

Communication

Calix[4]crowns with Methoxynaphthoymethyl Pendant Groups

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The novel calix[4]crowns with two pendant groups were prepared by the alkylation of calix[4]crowns with 6-methoxy-2-bromoacetylnaphthalene. ^1H NMR titration and picrate extraction experiments indicated that they exhibit higher complexing efficiency than their parent compounds and possess obvious selectivity for Na^+ or K^+ , respectively, and that the cation is encapsulated inside the preorganized ionophoric cavity defined by carbonyl oxygens, the crown ether and the phenoxy oxygens. From UV and fluorescent spectra it is revealed that calix[4]-crown-4 **3a** with 6-methoxy-2-naphthoymethyl pendant groups exhibits remarkable cation-induced photophysical effects and it could be utilized as a selective fluorescent sensor for Ca^{2+} .

Keywords calix[4]arene, ^1H NMR spectra, picrate extraction, fluorophore, calcium cation

Calixcrowns, combination of calixarene and crown ether in a single molecule, are a novel class of macrocyclic host compounds which have attracted increasing attention because of their increased ability for selective complexation of cations as compared with crown ethers or calixarenes.^{1,2} Recently, various calixcrowns³⁻⁶ including calix(aza)-crowns⁷⁻⁹, calix(thia)crowns¹⁰ have been synthesized. It is now well known that some of them exhibit outstanding recognition abilities towards cations. For example, the selectivity of diethylcalix[4]crown-4 and diethylcalix[4]crown-5 with 1,3-alternate conformation for Na^+/K^+ is $10^{5.3}$ and $10^{4.07}$ for K^+/Na^+ , respectively.¹¹ Therefore, calixcrowns have been applied as selective ionophores in extractive processes,^{3,12} as active carriers in ion selective electrodes^{11,13} and as selective fluorophore in the optical detection of trace metal cations.¹⁴

In the lariat crown ether, the donor atoms of the macroring and sidearms cooperatively complex with metal cation to form a three dimensional intramolecular array of binding sites. Consequently, the complexing capacity of the lariat crown ether is greater than the parent crown ether.¹⁵ If in lower-rim-1,3-bridged calix[4]crown with a cone conformation, appropriate pendant groups with the donor atoms are introduced by the alkylation of other two phenolic hydroxyl groups, then in such calix[4]crown, the

pendant groups with the donor atoms are situated at both sides of crown ring. Consequently, the guest cation trapped in the crown ring may be wrapped in such a way that the additional donor atoms on the pendant groups provide further co-ordination, as do lariat crown ethers. However, the studies of such calix[4]crown with pendant groups are relatively rare. There are only a few papers that report the synthesis and metal cation complexation ability of calixcrown with pendant groups, in which the pendant groups are alkyloxy (additional O donor sites for alkali and alkaline earth metal cations),^{14,16,17} picolyl¹⁸ and phosphinyl¹⁹ (additional N or P donor sites for transition metal).

In the present work, two novel calix[4]crowns with two pendant groups **3a** and **3b**²⁰ were synthesized (Scheme 1) by the alkylation of calix[4]crown-4 **2a** or calix[4]crown-5 **2b** with 6-methoxy-2-bromoacetylnaphthalene **4**.²¹ The yields of **3a** and **3b** are ~30% and ~55%, respectively. The compounds **3a** and **3b** were characterized by ^1H NMR, ESIMS, IR and elemental analysis.²⁰ In the ^1H NMR spectra, the methylene protons of ArCH_2Ar of **3a** and **3b** appeared as one pair of doublets. The chemical shift values are 3.14 and 4.52, 3.18 and 4.62, respectively, and all coupling constants are about 12.7 Hz. The two singlets of the aromatic protons appeared at 6.51 and 7.12, 6.57 and 7.04, the two singlets of the ^tBu group protons appeared at 0.83 and 1.33, 0.90 and 1.27, respectively. Obviously, this is consistent with the pinched-cone conformation having C_{2v} symmetry.²²⁻²⁵

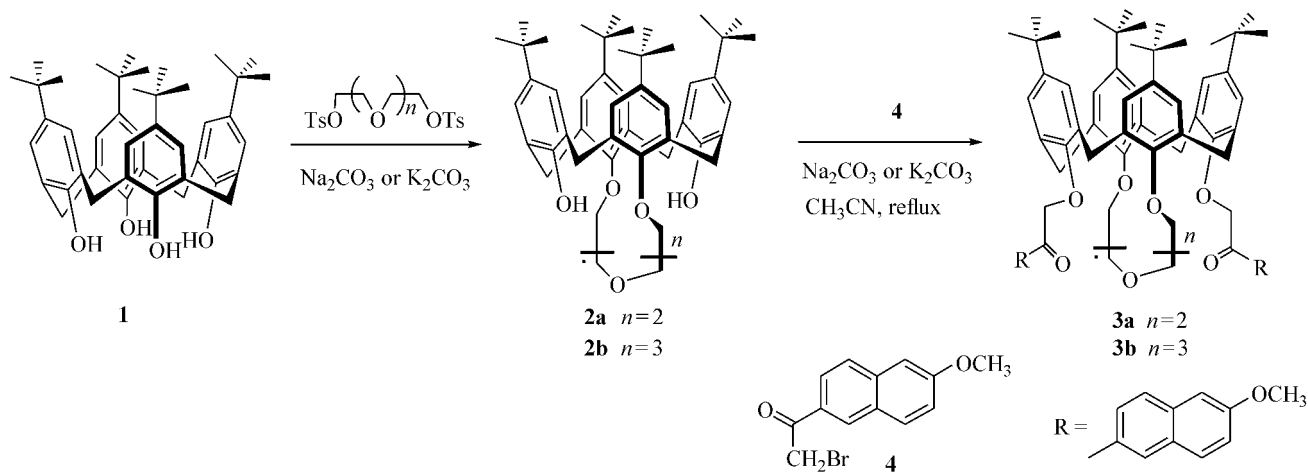
The extraction experiments of **3a**, **3b** and corresponding parent calix[4]crowns **2a**, **2b** for alkali metal picrates from water to chloroform were performed according to Pedersen's procedure.²⁶ The extraction percentages ($E\%$) are given in Table 1.

It is clear from Table 1 that the complexation abilities of calix[4]crowns **3a** and **3b** bearing the pendant groups with the donor atoms are dramatically increased as compared with the corresponding parent calix[4]crowns **2a** and **2b**, which can be ascribed to the participation of the carbonyl group oxygen atoms at the pendant groups in the

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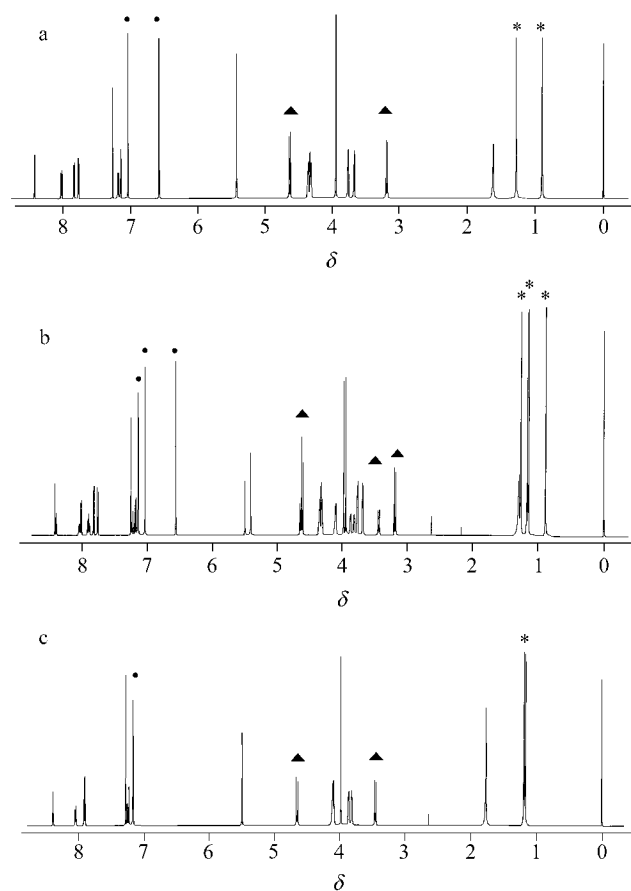
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Scheme 1 Synthesis of calix[4]crowns bearing pendant groups**Table 1** Extraction percentages ($E\%$) of alkali metal picrates from water into chloroform at 20 °C

Host	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
2a	0.23	3.50	0.32	0.26	0.11
3a	1.30	23.9	0.41	0.30	0.22
2b	0.19	0.24	3.11	0.32	0.09
3b	5.70	4.80	30.4	10.3	3.01

formation of the complexes. In addition, it is notable that calix[4]crown-4 **3a**, calix[4]crown-5 **3b** have higher Na⁺ or K⁺ selectivity, respectively. Obviously, it can be attributed to the cavity size of calix[4]crown-4 and calix[4]crown-5. In contrast to the selectivity of 12-crown-4, 15-crown-5 and 18-crown-6 for Li⁺, Na⁺ and K⁺, respectively, the calix[4]crowns show a preference for the corresponding larger cations.

To afford precise insight into the binding sites, stoichiometry and solution structures of calix[4]crown bearing two pendant groups with alkali metal ion, ¹H NMR titration experiments of **3a** and **3b** with potassium and sodium thiocyanate were carried out in CDCl₃-CD₃OD (V/V, 1:1). In the presence of KSCN, the signals in the ¹H NMR spectrum of **3b** change greatly. When the molar ratio of KSCN to **3b** is less than 1, signals for both complexed and uncomplexed host **3b** are present in the spectrum [Fig. 1 (b)], whereas as the molar ratio of KSCN to **3b** reaches 1:1, all the signals for the free host, except for protons in naphthyl and methoxy group, disappear [Fig. 1 (c)]. An increase in the potassium thiocyanate:**3b** molar ratio beyond unity results in no further spectral changes. It suggests that complex stoichiometry of calix[4]crown-5 host **3b** to K⁺ is 1:1. From Fig. 1 (c), two peaks of phenyl rings in calix[4]crown-5 moiety have been merged into a single peak and the chemical shifts move from 6.57, 7.04 to 7.17. Two peaks of *t*-butyl groups at 0.90, 1.27 appear at almost the same position (1.166, 1.175). The splitting pattern of the methylene protons of ArCH₂Ar in calix[4]crown-5 moiety has not changed, but the chemical shifts move from 3.18, 4.62 to 3.44, 4.65, respectively. These changes indicate that the C_{2v} symmetry in the free

**Fig. 1** ¹H NMR spectra (600 MHz, CDCl₃-CD₃OD, 1:1 V/V, 25 °C) of **3b** (a) and spectral changes upon addition of 0.5 (b) and 1.0 equiv. (c) of KSCN (* = *t*-butyl, ▲ = ArCH₂Ar, ● = phenyl).

host has been changed into a pseudo-4-fold symmetry (C_{4v}) due to complexing with K⁺. Moreover, the chemical shift of the methylene protons adjacent to carbonyl group moves downfield from 5.42 to 5.53 and the multiplet of methylene protons of crown ether has also shifted downfield or upfield about 0.25. From these facts it is suggested the participation of the carbonyl group oxygen atoms in the formation of the complex, in which the rota-

tion of the carbonyl groups takes place to reach a suitable orientation of the carbonyl group oxygen atoms towards the cation (Fig. 2). Similar situation can be observed from ^1H NMR spectra in the titration experiments of **3a** with sodium thiocyanate. Therefore, it is believed that K^+ or Na^+ be encapsulated inside the preorganized three-dimensional cavity defined by the oxygen atoms in the carbonyl group, the crown ether and the phenoxy groups.

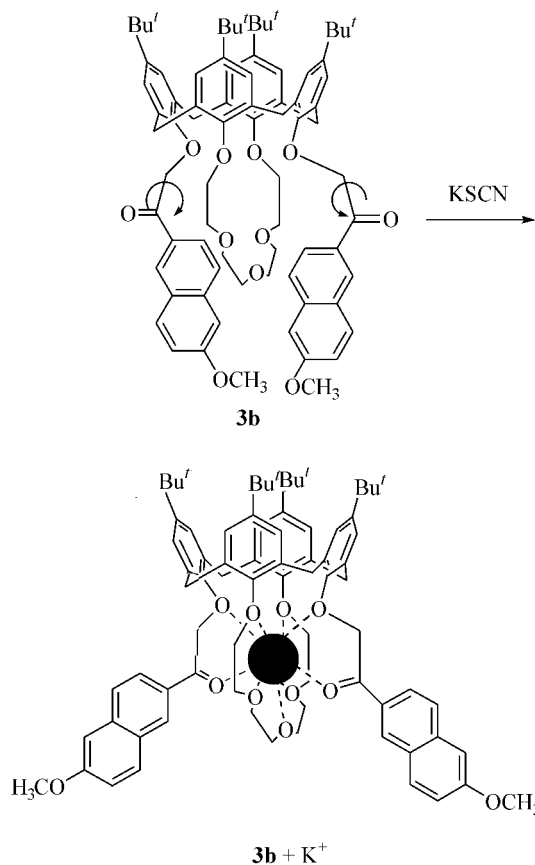


Fig. 2 The encapsulation process of host **3b** with K^+ ion.

Electrospray ionization mass spectroscopy (ESIMS) has been used to determine the complex stoichiometry of host and guest.²⁷ For the present study, the only one peak was found in the ESIMS spectra of the complexes of calix[4]crowns with Na^+ or K^+ , which appeared at m/z 1181.7 (**3a** ~ Na^+ , calcd 1181.6), 1241.6 (**3b** ~ K^+ , calcd 1241.6), respectively. Therefore, it is further demonstrated that the complex stoichiometry of calix[4]crowns bearing two pendant groups with alkali metal cations Na^+ or K^+ is 1:1.

The 6-methoxy-2-naphthylmethyl was chosen as pendant groups because of its distinguished photophysical characteristics. The photoactive group includes an electron-donating substituent (methoxy group) conjugated to an electron-withdrawing substituent (carbonyl group). It undergoes intramolecular charge transfer upon excitation and is thus expected to have marked changes in UV absorption and fluorescence emission spectra upon the participation of carbonyl group oxygen atoms in the complexation

process. The effects upon addition of Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} perchlorates to **3a** and **3b** were examined in acetonitrile solution. An increase in the molar absorption coefficients together with red shifts of the absorption and emission spectra was observed upon cation binding and the trends are almost identical in both spectra. The maximum absorption and emission wavelengths of **3a** and its complexes with the cations are 310 nm, 400 nm for the free **3a**, 328 nm, 434 nm for **3a** ~ Ca^{2+} , 331 nm, 426 nm for **3a** ~ Sr^{2+} , 316 nm, 418 nm for **3a** ~ Na^+ , 314 nm, 406 nm for **3a** ~ Mg^{2+} , 314 nm, 410 nm for **3a** ~ Li^+ , 312 nm, 407 nm for **3a** ~ Ba^{2+} , 312 nm, 403 nm for **3a** ~ K^+ complex. Fig. 3 shows the fluorescence spectra of **3a** and its complexes in CH_3CN (excitation wavelength is 308 nm). The fluorescence strength remarkably increases upon Ca^{2+} cation binding. It is clear that **3a** exhibits a larger photophysical effect upon Ca^{2+} binding. The reasons are that Ca^{2+} not only possesses the higher charge density which results in the cation-induced enhancement of the electron-withdrawing character of the carbonyl,²⁸ but also its diameter (0.212 nm) is suitable for the cavity of calix[4]crown-4 **3a** in the formation of the complex. Therefore, **3a** could be utilized as a selective fluorescent sensor for Ca^{2+} . When the Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} perchlorates were added to **3b** in acetonitrile solution, an increase in the molar absorption coefficients together with red shifts of the absorption and emission spectra was also observed upon cation binding. The obvious difference is that the fluorescence strength remarkably increases upon Sr^{2+} cation rather than Ca^{2+} . It further demonstrates that the suitability of cation diameter and the cavity of calix[4]crown and the higher charge density of cation result in cation-induced photophysical effects.

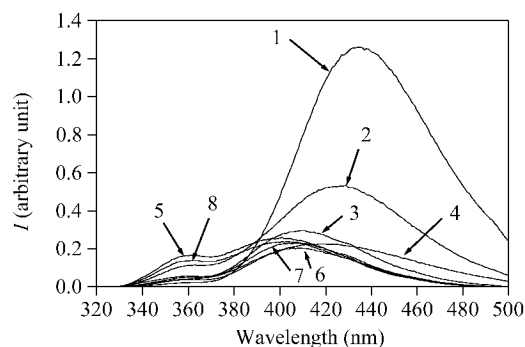


Fig. 3 Fluorescence spectra of **3a** and its complexes in CH_3CN (excitation wavelength is 308 nm) of (1) $\text{Ca}(\text{ClO}_4)_2$, (2) $\text{Sr}(\text{ClO}_4)_2$, (3) LiClO_4 , (4) NaClO_4 , (5) host **3a**, (6) $\text{Mg}(\text{ClO}_4)_2$, (7) $\text{Ba}(\text{ClO}_4)_2$ and (8) KClO_4 .

In conclusion, experiments of picrate extraction and ^1H NMR titration demonstrated that **3a** and **3b** exhibit higher complexing efficiency than their parent compounds and possess obvious selectivity for Na^+ and K^+ , respectively. ^1H NMR and ESIMS spectra indicated that the complex stoichiometry of host **3a** to Na^+ , **3b** to K^+ is 1:

1. It can be believed that the carbonyl group oxygen atoms at pedant groups participate in the formation of the complex and the metal cation is encapsulated inside the preorganized three-dimensional cavity defined by carbonyl oxygens, the crown ether and the phenoxy oxygens. The determinations of UV and fluorescent spectra of the hosts and their complexes with perchlorate salts indicated that **3a** shows remarkable Ca^{2+} cation-induced photophysical effects and thus it could be utilized as a selective fluorescent sensor for Ca^{2+} .

References and notes

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