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Stable supramolecular complex of porphyrin macroring with pyridyl and fullerenyl ligands

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ABSTRACT

Binding constants and thermodynamic parameters for 1:1 complexation of a porphyrin macroring, self-assembled from three trisporphyrinatozinc through imidazole–Zn coordination on the terminal porphyrins, with several multidentate pyridyl and fullerenyl ligands were examined. In benzonitrile, the ligand having one fullerenyl and two coordinative pyridyl moieties surprisingly afforded the highest affinity. The thermodynamic data of the complexation indicated that an unusual and fairly large positive entropic change, which may be attributed to extensive desolvation of the solutes especially from the large cavity of porphyrin macroring and fullerene surface, significantly contributed to the enhancement of the binding constant.

Natural and synthetic macrocyclic molecules such as cyclodextrin,[1,2] calixarene,[3] cucurbituril,[4,5] cyclic paraphenyleneacetylene,[6] cyclotriveratrylene,[7] and cyclic multiporphyrin[8–10] have attracted much attention in supramolecular science, since they are able to incorporate various guest molecules inside their rings with high association constants. We have reported several supramolecular macrorings self-assembled from bis(imidazolylporphyrinatozinc)s through imidazole coordination.[11,12] The robust macroring skeletons provided stable nanometer-size pores even on metal surfaces[13,14] and in a bilayer lipid membrane.[15]

A very strong complexation behavior of macroring **1** was observed with **6** having tripyridyl and fullerenyl moieties (Fig. 1).[16] The complex showed an unusual geometry, where fullerene overwhelmed the pyridyl coordination and was entrapped in the macroring. Here, we synthesized various multipyridyl and fullerenyl ligands **2**–**9**, in which the number of pyridine(s) and fullerene(s) was varied systematically (Fig. 2). The thermodynamic parameters evaluated for ligands **2**, **3**, **5**, and **6** elucidated that the binding of the porphyrin macroring with the multipyridyl and fullerenyl ligands was stronger than that estimated from the conventional enthalpy–entropy compensation plot. The combination of two coordinating pyridyl moieties and one fullerenyl moiety afforded the highest affinity with macroring **1**.

Porphyrin macroring **1**[17] and fullerene derivatives **7** and **8**[18] were synthesized according to the reported procedures. Ligands **2**, **3**, **5**, and **9** were synthesized from 1,1,1-tri(4-iodophenyl)-3-ethylheptane by palladium-catalyzed coupling with 4-ethynylpyridine and fullerene attachment (Scheme S1 in Supplementary data). The ligands were characterized by NMR and MALDI-TOF mass spectra, and their purities were checked chromatographically.

The binding affinities of macroring **1** with the ligands were examined by UV–vis and fluorescence titrations in benzonitrile, which has been frequently used as an aprotic polar solvent in photo-induced electron transfer studies related to artificial photosynthesis.[19,20] Since benzonitrile coordinates to the porphyrinatozinc moiety,[16] it should act as a competitive ligand for ligands **2**–**9**.

UV–vis spectral change of macroring **1** upon the addition of ligand **5** is shown in Figure 3a. The intensities of the Soret bands at both 413 and 445 nm decreased gradually, and the change became subtle when more than 1 equiv of **5** was added. The absorption change, $|\Delta A|$, at 413 nm is plotted in the inset of Figure 3a. The change corresponded very well with an assumption of 1:1 complexation between macroring **1** and **5**. This result was consistent with the previous results obtained for **4** and **6**.[16,17] From the curve fitting analysis,[21] the binding constant was determined to be 8.0×10^7 M^{-1}. Along with the UV–vis spectral change, decrease in the fluorescence intensity due to energy and/or electron transfer from the excited porphyrin to the fullerene moiety was also

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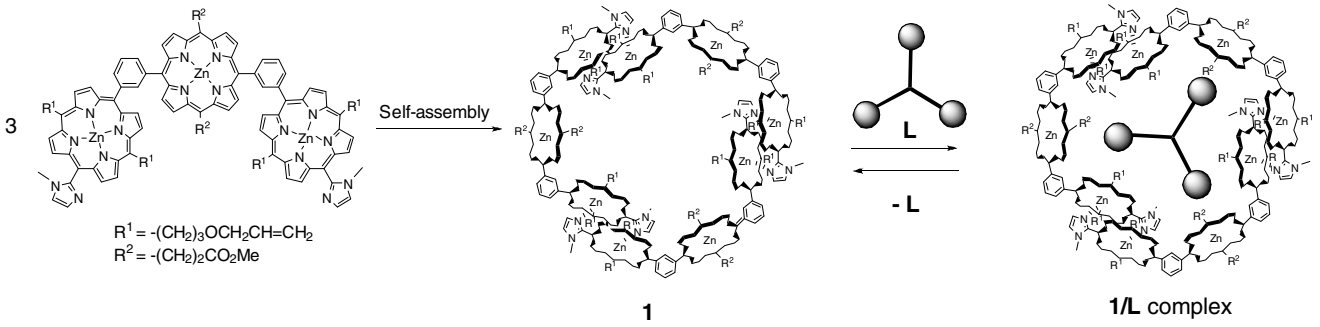

Figure 1. Schematic image of the equilibrium between the porphyrin macroring **1** and a guest ligand **L**.

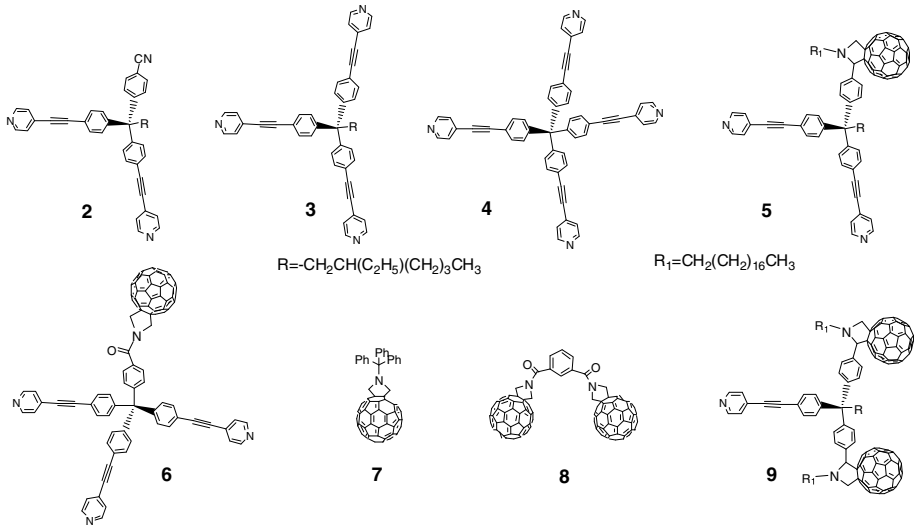

Figure 2. Guest ligands **L** for the porphyrin macroring **1**.

observed (Fig. 3b). In the inset of Figure 3b, the integrated fluorescence intensity is plotted as a function of the concentration of the added ligand. The change became subtle upon the addition of 1 equiv of **5**, and the fluorescence was quenched by 82% at the addition of 1 equiv of **5**. The binding constant ($8.0 \times 10^7\ M^{-1}$) estimated from the fluorescence titration was identical with that obtained from the UV–vis titration.

In a similar manner, binding constants of **1** with other ligands were estimated by UV–vis titration along with fluorescence titration for fullerene-containing ligands. In the case of monofullerene **7**, the fluorescence was quenched by only 9% when 300 equiv of **7** were added, and the binding constant was too small to determine (the data are listed in Table 1).

The binding constant of **1** with **2** ($2.2 \times 10^6\ M^{-1}$) is three orders of magnitude larger than that of tetraarylporphyrinatozinc with pyridine in non-coordinative solvents.[22,23] This enhancement is due to cooperative coordinations between the two pyridyl moieties and the two zinc porphyrin sites in **1**. Introduction of further pyridyl moieties in the trispyridyl ligand **3** and the tetrapyridyl ligand **4** increased their binding constants only by approximately 5–10 times compared to that of ligand **2**, which suggests that the binding ability is also affected by a factor other than the coordination. Bidentate interaction was also effective in the bisfullerene ligand **8** to give a moderate binding constant, $3 \times 10^4\ M^{-1}$, in contrast to the weak binding of the monofullerene ligand **7**. Although introduction of a pyridyl group to ligand **8** improved the affinity by approximately 4 times in **9**, the effect was smaller than that expected from the binding constant of porphyrinatozinc and pyridine (ca. $10^3\ M^{-1}$).[22,23]

To investigate the factors affecting the complexation, thermodynamic parameters for the formation of complexes between macroring **1** and the ligands (**2**, **3**, **5**, and **6**) were estimated from variable temperature UV–vis titrations (Table 2). The enthalpy and entropy terms were determined by the van't Hoff plot as shown in Figure S19 and in

$$-\ln K = \frac{\Delta H^0}{R}\frac{1}{T} - \frac{\Delta S^0}{R} \quad (1)$$

where K, R, and T are binding constant, gas constant, and temperature, respectively.

Complexation of **1** with bis- and trispyridyl ligands **2** and **3** in benzonitrile exhibited large negative ΔH^0 values. A positive and significantly large ΔS^0 value is unusual for such a strong coordination event and is best explained by hypothesizing that a certain amount of benzonitrile molecules solvated to the host was released upon complexation. Introduction of additional pyridyl moiety in **3** increased the ΔH^0 value by 1.5 times but decreased the ΔS^0 value to almost half of that of **2**. The behavior indicates that the three pyridyl coordination is advantageous for stronger overall binding in terms of ΔH^0, but must be compensated to some extent by the loss of flexibility due to the formation of a rigid three-dimensional complex. This is normal enthalpy–entropy compensation behavior observed in various host–guest systems.[1,2] When the measurement was undertaken in chloroform, the ΔH^0 value of **3** became

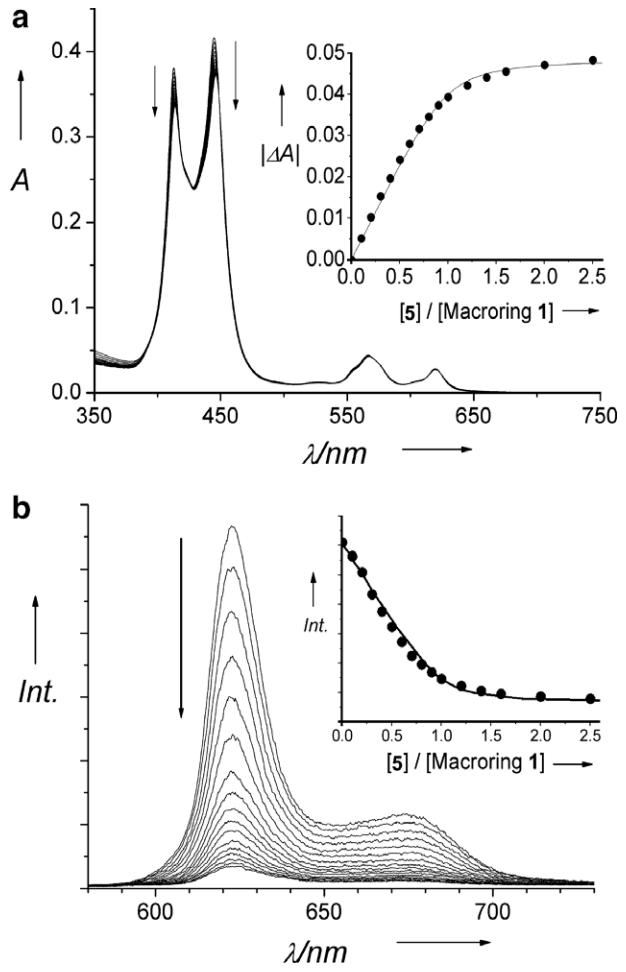

Figure 3. (a) UV–vis and (b) fluorescence (ex. 558 nm) titrations for macroring 1 with ligand 5 in benzonitrile. [**1**] = 3.05×10^{-7} M, [**5**] = 0–2.5 equiv, 25 °C. Inset in (a) absorption change at 413 nm (filled circle) and the theoretical curve for $K_a = 8.0 \times 10^7$ M^{-1} (plain line), inset in (b) the change of the signal integration (570–750 nm) (filled circle) and the theoretical curve for $K_a = 8.0 \times 10^7$ M^{-1} (plain line).

Table 1
Binding constants (K_a) and fluorescence quenching ratios of macroring **1** for complexation with ligands **2**–**9** in benzonitrile

L	Number of moieties		K_a (M^{-1})[a]	Fluorescence quenching[a,b]	Reference
	Py	C_{60}			
2	2	0	2.2×10^6	—	This work
3	3	0	2.5×10^7	—	This work
4	4	0	1.2×10^7	—	16
5	2	1	8.0×10^7	82% (1 equiv)	This work
6	3	1	9.0×10^7	85% (1 equiv)	This work
7	0	1	—	9% (300 equiv)	This work
8	0	2	3.0×10^4	77% (300 equiv)	This work
9	1	2	1.1×10^5	77% (40 equiv)	This work

[a] At 25 °C.
[b] F/F_0 (%), where F_0 is the initial fluorescence intensity of **1** in the absence of a ligand, and F is the fluorescence intensity on the addition of a ligand ([**L**]/[**1**] equiv).

more negative and the ΔS^0 value was reversed to a large negative value. The strong solvent effect supports that benzonitrile is coordinated to the macroring.

The thermodynamic parameters for complex formation of **1** with **5** or **6** showed an interesting tendency. The large incremental ΔH^0 values (−8.7 and −8.2 kJ mol^{-1}) from that of **2** suggest three-point interaction of **5** and **6** probably due to additional π–π interaction between the fullerene moiety and the porphyrins. Although the ΔH^0 values increase, their ΔS^0 values are almost the same as that of **2**. This seems to be contradictory to the enthalpy–entropy compensation observed in the case of **2** and **3**. The behavior can be explained if more benzonitrile molecules interact with the fullerene ligands, **5** and **6**, compared to ligand **2** prior to the ligand-to-macroring coordination. Therefore, the configurational entropy penalty for the three-point interaction of **1** with **5** or **6** must be compensated by the larger positive entropy change gained by the desolvation of fullerenyl moieties upon complexation. Actually, ligands containing two pyridyl and one fullerenyl moieties, **5** and **6**, interacted more strongly than trispyridine **3** (Table 1), although interaction of monofullerene with porphyrinatozinc is usually significantly weaker than that of the pyridine ligand.[22,23] These results show the importance of the desolvation effect of fullerene[24,25] along with the fullerene–porphyrin interaction upon the complex formations. The results also support the previous suggestion from fluorescence quenching experiment of macroring **1** by ligand **6**, where two pyridyl and one fullerenyl moieties were accommodated, excluding coordination of one of the pyridyl moieties.[16]

Table 2
Thermodynamic parameters for complex formation of macroring **1** with ligands **2**, **3**, **5**, and **6** in benzonitrile and chloroform[a]

L	Number of moieties		ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	R^{2c}, $p = 4$
	Py	C_{60}			
2	2	0	−24.1	40.7	0.999
3	3	0	−36.3	19.8	0.999
5	2	1	−32.8	41.1	0.997
6	3	1	−32.3	43.8	0.998
3[b]	3	0	−75.7	−66.5	0.999

[a] Standard deviation <5%.
[b] In chloroform.
[c] R^2: value for the linear fit of the van't Hoff plot.

To gain further insight into the complexation of macroring **1** with the ligands, the present data are compared with the enthalpy–entropy compensation plots for complexation of zinc porphyrin derivatives[26] (Fig. 4) and α-, β-, and γ-cyclodextrins[1] (not shown) with various guest molecules. The data obtained in the complexation of **1** exhibited similar slopes to those of other zinc porphyrin enthalpy–entropy compensation plots. However, the present data series locate at much higher positions over these enthalpy–entropy compensation plots.[1,9,26] The results suggest that macroring **1** is more advantageous than other hosts for binding ligands due to

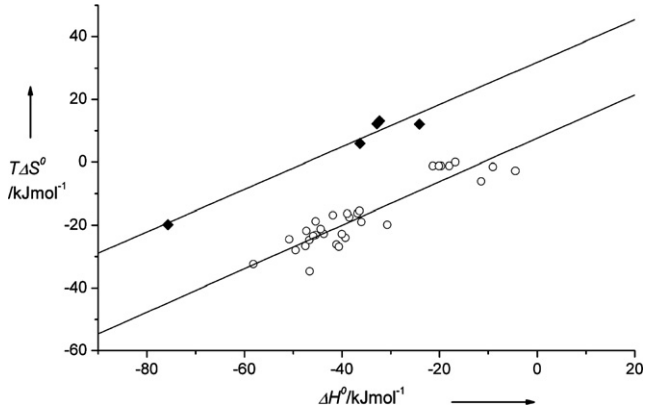

Figure 4. The thermodynamic data ($T = 298$ K) obtained for porphyrin macroring **1** and ligands (**2**, **3**, **5**, and **6**) complexation (diamonds), and tetraarylporphyrinatozinc with amine ligands[26] (open circles).

the positive entropy effect, which may be attributed to desolvation from the robust and large macrocyclic structure. The pore size of **1** (diameter, *D*, >2 nm) is much larger than that of γ-cyclodextrin (D 0.96 nm),[2] which is one of the largest well-known macrocycles. Therefore, **1** can include more solvent molecules and the entropy gained by the release of solvent molecules upon complexation must be significant. The plot obtained in $CHCl_3$ is also on the line in Figure 4, suggesting that the mobility of the chloroform molecules inside the pore might be restricted prior to complexation.

In conclusion, the robust porphyrin macroring **1** exhibited strong binding of several polypyridyl and fullerenyl ligands. In benzonitrile, combination of two coordinative pyridyl and one fullerenyl moieties afforded higher affinities with macroring **1** than the trispyridyl ligands. In this system, the positive entropic term contributed significantly along with negative enthalpies. The positive entropy deviating from conventional enthalpy–entropy compensation plots may come from desolvation upon complexation.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.07.038.

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