A New Water-soluble Host Molecule, a *p-tert*-Butylcalix[8]arene bearing Polyoxyethylene Chains

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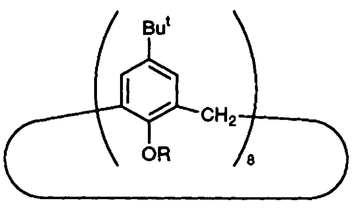
Reaction of *p-t*-butylcalix[8]arene with ethylene oxide gives a water-soluble host compound with a hydrophobic cavity that is capable of including organic molecules in aqueous solution.

A great deal of interest has recently been shown in calixarenes[1,2] because they exhibit inclusion ability with organic molecules and ions. Water-soluble calixarenes are most interesting because of their potential to act as enzyme mimics. Several water-soluble calixarene derivatives with water-soluble alkali-metal and ammonium salts have been reported.[3–8] This communication describes a new water-soluble calixarene (**C3**), which consists of a hydrophobic *p-tert*-butylcalix[8]arene cavity and flexible hydrophilic polyoxyethylene chains.

C1, obtained according to Gutsche's method,[1] was treated with 8 equiv. of potassium *tert*-butoxide in dry toluene and refluxed for 8 h; this produced **C2** after the solvent had been removed. **C2** was placed in a 250 ml stainless-steel autoclave and purged with dry nitrogen, then ethylene oxide was added, and the autoclave was heated at 170–180 °C in an oil bath until the pressure fell to zero. Potassium ions in the product (**C3**) were removed by the addition of ion-exchange resins.



C1; R = H
C2; R = K
C3; R = $(CH_2CH_2O)_nH$

C3 is soluble in water and its molecular structure was confirmed by IR and ^{1}H NMR spectroscopy. The polyoxyethylene ether chain length has a distribution fairly close to the Poisson distribution deduced by Flory for polymerizations of this type.[9] The absorption spectra of **C3** show that there is no free phenolic group.‡

1-Anilino-8-naphthalenesulfonate (ANS) shows a very weak fluorescence in water with a quantum yield as low as 0.004 and an emission maximum at 515 nm, while in organic solvents such as ethanol it exhibits a very strong fluorescence and an emission maximum at 468 nm.[10] Fig. 1 shows that the fluorescence of ANS increases markedly on addition of **C3**. The quantum yield increases more than 40-fold and the emission maximum shifts from 515 to 460 nm. This suggests that ANS is transported into the hydrophobic cavities of *p-tert*-butylcalix[8]arene to form an inclusion complex. The equilibrium constant of complex formation (1 : 1 guest–host) according to the Hildbrand–Benesi equation is about 3.5 × 10^4 dm^3 mol^{-1}.

N-Phenyl-2-naphthylamine (NPN) is a completely hydrophobic version of ANS. NPN also shows large fluorescence enhancements and blue shifts in hydrophobic environments and is used widely in fluorescence polarization studies.[11] Fig. 2 shows that the emission maximum of NPN in aqueous solution shifts from 446 to 410 nm when **C3** is added and the fluorescence intensity also increases as much as 7 times when 6 × 10^{-5} mol dm^{-3} **C3** is added. These data imply that NPN is very well shielded from the surrounding water molecules and thus it must be included in the hydrophobic cavity of **C3**. In view of the concentration ratio of host to guest at the discontinuity in curve 1, it is likely that each host molecule includes one NPN molecule. Examination of CPK molecular

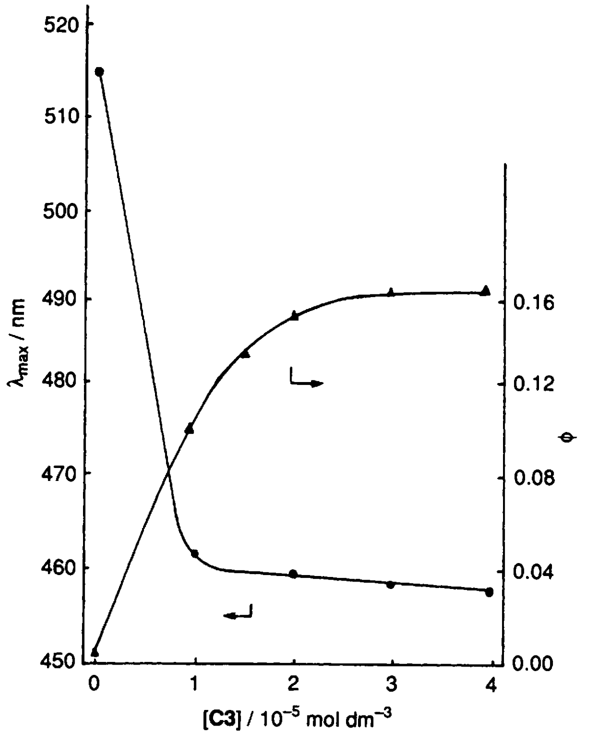


Fig. 1 Fluorescence emission maxima and quantum yields of ANS *vs.* **C3** concentration in aqueous solution [ANS] = 1.0 × 10^{-5} mol dm^{-3}; excitation 280 nm

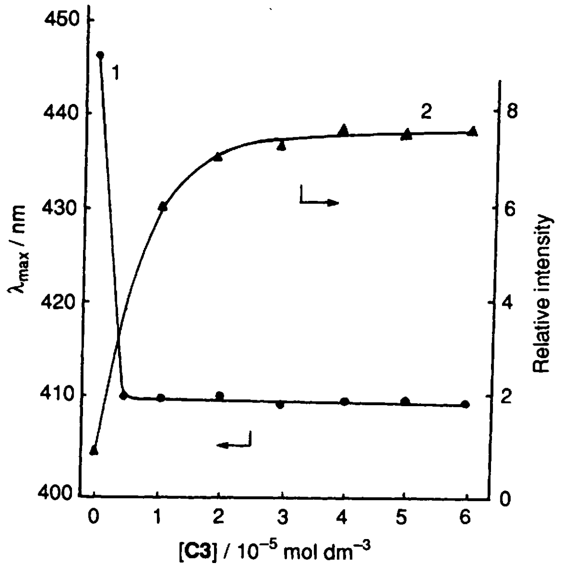


Fig. 2 Fluorescence emission maxima and relative intensity of NPN with **C3** concentration in aqueous solution [NPN] = 5 × 10^{-6} mol dm^{-3}; excitation 280 nm

models suggests that the cavity of *p-tert*-butylcalix[8]arene is large enough to house NPN and can enclose the molecule. A Hildebrand–Benesi plot based on 1:1 host–guest complexation was linear, and the formation constant for inclusion of NPN by **C3** is *ca.* 1.4×10^5 dm^3 mol^{-1}.

In conclusion, a new-water soluble host molecule derived from *p-tert*-butylcalix[8]arene can accept organic molecules and ions in aqueous solution and enhance the fluorescence of guest molecules.

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Footnote

† In an alcoholic solution of potassium hydroxide any free phenolic group exhibits a strong phenoxide ion absorption at 300 nm, whereas the phenolic ethers show a characteristic double peak around 275–282 nm both in neutral and in alkanline aqueous solutions.

References

1 C. D. Gutsche, B. Dhawan, K. H. No and R. Mutukrishnan, *J. Am. Chem. Soc.*, 1981, **103**, 3782.

2 R. Ungaro and A. Pochinia, *Frontiers in Supramolecular Organic Chemistry and Photochemistry*, ed. H.-J. Schreider and H. Dur, VCH, New York, 1991.

3 A. Arduini, A. Pochini, S. Reverberi and R. Ungaro, *J. Chem. Soc., Chem. Commun.*, 1984, 981.

4 S. Shinkai, S. Mori, T. Tsubaki, T. Sone and O. Manabe, *Tetrahedron Lett.*, 1984, **25**, 5315.

5 S. Shinkai, H. Kawabata, T. Arimura, T. Matsuda, H. Satoh and O. Manabe, *J. Chem. Soc., Perkin Trans. 1*, 1989, 1073.

6 S. Shinkai, S. Mori, H. Koreishi, T. Tsubaki and O. Manabe, *J. Am. Chem. Soc.*, 1986, **108**, 2409.

7 C. D. Gutsche and I. Alam, *Tetrahedron*, 1988, **44**, 4689.

8 I. Alam and C. D. Gutsche, *J. Org. Chem.*, 1990, **55**, 4487.

9 J. W. Cornforth, E. D. Morgan, K. T. Potts and R. J. W. Ress, *Tetrahedron*, 1973, **29**, 1659.

10 L. Stryer, *J. Mol. Biol.*, 1965, **13**, 482.

11 Y. Muraki, J. Kikuchi, T. Ohno, O. Hayashida, Y. Hisaeda, H. Nishimura, J. P. Snyder and K. Steliou, *J. Am. Chem. Soc.*, 1991, **113**, 8228.