SHORT PAPER

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Synthesis and binding properties of calix[4]arene dual porphyrin conjugate: tweezers for DABCO†

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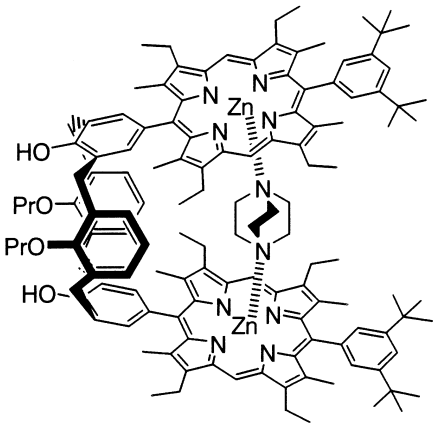
A dual porphyrin system built on a calix[4]arene spacer was prepared and the corresponding Zn(II) complex **4** showed a marked affinity for 1,4-diazobicyclo[2.2.2]octane (DABCO) as compared with other amines.

Keywords: calix[4]arene, porphyrin, tweezers, DABCO, supramolecule

The superamolecular chemistry of calixarenes has been studied,[1] because they are useful building-blocks in the design of functionalised supramolecules and ultimately of synthetic enzyme mimics. It is well-known that porphyrin derivatives play an important role in biological systems[2] and their coordination properties permit the construction of unique supramolecular structures. Calixarene-porphyrin conjugates have been synthesized as host molecules[3] and anion sensors with this objective.[4] Furthermore, we have shown that the calixarene-porphyrin conjugate served as tweezers to complex with a benzoquinone and formed non-covalently electron donor-acceptor system.[5] In this paper, we describe the synthesis of Zn(II)porphyrin-substituted calix[4]arene **4** and its selective binding property for several diamines. Compound **4** serves as tweezers for DABCO selectively, which led to the formation of ensemble **I** (Scheme 1).



Scheme 1

Results and discussion

The starting material, cone-5,17-diformyl-25,27-dipropoxy-26,28-dihydroxycalix[4]arene **1** was prepared according to the literature.[6] The preparation of Zn(II) porphyrin di-substituted calix[4]arene **4** is shown in Scheme 2. The cross-condensation of calix[4]arene **1**, dipyrromethane **2** and 3,5-di-*tert*-butylbenzaldehyde **3** gave the target compound **4** in 20% yield. At the same time, mono-substituted compound **5** (2.4%) and Zn(II) 5,15-bis(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (trace amount) were also obtained. The ^{1}H NMR spectrum revealed that the structure of **4** was fixed in a cone-conformation,[1b] and that the hydroxyl groups formed intramolecular hydrogen bonds.

Amines are known as a good axial ligand for Zn(II) porpyrins.[7] In order to examine a binding property of **4**, a titrimetric study of several diamines, DABCO, 1,2-bis(4-pyridyl)ethane, 4,4-dipyridyl, pyrazine and 4,7-phenenthroline, was carried out by UV–visible absorption spectroscopy in the presence of **4** (5.0×10^{-6} M). On the addition of DABCO in the concentration range from 0 up to 5.0×10^{-5} M, the coordination shift of the Soret band from 415 nm to 419 nm was observed. The analysis by standard curve fitting methods8 showed that 1:1 complex was formed with a binding constant of 3.7×10^5 M^{-1} (Table 1). Further addition of more than 20 equiv of DABCO, the additional shift of the Soret band to 421 nm was also observed as a result from formation of 1:2 complex. All amines except for 4,7-phenenthroline displayed the red shift of the Soret band, so the compound **4** is capable of binding various amines through zinc nitrogen coordination. K_1 and K_2 were estimated on the assumption that 1:1 complex was formed in low concentrations (up to 10 equiv mole) of amines, and 1:2 complex in high concentrations (more than 100 equiv mole). Porphyrin tweezers **4** have a larger stability constant .(3.7×10^5 M^{-1}) for DABCO than those of the other amines. The large K_1 for DABCO suggests that the skeleton of calix[**4**]arene can provide a sterically more favoured coordination geometry for the binding of DABCO.

Table 1 Binding constants with 4[a]

Amines	K_1 (M^{-1})	K_2(M^{-1})
DABCO	3.7×10^5	1.0×10^2
1,2-Bis(4-pyridyl)ethane	2.1×10^3	8.8×10^2
4,4-Dipyridyl	1.9×10^3	1.0×10^3
Pyrazine	3.4×10^2	–[c]
4,7-Phenenthroline	–[b]	–[b]

[a]All measurements were carried out with 5×10^{-6} M of **4** in CH_2Cl_2 at 20°C. [b]No formation of complex was observed. [c]Absorbance change was too small to determine K_2.

Next, ^{1}H NMR titration studies for the complexation of **4** and DABCO were carried out in chloroform-d_1. The concentration of **4** was maintained constant (5.0×10^{-3} M) while the ratio of [DABCO]/[**4**] was varied (0, 0.2, 0.4, 0.6, 0.8, 1, 2 and 15). In the presence of DABCO, new signals assigned to the *meso* protons of the porphyrins of ensemble **I** appeared in the spectra (b) and (c) in Fig. 1. The peaks for meso protons of complex species appeared at 9.65 and 9.70 ppm and the peak for hydroxyl protons appeared at 8.82 ppm, and the peaks for free species **4** disappeared from the spectra (c) in Fig. 1. The differences between chemical shifts for free species and

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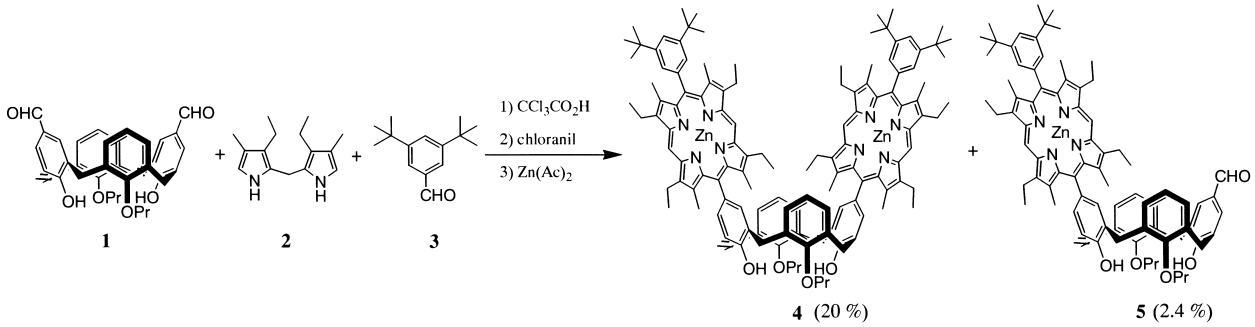

Scheme 2

complex, $\Delta\delta = \delta(\text{free}) - \delta(\text{complex})$, were *ca* 0.60 ppm for meso protons and 0.11ppm for hydroxyl protons, respectively.

The peak at –4.96 ppm was assigned to the typical methylene protons of DABCO in the ternary porphyrin–DABCO–porphyrin complexes.[9] Interestingly, the disappearance of the peak at –4.96 ppm due to ternary complex was observed in the presence of a large excess amount of DABCO and then 1:2 complex should be formed. In the 1:2 complex, the peaks at 9.65 and 9.70 ppm assigned for the meso protons of ensemble I shifted downfield to the broad peaks at 10.10 and 10.15 ppm. On the other hand, upon addition of other amines such as 4,4-dipyridyl even at low concentrations, the original meso proton signals of free species **4** were shifted to upfield slightly and finally reached at 10.10 and 10.15 ppm ($\Delta\delta = 0.15$ ppm). These small upfield shifts resulted from the coordination of two amines. The $\Delta\delta$ (= 0.60 ppm) for meso protons of the complex with 1:1 [**4**]/[DABCO] stoichiometry was much bigger than $\Delta\delta$ (=0.15 ppm) for the complex with 1:2 [**4**]/[DABCO] and [**4**]/[other amine] stoichiometry. This large shift ascribed to the ring current effect from two porphyrin moieties and revealed the formation of ensemble **I**. The present paper shows that two porphyrin moieties of **4** serve as tweezers to capture the DABCO selectively in two-point coordination.

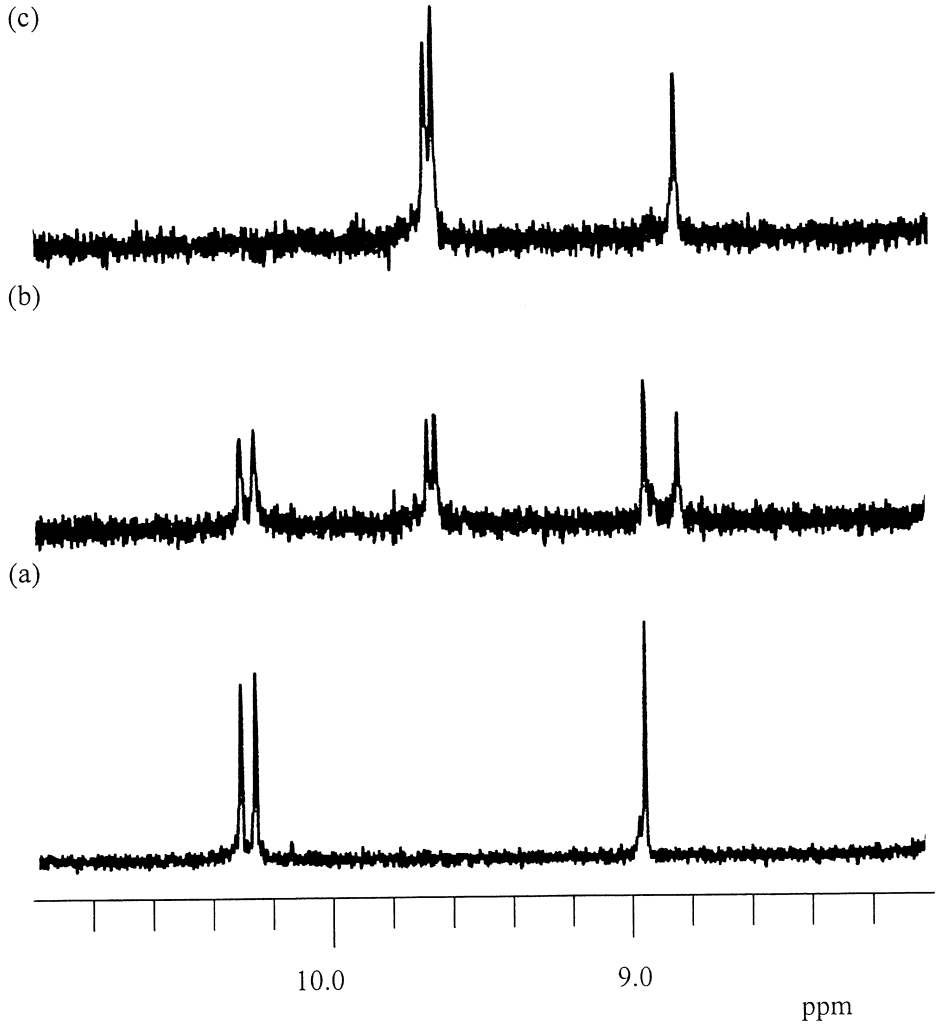

Fig. 1 Partial ^{1}H NMR spectra of **4**-DABCO complex in $CDCl_3$ on the ratio [DABCO]/[**4**]: (a) 0, (b) 0.4 and (c) 1.0.

Experimental

Melting points were determined with a Yanagimoto melting point apparatus. UV-visible spectra were obtained with a Shimadzu UV-3101PC spectrometer. ^{1}H NMR spectra were recorded on a Varian Gemini-300 spectrometer operated at 300 MHz at room temperature (20°C) in the Fourier transform mode. Chloroform-d_1 was used as a solvent and tetramethylsilane was used as an internal reference for ^{1}H NMR measurement. FAB mass spectra were recorded on JEOL-DX 303. Dichloromethane was freshly distilled over calcium hydride.

Zn(II)porphyrin-substituted calix[4]*arene* (**4**): Diformylcalix[4]-arene **1** (1.3 g, 2.3 mmol), dipyrromethane **2** (2.6 g, 11 mmol) and 3,5-di-*tert*-butylbenzaldehyde 3 (1.5 g, 6.8 mmol) were dissolved in dichloromethane-acetonitrile (360–400 ml). After the addition of trichloroacetic acid (500 mg, 3.1 mmol) in acetonitrile (10ml), the mixture was stirred for 20 h under an argon atmosphere. After that chloranil (5.0g, 20 mmol) in 60 ml of dichloromethane was added and the reaction mixture was stirred for an additional 3 h. The reaction mixture was then washed with aqueous sodium bicarbonate followed by H_2O. The organic layer was then dried over sodium sulfate. After the solvent was removed, the residue was dissolved in 200 ml of dichloromethane and saturated zinc acetate in methanol (5ml) was added. After stirring for 30 min, the solvent was evaporated under reduced pressure. The residue was separated by column chromatography with silica gel (eluting with hexane-dichloromethane) to afford **4** (900 mg, 20 %) and **5** (70 mg, 2.4 %).

Compound **4** purple powder; m.p. > 300°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53 (36H, s, $C(CH_3)_3$), 1.60 (6H, t, $OCH_2CH_2CH_3$), 1.74–1.89 (24H, m, pyrrole β-CH_2CH_3), 2.00, 2.47, 2.49, 2.78 (each 6H, s, pyrrole β-CH_3), 2.24-2.41 (4H, m, $OCH_2CH_2CH_3$) , 3.68, 4.80 (each 4H, d, J = 13 Hz, ArCH_2Ar), 3.99–4.24 (20H, m, $OCH_2CH_2CH_3$, pyrrole β-CH_2CH_3), 6.91 (2H, t, Ar*H*), 7.18 (4H, d, J = 7.5 Hz, Ar*H*), 7.84 (2H, t, J = 1.5 Hz, meso-Ar*H*), 7.92 (4H, s, Ar*H*), 7.98 (8H, d, J = 1.5 Hz, meso-Ar*H*), 8.93 (2H, s, O*H*), 10.25, 10.30 (each 2H, s, meso-*H*); FAB/MS *m*/*z* 1962 (M^+) (Found: C, 74.64; H, 7.03; N, 5.30. $C_{126}H_{144}N_8O_4Zn_2$•0.5$CHCl_3$ requires C, 75.03; H, 7.19; N, 5.53%.).

Compound **5** purple powder; m.p. > 300°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (6H, t, J = 7.4 Hz, $OCH_2CH_2CH_3$), 1.51 (18H, s, $C(CH_3)_3$), 1.67–1.83 (12H, m, pyrrole β-CH_2CH_3), 1.95, 2.44, 2.45, 2.66 (each 3H, s, pyrrole β-CH_3), 2.17–2.25 (4H, m, $OCH_2CH_2CH_3$), 3.58, 3.60, 4.45, 4.64 (each 2H, d, J = 13 Hz, ArCH_2Ar), 3.88–4.16 (12H, m, $OCH_2CH_2CH_3$, pyrrole β-CH_2CH_3), 6.86 (2H, t, Ar*H*), 7.02, 7.08 (each 2H, d, Ar*H*), 7.78, 7.80 (each, 2H, s, Ar*H*), 7.81 (1H, t, J = 1.8 Hz, meso-Ar*H*), 7.94 (2H, d, J = 1.8 Hz, meso-Ar*H*), 8.46, 9.36 (each 1H, s, O*H*), 9.92 (1H, s, CH*O*), 10.17, 10.21 (each 1H, s, meso-*H*); FAB/MS *m*/*z* 1263 (M^+) (C, 71.37; H, 6.44; N, 3.92. $C_{81}H_{90}N_4O_5Zn$•$CHCl_3$ requires C, 71.14; H, 6.63; N, 4.05%.).

In order to construct Table 1, the binding constants were evaluated by a curve fitting method[10] on assumption that 1:1 complex was formed in low concentration (up to 10 equiv. mole) of amines, and 1:2 complex in high concentration (more than 100 equiv. mole). The concentration of the porphyrin dimer **4** was maintained constant (5.0×10^{-6} M) while that of the amines was varied ($0 - 1.5 \times 10^{-2}$ M). The equations are as follows:

$$K_1 = \frac{x}{\{[\text{porphyrin}]_0 - x\}\ \{[\text{diamine}]_0 - x\}} \quad (1)$$

$$K = K_1K_2 = \frac{x}{\{[\text{porphyrin}]_0 - x\}\ \{[\text{diamine}]_0 - 2x\}^2} \quad (2)$$

where $[\text{porphyrin}]_0$ and $[\text{diamine}]_0$ are total concentration of porphyrin and diamine, respectively. The x was determined by following equation:

$$x = \frac{A - A_0}{A_c - A_0}$$

where A_0 is absorption of initial solution and AC is absorption of complex species.

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