CHEMISTRY LETTERS, pp. 989-992, 1994.

Calix[4]arene-Capped Tetraphenylporphyrin.
Synthetic Approach to a Chiral Capped Porphyrin with Regular C_4 Symmetry

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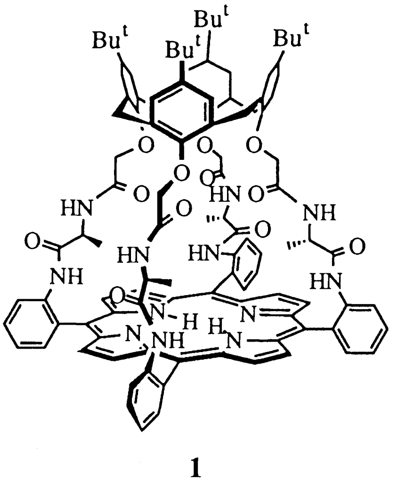
A tetraphenylporphyrin capped with a calix[4]arene through four chiral pillars has been synthesized. This molecule retains C_4 symmetry characteristic of porphyrins. The preliminary experiments indicated that the cavity shows unique guest-binding properties.

It has been demonstrated that capped porphyrins are very useful to mediate the binding of small molecules, oxygenation of olefins, molecular recognition, *etc.*[1)] When one wish to add the function of chiral discrimination to capped porphyrins, they should be of course chiral and desirably, high molecular symmetry should be retained to achieve high enantiomeric selectivity: this situation is well demonstrated by the importance of C_2 symmetry in asymmetric syntheses. Porphyrins *a priori* have C_4 symmetry, so that the expeditious answer to this requirement is to use a C_4-symmetric cap.

Bruice *et al.*[2)] synthesized porphyrins capped with a 1,2,4,5-tetra-substituted benzene but the molecular symmetry is lowered to C_2 symmetry. Cyclodextrin-capped porphyrins were also synthesized[3),4)] but these compounds almost lose the molecular symmetry. We noticed that calix[4]arene-25,26,27,28-tetrols, cyclic tetramers made of phenol and formaldehyde, exactly satisfies this requirement. We thus designed compound **1** as a synthetic target. This compound has several novel structural characteristics: that is, (i) it has neat C_4 symmetry, (ii) a porphyrin ring is linked to a calix[4]arene ring by four chiral pillars, and (iii) an alkali-metal binding site composed of four OCH_2CO groups and a transition-metal binding site composed of a porphyrin are



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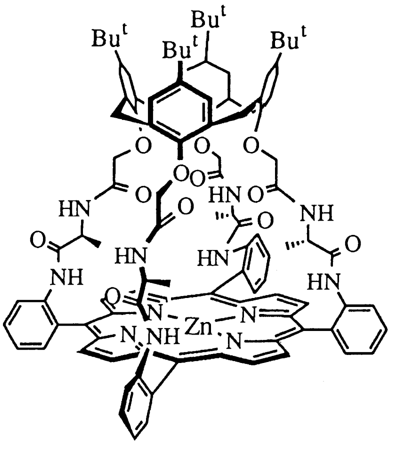
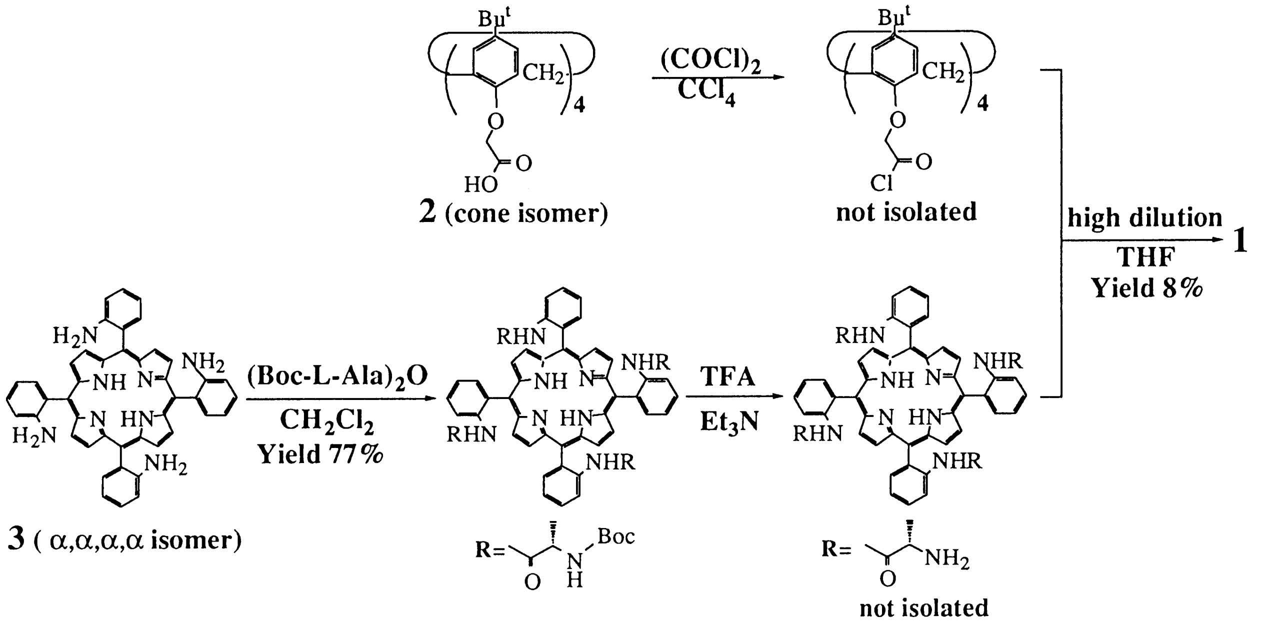


1•Zn(II)



Scheme 1.

closely located within a molecule. We report hereafter the synthesis of the first calix[4]arene-capped porphyrin, its spectroscopic properties, and preliminary studies on molecular recognition.5)

Compound **1** was synthesized from 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(hydroxycarbonylmethoxy)calix[4]arene (**2**)6) and 5,10,15,20-tetrakis(2-aminophenyl)porphyrin (**3**)7) according to Scheme 1. The product (mp > 300 °C) was identified by ^1H NMR, mass, and absorption spectral evidence and elemental analysis.8)

Compound **1** gave a relatively simple ^1H NMR spectrum ($CDCl_3$, 24 °C, 250 MHz)8) because of the C_4 symmetry. In particular, it is worthy to mention that the δ_H for the methyl groups in the alanyl pillars appears at unusually higher magnetic field (-1.17 ppm). This suggests that the methyl groups reside in the cavity and undergo the ring current effect of the porphyrin π-system. In calix[4]arenes bearing OCH_2CONHR groups the δ_H for the NH protons appears at 7-9 ppm because of the intramolecular hydrogen-bonding interactions.9) In **1**, on the other hand, it appears at 3.65 ppm, indicating that the intramolecular hydrogen-bonding interaction is suppressed by rigidification of the chains. The absorption spectrum of **1** is shown in Fig. 1. The typical Q bands appear at 511, 542, 585, and 640 nm. In the mass spectrum (positive SIMS) we could observe a strong 1791 peak assignable to [**1** + Na]$^+$.

The treatment of **1** with $ZnCl_2$ in DMF at room temperature for 10 h gave the **1**•Zn(II) complex (mp > 300 °C) in 97% yield.10) The absorption spectrum is shown in Fig. 1. The Soret band characteristic of a porphyrin•Zn(II) complex appears at 436 nm: this λ_{max} shifts to longer wavelength than those for conventional porphyrin•Zn(II) complexes. In the mass spectrum (positive SIMS) we could detect a 1871 peak assignable to [**1**•Zn(II) + Na + H_2O]$^+$ in addition to a 1853 peak assignable to [**1**•Zn(II) + Na]$^+$. The elemental analysis also supports inclusion of one water molecule.10) This water molecule could not be removed by vaccum drying. Probably, the water molecule is bound into the cavity, interacting with Zn(II) and NH (or C=O) in the pillars. Since the λ_{max} of tetraphenylporphyrin•Zn(II) complexes with an axial ligand usually shifts to longer wavelength, this proposal is compatible with the above spectral data.

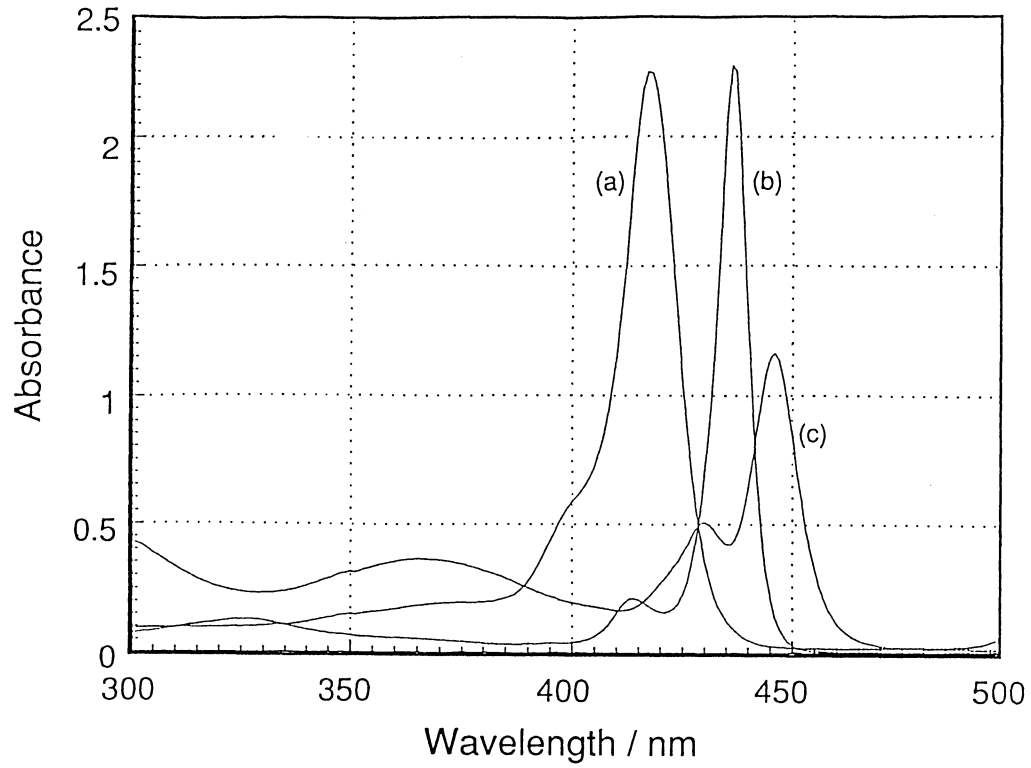
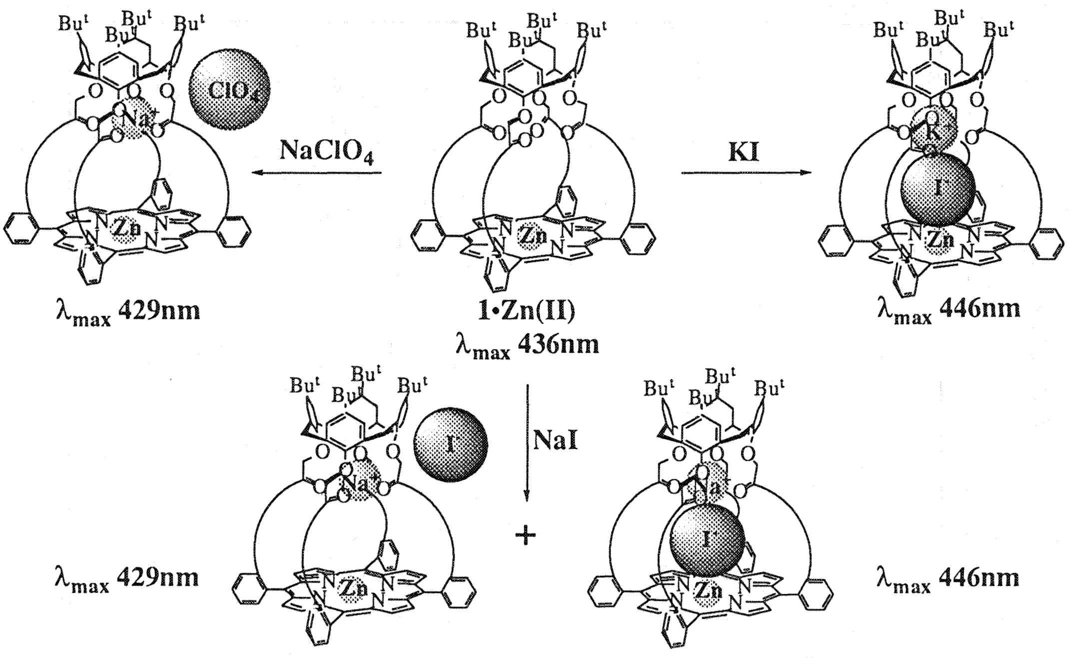


Fig. 1. Absorption spectra of (a) **1**, (b) **1**•Zn(II), and (c) **1**•Zn(II) + NaI at 25 °C: [**1** or **1**•Zn(II)] = 1.00 x 10^{-5} M, [NaI] = 5.00 x 10^{-4} M. The solvent is chloroform for **1** and **1**•Zn(II) and chloroform:acetonitrile = 4:1 v/v for **1**•Zn(II) + NaI.

The preliminary investigation has disclosed that the cavity in **1**•Zn(II) shows unique guest-binding properties. When $NaClO_4$ (50 equiv. to **1**•Zn(II)) was added to a $CHCl_3$-CH_3CN (4:1 v/v) solution of **1**•Zn(II), the Soret band (436 nm) shifted to 429 nm whereas when NaI (50 equiv.) was added, two absorption maxima appeared at 429 and 446 nm (Fig. 1). On the other hand, when KI (50 equiv.) was added, only the 446 nm band appeared. The fluorescence measurement ([**1**•Zn(II)] = 1.00 x 10^{-5} M, 25 °C, $CHCl_3$-CH_3CN = 4:1 v/v, excitation 437 nm, emission 619 nm) revealed that the fluorescence is scarcely quenched by $NaClO_4$ (20 equiv.) but significantly quenched by NaI and KI (20 equiv. each) (I/I_0 = 0.85 and 0.06, respectively). When a tetraphenylporphyrin•Zn(II) complex was used instead of **1**•Zn(II), neither the absorption spectrum nor the fluorescence intensity was changed. These observations are reasonably explained by Scheme 2: in $NaClO_4$ Na^+ is bound to the calix[4]arene cavity and ClO_4^- exists as a counteranion to give the 429 nm band whereas in KI K^+ is bound to the calix[4]arene cavity and I^- coordinates to Zn(II) to give the 446 nm band. In NaI both species can co-exist. These results indicate that the cavity with a hard-soft ditopic binding site is very suitable to "recognition" of I^- ion.



Scheme 2.

In conclusion we succeeded in the synthesis of **1** and **1**•Zn(II), the cavity of which has a hard-soft ditopic binding-site, chirality, C_4 symmetry, *etc*. We are now trying the application to chiral molecular recognition, asymmetric syntheses, *etc*.

References

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8) ^{1}H NMR ($CDCl_3$, 24 °C, 250 MHz)δ -2.70 (2H, s, NH), -1.17 (12H, s, CH_3), 1.01 (36H, s, Bu^t), 3.03 and 3.65 (4H each, d each, $ArCH_2Ar$), 3.41 and 3.65 (4H each, s each, CONH), 4.04 (8H, s, OCH_2), 5.99 (4H, s, CH), 6.91 (8H, s, ArH), 7.70 and 7.84 (4H each, t each, ArH), 8.17 and 8.47 (4H each, d each, ArH), 8.78 (8H, s, PyH); Anal. Found: C, 65.32; H, 6.27; N, 8.00%. Calcd for $C_{108}H_{110}N_{12}O_{12}\cdot CHCl_3\cdot 7H_2O$: C, 65.02; H, 6.26; N, 8.35%.

9) H. Murakami and S. Shinkai, *Tetrahedron Lett.*, **34**, 4237 (1993).

10) Anal. Found: C 60.64, H 5.72, N 7.53%. Calcd for $C_{108}H_{108}N_{12}O_{12}Zn\cdot 2CHCl_3\cdot 6H_2O$: C, 60.65; H, 5.65; N, 7.72%.

(Received February 18, 1994)