Control of *Face-to-face* and Extended Aggregations of Crown Ether-Appended Metalloporphyrins

Hideyuki Shinmori,*[a] Yuzo Yasuda,[a] and Atsuhiro Osuka*[a]

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Metalloporphyrins bearing two crown ether moieties (benzo-15-crown-5) at the 5- and 15-postions have been prepared by condensation of 4′-formyl-benzo-15-crown-5 with either unsubstituted or *meso*-aryl-substituted dipyrromethanes, followed by oxidation and metallation. The *meso*-*meso*-coupled Zn^{II} diporphyrin **Zn4** was prepared by the oxidative coupling of **Zn1** with $AgPF_6$. UV/vis, fluorescence, and ^1H NMR spectroscopic studies revealed that addition of K^+ and Rb^+ to solutions of monomeric porphyrin derivatives **M1** (M = 2 H, Zn, Co, Ni, Pd, Cu) in $CHCl_3$:MeCN (2:1 v/v) induced *face-to-face* dimerization with high stability constants (ca. 10^{15}–10^{19} M^{-3}). ^1H NMR analysis showed that the two **Zn1** molecules in the *face-to-face* dimer were packed more closely than in TPP-type Zn^{II} porphyrin bearing four crown ethers (Krishnan et al, *J. Am. Chem. Soc.* **1982,** *104*, 3643), but such dimerization was hardly detected for 10,20-diphenylated Zn^{II} porphyrin **Zn2**, probably due to steric hindrance exerted by the *meso* phenyl groups. *meso*-Monoarylated Zn^{II} porphyrin **Zn3** exhibited a comparably large stability constant for formation of the *face-to-face* dimer with the *meso*-aryl substituents pointing outward. Coordination of 4-dimethylaminopyridine to Co^{II} porphyrin was shown to be stronger than the interaction of K^+ with the crown ether, thereby dissociating the *face-to-face* dimer $(\mathbf{Co1})_2$ into six-coordinated monomeric Co^{II} porphyrin **5**. The diporphyrin **Zn4** formed extended linear aggregates upon addition of K^+ and Rb^+, owing to the divergent disposition of the crown ether substituents.

Introduction

Molecular assembly by means of intermolecular interactions have been of wide interest as a means for constructing large molecular architectures quickly and efficiently,[1,2] but control of these assembling process is not necessarily easy. Among many molecules involved in assemblies, porphyrin is an attractive component because of its fascinating photophysical,[3,4] electrochemical, catalytic,[5] and geometrical properties.[6–10] Porphyrin assemblies are also interesting in terms of their possible relevance to important biological proteins such as the photosynthetic reaction center, light-harvesting complexes,[11] and cytochromes.[12]

Here we report that K^+-induced dimerization of benzo-15-crown-5-appended metalloporphyrins can be controlled by the introduction of peripheral substituents and the choice of central metals in the porphyrin core, and by the addition of a ligand capable of coordinating to the central metal. We also report that a skeletal change from porphyrin monomer to *meso*-*meso*-linked diporphyrin results in a dramatic change in the manner of assembly, from *face-to-face* dimerization to an extended aggregation into a linear supramolecular network by virtue of the divergent disposition of the crown ethers. Krishnan et al. have reported[9] the K^+-induced *face-to-face* dimerization of Zn^{II} 5,10,15,20-tetrakis(benzo-15-crown-5)porphyrin (**ZnTCP**), with a stability constant of ca. 10^{23} M^{-5}. It has been suggested that cooperative interaction between the crown ethers and K^+ gives rise to such a large stability constant. The stability constant therefore decreases with a decrease in the number of the crown ethers: 10^{16} M^{-4} for Zn^{II} 5,10,15-tris(benzo-15-crown-5)-20-phenylporphyrin, and below noticeable levels for Zn^{II} 5,15-bis(benzo-15-crown-5)-10,20-diphenylporphyrin and Zn^{II} 5-(benzo-15-crown-5)-10,15,20-triphenylporphyrin.

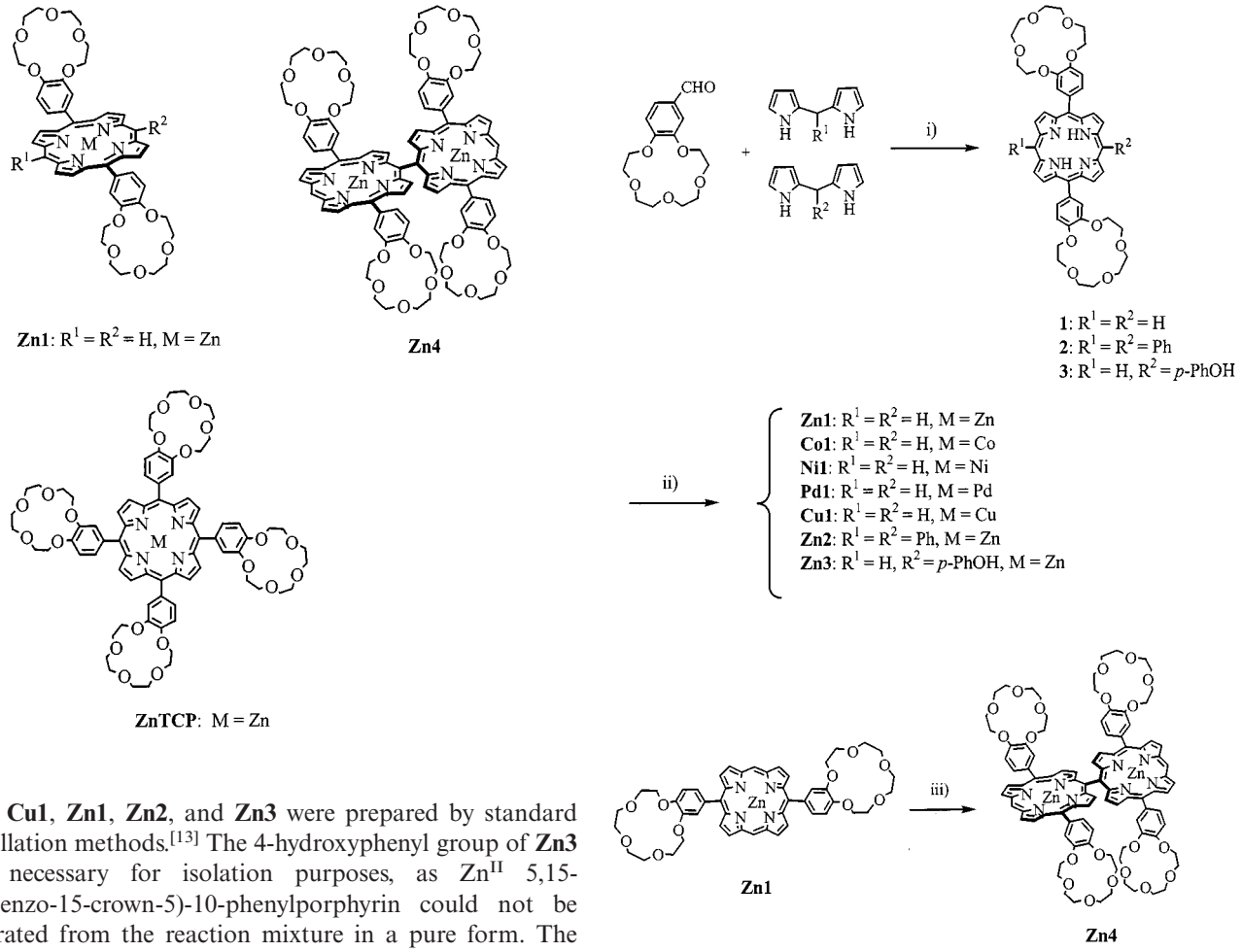
In this paper we focus on the dimerization and aggregation behavior of Zn^{II}-5,15-bis(benzo-15-crown-5)porphyrin **Zn1** and *meso*-*meso*-linked Zn^{II} diporphyrin **Zn4**, which lack *meso*-phenyl substituents. As described below, **Zn1** shows the larger stability constant for formation of *face-to-face* dimer, despite there being only two crown ethers available for aggregation.

Results and Discussion

Synthesis of Crown Ether-Appended Porphyrins 1–3 and *meso*–*meso*-Coupled Diporphyrin Zn4

Synthetic routes to the crown ether-appended porphyrins **1**, **2**, and **3** and the *meso*-*meso*-linked Zn^{II} diporphyrin **Zn4** are shown in Scheme 1. Metal complexes such as **Co1**, **Ni1**,

[a] Department of Chemistry, Graduate School of Science, Kyoto University,
Kyoto 606-8502, Japan
Fax: (internat.) + 81-75/753 3970
E-mail: shinmori@kuchem.kyoto-u.ac.jp



Scheme 1. Synthesis of crown ether-appended porphyrin and diporphyrin: i) $BF_3{\cdot}Et_2O$, $CHCl_3$ then DDQ; ii) $M(OAc)_2$, $CHCl_3$/MeOH; iii) $AgPF_6$/MeCN, $CHCl_3$/MeOH

Pd1, **Cu1**, **Zn1**, **Zn2**, and **Zn3** were prepared by standard metallation methods.[13] The 4-hydroxyphenyl group of **Zn3** was necessary for isolation purposes, as Zn^{II} 5,15-bis(benzo-15-crown-5)-10-phenylporphyrin could not be separated from the reaction mixture in a pure form. The *meso*-*meso*-linked diporphyrin **Zn4** was obtained in 13% yield by treatment of **Zn1** with $AgPF_6$.[10]

Face-to-face Dimerization of Crown Ether-Appended Porphyrins

While addition of Na^+ ions to a solution of **Zn1** in $CHCl_3$/MeCN (2:1 *v*/*v*) did not induce any significant UV/vis or fluorescence spectral changes, addition of K^+ ions caused a noticeable blue shift of the Soret band from 415 to 396 nm, with an isosbestic point at 404 nm (Figure 1),[14] as well as a monotonous decrease in the fluorescence intensity (Figure 2). The fluorescence quantum yields of **Zn1** and **Zn1** plus K^+ ions (7.6×10^{-5} M) determined relative to ZnTPP (0.03)[15] are 0.022 and 0.004, respectively. These spectral changes can be explained in terms of the formation of *face-to-face* dimer $(\mathbf{Zn1})_2$, which was also identified by ^{1}H NMR spectroscopy (Figure 3). The ^{1}H NMR spectrum of $(\mathbf{Zn1})_2$ showed sharp signals that could be assigned to two kinds of *meso*-H signals (at δ = 10.27 and 6.73) and four kinds of β-H signals (at δ = 9.43, 8.89, 8.26, and 7.38) in the aromatic region, indicating that $(\mathbf{Zn1})_2$ had adopted a slipped *face-to-face* structure as shown in Scheme 2. The observed different chemical shifts [inner protons (*i*) and outer protons(*o*)] for the two *meso*-H and upfield-shifted β-H protons were consistent with this slipped geometry. In addition, the aromatic proton H_a in the phenyl bridge was shifted downfield and the H_b and H_c were shifted upfield, probably suggesting fixation of the crown ether-appended phenyl bridge as shown in Scheme 2, with the H_a proton located outward and the H_b and H_c protons located inward with respect to the complexed porphyrin counterpart. This means that $(\mathbf{Zn1})_2$ was fixed in a *syn* conformation with both crown loops on one side of the porphyrin plane, because each aromatic proton signal (H_a, H_b, and H_c) was of one kind in the ^{1}H NMR spectrum. The stoichiometry of the **Zn1**−K^+ ion complex was confirmed by a Job plot[16] of the absorbance at 396 nm against [**Zn1**]/([**Zn1**]+[K^+]) (Figure 4), which gave a maximum at 0.50 mol/mol, indicating 1:1 or 2:2 stoichiometry. The above ^{1}H NMR results supported the view that the stoichiometry of the **Zn1**−K^+ ion complex was 2:2. The changes in the intensity of the Soret band at 415 nm and in the fluorescence intensity of **Zn1** at 640 nm upon addition of alkali metal ions (Na^+, K^+, Rb^+, and Cs^+) are depicted in Figure 5. Only marginal effects were seen for the addition of Na^+ and Cs^+ ions, while intense changes were observed for Rb^+ ions. However, the strongest influence was noted for K^+ ions. A slightly enhanced fluorescence intensity upon addition of

Na^+ ions may indicate suppression of aggregation owing to the positive charge arising from complexed Na^+. Analysis of the metal-binding profile by a nonlinear least-squares method gave the stability constants (K) 2.2 ± 0.3 × 10^{18} M^{-3} for **Zn1**-K^+ and 4.2 ± 0.2 × 10^{15} M^{-3} for **Zn1**-Rb^+.

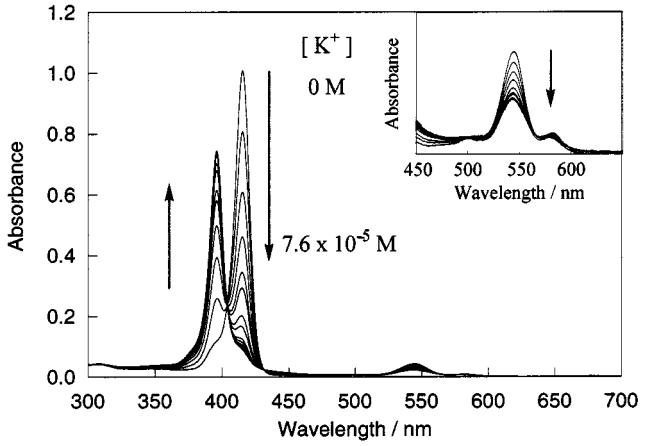


Figure 1. Absorption spectra of **Zn1** on addition of $KClO_4$ in $CHCl_3$/MeCN, 2:1 at room temperature; [**Zn1**] = 1.9 × 10^{-6} M

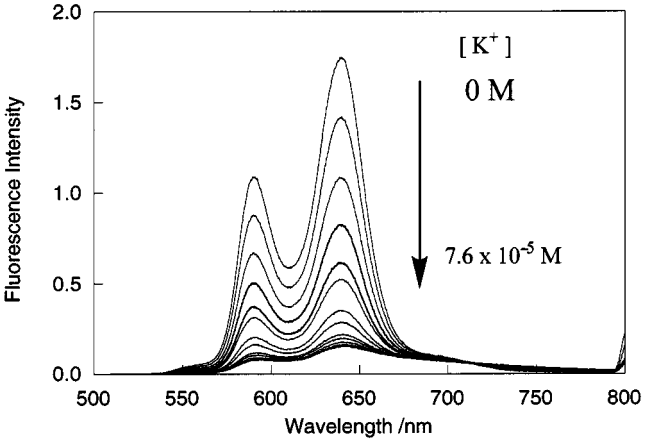


Figure 2. Fluorescence spectra of **Zn1** on addition of $KClO_4$ in $CHCl_3$/MeCN, 2:1 at room temperature; [**Zn1**] = 1.9 × 10^{-6} M., λ_{ex} = 404 nm

$$2\ \mathbf{Zn1} + 2\ M^+ \rightarrow (\mathbf{Zn1})_2[M^+]_2 \quad (1)$$

Similar UV/vis spectral changes were observed for **1**, **Co1**, **Ni1**, **Pd1**, and **Cu1**. The stability constants (K) with K^+ were determined from plots of K^+ concentration against ΔA in the same way (Figure 6), and the results are summarized in Table 1. The stability constants are, at 10^{18} M^{-3}, several orders of magnitude greater than those observed in the interaction between the crown ether and K^+,[17] suggesting that there are additional interactions that favor *face-to-face* dimerization. A much larger stability constant (≈ 10^{23} M^{-5}) was reported[9] for **ZnTCP** and was ascribed to cooperative interaction of the four crown ether binding sites. However, when we consider the relative

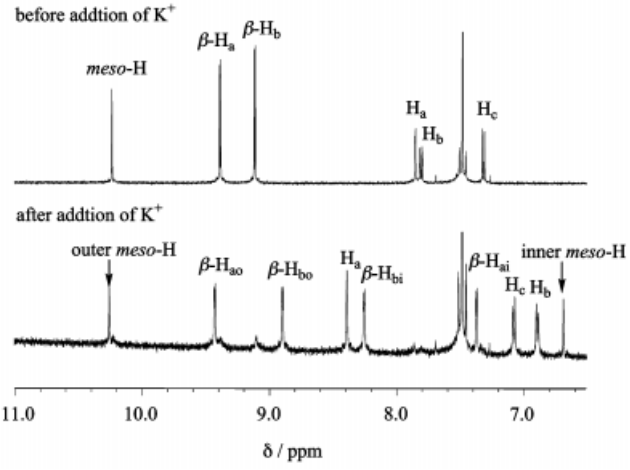
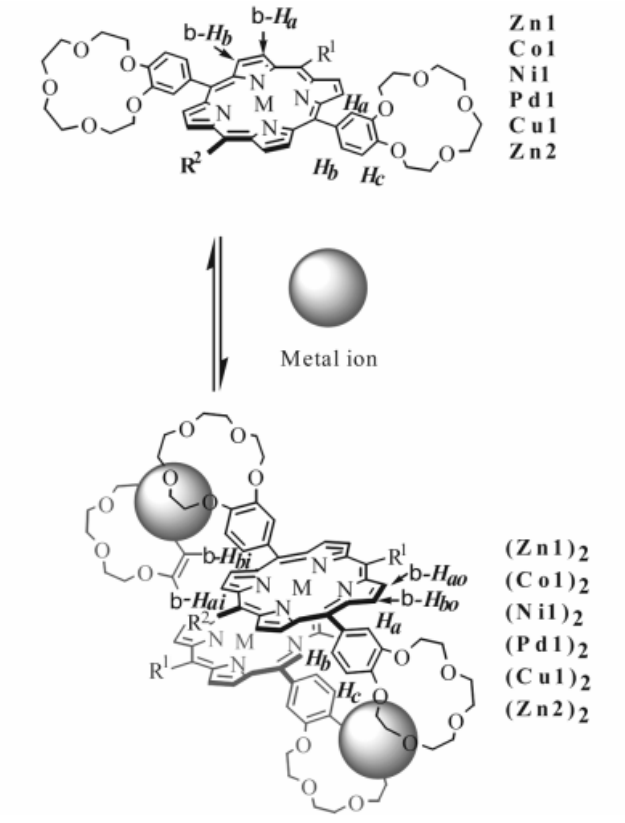


Figure 3. ^1H NMR spectra of **Zn1** (top) and **Zn1** plus $KClO_4$ (bottom) in $CDCl_3/CD_3OD$, 2:1 at room temperature; [**Zn1**] = 1.0 mM, [$KClO_4$] = 2.0 mM



Scheme 2. Proposed structure of porphyrin dimers induced by metal ion

stability constants *per binding site consisting of two crown ethers and one K^+ ion*, for which the value of ≈10^6 M^{-1} can be derived for **ZnTCP**, and that for **Zn1**, which we determined to be ≈10^9 M^{-1}, the latter is 10^3 times larger. One possible explanation for this enhancement may be that there is less steric hindrance in the *face-to-face* dimerization for **Zn1** than for **ZnTCP**. It has been demonstrated well that π-π interactions are strongest at a rather close approach (ca. 3.4−3.6 Å) of the interacting π-planes, and these are very

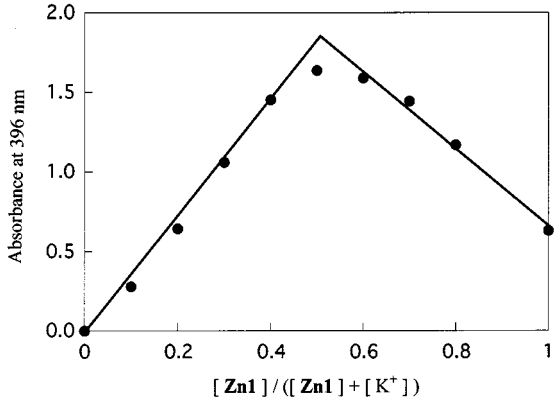


Figure 4. Job plot; [**Zn1**] + [K^+] = 1.1×10^{-4} M

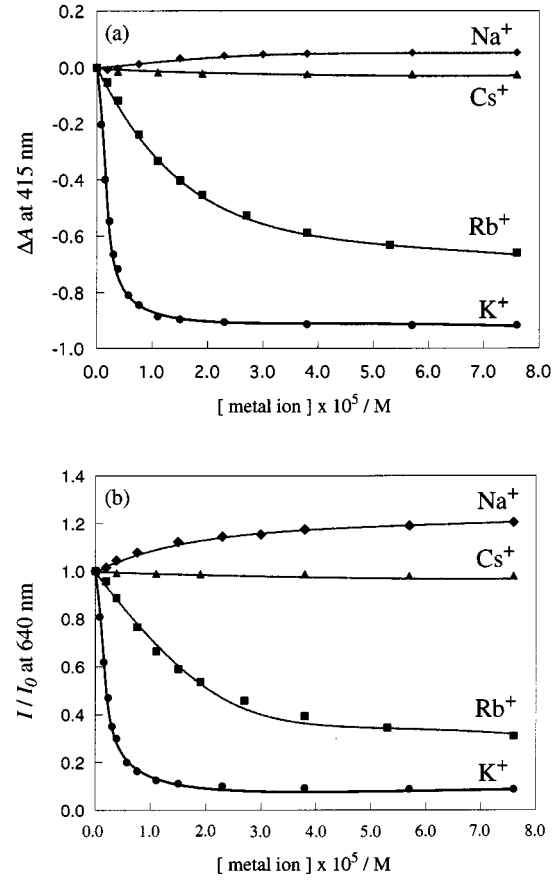


Figure 5. Plots of [metal ion] against ΔA at 415 nm (a) and I/I_0 at 640 nm (b) for **Zn1** in $CHCl_3$/MeCN, 2:1 at room temperature; [**Zn1**] = 1.9×10^{-6} M, λ_{ex} = 404 nm

sensitive to geometric changes.[18] In view of this, bis(5,15-benzo-15-crown-5)porphyrin systems such as **Zn1** may be favorable for π-π interactions, owing to their lack of two *meso*-phenyl substituents, which exert some steric hindrance. In line with this, the observed upfield chemical shift changes, Δδ, of the peripheral β-protons in **Zn1** were larger (2.01 ppm for β-H_{ai} and 0.86 ppm for β-H_{bi}) than those of **ZnTCP** (Δδ; 0.41 and 0.25 ppm for β-H). These results suggested that the interporphyrin distance was shorter in (**Zn1**)$_2$ than in the dimer of **ZnTCP**, and that additional cooperative π-π interaction was giving rise to the enhancement of the stability constant of (**Zn1**)$_2$ per binding site.

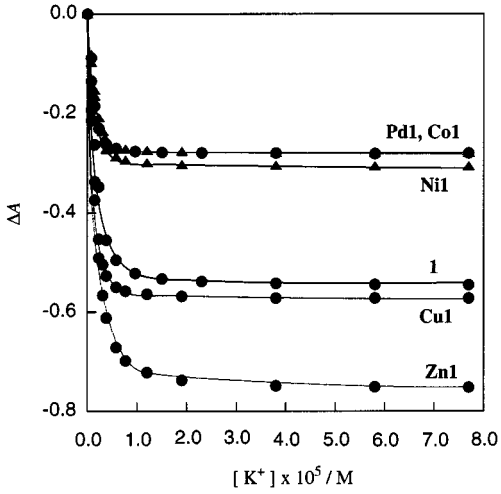


Figure 6. Plots of [K^+] against ΔA for crown ether-appended metalloporphyrins in $CHCl_3$/MeCN, 2:1 at room temperature; [Metalloporphyrins] = 1.9×10^{-6} M

Table 1. Stability constants of crown ether-appended metalloporphyrins with potassium ion

Metalloporphyrins	$K \times 10^{18}$ M^{-3}
1	1.9 ± 0.1
Zn1	2.2 ± 0.3
Co1	3.3 ± 0.9
Ni1	3.5 ± 0.5
Pd1	1.7 ± 0.9
Cu1	18.0 ± 4.8

We next examined the dimerization behavior of **Zn2** and **Zn3**. Addition of K^+ ions to a solution of **Zn2** in $CHCl_3$/MeCN (2:1) induced no significant change in the UV/vis and fluorescence spectra (Figure 8), consistently with Krishnan's results.[9] The fluorescence quantum yields of **Zn2** and **Zn2** plus K^+ ions (2.0×10^{-4} M) determined relative to ZnTPP (0.03)[15] were 0.020 and 0.020, respectively This result also highlighted the sensitivity of this dimerization towards steric factors, showing that the introduction of the 10,20-diphenyl substituents posed some steric congestion that suppressed the *face-to-face* dimerization. In contrast, addition of K^+ ions to a solution of **Zn3** in $CHCl_3$/MeCN (2:1) caused a blue shift of the Soret band from 422 to 403 nm, with an isosbestic point at 411 nm (Figure 7), as well as a decrease in the fluorescence intensity, indicating the assembly of a *face-to-face* diporphyrin (**Zn3**)$_2$ similar to that observed for **Zn1**. The fluorescence quantum yields of **Zn3** and **Zn3** plus K^+ ions (9.0×10^{-5} M) determined relative to ZnTPP (0.03)[15] were 0.029 and 0.013, respectively. Analysis of a plot of K^+ concentration against ΔA for **Zn3** (Figure 8) revealed the stability constant to be $1.3 \pm 0.3 \times 10^{17}$ M^{-3}, similar to the values for the 5,15-bis(benzo-15-crown-5)porphyrin systems. This

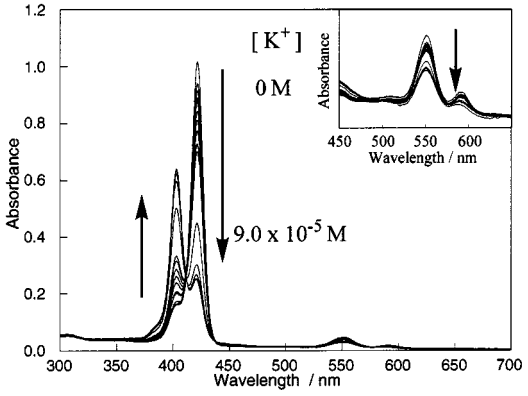


Figure 7. Absorption spectra **Zn3** on addition of $KClO_4$ in $CHCl_3$/MeCN, 2:1 at room temperature; [**Zn3**] = 1.9×10^{-6} M

dimerization process was also studied by ^{1}H NMR (Table 2), which revealed a large upfield shift of the *meso*-H signal from δ = 10.13 to δ = 6.84, combined with a splitting of the β-H signals: two β-H signals were observed at high-field chemical shifts (δ = 8.22 and 7.44) while another set of β-H signals were shifted only slightly upfield, appearing at δ = 9.02 and δ = 8.74. These results were consistent with the formation of a slipped, offset *face-to-face* dimer **(Zn3)**$_2$, in which the *meso*-aryl substituents were directed outward to avoid steric hindrance. It may therefore be concluded that K^+ ions can trigger the dimerization

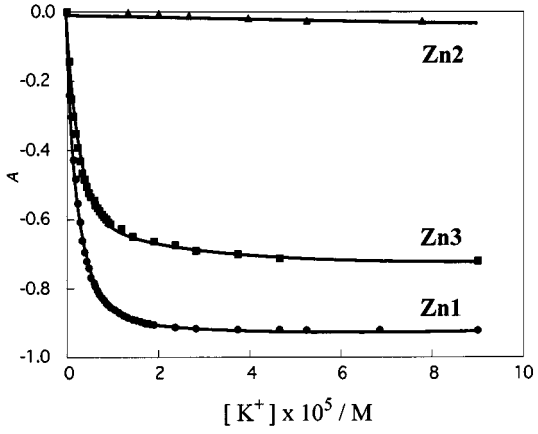


Figure 8. Plots of [K^+] against Δ*A* for **Zn1** at 415 nm; **Zn2** at 425 nm, and **Zn3** at 422 nm in $CHCl_3$/MeCN, 2:1 at room temperature; [**Zn1**] = [**Zn2**] = [**Zn3**] = 1.9×10^{-6} M

of5,15-bis(benzo-15-crown-5) Zn^{II}-porphyrin in a restricted offset geometry without a substantial reduction in the stability constant.

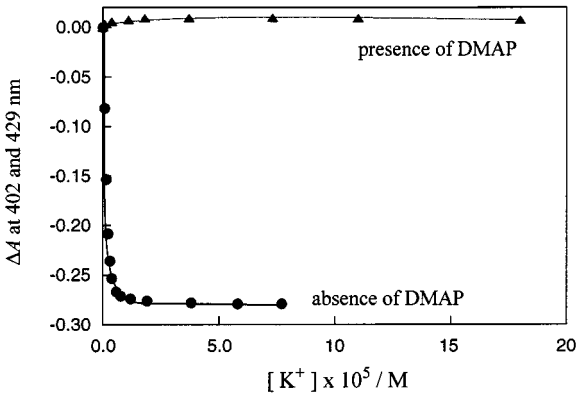


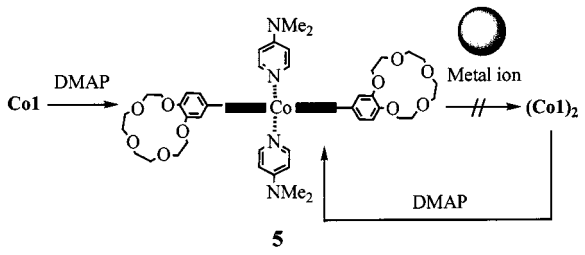
Figure 9. Plots of [K^+] against Δ*A* for **Co1** in the absence and presence of DMAP in $CHCl_3$/MeCN, 2:1 at room temperature; [**Co1**] = 1.9×10^{-6} M, [DMAP] = 0 or 2.0×10^{-2} M

Dimerization Control by Coordination at the Central Metal

In the case of six-coordinated metalloporphyrins such as **Co1**,[19] the K^+ ion-induced dimerization may be competitive with coordination of the central metal atom. We thus examined the dimerization behavior of **Co1** in the presence of nitrogen-containing ligands. As seen with **Zn1**, addition of K^+ ions to **Co1** caused a blue shift of the Soret band from 402 to 389 nm, with an isosbestic point at 395 nm, as a result of *face-to-face* dimer-formation ($K = 3.3 \pm 0.9 \times 10^{18}$ M^{-3}). In the presence, on the other hand, of 2.0×10^{-2} M 4-dimethylaminopyridine (DMAP), the UV/vis spectrum of **Co1** showed no change upon addition of K^+ ions (Figure 9), indicating that *face-to-face* dimer-formation was completely inhibited by 2.0×10^{-2} M DMAP, probably due to the both-sides coordination of DMAP to Co^{II} porphyrin (Scheme 3). Interestingly, addition of DMAP to the *face-to-face* dimer of **Co1** in $CHCl_3/CH_3CN$ induced the monomerization of **(Co1)**$_2$ to **5**, through coordination of two DMAP molecules. This transformation can be followed by the spectral changes, including a Soret band red shift from 389 to 429 nm (Figure 10). The final absorption spectrum was identical with that of six-coordinated **Co1**.

Table 2. ^{1}H NMR spectroscopic data for **Zn1−3**

Compound	Chemical shifts (δ values)			
	absence of K^+		presence of K^+	
	meso-H	β-H	*meso*-H	β-H
Zn1	10.24	9.39, 9.12	10.27, 6.73	9.43, 8.89, 8.26, 7.38
Zn2	–	8.93, 8.87	–	8.92, 8.86
Zn3	10.13	9.33, 9.05, 8.95, 8.94	6.84	9.02, 8.74, 8.22, 7.44



Scheme 3. Complexation behavior of **Co1**

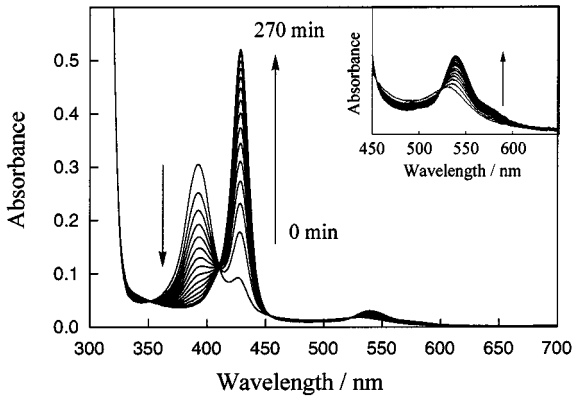


Figure 10. Change over time of absorption spectra of **Co1** plus K^+ on complexation of DMAP in $CHCl_3$/MeCN, 2:1 at room temperature; [**Co1**] = 1.9×10^{-6} M, [$KClO_4$] = 3.8×10^{-5} M, [DMAP] = 2.0×10^{-2} M

Extended Molecular Assembly of Porphyrin

The UV/vis spectral changes of **Zn4** upon addition of K^+ ions were more complicated (Figure 11). In the absence of metal ion, **Zn4** exhibited split Soret bands due to exciton coupling, at 421 and 453 nm.[10] On addition of K^+ ions up to 1.0×10^{-5} M, the intensities of the Soret band at 421 and 453 nm were decreased, and further addition resulted in a slight red shift of the Soret band to 423 from 421 nm, followed by an increase in its absorbance and a slight blue

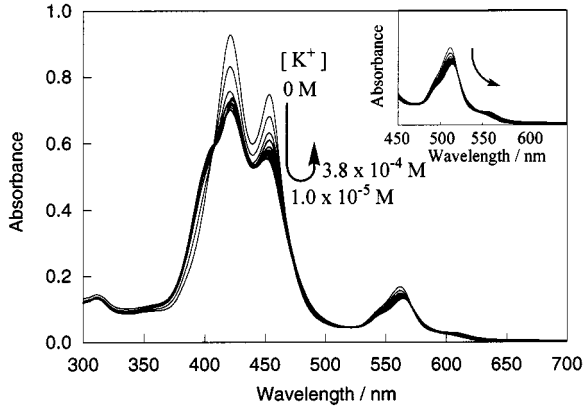


Figure 11. Absorption spectra of **Zn4** on addition of $KClO_4$ in $CHCl_3$/MeCN, 2:1 at room temperature; [**Zn4**] = 3.8×10^{-6} M

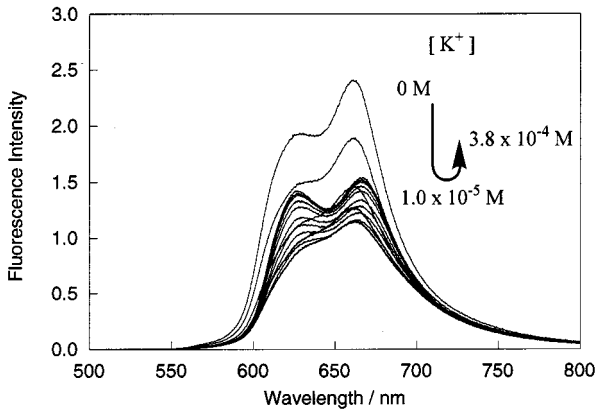


Figure 12. Fluorescence spectra of **Zn4** on addition of $KClO_4$ in $CHCl_3$/MeCN, 2:1 at room temperature; [**Zn4**] = 3.8×10^{-6} M, λ_{ex} = 408 nm

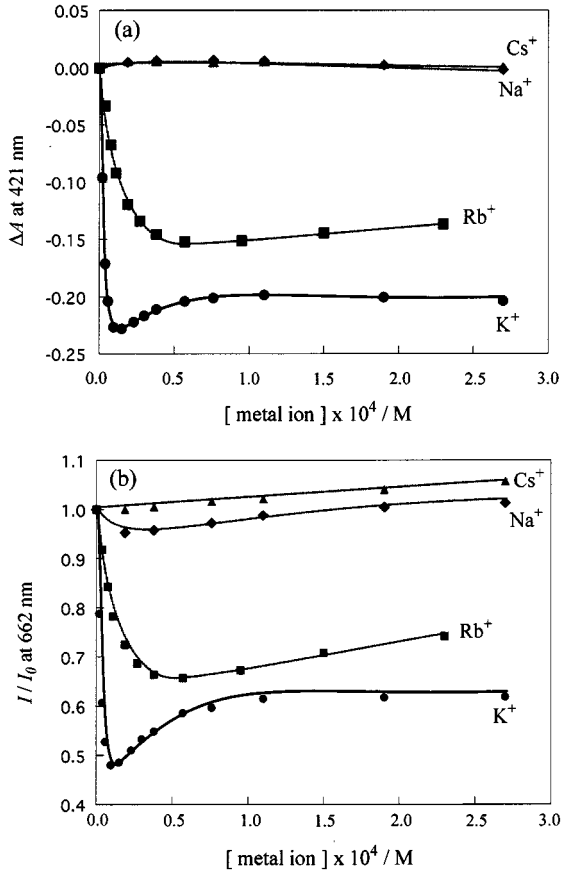
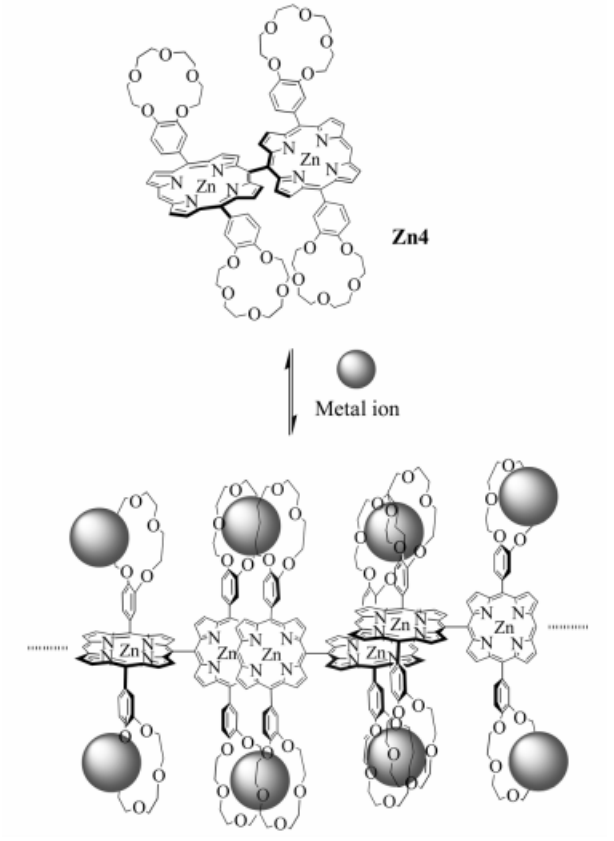


Figure 13. Plots of [metal ion] against ΔA at 421 nm (a) and I/I_0 at 662 nm (b) for **Zn4** in $CHCl_3$/MeCN, 2:1 at room temperature; [**Zn4**] = 3.8×10^{-6} M, λ_{ex} = 408 nm

shift of the Soret band to 451 from 453 nm, followed in turn by an decrease in its absorbance. In the course of these changes, a shoulder appeared at the high-energy side of the Soret band, with an isosbestic point at 408 nm. The fluorescence intensity changed in a complicated manner (Figure 12). On addition of K^+ ions up to 1.0×10^{-5} M, the fluorescence intensity at 628 (shoulder) and 662 nm was reduced, and further addition resulted in a slight shift of the

emission band to 626 from 628 nm (shoulder) and to 666 from 662 nm, followed by an increase in its fluorescence. The fluorescence quantum yields of **Zn1** and **Zn1** plus K^+ ions determined relative to ZnTPP (0.03)[15] were 0.030, 0.009 ($[K^+] = 1.0 \times 10^{-5}$ M), and 0.012 ($[K^+] = 3.8 \times 10^{-4}$ M), respectively. Similar UV/vis and fluorescence spectral behavior was observed upon addition of Rb^+ ions, but not on addition of Cs^+ ions or Na^+ ions. Plots of $[K^+]$ against ΔA at 421 nm and I/I_0 at 662 nm for **Zn4** are shown in Figure 13, indicating a steep decrease in intensity upon addition of potassium ions up to 1.0×10^{-5} M, followed by a slight restoration upon further addition. These changes were in contrast to a rather monotonous and saturated fluorescence intensity decrease of **Zn1** on addition of potassium ions (Figure 5). In the UV/vis study, appearance of a shoulder on the high-energy side of the Soret band suggested the formation of *face-to-face* stacked diporphyrin, as for **Zn1**. It was therefore plausible that the intermolecular interaction mode of the appended crown ether with potassium ion might be the same for **Zn1** and **Zn4**, but the resultant molecular architectures for **Zn1** and for **Zn4** were entirely different. Whereas the complexation between two crown ether sites and K^+ ion resulted in *face-to-face* dimerization in the case of **Zn1**, such self-complementary complexation was impossible for **Zn4**, which thus tended to prefer linear extended aggregation. The observed complicated profiles of the UV/vis spectral and fluorescence intensity changes for **Zn4** on addition of K^+ ions indicated multistage equilibria. The initial steep decrease in fluorescence intensity for complexation of **Zn4** with K^+ ion (Figure 13b) might suggest fluorescence quenching originating from the formation of the complexed *face-to-face* diporphyrin in **Zn4**. Subsequent slight increase in the fluorescence intensity might be caused by the interaction between the crown ethers at the edges of the linear aggregate and metal ions. A result in favor of this interpretation is to be found in Figure 5b, in which the fluorescence intensity was enhanced by interaction between Na^+ ions and crown ether sites in **Zn1**. Consistently with the proposed polymeric structure, the ^1H NMR spectrum of **Zn4** (1.0 mM) became very broad on addition of potassium ions, and no assignment of signals was possible. The polymeric nature of the aggregate formed from **Zn4** was confirmed by a light-scattering measurement, which indicated a molecular weight of approximately 10^5 for the aggregate, corresponding to an aggregation number of ca. 50 (Scheme 4).



Scheme 4. Possible structure of metal-assisted supramolecular assembly of **Zn4**

Conclusions

It has been demonstrated that strong *face-to-face* dimerization of 5,15-bis(benzo-15-crown-5) metalloporphyrins was effected through self-complementary interactions between K^+ ion and the two crown ethers and additional π-π interactions between the sterically uncongested metalloporphyrins. The dimer formation was found to be particularly sensitive to steric effects at the *meso*-position, which could be used for construction of a conformationally well defined dimer from **Zn3**. Moreover, dimer-to-monomer interconversion was achieved by addition of an excess of ligating base to $(\mathbf{Co1})_2$. Finally, a change in the aggregation mode, from dimerization to extended linear assembly, was observed for the *meso-meso* coupled diporphyrin **Zn4**.

Experimental Section

General: Starting chemicals were either prepared according to literature procedures or were commercially available and used without further purification. All solvents were purified and dried by standard methods. ^1H NMR spectra (500 MHz) were recorded on a JEOL ALPHA-500 FT NMR spectrometer, chemical shifts being referenced to tetramethylsilane ($\delta = 0.00$). FAB mass spectra were measured on a JEOL HX-110 spectrometer by the positive-FAB ionization method with a 3-nitrobenzyl alcohol matrix. MALDI-TOF mass spectra were measured on a Shimadzu/KRATOS MALDI 4 spectrometer. UV/vis spectra were measured on a Shimadzu UV-2400PC UV/vis recording spectrophotometer. Fluorescence spectra were measured on a Shimadzu RF-5300PC spectrofluorophotometer. Aggregation behavior was studied with a light-scattering photometer (Otsuka Electronics ELS-800).

Porphyrin 1: 4′-Formyl-benzo-15-crown-5 (420 mg, 1.23 mmol) and 2,2′-dipyrrylmethane (180 mg, 1.23 mmol) were dissolved in $CHCl_3$ (80 mL). After addition of $BF_3{\cdot}Et_2O$ (2.5 M in $CHCl_3$, 0.16 mL, 4.0 mmol) the solution was stirred for 2 h at room temperature under N_2 in the dark. DDQ (450 mg, 2.0 mmol) was then added to

the solution, and stirring was continued for an additional 2 h. After addition of triethylamine, the reaction mixture was passed through an alumina column. Chromatography on a silica gel column (eluent 10% MeOH in CH_2Cl_2) gave porphyrin **1** (101 mg, 0.12 mmol, 20%): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.29 (s, 2 H, *meso*-H), 9.38 (d, *J* = 5.0 Hz, 4 H, β-H), 9.12 (d, *J* = 5.0 Hz, 4 H, β-H), 7.89 (s, 2 H, Ar), 7.79 (d, *J* = 8.0 Hz, 2 H, Ar), 7.29 (d, *J* = 8.0 Hz, 2 H, Ar), 4.48−3.88 (m, 32 H, methylene), −3.10 (s, 2 H, inner NH). Mass (FAB): found 842.4, calcd. for $C_{48}H_{50}N_4O_{10}$, 842.9. UV/vis ($CHCl_3$/MeCN, 2:1): λ_{max} (logε) = 410 (5.54), 504 (4.24), 540 (3.87), 577 (3.72), and 636 (3.25) nm. Fluorescence ($CHCl_3$/MeCN, 2:1): λ_{max} = 636 and 696 nm. $C_{48}H_{50}N_4O_{10}$: calcd. C 68.39, H 5.98, N 6.65; found C 68.27, H 5.95, N 6.68.

Zn1: The porphyrin **1** (40 mg, 0.047 mmol) was dissolved in $CHCl_3$ (20 mL). A saturated solution of Zn^{II} acetate in MeOH was added to the solution, and the resulting mixture was refluxed for 3 h and poured into water. The reaction mixture was washed several times with water and dried over anhydrous $MgSO_4$. Chromatography on a silica gel column (eluent 10% MeOH in $CHCl_3$) gave porphyrin **Zn1** (37 mg, 0.041 mmol, 87%): ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 10.24 (s, 2 H, *meso*-H), 9.39 (d, *J* = 5.0 Hz, 4 H, β-H), 9.13 (d, *J* = 5.0 Hz, 4 H, β-H), 7.84 (s, 2 H, Ar), 7.82 (d, *J* = 8.0 Hz, 2 H, Ar), 7.30 (d, *J* = 8.0 Hz, 2 H, Ar), 4.49−3.87 (m, 32 H, methylene). Mass (FAB): found 906.5, calcd. for $C_{48}H_{48}N_4O_{10}Zn$, 906.3. UV/vis ($CHCl_3$/MeCN, 2:1): λ_{max} (logε) = 415 (5.73), 545 (4.35), and 583 (3.68) nm. Fluorescence ($CHCl_3$/MeCN, 2:1): λ_{max} = 590 and 640 nm. $C_{48}H_{48}N_4O_{10}Zn{\cdot}0.1H2O$: calcd. C 63.25, H 5.37, N 6.15; found C 63.02, H 5.29, N 6.08.

Co1: This compound was prepared from **1** and Co^{II} acetate in 90% yield according to the procedure outlined above for **Zn1**: Mass (FAB): found 899.3, calcd. for $C_{48}H_{48}N_4O_{10}Co$, 899.9. UV/vis ($CHCl_3$:MeCN = 2:1): λ_{max} (logε) = 402 (5.35), and 519 (4.18) nm. $C_{48}H_{48}N_4O_{10}Co{\cdot}0.5CH_2Cl_2$: calcd. C 61.81, H 5.25, N 5.95; found C 61.58, H 5.24, N 6.22.

Ni1: This compound was prepared from **1** and Ni^{II} acetate in 94% yield according to the procedure outlined above for **Zn1**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.92 (s, 2 H, *meso*-H), 9.17 (d, *J* = 5.0 Hz, 4 H, β-H), 8.98 (d, *J* = 5.0 Hz, 4 H, β-H), 7.61 (s, 2 H, Ar), 7.59 (d, *J* = 8.0 Hz, 2 H, Ar), 7.20 (d, *J* = 8.0 Hz, 2 H, Ar), 4.44−3.85 (m, 32 H, methylene). Mass (FAB): found 899.6, calcd. for $C_{48}H_{48}N_4O_{10}Ni$, 899.6. UV/vis ($CHCl_3$/MeCN, 2:1): λ_{max} (logε) = 404 (5.39), 516 (4.30), and 547 (3.93) nm. $C_{48}H_{48}N_4O_{10}Ni{\cdot}0.5H2O$: calcd. C 63.44, H 5.45, N 6.17; found C 63.49, H 5.31, N 6.19.

Pd1: This compound was prepared from **1** and Pd^{II} acetate in 71% yield according to the procedure outlined above for **Zn1**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.26 (s, 2 H, *meso*-H), 9.28 (d, *J* = 5.0 Hz, 4 H, β-H), 9.05 (d, *J* = 5.0 Hz, 4 H, β-H), 7.76 (s, 2 H, Ar), 7.74 (d, *J* = 8.0 Hz, 2 H, Ar), 7.27 (d, *J* = 8.0 Hz, 2 H, Ar), 4.48−3.87 (m, 32 H, methylene). Mass (FAB): found 947.3, calcd. for $C_{48}H_{48}N_4O_{10}Pd$, 947.4. UV/vis ($CHCl_3$/MeCN, 2:1): λ_{max} (logε) = 407 (5.36), 514 (4.37), and 545 (3.84) nm. $C_{48}H_{48}N_4O_{10}Pd{\cdot}1.3CH_2Cl_2$: calcd. C 55.97, H 4.83, N 5.37; found C 56.16, H 4.79, N 5.08.

Cu1: This compound was prepared from **1** and Cu^{II} acetate in 89% yield according to the procedure outlined above for **Zn1**: Mass (FAB): found 904.7, calcd. for $C_{48}H_{48}N_4O_{10}Cu$, 904.5. UV/vis ($CHCl_3$/MeCN, 2:1): λ_{max} (logε) = 406 (5.56), 528 (4.28), and 561 (3.57) nm. $C_{48}H_{48}N_4O_{10}Cu{\cdot}0.5CH_2Cl_2$: calcd. C 61.51, H 5.23, N 5.91; found C 61.58, H 5.15, N 5.72.

Porphyrin 2: 4′-Formyl-benzo-15-crown-5 (200 mg, 0.67 mmol) and 5-phenyldipyrromethane (150 mg, 0.67 mmol) were dissolved in $CHCl_3$ (50 mL). After addition of $BF_3{\cdot}Et_2O$ (2.5 M in $CHCl_3$, 0.1 mL, 2.5 mmol) the solution was stirred for 2 h at room temperature under N_2 in the dark. DDQ (230 mg, 1.0 mmol) was then added to the solution, and stirring was continued for an additional 2 h. After addition of triethylamine, the reaction mixture was passed through an alumina column. Chromatography on a silica gel column (eluent 10% MeOH in $CHCl_3$) gave porphyrin **2** (50 mg, 0.05 mmol, 15%): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.89 (d, *J* = 5.0 Hz, 4 H, β-H), 8.83 (d, *J* = 5.0 Hz, 4 H, β-H), 8.21 (d, *J* = 8.0 Hz, 4 H, Ar), 7.79 (s, 2 H, Ar), 7.76 (d, *J* = 8.0 Hz, 2 H, Ar), 7.75 (d, *J* = 8.0 Hz, 2 H, Ar), 7.29 (d, *J* = 8.0 Hz, 2 H, Ar), 7.24 (d, *J* = 8.0 Hz, 4 H, Ar), 4.44−3.86 (m, 32 H, methylene), −2.77 (s, 2 H, inner NH). Mass (FAB): found 996.2, calcd. for $C_{60}H_{58}N_4O_{10}$, 995.1. UV/vis ($CHCl_3$/MeCN, 2:1): λ_{max} (logε) = 417 (5.54), 510 (3.90), 540 4.23), 572 (3.70), and 646 (3.48) nm. Fluorescence ($CHCl_3$/MeCN, 2:1): λ_{max} = 650 and 713 nm. $C_{60}H_{58}N_4O_{10}$: calcd. C 72.42, H 5.87, N 5.63; found C 72.46, H 5.92, N 5.76.

Zn2: This compound was prepared from **2** in 93% yield according to the procedure outlined above for **Zn1**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.94 (d, *J* = 5.0 Hz, 4 H, β-H), 8.88 (d, *J* = 5.0 Hz, 4 H, β-H), 8.22 (d, *J* = 8.0 Hz, 4 H, Ar), 7.81 (s, 2 H, Ar), 7.76 (d, *J* = 8.0 Hz, 2 H, Ar), 7.75 (d, *J* = 8.0 Hz, 2 H, Ar), 7.27 (d, *J* = 8.0 Hz, 2 H, Ar), 7.19 (d, *J* = 8.0 Hz, 4 H, Ar), 4.48−3.87 (m, 32 H, methylene). Mass (FAB): found 10^{60}.1, calcd. for $C_{60}H_{56}N_4O_{10}$, 10^{58}.5. UV/vis ($CHCl_3$/MeCN, 2:1): λ_{max} (logε) = 425 (5.71), 557 (4.38), and 598 (4.11) nm. Fluorescence ($CHCl_3$/MeCN, 2:1): λ_{max} = 605 and 658 nm. $C_{60}H_{56}N_4O_{10}Zn$: calcd. C 68.08, H 5.33, N 5.29; found C 68.07, H 5.45, N 5.15.

Porphyrin 3: 4′-Formyl-benzo-15-crown-5 (1.0 g, 3.37 mmol), 2,2′-dipyrrylmethane (250 mg, 1.70 mmol), and 5-(4-hydroxyphenyl)dipyrromethane (405 mg, 1.70 mmol) were dissolved in $CHCl_3$ (400 mL). After addition of $BF_3{\cdot}Et_2O$ (2.5 M in $CHCl_3$, 0.9 mL, 23 mmol), the solution was stirred for 2 h at room temperature under N_2 in the dark. DDQ (1.36 g, 6.0 mmol) was then added to the solution, and stirring was continued for an additional 8 h. After addition of triethylamine, the reaction mixture was passed through an alumina column. Chromatography on a silica gel column (eluent 10% MeOH in CH_2Cl_2) gave porphyrin **3** (100 mg, 0.11 mmol, 7%): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.13 (s, 1 H, *meso*-H), 9.28 and 9.03 (d, *J* = 5.0 Hz, 4 H, β-H), 8.90 and 8.89 (d, *J* = 5.0 Hz, 4 H, β-H), 8.03 (d, *J* = 8.0 Hz, 2 H, Ar), 7.78−7.68 (m, 6 H, Ar and OH), 7.18 (d, *J* = 8.0 Hz, 2 H, Ar), 4.42−3.84 (m, 32 H, methylene), −3.01 (s, 2 H, inner NH). Mass (FAB): found 935.4, calcd. for $C_{54}H_{54}N_4O_{11}$, 935.0. UV/vis ($CHCl_3$/MeCN, 2:1): λ_{max} (logε) = 413 (5.53), 505 (3.90), 534 (4.23), 563 (3.70), and 637 (3.48) nm. Fluorescence ($CHCl_3$/MeCN, 2:1): λ_{max} = 647 and 707 nm. $C_{54}H_{54}N_4O_{11}{\cdot}0.9CH_2Cl_2$: calcd. C 65.21, H 5.56, N 5.53; found C 65.45, H 5.87, N 5.23.

Zn3: This compound was prepared from **3** in 95% yield according to the procedure outlined above for **Zn1**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.3 (s, 1 H, *meso*-H), 10.21 (s, 1 H, *meso*-H), 9.37 (d, *J* = 4.5 Hz, 2 H, β-H), 9.13 (d, *J* = 4.5 Hz, 2 H, β-H), 9.03 (d, *J* = 4.5 Hz, 2 H, β-H), 9.02 (d, *J* = 4.5 Hz, 2 H, β-H), 8.07 (d, *J* = 8.0 Hz, 4 H, Ar), 7.82 (s, 2 H, Ar), 7.76 (d, *J* = 8.0 Hz, 2 H, Ar), 7.27 (d, *J* = 8.0 Hz, 2 H, Ar), 7.22 (d, *J* = 8.0 Hz, 4 H, Ar), 4.48−3.87 (m, 32 H, methylene). Mass (FAB): found 999.5, calcd. for $C_{54}H_{52}N_4O_{11}Zn$, 998.4. UV/vis ($CHCl_3$/MeCN, 2:1): λ_{max} (logε) = 422 (5.71), 551 (4.38), and 590 (4.00) nm. Fluorescence ($CHCl_3$/MeCN, 2:1): λ_{max} = 600 and 650 nm. $C_{54}H_{52}N_4O_{11}Zn{\cdot}0.2CH_2Cl_2$: calcd. C 60.30, H 4.98, N 5.10; found C 60.31, H 5.24, N 4.82.

Diporphyrin Zn4: Porphyrin **Zn1** (50 mg, 0.06 mmol) was dissolved in 5% MeOH in $CHCl_3$ (100 mL). After addition of $AgPF_6$ (0.1 M in MeCN, 3.0 mL, 0.30 mmol), the solution was stirred for 8 h at room temperature in the dark. The reaction mixture was washed several times with water and dried over anhydrous $MgSO_4$. Chromatography on a silica gel column (eluent 10% MeOH in CH_2Cl_2) gave porphyrin **Zn4** (13 mg, 0.007 mmol, 13%): ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 10.37 (s, 2 H, *meso*-H), 9.52 (d, *J* = 5.0 Hz, 4 H, β-H), 9.02 (d, *J* = 5.0 Hz, 4 H, β-H), 8.62 (d, *J* = 5.0 Hz, 4 H, β-H), 7.89 (d, *J* = 5.0 Hz, 4 H, β-H), 7.80−7.67 (m, 8 H, Ar), 726 (d, *J* = 8.0 Hz, 4 H, Ar), 4.38−3.44 (m, 64 H, methylene). Mass (MALDI-TOF): found 1809.1, calcd. for $C_{96}H_{94}N_8O_{20}Zn_2$, 1810.6. UV/vis ($CHCl_3$/MeCN, 2:1): λ_{max} (log ε) = 421 (5.39), 453 (5.60), and 562 (4.65) nm. Fluorescence ($CHCl_3$/MeCN, 2:1): λ_{max} = 628 and 662 nm. $C_{96}H_{94}N_8O_{20}Zn_2 \cdot 6.5H_2O$: calcd. C 59.80, H 5.61, N 5.81; found C 60.05, H 5.39, 5.52.

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