Design of Homooxacalix[3]arene–Porphyrin Heterocapsules Which Provide Novel Cavities for Molecular Recognition

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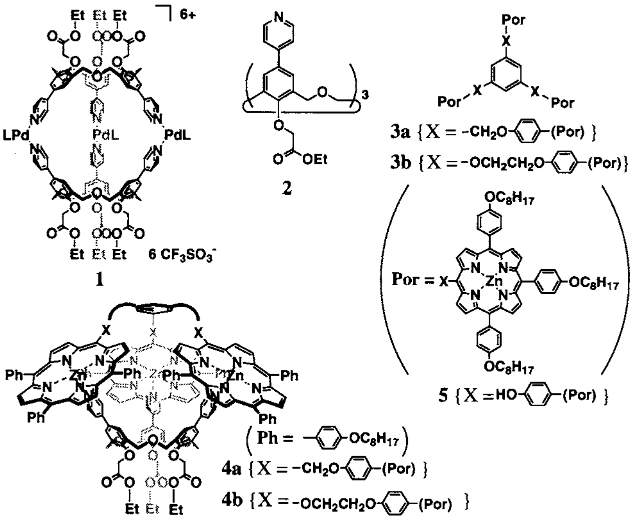
A novel heterocapsular molecule has been obtained in a self-assembled manner by a multi-point interaction between pyridine-appended homooxacalix[3]arene and a Zn(II) porphyrin trimer. The cavity delineated by π-basic components can accept [60]fullerene with $K = 60$ dm^3 mol^{-1} at –30 °C.

Half-bowl-shaped calixarenes and their analogues[1] are useful building units for constructing molecular capsules[2] which represent a very attractive type of host molecules with well-defined three-dimensional internal cavities. An early example is the sulfide-bonded calix[6]arene dimer reported in 1991.[3] It was later found that two complementarily functionalized calixarenes can dimerize to form molecular homocapsules crosslinked by either covalent bonds or hydrogen-bonding interactions.[4] For example, we found that triple linkage of two homooxacalix[3]arenes with covalent bonds creates novel molecular homocapsules with a self-threading function.[5] Rebek et al.[6] and Böhmer et al.[7] systematically studied multiurea-functionalized calix[4]arene homodimers. Compared with the molecular design of these homodimeric capsules, that of heterodimeric capsules is more difficult, because in the former system each monomer is necessarily complementary to each other whereas in the latter system one has to adjust the crosslinking points of different monomers complementary to form a capsule. Accordingly, the examples are very limited.[8–10] In spite of this difficulty, heterodimeric capsules provide very novel functions which cannot be expected for homodimeric capsules. For example, Reinhoudt et al.[8] successfully established a procedure to construct resorcinarene–calixarene heterocapsules using covalent bonds and Rebek et al.[9] and Böhmer et al.[10] prepared hydrogen-bonded heterocapsules. Very recently, we reported a novel homooxacalix[3]arene-based dimeric capsule (**1**), which can include [60]fullerene in the three-dimensional cavity. It thus occurred to us that when these pyridine units in the half-bowl-shaped homooxacalix[3]arene act as axial ligands for a Zn(II) porphyrin trimer to form a 1:1 complex, the resultant heterocapsular molecule would provide a novel three-dimensional cavity surrounded with porphyrins. We thus designed a pyridine-containing homooxacalix[3]arene (**2**) and Zn(II) porphyrin trimers (**3a** and **3b**) and evaluated whether homooxacalix[3]arene-capped capsular molecules are really constructed in a self-assembled manner. The novel capsular molecule (**4**), if it is obtained, are delineated half by homooxacalix[3]arene and half by Zn(II) porphyrins. One may expect for this capsular molecule that (i) fullerene homologs which are known to be included in **1**[11] may be also trapped in this cavity, (ii) viologen derivatives which are known to be included in homooxacalix[3]arenes and their dimeric capsular molecules[5] may be trapped in this cavity and electron transfer from the photoexcited Zn(II) porphyrins to the guest may be facilitated as a pseudo-intramolecular process, and (iii) C_3-symmetrical guests (*e.g.*, R-NH$_3^+$) may be selectively bound to the lower rim of the homooxacalix[3]arene and change the cavity shape.[11] As a preliminary step to these lines of expectation we thoroughly examined the complexation properties between **2** and **3a** or **3b**.[11] Pyridine and **5** were used as reference compounds.



The synthesis of **2** was reported previously.[11] Compounds **3a** {mp > 300 °C (decomp)} and **3b** {mp > 300 °C (decomp)} were identified by IR, ^{1}H NMR, and mass ([M+H]$^+$ = 3350.12 and 3441.06 for **4a** and **4b**, respectively) spectral evidence and elemental analyses.

Figure 1 shows the absorption spectral change of **3b** at a constant concentration, caused by the addition of **2** (25 °C, toluene). It is seen from Figure 1 that the λ_{max} for the Soret band (426.5 nm) shifts to longer wavelength (431 nm) with a tight isosbestic point (430 nm in the Soret band region). The result supports the view that three pyridine units in **2** simultaneously coordinate to Zn(II) in **3b**. The stoichiometry was estimated by a Job plot. The peak top observed at [**2**]/([**2**] + [**3b**]) = 0.5 clearly supports that they form a 1:1 complex. From a plot of A_{426} vs [**2**] (the plot is not shown here), one can obtain $K = 8.5 \times 10^5$ dm^3 mol^{-1} for the formation of the 1:1 complex from **2** and **3b**. Since the K for the formation of the 1:1 complex from pyridine and **5** (estimated under the same conditions) is 2.9×10^3 dm^3 mol^{-1}, one can regard that the three-point simultaneous binding dramatically enhances the K value.

From the similar spectroscopic method, the K values were estimated to be 5.6×10^5 dm^3 mol^{-1} for **2** + **3a** in toluene and 7.2×10^4 dm^3 mol^{-1} for **2** + **3a** in 1,1,2,2-tetrachloroethane. The results indicate that **3b**, which can give a larger cavity than **3a**, is more suitable to the 1:1 complex formation. However, the difference is relatively small probably owing to the flexibility of the homooxacalix[3]arene ring.[11]

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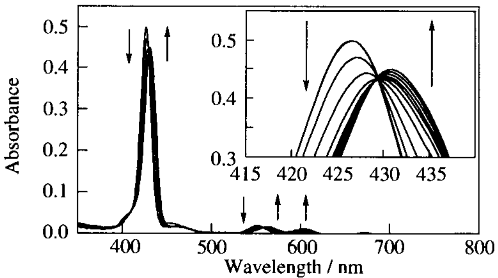


Figure 1. Absorption spectral change in **3b** (5.0×10^{-7} mol dm^{-3}) in toluene at 25 °C: [**2**] = 0~2.5×10^{-5} mol dm^{-3}.

The structure of the **2**/**3b** 1:1 complex was further characterized by ^{1}H NMR spectroscopy. It is known that homooxacalix[3]arenes with a cone conformation affords a pair of doublets for the $ArCH_2O$ methylene protons because of the germinal coupling.[11] The ^{1}H NMR spectrum for the **2**·**3b** complex in toluene-d_8 is shown in Figure 2a. It is seen from Figure 2a that these peaks (4.43 and 3.80 ppm) are significantly broadened. This broadening effect is due to the slowered molecular motion of the homooxacalix[3]arene moiety caused by capsule formation with **3b**. The large upfield shift is induced for α- and β-protons in the pyridyl groups and *m*-protons in the calixarene phenyl groups. These changes are ascribed to the strong shielding effect of the porphyrin π-systems.

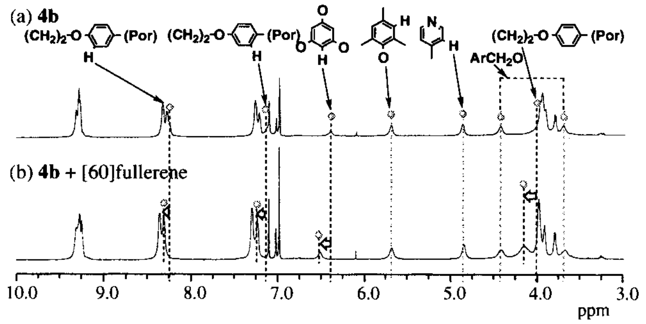
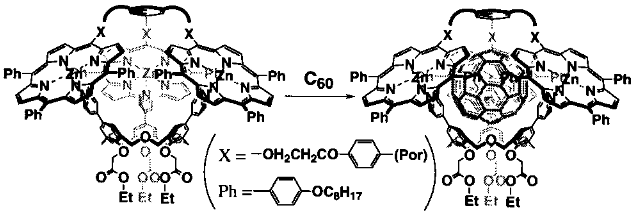


Figure 2. Partial ^{1}H NMR spectrum of (a) the **2** + **3b** system (1.5×10^{-3} mol dm^{-3} each) and (b) **4b** + [60]fullerene system ([**4b**] = 1.5×10^{-3} mol dm^{-3}, [60]fullerene = 5.8×10^{-3} mol dm^{-3}) in toluene-d_8 at 25 °C. The assignment was accomplished by ^{1}H-^{1}H COSY method.

NMR spectroscopic studies have provided clear evidence that **4b** can form complex with [60]fullerene. The ^{1}H NMR spectrum of **4b** in the presence of [60]fullerene is shown in Figure 2b. Although the proton signals for free **4b** and **4b**·[60]fullerene complex did not appear separately, the downfield shift values are as much as 0.20 and 0.12 ppm for the $ArOCH_2CH_2OAr$ and phloroglucinol protons. The large downfield shift can be explained by a deshielding effect of the included [60]fullerene on the core moiety of **2b** (Scheme 1). In the ^{13}C NMR spectrum in toluene-d_8 at 25 °C, ^{13}C-enriched (10–15%) [60]fullerene gave a peak at 143.20 ppm. In the presence of **4b** (0.25 equiv), the peak did not separate but just shifted to 142.75 ppm at room temperature: however, a new separate peak assingable to the **4b**·[60]fullerene complex appeared at 140.18 ppm at –30 °C. The association constant (K_{C60}) for [60]fullerene could be readily estimated from the ratio of the peak intensity of free [60]fullerene and the **4b**·[60]fullerene complex in the ^{13}C NMR spectra to be 60 dm^3 mol^{-1} at –30 °C.

Scheme 1.



In conclusion, the present study showed that the multi-point interaction between pyridine-appended homooxacalix[3]arene and a Zn(II) porphyrin trimer result in a novel heterocapsular molecule, the inner cavity of which can accept [60]fullerene as a guest. Further characterization of this novel capsule molecule has currently been continued: in particular, K_{C60} improvement and applications to electron-transfer systems should be of great significance.

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