splitting of the B band of **Zn1** appeared only below −7 °C at 2 mM, but for **Zn2** it occurred even at ambient temperature at the same concentration. These differences between **Zn1** and **Zn2** are most likely caused by the stronger basicity of 3,5-dimethylpyrazole compared to pyrazole. Furthermore, an interesting difference between these porphyrins was observed in the Saunders–Hyne analysis of the concentration dependence of the observed molar coefficient of the Q band (ε at 552 nm, in $CDCl_3$). The analysis for **Zn2** gave a best fit to the tetramer model, and not to a dimer, trimer or non-cooperative polymer model (Fig. 6), in contrast to the trimer model found for **Zn1**. These results for **Zn2** also agree well with those from the VPO measurements recorded under the same conditions as for **Zn1**. The average molecular weight of 4570 ± 340 obtained corresponds to the molecular weight of the tetramer of **Zn2** (FW = 4324 g mol^{-1}). The curve fitting to the tetramer model gave a binding constant $K_4 = 3.0 \pm 1.0 \times 10^{13}$ M^{-3} (295 K, in $CDCl_3$) which is too large to correspond to the formation of a liner tetramer.[19] As a result, the cooperative formation of a cyclic tetramer structure of **Zn2** by mutual coordination (Fig. 7) is strongly suggested by the ^1H NMR, UV/Vis spectra and VPO measurements.

Consideration of assembled structures

The fact that the association number of **Zn1** ($n = 3$) is different from that of **Zn2** ($n = 4$) was somewhat unexpected because both **Zn1** and **Zn2** have a similar pyrazol-4-yl group while the two methyl groups on the pyrazole ring seemed to affect only the pK_a value, which influences the binding affinities only.
To discuss why different assemblies are formed for **Zn1** and **Zn2** and why **Zn1** forms a trimer and **Zn2** forms a tetramer rather than other oligomers, we calculated the geometry of an axially coordinated pyrazole ligand to zinc(II) tetra-

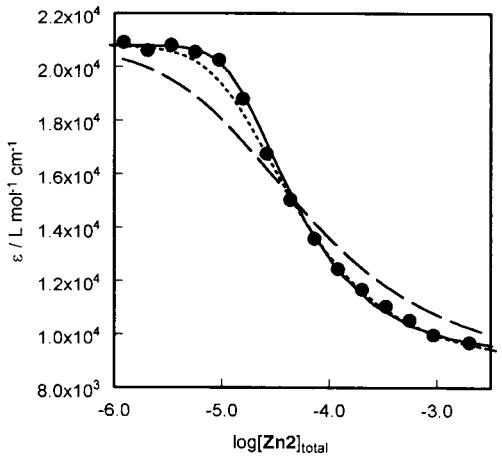


Fig. 6 Curve fitting analysis of the concentration dependence of the molar absorption coefficient of **Zn2** at 552 nm in $CDCl_3$: (●) experimental data, (– – –) dimer model, (· · ·) trimer model, (——) tetramer model.

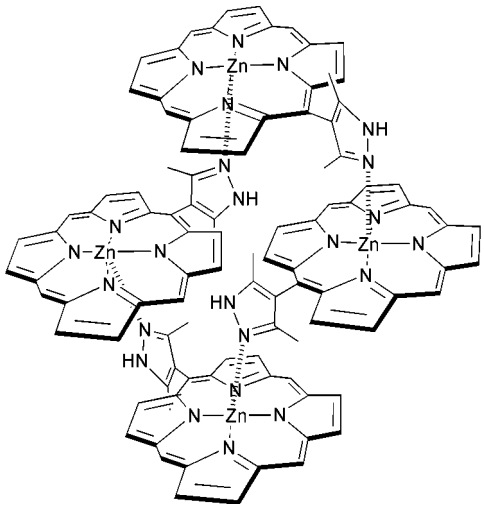


Fig. 7 Proposed structure of the self-assembled cyclic tetramer of **Zn2**. The *meso p*-octyloxyphenyl groups are omitted for clarity.

phenylporphryin as a model system by geometry optimization using the MOPAC program.[20] The calculated results of the model system are that the coordination angle α is 59° for an unsubstituted pyrazole ligand and 65° for 3,5-dimethylpyrazole, where α is defined as the angle between the porphyrin mean plane and the CH bond at position 3 in an axially coordinated pyrazole ring (Fig. 8). These results clearly showed that α is different for these two ligands, probably due to the steric repulsion of the methyl groups. Furthermore, if the angle α is assumed to be the angle between porphyrin mean planes in the self-assembled pyrazolylporphyrins, a trimer structure seems reasonable for self-assembled **Zn1** since the internal angle in a triangle is 60°. The formation of a tetramer of **Zn2** rather than a trimer might also be explained by the value of the angle α, 65°, which is not the preferred one for the trimer. Of course, some extent of deviation in the coordination angle may occur to form a thermodynamically stable structure. However, space filling modeling indicated that the core of the cyclic trimer structure of **Zn1** is very small and severe steric repulsion in the **Zn2** assembly could occur between methyl groups belonging to neighboring porphyrins in the trimer. From this consideration, a cyclic tetramer structure can be regarded as the most preferable structure for **Zn2** as the smallest cyclic structure which is stable in solution from the thermodynamic point of view.[21] Considering the coordination angle α of the 3,5-dimetylpyrazole ring, the cyclic tetramer structure of **Zn2** must not be square and it seems to form a twisted parallelogram in a "flexible" geometry, which agrees well with the NMR spectral results.

Conclusion

Novel zinc(II) pyrazolylporphyrins were synthesized and their self-assembled structures were studied. ^{1}H NMR spectra, VPO measurements and curve-fitting analyses for the concentration dependence of their UV/Vis spectra demonstrated the formation of the cyclic trimer and tetramer by mutual coordination. These results reveal that pyrazoles can be utilized as versatile building blocks in coordination porphyrin architecture and the structure can be easily controlled by the substituent at the 3,5-positions of the pyrazole ring. We are currently studying the porphyrin architecture using both metal coordination and hydrogen bonding in a cooperative fashion. The results will be published elsewhere.

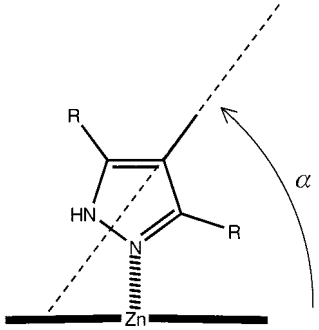


Fig. 8 Schematic view of the axially coordinated pyrazole ligand. The porphyrin plane is shown as a thick line.

Experimental

Instrumental

^{1}H NMR spectra were recorded on a Jeol 300 MHz LABDA-300 spectrometer, and chemical shifts are reported relative to internal TMS at 0.0 ppm. VPO measurements were carried out with a Knauer K-7000 vapor pressure osmometer. UV/Vis spectra were obtained with a Jasco V-570 spectrometer. $CDCl_3$ stabilized with silver foil was used to prevent demetallation of zinc(II) porphyrins.

Synthesis

The two pyrazolecarboxaldehydes used in this study were synthesized using reported procedures.[22]

5-(1-*p*-Methoxybenzylpyrazol-4-yl)-10,15,20-tris(*p*-octyloxyphenyl)porphyrin (*p*MB-H$_2$1). 1-*p*-Methoxybenzylpyrazole-4-carboxaldehyde (2.6 g, 12.3 mmol) and *p*-octyloxybenzaldehyde (8 ml, 33 mmol) were added to 310 mL refluxing propionic acid. Freshly distilled pyrrole (3.1 mL, 45 mmol) was then added and the mixture was refluxed for 10 h. The propionic acid was removed by distillation under reduced pressure to give a dark residue. This was taken up into the minimum amount of chloroform and transferred to a 500 mL round bottomed flask, *ca.* 100 g of alumina (grade I, Merck) was added, and the solvent was removed *via* rotary evaporation. The resulting dry powder was placed on the top of a dry silica column and the porphyrins were eluted with toluene and then with toluene–ethyl acetate (10 : 1). The second band was collected and crystallized from dichloromethane–methanol to give the title compound (0.7 g). Yield: 8%. ^{1}H NMR ($CDCl_3$): δ −2.72 (s, 2H, inner NH), 0.93 (t, 9H, CH_{3h}, J = 6.6), 1.30–1.51 (m, 24H, CH_{2d-g}), 1.64 (quint, 6H, J = 6.8, CH_{2c}), 1.99 (quint, 6H, J = 6.8, CH_{2b}), 3.88 (s, 3H, OMe), 4.26 (t, 6H, J = 6.6, CH_{2a}), 5.56 (s, 2H, NCH_2), 7.02 (d, 2H, J = 8.5 ArH, *p*-methoxyphenyl), 7.28 (d, 6H, J = 7.3 ArH_m, *p*-octyloxyphenyl), 7.37 (d, 2H, J = 8.5 ArH, *p*-methoxyphenyl), 8.10 (d, 6H, J = 7.3 ArH, *p*-octyloxyphenyl), 8.14, 8.35 (each s, pyrazole-$H_{3,5}$), 8.85–8.88 (m, 6H, pyrrole-H_β), 9.04 (d, 2H, J = 4.6 Hz pyrrole-H_β). Anal. calc. for $C_{73}H_{84}N_6O_4 \cdot 0.5H_2O$: C 78.39, H 7.66, N 7.51. Found: C 78.39, H 7.61, N 7.40%. Mp = 154–155 °C.

5-(1-*p*-Methoxybenzyl- 3,5-dimethylpyrazol- 4-yl)- 10,15,20-tris(*p*-octyloxyphenyl)porphyrin (*p*MB-H$_2$2). This compound was synthesized in the same manner as ***p*MB-H$_2$1** using 1-*p*-methoxybenzyl-3,5-dimethylpyrazole-4-carboxaldehyde, *p*-octyloxybenzaldehyde and pyrrole. Yield: 5%. ^{1}H NMR ($CDCl_3$): δ −2.74 (s, 2H, inner NH), 0.94 (t, 9H, J = 6.6 CH_{3h}), 1.25–1.50 (m, 24H, CH_{2d-g}), 1.64 (quint, 6H, J = 6.8, CH_{2c}), 1.99 (quint, 6H, J = 6.8, CH_{2b}), 2.09, 2.22 (each s, 6H, pyrazole-$Me_{3,5}$), 3.87 (s, 3H, OMe), 4.26 (t, 6H, J = 6.6, CH_{2a}), 5.56 (s, 2H, NCH_2), 7.02 (d, 2H, J = 8.5 ArH, *p*-methoxyphenyl), 7.27 (d, 6H, J = 7.3 ArH_m, *p*-octyloxyphenyl), 7.36 (d, 2H, J = 8.5 ArH, *p*-methoxyphenyl), 8.10 (d, 6H, J = 7.3 ArH_o, *p*-octyloxyphenyl), 8.97 (s, 4H, pyrrole-H_β), 8.98 (d, 2H, J = 4.6 pyrrole-H_β), 9.00 (d, 2H, J = 4.6 pyrrole-H_β). Anal. calc. for $C_{75}H_{88}N_6O_4 \cdot 3CH_3OH$: C 75.94, H 8.17, N 6.81. Found: C 75.78, H 7.56, N 6.65%. Mp = 100–103 °C.

5-(Pyrazol-4-yl)- 10,15,20-tris(*p*- octyloxyphenyl)porphyrin ($H_2$1). In 60 mL of trifluoroacetic acid, 1.1 g of ***p*MB-$H_2$1** (0.9 mmol) was dissolved and the mixture was refluxed for 3 days. The mixture was neutralized with a saturated solution of $NaHCO_3$. The porphyrin was extracted with chloroform and washed with water. The organic layer was dried with anhydrous Na_2SO_4 and the solvent was removed *via* rotary evaporation. The crude porphyrin was loaded onto a SiO_2 column and the desired porphyrin was eluted with toluene–ethyl acetate (3 : 1). Crystallization from dichloromethane–methanol gave the title compound (530 mg). Yield: 56%. ^{1}H NMR ($CDCl_3$): δ −2.74 (s, 2H, inner-NH), 0.94 (t, 9H, J = 6.8 CH_{3h}), 1.30–1.50 (m, 24H, CH_{2d-g}), 1.63 (quint, 8H, J = 6.8 CH_{2c}), 1.98 (quint, 8H, J = 6.8 CH_{2b}), 4.23 (t, 6H, J = 6.3 CH_{2a}), 7.26 (d, 6H, J = 8.6 ArH_m), 8.09 (d, 6H, J = 8.6 ArH_o), 8.37 (s, 2H, pyrazole-$H_{3,5}$), 8.86 (s, 4H, pyrrole-H_β), 8.89 (d, 2H, J = 4.9 pyrrole-H_β), 9.03 (d, 2H, J = 4.9 Hz pyrrole-H_β). Anal. calc. for $C_{65}H_{76}N_6O_3$: C 78.91, H 7.74, N 8.46. Found: C 78.87, H 7.53, N 8.39%. Mp > 300 °C.

5-(3,5-Dimethylpyrazol-4-yl)-10,15,20-tris(*p*-octyloxyphenyl)-porphyrin ($H_2$2). This compound was synthesized in the same manner as **$H_2$1** using ***p*MB-$H_2$2** as the starting material. Yield: 65%. ^{1}H NMR ($CDCl_3$): δ −2.74 (s, 2H, inner NH), 0.94 (t, 9H, J = 6.6, CH_{3h}), 1.30–1.55 (m, 24H, CH_{2d-f}), 1.63 (quint, 6H, J = 6.8, CH_{2c}), 1.98 (quint, 6H, J = 6.8, CH_{2b}), 2.19 (s, 6H, pyrazole-$Me_{3,5}$), 4.24 (t, 6H, J = 6.5, CH_{2a}), 7.27 (d, 6H, J = 8.6, ArH_m), 8.10 (d, 6H, J = 8.6, ArH_o), 8.84 (d, 2H, J = 4.6, pyrrole-H_β), 8.86 (s, 4H, pyrrole-H_β), 8.89 (d, 2H, J = 4.6, Hz pyrrole-H_β). Anal. calc. for $C_{67}H_{80}N_6O_3 \cdot H_2O$: C 77.72, H 7.98, N 8.11. Found: C 77.47, H 7.85, N 7.73%. Mp = 140–142 °C.

[5-(Pyrazol-4-yl)-10,15,20-tris(*p*-octyloxyphenyl)porphyrinato] zinc(II) (Zn1). To a stirred solution of 0.19 g (0.19 mmol) of **$H_2$1** in 100 mL of CH_2Cl_2 was added 0.85 g (3.9 mmol) of $Zn(OAc)_2$ in 50 ml MeOH. The mixture was stirred and refluxed for 10 h. The solvent was diluted with CH_2Cl_2 and washed with water. The organic phase was separated, then dried over Na_2SO_4. The solvent was removed *in vacuo* and recrystallization from CH_2Cl_2–MeOH gave the title compound (0.19 g). Yield: 95%. ^{1}H NMR (CD_2Cl_2, 10 mM, 295 K): δ 0.89 (t, 3H, J = 6.8, CH_{3h}), 0.97 (t, 6H, J = 6.8, CH_{3h}), 1.26–1.54 (m, 24H, CH_{2d-f}), 1.70 (m, 6H, CH_{2c}), 1.91 (quint, 2H, J = 6.8, CH_{2b}), 2.06 (quint, 4H, J = 6.8, CH_{2b}), 4.14 (t, 2H, J = 6.4, CH_{2a}), 4.31 (t, 4H, J = 6.4, CH_{2a}), 4.52 (br, 2H, pyrazole-$H_{3,5}$), 7.18 (d, 4H, overlapping of pyrrole-H_β with ArH_m), 7.30 (d, 4H, J = 8.3, ArH_m), 8.06 (d, 2H, J = 8.3, ArH_o), 8.14 (d, 4H, J = 8.3, ArH_o), 8.64 (d, 2H, J = 4.7, pyrrole-H_β), 8.91, 8.94 (each d, 2H × 2, J = 4.7 Hz, pyrrole-H_β). Anal. calc. for $C_{65}H_{75}N_6O_3Zn$: C 74.09, H 7.17, N 7.98. Found: C 73.80, H 7.07, N 7.85% Mp = 145–150 °C.

[5-(3,5-Dimethylpyrazol-4-yl)-10,15,20-tris(*p*-octyloxyphenyl)porphyrinato] zinc(II) (Zn2). This compound was synthesized as for **Zn1** using **$H_2$2**. Yield: 98%. ^{1}H NMR (pyridine-d_5): δ 0.88 (t, 9H, J = 6.6, CH_{3h}), 1.20–1.40 (m, 24H, CH_{2d-f}), 1.57 (br, 6H, CH_{2c}), 1.93 (quint, 6H, J = 6.8, CH_{2b}), 2.51 (s, 6H, pyrazole-$Me_{3,5}$), 4.22 (t, 6H, J = 6.5, CH_{2a}), 7.46 (m, 6H, ArH_m), 8.36 (m, 6H, ArH_o), 9.30 (m, 6H, pyrrole-H_β), 9.41 (d, 2H, J = 4.6 Hz, pyrrole-H_β). Anal. calc. for $C_{67}H_{78}N_6O_3Zn \cdot MeOH$: C 73.39, H 7.43, N 7.55. Found: C 73.72, H 7.09, N 7.39%. Mp > 300 °C.

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10 Almost the same spectra were obtained in $CDCl_3$ or toluene-d_5. We used CD_2Cl_2 here to avoid the overlapping of the residual solvent peak with aryl proton peaks around 7.2 ppm.

11 $\Delta\delta$ is defined as $\Delta\delta = \delta$(metal free porphyrin) − δ(zinc(II) complex).

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