Original

The metal binding properties of photoresponsive calix [4] arene modified with an azobenzene

by

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Abstract

The photoresponsive calix [4] arene (2), which is modified with azobenzene moiety on the lower rim of the calix, has been prepared. Photoisomerization of 2 was performed with photoirradiation by 500 W-Xe lamp using Corning 7-37 filter. The liquid-liquid extraction of various metal cations by 2 in the fashion of photoirradiated isomers and non-photoirradiated isomer (trans one) using picrate counter ions has been studied. The calixarene (2) shows higher binding ability for almost all metal cations examined in the 12 h photoirradiated isomer than those of trans isomer and non-modified calix [4] arene (3), which has a same structure on the upper rim of the calix.

Key Words : Photoirradiation, Calix [4] arene, Solvent Extraction, Metal Cations.

Introduction

In last decades, photochemical control of complexation phenomena has been a topic in host-guest chemistry, and various photoresponsive ligands have been used to regulate the binding of organic compounds or metal cations in an on-off fashion. The photoresponsive host has a binding site and photochromic one, which is changed to the another isomer under photoirradiation, and the structural change results in the change of affinity of the binding site for the guest molecules. So far, extensive studies in this field have been done by using cyclodextrins¹⁾ or crown ethers²⁾ as guest binding sites and azobenzene as a photochromic site. However, while calixarenes³⁾ have been used as versatile host molecules for the last two decades, the area of photo-regulated calixarenes with a view to complexing metal cations has been slow to develop. Calixarenes are composed benzene rings, linked via methylene bridges, with functional groups forming the upper and lower rims of calix (Figure 1). Recently, we reported on the photoresponsive calix(1), 5, 11, 17, 23-tetrakis (N'-benzyl-N-piperazino) methy-25, 26, 27, 28-tetrahydroxy calix [4] arene modified with azobenzene⁴⁾. 1 shows reverse photochromism and larger

Fig. 1 Schematic structure of calix [4] arenes.

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metal affinity in the trans than that of cis form. For further extension of the work, we prepared a new calixarene derivative (2), which has morpholine moieties on the upper rim and modified with azobenzene moiety at the lower rim. Here we would like to report the metal binding ability and complexation pattern of 2 in the form of cis-trans isomers for alkali and transition metal cations in a liquid-liquid extraction system.

Experimental Section

Preparation of Azobenzene-capped calix[4]arene (2).

A reaction mixture of 5, 11, 17, 23-tetakis morpholino-methyl 25, 26, 27, 28-tetrahydroxy-calix[4]arene (3)⁵⁾ (5.0 g, 6.1 mmol) and azobenzene-4, 4'-dicarboxyl chloride (4) (2.05 g, 6.7 mmol)⁷⁾ in the presence of triethylamine (0.92 g, 9.1 mmol) in the chloroform (200 mL) was stirred at room temperature for 4 h. The reaction mixture was washed twice with water and the organic layer was dried over Na₂SO₄. After filtration, the organic layer was evaporated in vacuo to yield an orange powder, which was purified with silica gel column chromatography using chloroform, and methanol, and finally chloroform was used as eluting solvent. The last chloroform eluting fractions were combined and evaporated to yield pure 2. Yield : 17.6 %. ¹H-NMR (CDCl₃) : 8.47 (4H, d, J = 8.25 Hz, azobenzene-H), 8.01 (4H, d, J = 8.58 Hz, azobenzene-H), 7.01 (4H, s, Ar-H), 6.94 (4H, s, Ar-H), 3.94 (4H, d, J = 14.24 Hz, Ar-CH₂-Ar) 3.40-3.80 (28H, br.s, overlapped with Ar-CH₂-Ar, CH₂O and ArCH₂N), 3.30 (4H, s, CH₂N), 3.20 (4H, s, CH₂N), 2.35 (4H, s, CH₂N), 2.22 (4H, s, CH₂N). Found : C, 69.21 ; H, 6.48, N, 7.80. Calcd. for C₆₂H₆₆O₁₀N₆ · H₂O : C, 69.38 ; H, 6.38 ; N, 7.82. IR (KBr) : 3450 (OH), 1710 (ester) cm⁻¹.

Photoisomerization of 2.

A dichloromethane solution containing 2 (2.0 mL, 1 × 10⁻³ mol dm⁻³) was UV-photoirradiated with a 500 W-Xe lamp using a USHIO ELECTRIC INC UI-502 Q with a Goring 7-37 filter.

Liquid-liquid extraction ability of 2.

After 6, 12, 28, 24, 36 h-photoirradiation of a dichloromethane solution of 2 (2 mL, 1 × 10⁻³ mol dm⁻³), an aqueous solution (2 mL) containing 2 × 10⁻⁵ mol dm⁻³ of picric acid and 1 × 10⁻² mol dm⁻³ of metal nitrate were added and stirred for 30 min under UV-photoirradiation. An aliquot of the upper aqueous solution was withdrawn, and the UV spectrum was recorded. The extractability was determined on the basis of the absorbance of picrate ion in aqueous solutions by the following equation.

$$\text{Extractability (\%)} = [(A_0 - A)/A_0] \times 100^{4)}$$

where A and A₀ are the absorbance at 354 nm in the presence and the absence of 2, respectively.

Scheme 1

Results and Discussion

In the field of photoresponsive host-guest chemistry, azobenzene has been used as a photochromic moiety because trans-cis isomerization will happen easily under photoirradiation. When the azobenzene moiety is under UV-photoirradiation, azobenzene is changed from trans form to cis isomer as shown in Scheme 2. Calix[4]arenes are found in one of four possible extreme conformations: the cone, partial cone, 1,2-alternate, and 1,3-alternate (Fig. 2). Most of the published examples to make host-guest complexation have so far been of the cone conformation. We selected 5, 11, 17, 23-tetrakis (N-morpholinomethyl)-25, 26, 27, 28-tetrahydroxy calix[4]arene (3), which was reported by Gutsche group, for our study as a part of guest binding site, because 3 has a cone conformation and might be an excellent ligand for complexation with alkali and transition metal cations

Scheme 2

Fig. 2 Four extreme conformations of calix[4]arenes.

Scheme 3

because **3** has nitrogen and oxygen in the upper structure⁵). The synthesis of **2**, which was modified with azobenzene on the lower rim, is shown in Scheme 3. The ¹H-NMR of **2** shows doublet at 3.94 ppm arising from the bridging methylene group with $J_{AB} = 14.24$ Hz at 25°C, which means **2** exists in the cone conformation⁶). Unfortunately, we couldn't assigned the other signal from another pair of bridging methylene group, because the signal is overlapped with ones from CH_2 O- and ArCH_2N -moieties. The photoisomerization of **2** was performed under photoirradiation with 500 W-Xe lamp using a Corning 7-37 filter, which selects the UV region ($310 < \lambda < 390$ nm). Figure

Fig. 3 Absorption spectra of **2** obtained under photoirradiation ;
(photoirradiation time ; 1, 0 h ; 2, 12 h ; 3, 24 h ; 4, 36 h)

3 shows the absorption spectra of **2** obtained by UV-photoirradiation and non-photoirradiation. After UV irradiation, the absorption spectra at 260 nm was increased and that around 330 nm was decreased, which means trans to cis isomerization occurred. The photostationary state was almost performed by 36 h-UV photoirradiation, which is three times longer period than that of **1**. We defined this photostationary state as the cis form. The cis percentage of **2** at the photostationary state was calculated to be 64 % using the absorbance at 330 nm⁷. The cis form is converted back into the original trans one if kept in the dark, with a half life time of 6 h at 25°C, which is shorter period than that of **1**⁴. This fact suggested that **2** is more flexible host than **1**, because appended moiety on the upper rim is smaller molecule than that of **1**. Photoisomerization of the capped moiety on the lower rim of **2**, probably, works to change the configuration at the upper rim of **2**. This might effect regulation of the metal affinity of **2**. The molecular model suggests that A-C rings at the upper rim will be getting far away and B-D rings are getting closer respectively with trans to cis isomerization as shown in Figure 4, if we named 4 benzene ring composed of calixarene as A, B, C, and D in clockwise. We studied the affinity of **2** for several metal cations in each the configuration. Figure 5 shows the liquid-liquid extractability of the trans form of **2**, 12 h-photoirradiated **2**, and non-

Fig. 4 Schematic representation of trans and cis forms of **2**.

Fig. 5 The extractability of **2** in the trans (□), 12 h-photoirradiated state (▨), and **3** (■) for the various metal cations.

modified calix[4]arene (3). Here, the trans form of 2 is the non-photoirradiated fraction; 12 h-photoirradiated 2 is obtained by UV photoirradiation for 12 h. 2 in the trans form does show only small extractability ranging from 4 % to 6 % for metal cations and little one for Cu^{2+} . On the other hand, the 12 h-photoirradiated calix[4]arene (3) shows higher affinity in the sequence of $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{K}^+ > \text{Cd}^{2+}$ than those of trans form of 2 and 3, and does a little ability for Ni^{2+} and none for K^+ . As mentioned before, it is supposed that the configuration of 2 will be changed from trans form to another isomer and finally to photostationary isomer (= cis isomer), when 2 was kept under photoirradiation. This suggested that 2 in a different configuration should show a different extractability for metal cations. We studied the affinities of 2 for Cu^{2+} and K^+ in different configurations obtained by under 0, 6, 12, 18, 24, and 36 h-photoirradiation of 2. Figure 6 shows that 2 shows the highest affinity for Cu^{2+} in the state obtained by 12 h-photoirradiation and smaller one in the state obtained by longer photoirradiation and finally zero by 36 h-photoirradiation. On the other hand, 2 shows different metal complexation pattern when K^+ was used as a guest metal cation, in which the extractability is 2.3 % at non-photoirradiated state and getting larger values under longer photoirradiation and finally 12 % under 36 h-photoirradiation. This means that how much the extraction ability of 2 for metal cations in each configuration produced by photoirradiation will be depended on how is the configuration of 2 and how much the ionic radius of metal cations used as guest.

In conclusion, the present results show that photoregulated, selective metal cations extraction can be realized by the use of the photoresponsive calix[4]arene system. Further work with many metal cations as a guest is needed to clarify the relationship guest property and affinity of this system.

Fig. 6 The extractability of 2 obtained under from 0 h to 36 h photoirradiation for Cu^{2+} (—■—) and K^+ (—○—).

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