Porphyrin Polygons: A New Synthetic Strategy for Cyclic Porphyrin Oligomers Utilizing a Porphyrin Double Decker Structure

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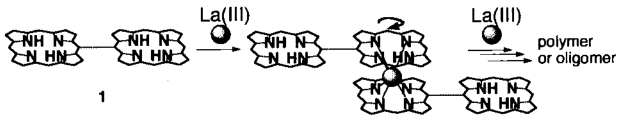
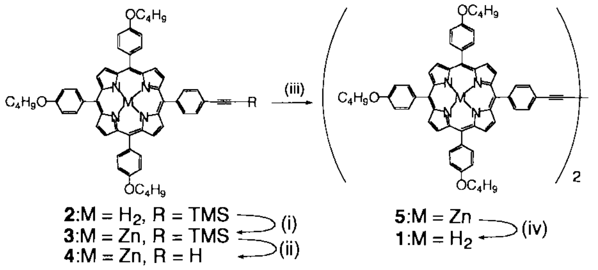
A novel synthetic scheme for constructing cyclic porphyrin oligomers is presented: bisporphyrin derivative **1** reacts with La(acac)$_3$ in 1,2,4-trichlorobenzene to yield porphyrin polygons, such as cyclic dimer $\mathbf{1}_2\cdot$2La(III) and cyclic trimer $\mathbf{1}_3\cdot$3La(III).

The design of porphyrin arrays toward artificial photosynthetic systems, molecular photonic devices, molecular containers or capsules is a hot challenging research area.[1–7] Such polymeric or oligomeric porphyrins have been prepared by either covalent linkage of monomeric porphyrins or programmed self-assembling methods. The pursuit of new schemes for preparing porphyrin arrays with defined structures which frequently lead to new photochemical and electrochemical properties has been paid much attention by many research groups.[1–7] For example, Sanders et al. demonstrated that template synthesis is a powerful scheme for cyclic porphyrin oligomers.[1a] Linear porphyrin arrays have been synthesized by Anderson et al.[1b–d] and Osuka et al.,[1g–i] independently. Recently, Hunter et al. showed an elegant self assembling approach toward cyclic oligomeric porphyrin rings utilizing a pyridine-appended cobalt porphyrin.[1e–f] Lindsey et al. reported that porphyrin arrays with double- and triple-decker porphyrin complexes are useful as novel candidates for a multibit information storage system because of their unique electrochemical characteristics.[7] Here we describe a new synthetic strategy for constructing cyclic porphyrin oligomers utilizing La(III) metal and porphyrin ligands complexation. It has been known that La(III) results in a double decker structure with porphyrins bearing four *meso*-aryl substituents by a simple treatment (e.g., refluxing of a reaction mixture).[8,9] It thus occurred to us that the reaction of La(III) with covalently-linked bisporphyrin should produce linear or cyclic oligomeric porphyrin arrays (Scheme 1).[10] This system is undoubtedly advantageous in producing porphyrin arrays because (i) the orientation of two porphyrin planes in a double decker complex is controlled by the inherent coordination geometry of La(III) and (ii) since the porphyrin ligands in the La(III) bis(porphyrinate)s can rotate in NMR time scale,[8–10] the porphyrin corners can adopt various angles, which is suitable for the polygon formation. These characteristics of La(III) coordination to porphyrin ligands have enabled us, for the first time, to synthesize a large variety of cyclic porphyrin oligomers from bisporphyrin **1**. As far as we are aware, this is the first example for the molecular design of double decker porphyrin-based cyclic porphyrin arrays.



Scheme 1.

Compound **1** was prepared from 5,10,15-tris(4-*n*-buthoxyphenyl)-20-[4-(trimethylsilylethynyl)phenyl]porphyrin according to Scheme 2 and identified by ^{1}H NMR and MALDI-TOFMS (MALDI = Matrix-Assisted Laser Desorption Ionization) spectral evidence and elemental analysis.[11] A solution of **1** (3.5 mmol dm^{-3} (condition A) or 7.0 mmol dm^{-3} (condition B)) and three equivalents of La(acac)$_3$ (acac = acetylacetonato) in 5 mL of 1,2,4-trichrolobenzene was heated at reflux temperature. The time course of the reaction between La(acac)$_3$ and **1** was monitored by GPC and MALDI-TOFMS. The reaction was terminated after 24 h and 14 h in condition A and condition B, respectively. Further addition of La(acac)$_3$ to this reaction mixture caused no GPC chromatogram change, indicating that unreacted freebase porphyrin no longer exists in the mixture and resultant oligomers have cyclic structures (vide infra). The typical GPC chromatograms are shown in Figure 1.



Scheme 2. (i) Zn(OAc)$_2$, CHCl$_3$-CH$_3$OH, 97 %, (ii) CsF, THF–CH$_3$OH, 66 %, (iii) Cu(OAc)$_2$, pyridine, 96%, (iv) TFA, THF, 90%.

The peaks which could be assigned to dimeric species (retention time 33.6 min) and trimeric species (retention time 31.0 min) in Figure 1A were isolated by size exclusion chromatography (Bio-beads SX-1, THF) and the samples were subjected to analysis by GPC and MALDI TOF MS spectroscopies (Figure 1). MALDI TOF MS spectra shows that these peaks are assignable to the cyclic structures, $\mathbf{1}_2\cdot$2La(III) (*m/z* 3688.36) and $\mathbf{1}_3\cdot$3La(III) (*m/z* 5532.1), respectively.[12] The trimer fraction showed a small, additional peak assignable to cyclic tetramer $\mathbf{1}_4\cdot$4La(III) (*m/z* 7376.6 ([M]$^+$ = 7376.06)), which was estimated to less than 10 mol% from GPC analysis (Figure 1D). The measurements of MALDI TOF MS for condition A established that the relative intensities of the peaks attributed to **1** (retention time 35.0 min), $\mathbf{1}_2\cdot$2La(III) and $\mathbf{1}_3\cdot$3La(III) is in a 1.0:2.5:1.0 ratio, respectively, in addition to a very small tetramer peak. Condition B featuring the higher feed concentration of **1** also yielded cyclic dimer, trimer and tetramer in a 2.6:1.0:1.0 ratio in addition to the peaks attributable to pentamer and hexamer. It is seen from Figure 1 and ^{1}H NMR spectra (vide infra) that no linear oligomeric porphyrin array remains both in the end of the reactions of condition A and con-

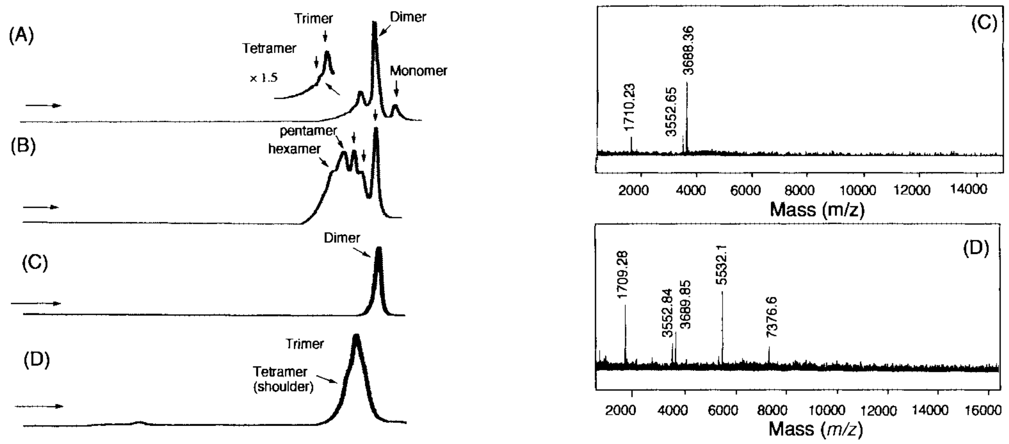


Figure 1. GPC chromatograms for the reaction mixture of La(acac)$_3$ and **1**: (A) condition A after 24 h, (B) condition B after 14 h, (C) second fraction of (A) ($\mathbf{1}_2$•2La(III)), and (D)first fraction of (A) ($\mathbf{1}_3$•3La(III) and a small amount of $\mathbf{1}_4$•4La(III)). GPC analysis was performed on a Shimadzu HPLC LC-9A with a TOSOH TSKgel G3000H$_{HR}$ and TOSOH TSKgel G4000H$_{HR}$. In MALDI TOF MS spectra, the fractions of (C) and (D) are shown.

dition B. Presumably, once linear $\mathbf{1}_n$•(n – 1)La(III) (n ≥ 2) is produced, the following intramolecular reaction between La(III) and freebase porphyrin to yield cyclic porphyrin arrays occurs in preference to the intermolecular reaction to yield linear porphyrin arrays under these reaction conditions.

We characterized cyclic dimer $\mathbf{1}_2$•2La(III) and trimer $\mathbf{1}_3$•3La(III) complexes by UV–vis and ^{1}H NMR spectroscopies. The λ_{max} of the Soret band in $\mathbf{1}_2$•2La(III) is slightly blue-shifted compared with that of **1** and the Q band is significantly broadened, which are characteristic of La(III) bis(porphyrinate)s.[8,9] The λ_{max} values of $\mathbf{1}_3$•3La(III) appear at 424, 518, 560, and 610 nm, which are comparable with those of $\mathbf{1}_2$•2La(III). In the ^{1}H NMR spectra of $\mathbf{1}_2$•2La(III),[12] it is confirmed that there is no pyrrole N–H proton assignable to freebase porphyrin (δ –2.54 ppm) and no mono-porphyrinated La(III)(acac)$_X$ species, whose proton signals should appear in higher magnetic field. These findings together with mass spectral evidence support our assertion that both the dimer and the trimer have the cyclic structures.

In conclusion, we have demonstrated a new synthetic strategy for constructing cyclic porphyrin arrays utilizing porphyrin dimerization with La(III). In this scheme, one can easily obtain porphyrin polygons, which should show multiple redox states. Electrochemical studies using these porphyrin oligomers are now in progress in our research group.

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10 We have tried to synthesize cyclic porphyrin oligomers by the reaction of **1** with Ce(acac)$_3$, because it is also known that Ce(acac)$_3$ results in a double decker structure with porphyrins. The reaction between Ce(acac)$_3$ and **1**, however, did not proceed at all under these reaction conditions. See recent references on Ce bis(porphyrinate) double decker complexes; a) M Takeuchi, T. Imada, and S. Shinkai, *Angew. Chem. Int. Ed.*, **37**, 2096 (1998). b) M. Takeuchi, T. Imada, and S. Shinkai, *Tetrahedron Lett.*, **39**, 7897 (1998). c) M. Ikeda, M. Takeuchi, A. Sugasaki, A. Robertson, T. Imada, and S. Shinkai, *Supramol. Chem.*, **12**, 321 (2000). d) M. Ikeda, T. Tanida, M. Takeuchi, and S. Shinkai, *Org. Lett.*, **2**, 1803 (2000). e) A. Sugasaki, M. Ikeda, M. Takeuchi, and S. Shinkai, *Angew. Chem. Int. Ed.*, **39**, 3839 (2000). f) K. Tashiro, K. Konishi, and T. Aida, *Angew. Chem., Int. Ed. Engl.* **36**, 856 (1997). g) K. Tashiro, T. Fujiwara, K. Konishi, and T. Aida, *Chem. Commun.*, **1998**, 1121. h) K. Tashiro, K. Konishi, and T. Aida, *J. Am. Chem. Soc.*, **122**, 7921 (2000).

11 **1**: Mp >300 °C, MALDI-TOFMS (CHCA) *m/z* 1709.23 ([M+H]$^+$ =1709.14). ^{1}H NMR (250 MHz, CDCl$_3$, TMS, 25 °C) δ –2.54 (s, 4H), 1.08–1.14 (m, 18H), 1.65–1.68 (m, 12H), 1.96–2.01 (m, 12H), 4.24–4.26 (m, 12H), 7.25–7.28 (m, 12H), 8.01 (d, *J* = 7.80 Hz, 4H), 8.09–8.12 (m, 12H), 8.23 (d, *J* = 7.74 Hz, 4H), and 8.85–8.98 (m, 16H).

12 For $\mathbf{1}_2$•2La(III): Yield 35%, MALDI-TOFMS (CHCA) *m/z* 3688.36 ([M+H]$^+$ = 3689.04), ^{1}H NMR (600 MHz, THF-d_8, TMS, 25 °C) δ 1.24–1.33 (m, 60H), 1.67–1.73 (m, 24H), 4.26–4.29 (m, 24H), 6.92–6.93 (m, 12H), 7.02–7.05 (m, 4H), 7.21–7.23 (m, 16H), 7.46–7.47 (m, 16H), 8.11–8.32 (m, 32H), and 8.76 (m, 16H). For $\mathbf{1}_3$•3La(III): MALDI TOF MS (CHCA) *m/z* 5532.1 (M$^+$ = 5532.04). NMR spectrum of $\mathbf{1}_3$•3La(III) gives serious line-broadened proton signals, especially for aromatic protons.