A Uranyl Ion-sensitive Chromoionophore based on Calix[6]arene

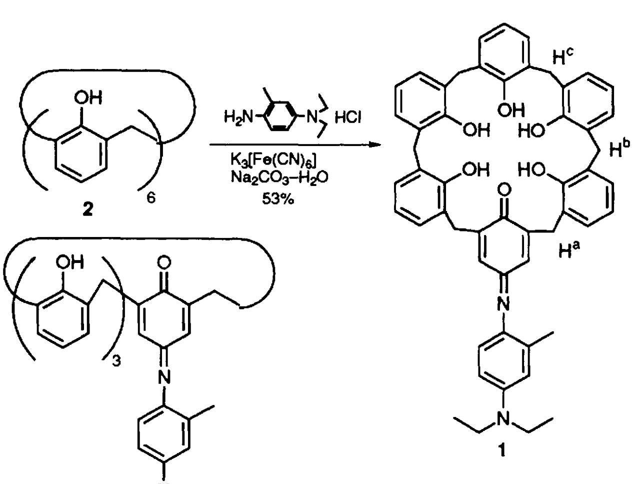
Yuji Kubo,* Shin'ya Maeda, Minoru Nakamura and Sumio Tokita

Department of Applied Chemistry, Faculty of Engineering, Saitama University, Shimo-okubo, Urawa, Saitama 338, Japan

A new type of chromoionophore, mono(indoaniline)-derived calix[6]arene **1**, has been synthesized, which shows a selective UO_2^{2+} ion-induced pronounced colour change (wavelength change *ca.* 60 nm) with increasing absorption intensity in 99% EtOH at 25 °C, making it of potential use as an optical sensor for UO_2^{2+} detection.

Synthetic chromoionophores that give rise to specific colour change on selective complexation with cations have attracted considerable attention as efficient spectrophotometric analytical reagents for the detection of particular species[1] as well as the design of (supra)molecular devices having 'recognition and optical sensing' functions.[2] Calixarenes have been important building blocks for constructing host molecules in supramolecular chemistry.[3] Of particular interest, among them, has been the use of calix[6]arenes because of the availability for the design of pseudoplanar hexadentate uranophiles.[4] To the best of our knowledge, however, no chromoionophore as an optical sensor for UO_2^{2+} detection has yet been prepared in spite of particular recent emphasis on the synthesis of chromogenic[5] and fluorogenic[6] calixarenes. The indoaniline chromophore system may be important in this area because its optical properties can be perturbed significantly by chemical stimuli. In particular, we found that the quinone carbonyl group of indoaniline-type ligands interacts strongly with divalent metal ions causing a colour change.[7] Thus the incorporation of this chromophore into a calixarene unit would be of great value in the design of a chromoionophore. Indeed, some indoaniline-derived calix[4]arenes show large spectral changes on selective complexation with alkali and alkaline-earth metal ions.[5d,g] By replacing the calix[4]arene with the calix[6]arene unit, a chromoionophore showing different characteristics could be produced. In this communication, we report the synthesis of the title compound **1** and our results for the new chromogenic calix[6]arene for the detection of UO_2^{2+}.

Condensing calix[6]arene **2**[8] with 1.2 equiv. of 4-diethylamino-2-methylaniline hydrochloride under alkaline conditions in the presence of 2.4 equiv. of $K_3Fe(CN)_6$ at room temp. afforded the mono(indoaniline)-derived calix[6]arene **1**[†] in 53% yield. Compound **1** has a visible absorption band with λ_{max} = 665 nm in 99% EtOH solution. However, addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base caused a hypsochromic shift of 37 nm and decreased absorption intensity, attributable to removal of intramolecular hydrogen bonding between the quinone carbonyl of indoaniline and the adjacent phenolic hydroxy groups. At a ratio [DBU] : [**1**] of 1000 : 1, the spectral change was established to be saturated, suggesting that the phenol group adjacent to the indoaniline chromophore was completely dissociated.[‡]



Scheme 1

We investigated to see if **1** would act as a chromoionophore for detection of UO_2^{2+}. Compound **1** has an absorption band at 628 nm in the presence of 10^3 equiv. of DBU in 99% EtOH

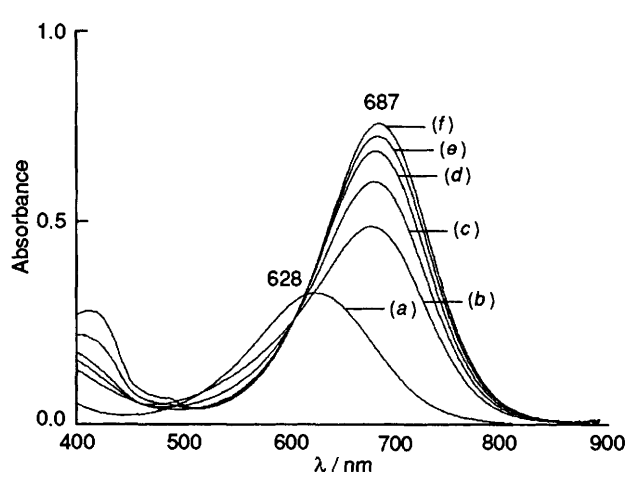


Fig. 1 Spectral changes upon addition of $UO_2(MeCO_2)\cdot 2H_2O$ (*a*) 0, (*b*) 5.0×10^{-5}, (*c*) 1.0×10^{-4}, (*d*) 2.0×10^{-4}, (*e*) 1.0×10^{-3}, (*f*) 2.0×10^{-3} mol dm^{-3}, to a 99% EtOH solution of **1** (2.0×10^{-5} mol dm^{-3}) in the presence of 10^3 equiv. of DBU

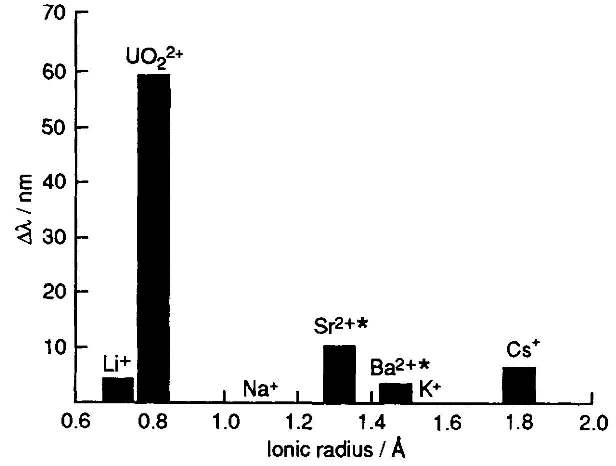


Fig. 2 Spectral responses [$\Delta\lambda_{max} = \lambda_{max}$(complex) $- \lambda_{max}$(ligand)] of **1** in the presence or absence of several metal ions at 25 °C; [**1**] = 2.0×10^{-5} mol dm^{-3}; [DBU]/(1] = 10^3. In the case of addition of Mg^{2+}, Ca^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, $\Delta\lambda_{max}$ could not be determined under these conditions owing to precipitation of the cations. However, when 5 equiv. of these metal ions (except for Cu^{2+}) were added to a 99% EtOH solution of **1** in the presence of DBU (300 equiv. for Ni^{2+}, Zi^{2+}, 10^3 equiv. for Mg^{2+}, Ca^{2+}) there was virtually no spectral response; the ionic radius of U^{VI} is 0.66–0.87 Å.[11] Asterisks indicate spectral response after solid[$M(MeCO_2)_2\cdot xH_2O$]–liquid (99% EtOH) two-phase solvent extraction.

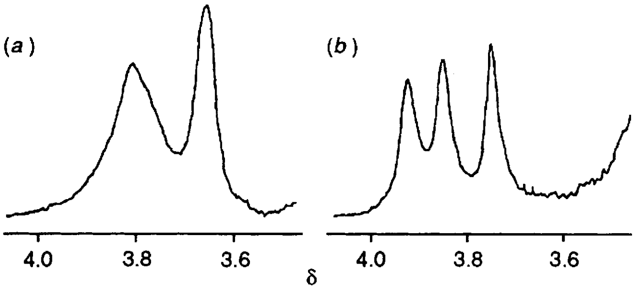


Fig. 3 ^1H NMR spectra in the presence of excess DBU in $CDCl_3$ at room temperature; (*a*) ligand **1**, (*b*) **1**–UO_2^{2+} complex

at 25 °C. Interestingly, as shown in Fig. 1, addition of UO_2^{2+} to such a solution of **1** causes a large bathochromic shift with an increase in absorption intensity. At a ratio $[UO_2^{2+}]:[\mathbf{1}]$ of 100:1, a new band at 687 nm was observed. Use of the continuous variation method[9] indicated the formation of a 1:1 complex between **1** and UO_2^{2+}. However, addition of other metal ions caused no or only minor changes in the absorption spectra (see Fig. 2). The results indicated that compound **1** exhibits a significant selectivity for UO_2^{2+}, which can be interpreted in terms of a specific coordination mode of the UO_2^{2+} ion with **1** since the selective colour change was not dependent on the ionic radius (Fig. 2). The apparent association constant for UO_2^{2+} from the spectral changes was established to be 8×10^4 dm^3 mol^{-1} using a Benesi–Hildebrand plot.[10]

^1H NMR (400 MHz) spectra were used in order to gain insight into the coordination structure. Compound **1** in the presence of excess DBU in $CDCl_3$ at room temperature displays a broad signal in the range δ 3.6–4.0 which is attributable to $ArCH_2Ar$ of the calix[6]arene segments, and indicates that conformational interconversion is somewhat slow on the NMR timescale at room temperature [Fig. 3(*a*)]. However, upon interaction with the excess $UO_2(MeCO_2)\cdot 2H_2O$, the spectral pattern was found to change to three singlets in a 1:1:1 ratio for the methylene protons (H^a, H^b and H^c: Scheme 1). These results suggest that UO_2^{2+} upon complexation with **1** might cause the ligand to adopt an unusual pseudoplanar structure in which the UO_2^{+} cation is six-coordinate. Indeed, the absence of an interaction between mono(indoaniline)-derived calix[4]arene **3** and UO_2^{2+} supports the premise that selectivity for UO_2^{2+} in the present case results from a good match of the rigid calix[6]arene skeleton to the coordination requirements of UO_2^{2+}. We are attempting to obtain a X-ray crystal-structure of the UO_2^{2+} complex with **1**.

Y. K. thanks the Ministry of Education, Science and Culture, Japan, for Grant-in-Aid for Encouragement of Young Scientists (No. 05750752).

Received, 7th March 1994; Com. 4/01348D

Footnotes

[†] Compound **1** was identified by NMR and mass spectroscopy, and elemental analysis. ^1H NMR [$(CD_3)_2SO$, 353 K], δ 1.13 (t, 6H), 2.14 (s, 3H), 3.36 (q, 4H), 3.69 (s, 4H), 3.81 (s, 4H), 3.86 (s, 4H), 6.04 (1H, dd, J = 2.2, 9.0 Hz), 6.15–6.19 (2H, m), 6.48 (2H, d, J = 7.1 Hz), 6.57 (1H, d, J = 2.7 Hz), 6.68–6.78 (6H, m), 6.87 (2H, d, J = 7.4 Hz), 7.00 (2H, d, J = 7.4 Hz) and 7.07–7.10 (4H, m).

[‡] The pK_a value for **1** could not be determined because of its poor solubility in water.

References

1 For comprehensive reviews see, M. Takagi and K. Ueno, *Top. Curr. Chem.*, 1984, **121**, 39; H.-G. Lohr and F. Vögtle, *Acc. Chem. Res.*, 1985, **18**, 65.
2 J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89.
3 C. D. Gutsche, *Calixarenes, Monographs in Supramolecular Chemistry*, ed. J. F. Stoddart, RSC, Cambridge, 1989; *Calixarenes, A Versatile Class of Macrocyclic Compounds*, ed. J. Vicens and V. Böhmer, Kluwer, Dordrecht, 1991.
4 S. Shinkai, H. Koreishi, K. Ueda, T. Arimura and O. Manabe, *J. Am. Chem. Soc.*, 1987, **109**, 6371; S. Shinkai, Y. Shirahama, H. Satoh, O. Manabe, T. Arimura, K. Fujimoto and T. Matsuda, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1167; T. Nagasaki and S. Shinkai, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1063; K. Araki, N. Hashimoto, H. Otsuka, T. Nagasaki and S. Shinkai, *Chem. Lett.*, 1993, 829.
5 (*a*) S. Shinkai, K. Araki, J. Shibata, D. Tsugawa and O. Manabe, *Chem. Lett.*, 1989, 931; (*b*) E. Nomura, H. Taniguchi and S. Tamura, *Chem. Lett.*, 1989, 1125; (*c*) H. Shimizu, K. Iwamoto, K. Fujimoto and S. Shinkai, *Chem. Lett.*, 1991, 2147; (*d*) Y. Kubo, S. Hamaguchi, K. Kotani and K. Yoshida, *Tetrahedron Lett.*, 1991, **32**, 7419; (*e*) A. M. King, C. P. Moore, K. R. A. S. Sandanayake and I. O. Sutherland, *J. Chem. Soc., Chem. Commun.*, 1992, 582; (*f*) M. McCarrick, B. Wu, S. J. Harris, D. Diamond, G. Barrett and M. A. McKervey, *J. Chem. Soc., Chem. Commun.*, 1992, 1287; (*g*) Y. Kubo, S. Hamaguchi, A. Niimi, K. Yoshida and S. Tokita, *J. Chem. Soc., Chem. Commun.*, 1993, 305; (*h*) M. McCarrick, S. J. Harris and D. Diamond, *J. Mater. Chem.*, 1994, 217.
6 T. Jin, K. Ichikawa and T. Koyama, *J. Chem. Soc., Chem. Commun.*, 1992, 499; I. Aoki, T. Sakai, S. Tsutsui and S. Shinkai, *Tetrahedron Lett.*, 1992, **33**, 89; I. Aoki, T. Sakai and S. Shinkai, *J. Chem. Soc., Chem. Commun.*, 1992, 730; K. Iwamoto, K. Araki, H. Fujishima and S. Shinkai, *J. Chem. Soc., Perkin Trans. 1*, 1992, 1885; C. P. Jimènes, S. J. Harris and D. Diamond, *J. Chem. Soc., Chem. Commun.*, 1993, 480; *J. Mater. Chem.*, 1994, 145.
7 Y. Kubo, K. Sasaki, H. Kataoka and K. Yoshida, *J. Chem. Soc., Perkin Trans. 1*, 1989, 1469.
8 C. D. Gutche and L.-G. Lin, *Tetrahedron*, 1986, **42**, 1633.
9 K. Ueno, *Nyumon Chelate Kagaku*, Nankodo, Tokyo, 1969, p. 56.
10 H. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.
11 *Kagaku Binran II*, ed. The Chem. Soc. Jpn., Maruzen, Tokyo, 1984, p. 717.