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Synthesis and Cation Complexation Properties of Calix[4]crowns Bearing Pendant Donor Sites

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Four novel calix[4]crowns-4 and calix[4]crowns-5 with two pendant groups were synthesized by the alkylation of calix[4]crowns-4 and calix[4]crowns-5 with 6-methoxy-2-bromoacetylnaphthalene and 2-methoxy-1-bromoacetylaminomethylnaphthalene, respectively in the presence of Na_2CO_3 or K_2CO_3. ^1H NMR titration and picrate extraction experiments indicated that the cation is encapsulated inside the preorganized ionophoric cavity constructed by the carbonyl oxygens, the crown ether and the phenoxy oxygens so that these calix[4]crowns-4 and calix[4]crowns-5 with two pendant groups exhibit higher complex efficiency than their parent compounds and possess obvious selectivity for Na^+ and K^+, respectively. The measurement of UV and fluorescent spectra of the hosts and their complexes with perchlorate salts revealed that calix[4]crowns-4 with the 6-methoxy-2-naphthoylmethyl pendant groups (2a) exhibits remarkable cation-induced photophysical effects and they could be utilized as a selective photophysical sensor for Ca^{2+}.

Keywords: Calixcrown; Picrate extraction; Fluorescent ionophore; Cation selectivity

INTRODUCTION

Calixcrowns carrying bridging polyethyleneoxy moieties on the lower rim, which combine calixarene and crown ether in a single molecule, are a novel class of host compounds which have attracted increasing attention because of their increased ability for selective complexation of cations and neutral molecules as compared with crown ethers or calixarenes [1–4]. During the past decade, various calixcrowns [5–12] including calix(aza)crowns [13–17] and calix(thia)crowns [18,19] 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 $K^+/Na^+ = 10^{4.07}$, respectively [20]. Therefore, calixcrowns have been applied as selective ionophores in extractive processes [7,10,19], as carriers through liquid membranes for metal ion separation [21,22] or across bilayer for metal ion transportation [23], as active carriers in ion selective electrodes or ion selective field effect transistors [20,24–26], and as selective fluorophores in the optical detection of trace metal cations [27].

Apart from the cavity geometry and the nature of donor sites, the co-operation of sidearms on the macrocycle also plays an important role in determining the selective complexation ability for metal cations. In this context, the lariat crown ether has long been studied. In the lariat crown ether, the donor atoms of the macroring and sidearms cooperatively complex with the 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 [28–30]. If in a lower-rim-1,3-bridged calix[4]crown with a cone conformation, appropriate pendant groups with donor atoms are introduced by the alkylation of two other phenolic hydroxyl groups, then in such a calix[4]crown, the pendant groups with the donor atoms are situated at both sides of the 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,

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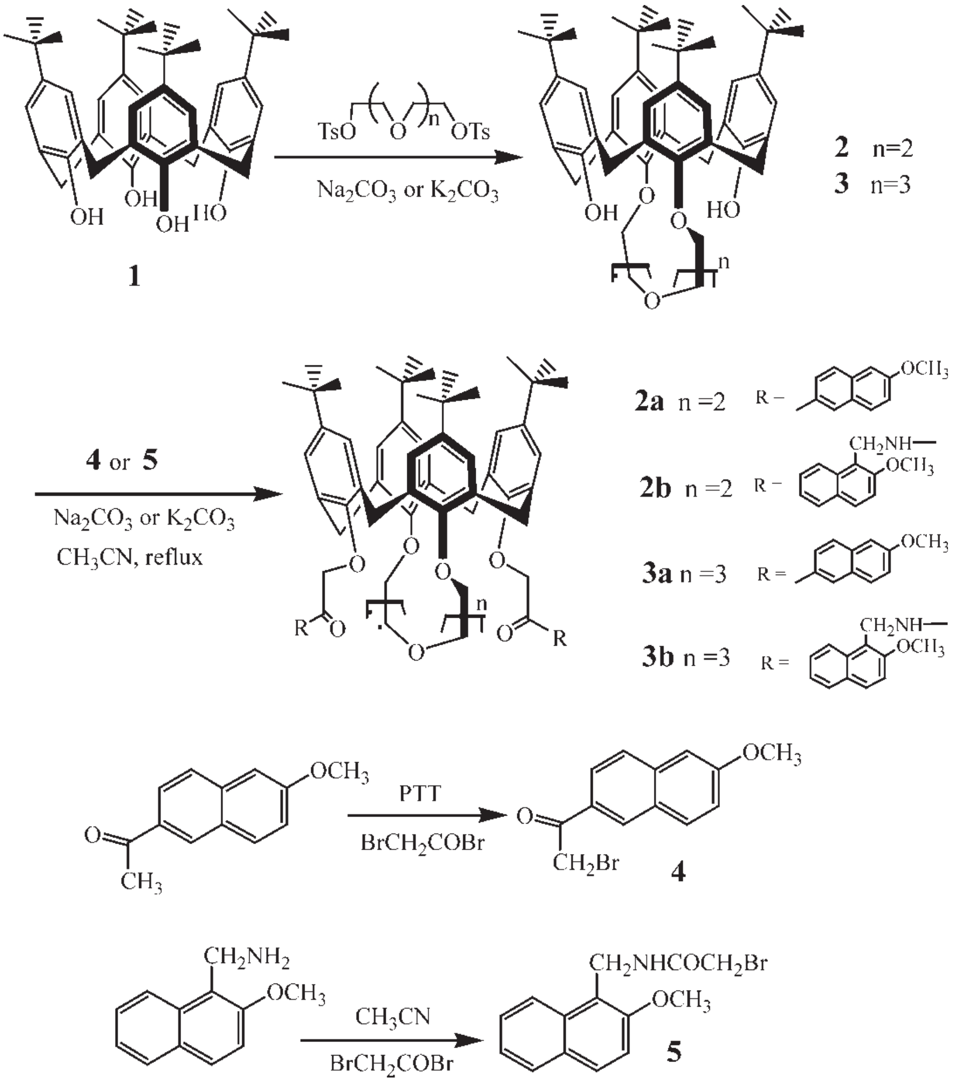

SCHEME 1 Synthesis of calix[4]crowns bearing pendant groups.

as do lariat crown ethers. However, the studies of such calix[4]crowns with pendant groups are relatively rare. There are only a few papers that report the synthesis and metal cation complexation ability of calixcrowns with pendant groups, in which the pendant groups are picolyl (additional N donor sites for transition metals) [31], phosphinyl (additional P donor sites for transition metals) [32], and alkyloxy (additional O donor sites for alkali and alkaline earth metal cations) [33–35].

In the present work, four novel calix[4]crowns with two pendant groups containing carbonyl group were synthesized (Scheme 1). 6-Methoxy-2-naphthoylmethyl and 2-methoxy-1-naphthylmethylaminoformylmethyl were chosen as pendant groups, respectively. The investigations of ^{1}H NMR, ESIMS and extraction experiments have revealed that carbonyl groups at the pendant groups participate in the complexation of metal cations and the selective complexation ability is much greater than that of the parent calix[4]crown. Furthermore, in the pendant group 6-methoxy-2-naphthoylmethyl, because the carbonyl group is in conjugation with the naphthalene ring, the cation binding results in changes in the photophysical characteristics. UV and fluorescence spectra have demonstrated that the calix[4]crown-4 **2a** with the pendant group 6-methoxy-2-naphthoylmethyl exhibits remarkable cation-induced photophysical effects with Ca^{2+}.

RESULTS AND DISCUSSION

Synthesis of Calix[4]crown with Two Pendant Groups

p-Tetra-*tert*-butyl calix[4]crowns with two pendant groups (**2a**, **2b** and **3a**, **3b**) were prepared in three steps (Scheme 1). *p*-Tetra-*tert*-butyl calix[4]crown-4 (**2**) or *p*-tetra-*tert*-butyl calix[4]crown-5 (**3**) were synthesized according to literature procedures [35]. 6-Methoxy-2-bromoacetylnaphthalene **4** was obtained by

Friedel–Crafts acylation of 2-methoxynaphthalene by bromoacetyl bromide [36]. 2-Methoxy-1-bromoacetylaminomethylnaphthalene **5** was obtained by the condensation of 2-methoxy-1-aminomethylnaphthalene [37] and bromoacetyl bromide. The dialkylation of 1,3-dihydroxy-*p*-tetra-*tert*-butyl calix[4]crowns **2** and **3** with 6-methoxy-2-bromoacetylnaphthalene **4** or 2-methoxy-1-bromoacetylaminomethylnaphthalene **5** was carried out in the presence of the weak base Na_2CO_3 or K_2CO_3 in acetonitrile, respectively. The yields for **2a** and **2b** were ~30%, and for **3a** and **3b** were ~55%. Compounds **2a**, **2b** and **3a**, **3b** were characterized by ^{1}H NMR, ^{13}C NMR, ESIMS, IR and elemental analysis. The IR absorption peaks in **2a**, **3a** and **2b**, **3b** at about 1700 and 1665 cm^{-1} are the characteristic bands of aromatic carbonyl and amide carbonyl groups, respectively. In the ^{1}H NMR spectra, the methylene hydrogens of $ArCH_2Ar$ appeared as one pair of doublets. The chemical shift values are 3.14 and 4.52, 2.97 and 3.99, 3.18 and 4.62, 2.92 and 4.21 ppm, respectively, and all the coupling constants are ~12.7 Hz. The ^{13}C chemical shift values of the methylene carbons of $ArCH_2Ar$ are at 31.0–32.0 ppm. Obviously, these are consistent with a cone conformation [38–40]. Moreover, in the ^{1}H NMR spectra of **2a**, **2b** and **3a**, **3b**, the two singlets of the aromatic protons appeared at δ6.51 and 7.12, 6.31 and 7.02, 6.57 and 7.04, 6.49 and 6.93, respectively, while the two singlets of the ^{t}Bu group protons appeared at δ0.83 and 1.33, 0.75 and 1.32, 0.90 and 1.27, 0.82 and 1.26, respectively, suggesting a pinched-cone conformation having C_{2v} symmetry in solution [31,38,40,41].

^{1}H NMR Titration Experiments

To afford precise insight into the binding sites, stoichiometry and solution structures of the complex of calix[4]crown bearing two pendant groups with alkali metal ions, ^{1}H NMR titration experiments for **2a**, **2b**, **3a** and **3b** with potassium and sodium thiocyanate were carried out in $CDCl_3$–CD_3OD (v/v, 1:1). Figure 1 shows the ^{1}H NMR spectral changes upon titration of **3a** with KSCN. In the absence of potassium thiocyanate, the ^{1}H NMR spectrum, Fig. 1(a), of **3a** is in agreement with the pinched-cone conformation with C_{2v} symmetry. In the presence of KSCN, the signals in the ^{1}H NMR spectrum change greatly. When the molar ratio of KSCN and **3a** is less than 1, signals for both complexed and uncomplexed host **3a** are present in the spectrum [Fig. 1(b)], whereas when the molar ratio of KSCN and **3a** reaches 1: 1, all the signals for the free host, except for the protons in naphthyl and methoxy group, disappear [Fig. 1(c)]. An increase in the potassium thiocyanate:**3a** molar ratio beyond unity results in no further spectral changes. This suggests that the complex stoichiometry of calix[4]crown-5 host **3a** to K^+ is 1:1. From Fig. 1, the two peaks of the phenyl rings in the calix[4]arene-5 moiety have merged into a single peak and the chemical shifts move from 6.57, 7.04 ppm to 7.17 ppm. The two peaks of the *t*-butyl groups at 0.90, 1.27 ppm appear at almost the same position (1.166, 1.175 ppm). The splitting pattern of the methylene protons of $ArCH_2Ar$ in calix[4]arene-5 moiety has not changed, but the chemical shifts move from 3.18, 4.62 ppm to 3.44, 4.64 ppm, respectively. These changes can be interpreted by assuming that the C_{2v} symmetry in the free host has been changed into a pseudo-four-fold symmetry (C_{4v}) [31] due to complexing with K^+. Moreover, the chemical shift of the methylene protons adjacent to the carbonyl group moves downfield from 5.42 to 5.49 ppm and the multiplet of methylene protons of crown ether have also shifted downfield or upfield by about 0.25 ppm. These facts suggest the participation of the carbonyl group oxygen atoms in the formation of the complex, in which the rotation of the carbonyl groups takes place to reach a suitable orientation of the carbonyl oxygen atoms towards the cation. A similar situation can be observed from ^{1}H NMR spectra in the titration experiments of calix[4]-crown-5 **3b** with potassium thiocyanate (Table I). Therefore, the oxygen atoms in the carbonyl group, in the crown ether and the phenoxy group provide a total of nine binding sites for the cation. It is believed that K^+ is encapsulated inside the preorganized three-dimensional cavity. The complexing process of calix[4]crown-5 **3a** and **3b** with K^+ and the structures of the complexes in solution are shown in Fig. 2.

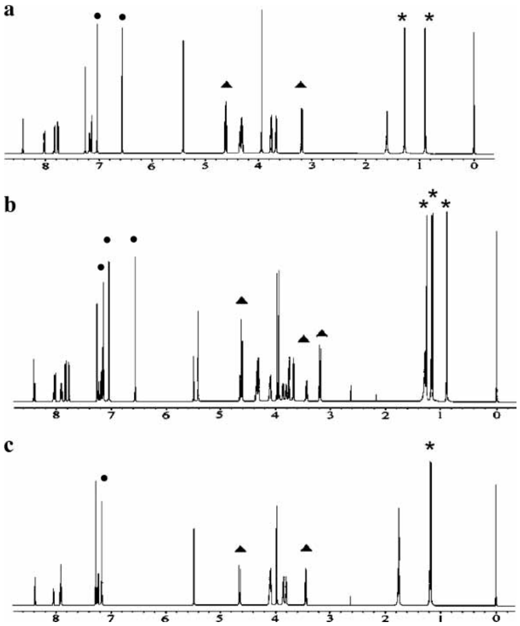

FIGURE 1 ^{1}H NMR spectra (600 MHz, $CDCl_3$–CD_3OD, 1:1 v/v, 25°C) of **3a** (a) and spectral changes upon addition of 0.5 (b) and 1.0 equiv (c) of KSCN (★ = *t*-butyl, ▲ = $ArCH_2Ar$, • = phenyl).

TABLE I Partial proton chemical shifts (δ, ppm) of calix[4]crowns bearing pendant groups and their complexes with alkali metal thiocyanates (600 MHz, $CDCl_3$–CD_3OD, v/v, 1:1, 25°C)

Compd.	ArH	$ArCH_2Ar$	Crown unit	OCH_2CO	*t*-Butyl
2a	6.51, 7.12	3.14 (d), 4.52 (d)	4.12 (t), 4.45 (t)	5.26	0.83, 1.33
2a–Na^+	6.94, 7.27	3.47 (d), 4.74 (d)	4.10(b), 4.33(b)	5.67	0.97, 1.29
2a–K^{+*}	6.52, 7.13	3.15 (d), 4.52 (d)	4.12 (t), 4.45 (t)	5.27	0.83, 1.33
2b	6.31, 7.02	2.97 (d), 3.99 (d)	3.70 (t), 4.35 (t)	4.32	0.75, 1.32
2b–Na^+	6.82, 7.13	3.28 (d), 4.32 (d)	3.26(b), 3.41(b)	4.58	0.94, 1.25
2b–K^{+*}	6.31, 7.02	2.97 (d), 3.98 (d)	3.70 (t), 4.34 (t)	4.31	0.75, 1.32
3a	6.57, 7.04	3.18 (d), 4.62 (d) 4.30 ∼ 4.37 (m)	3.67 (t), 3.76 (t)	5.42	0.90, 1.27
3a–K^+	7.17	3.44 (d), 4.64 (d) 4.08 ∼ 4.11(m)	3.82(b), 3.85(b)	5.49	1.17
3a–Na^+	7.16, 7.18	3.49 (d), 4.74 (d) 4.17(b)	3.80(b), 3.91(b)	5.74	1.17, 1.18
3b	6.49, 6.93	2.92 (d), 4.21 (d)	3.45 (t), 3.69 (t)	4.88	0.82, 1.26
3b–K^+	6.99	3.16 (d), 4.23 (d) 3.73 ∼ 3.78 (m)	3.51 ∼ 3.54 (m)	4.50	1.11
3b–Na^+	7.02, 7.06	3.22 (d), 4.24 (d)	3.58(b), 3.92(b)	4.58	1.10, 1.15

* **2a**–K^+ and **2b**–K^+; the molar ratio of potassium thiocyanate: **2a** or **2b** is 1: 1, ^1H NMR spectra have not any changes.

In the titration of **3a** or **3b** with sodium thiocyanate, some signals (aromatic, ^tBu) are broadened in the initial stage, followed by sharpening at a 1:1 ratio of NaSCN and host **3a** or **3b**. This indicates that the exchange rates for Na^+ with **3a** or **3b** are faster than those for K^+, which is similar to the proposal reported by Pappalardo *et al.* [31]. On the other hand, great changes occur in the ^1H NMR spectra of host **3a** or **3b** when the molar ratio of NaSCN and **3a** or **3b** reaches 1: 1. It is clear from Table I that the signals of the methylene protons adjacent to the carbonyl group in host **3a** and **3b** shift downfield and upfield by 0.32 and 0.30 ppm, respectively, because of the participation of their carbonyl group oxygen atoms in complex formation. Moreover, the signals of methylene protons in the crown ring and in $ArCH_2Ar$ also shift downfield pronouncedly. In the two signals of phenyl or *t*-butyl, the signals in the lower field shift upfield, whereas the signals in the higher field shift downfield, so that they become very close to each other at 7.16 and 7.17 ppm, 7.02 and 7.04 ppm for the phenyl protons of **3a**–Na^+ and **3b**–Na^+, 1.17 and 1.18 ppm and 1.12 and 1.15 ppm for *t*-butyl protons of **3a**–Na^+ and **3b**–Na^+, respectively. Therefore, the smaller Na^+ cation can also be encapsulated into the ionophoric

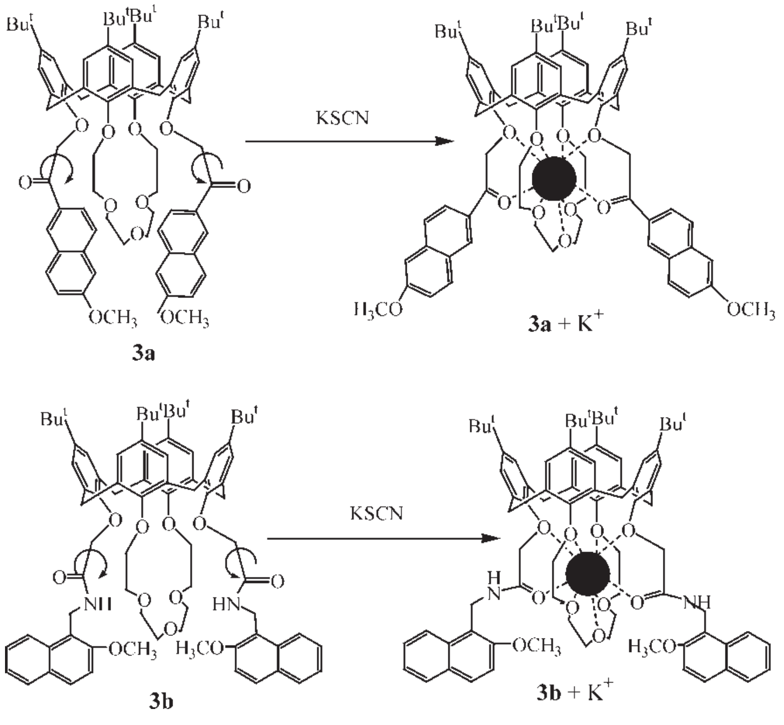

FIGURE 2 The encapsulation processes of hosts **3a** or **3b** with K^+ ion.

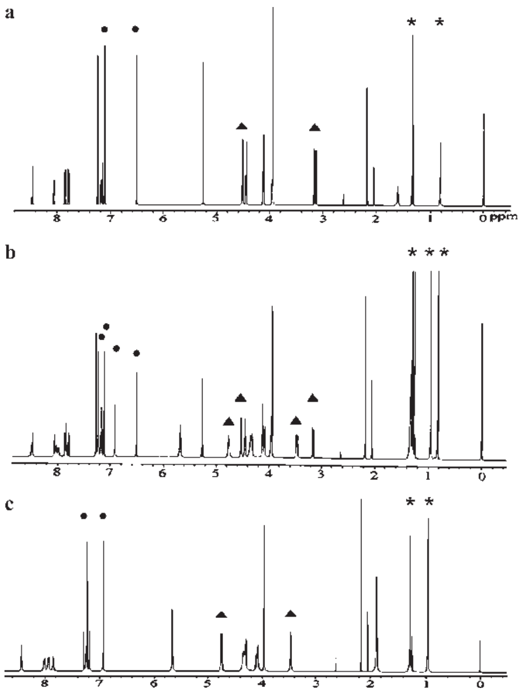

FIGURE 3 ^{1}H NMR spectra (600 MHz, $CDCl_3$–CD_3OD, 1:1 v/v, 25°C) of **2a** (a) and spectral changes upon addition of 0.5 (b) and 1.0 equiv (c) of NaSCN, ★ = *t*-butyl, ▲ = $ArCH_2Ar$, • = phenyl).

cavity defined by the carbonyl group, phenoxy and crown ethereal oxygens in a complex stoichiometry of 1:1.

Figure 3 shows the ^{1}H NMR spectral changes upon titration of calix[4]arene-4 **2a** with NaSCN. When the molar ratio of NaSCN and **2a** reaches 1:1, all the signals for the free host **2a** disappear and great changes occur in the spectra [Fig. 3(c), Table I]. The main changes are summarized as follows: the signals of the methylene protons adjacent to the carbonyl group shift downfield by 0.41 ppm. Two signals of the phenyl protons shift downfield by 0.12 and 0.09 ppm, respectively. One pair of doublets of the methylene protons of $ArCH_2Ar$ shift downfield by 0.22 and 0.33 ppm. For the *t*-butyl protons, the signals at lower field (1.33 ppm) shift upfield by 0.04 ppm, whereas the signals at higher field (0.83 ppm) shift downfield by 0.14. Similar phenomena are also observed from ^{1}H NMR spectra in the titration experiments of calix[4]crown-4 **2b** with NaSCN (Table I). The spectral changes suggest that the Na^+ cation is bound in the preorganized cavity defined by the crown ether ring, the carbonyl and the phenoxy group and the complex stoichiometry is considered as 1:1. The structures of calix[4]crown-4 **2a**–Na^+ and **2b**–Na^+ complexes in solution are similar to those of calix[4]crown-5 **3a**–K^+ and **3b**–K^+ complexes. Titration experiments of calix[4]crown-4 **2a** and **2b** with KSCN under same conditions have shown that the ^{1}H NMR spectra of **2a** and **2b** remain unchanged (Table I) when the molar ratio of KSCN and **2a** or **2b** reaches 1:1. This indicates that the K^+ cation is too large to be encapsulated into the ionophoric cavity of calix[4]crown-4 **2a** or **2b**. Therefore, the ionophoric cavity of **2a** and **2b** is best adapted for the Na^+ cation.

It is notable that the signals of the methoxy protons in the ^{1}H NMR spectra of **2b**–Na^+, **3b**–K^+ and **3b**–Na^+ complexes underwent no change compared with free hosts **2b** and **3b** although the methoxy was located at the β position of the naphthalene rings. This suggests that the methoxy oxygen atoms did not participate in the formation of the complex.

ESIMS Studies of Calix[4]crown with Two Pendant Groups

Electrospray ionization mass spectrometry (ESIMS) has been used to determine the complex stoichiometry of host and guest [42]. For the present study, 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 (**2a**–Na^+, Calcd 1181.6), 1239.7 (**2b**–Na^+, Calcd 1239.7), 1225.6 (**3a**–Na^+, Calcd 1225.6), 1241.6 (**3a**–K^+, Calcd 1241.6), 1283.5 (**3b**–Na^+, Calcd 1283.7) and 1299.6 (**3b**–K^+, Calcd 1299.7), 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.

Alkali Metal Picrate Extraction Studies of Calix[4]crown with Two Pendant Groups

The alkali metal binding properties of calix[4]crown **2**, **3** and calix[4]crown with two pendant groups **2a**, **2b**, **3a**, **3b** were investigated by two phase extraction experiments of alkali metal picrates from water to chloroform. The amount of picrate ion extracted into the organic phase was determined by UV absorption spectroscopy and from subtraction of the original aqueous phase. The extraction constants (K_e) and the distribution constants (K_d) were determined according to the following expressions, respectively [42–43]:

$$K_e = [M^+ \bullet\ Host \bullet\ Pic^-]_{org}/[M^+]_{aq}[Pic^-]_{aq}[Host]_{org}$$

$$K_d = [M^+ \bullet\bullet\ Pic^-]_{org}/[M^+]_{aq}[Pic^-]_{aq}$$

The association constant (K_{ass}) in chloroform was defined in the following expression and the values were calculated from K_e and K_d [42–43].

$$K_{ass} = [M^+ \bullet\ Host \bullet\ Pic^-]_{org}/[M^+ \bullet\bullet\ Pic^-]_{org}[Host]_{org}$$

$$K_{ass} = K_e/K_d$$

The association constants (K_{ass}) in chloroform are summarized in Table II.

TABLE II The association constants (K_{ass}) of calix[4]crowns **2**, **3**, **2a**, **2b**, **3a**, **3b** with alkali metal cations derived from metal picrate extraction

	2 $K_{ass} \times 10^{-5}\,M^{-1}$	**2a** $K_{ass} \times 10^{-5}\,M^{-1}$	**2b** $K_{ass} \times 10^{-5}\,M^{-1}$	**3** $K_{ass} \times 10^{-5}\,M^{-1}$	**3a** $K_{ass} \times 10^{-5}\,M^{-1}$	**3b** $K_{ass} \times 10^{-5}\,M^{-1}$
Li^+	1.35	2.41	15.4	1.05	7.51	2.50
Na^+	1.90	160	164	1.12	22.1	7.01
K^+	1.35	6.10	9.15	12.8	313	146
Rb^+	0.47	9.80	6.22	0.52	8.70	9.01
Cs^+	0.31	6.50	7.02	0.31	6.05	2.60

It is clear from Table II that the complexation abilities of calix[4]crowns **2a** and **2b**, **3a** and **3b** bearing the pendant groups with the donor atoms are dramatically increased compared with the corresponding parent calix[4]crowns **2** and **3**, which can be ascribed to the participation of the carbonyl group oxygen atoms at the pendant groups in the formation of the complexes. In addition, it is notable that calix[4]crown-4 **2a** and **2b** have higher selectivity for Na^+ than the corresponding calix[4]crown-5 **3a** and **3b**. In contrast, calix[4]crown-5 **3a** and **3b** have higher selectivity for K^+ than the calix[4]crown-4 **2a** and **2b**, 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.

UV and Fluorescent Spectra Studies of Calix[4]crown with Two Pendant Groups

In the present work, we chose methoxynaphthyl as the pendant group because it has distinguished photophysical characteristics. As for calix[4]crown **2a** and **3a**, the photoactive group 6-methoxy-2-naphthyl-acyl includes an electron-donating substituent (the methoxy group) conjugated to an electron-withdrawing carbonyl group. It undergoes intramolecular charge transfer upon excitation and is thus expected to exhibit marked changes in its UV absorption and fluorescence emission spectra upon the participation of the 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 calix[4]crown-4 **2a** were first examined in acetonitrile solution. The UV absorption and fluorescence spectra of **2a** and its complexes with Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} are shown in Figs. 4 and 5, respectively. An increase in the molar absorption coefficients together with red shifts of the absorption and emission spectra are observed upon cation binding and the trends are almost identical in both spectra. The maximum absorption and emission wavelengths of **2a** and its complexes with the cations are 310 and 400 nm for free **2a**, 328 and 434 nm for **2a**–Ca^{2+}, 331 and 426 nm for **2a**–Sr^{2+}, 316 and 418 nm for **2a**–Na^+, 314 and 406 nm for **2a**–Mg^{2+}, 314 and 410 nm for **2a**–Li^+, 312 and 407 nm for **2a**–Ba^{2+}, 312 and 403 nm for **2a**–K^+, respectively. It is clear that **2a** exhibits a larger photophysical effect upon Ca^{2+} binding. The reasons are that Ca^{2+} possesses a higher charge density, which results in the cation-induced enhancement of the electron-withdrawing character of the carbonyl, and also its diameter (2.12 Å) is suitable for the cavity of calix[4]crown-4 **2a**. Moreover, the fluorescence strength remarkably increases upon Ca^{2+} cation binding. Such an enhancement can be tentatively explained in terms of the relative energy of the singlet ππ* and nπ* states. In the presence of Ca^{2+} cation which strongly interacts with the lone pair of the carbonyl group, the nπ* state is likely to be shifted to higher energy so that the lowest excited state become ππ* [44]. However, as we expected, calix[4]crown **2b** and **3b** show no changes in the UV absorption and fluorescence emission spectra upon adding alkali and alkaline earth metal cations because the photoactive group 2-methoxy-1-naphthyl is unconjugated with the carbonyl group provided donor site in the formation of the complexes.

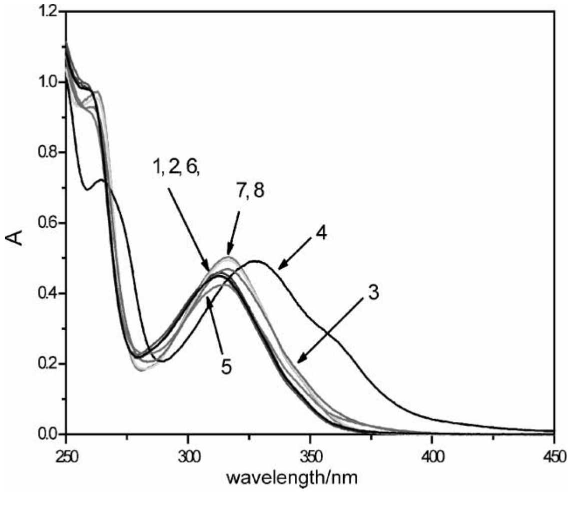

FIGURE 4 UV absorption spectra of host **2a** and its complexes in acetonitrile solution. The concentrations of the host **2a** and perchlorate salts are 2.0×10^{-5} M. (1) host **2a**, (2) $Ba(ClO_4)_2$, (3) $Sr(ClO_4)_2$, (4) $Ca(ClO_4)_2$, (5) $Mg(ClO_4)_2$, (6) $KClO_4$, (7) $NaClO_4$, (8) $LiClO_4$.

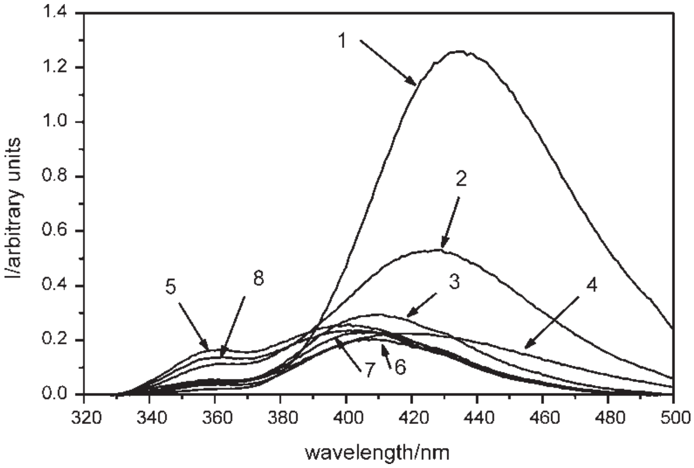

FIGURE 5 Fluorescence spectra of **2a** and its complexes in CH_3CN (excitation wavelength is 308 nm); (1) $Ca(ClO_4)_2$, (2) $Sr(ClO_4)_2$, (3) $LiClO_4$, (4) $NaClO_4$, (5) host **2a**, (6) $Mg(ClO_4)_2$, (7) $Ba(ClO_4)_2$, (8) $KClO_4$.

CONCLUSION

Four novel calix[4]crowns-4 or calix[4]crowns-5 with two pendant groups were synthesized by the alkylation of calix[4]crowns-4 or calix[4]crowns-5 with 6-methoxy-2-bromoacetylnaphthalene and 2-methoxy-1-bromoacetylaminomethylnaphthalene, respectively, in the presence of Na_2CO_3 or K_2CO_3. ^{1}H NMR titration and picrate extraction experiments have demonstrated that calix[4]crowns-4 or calix[4]-crowns-5 with two pendant groups exhibit higher complex efficiency than their parent compounds and possess obvious selectivity for Na^+ and K^+, respectively. It is also believed that the carbonyl group oxygen atoms on the pendant groups participate in the formation of the complex and the metal cation is encapsulated inside the preorganized three-dimensional cavity in which the oxygen atoms of the carbonyl group, the crown ether and the phenoxy provide a total of nine binding sites. Moreover, the determinations of UV and fluorescent spectra of the hosts and their complexes with perchlorate salts have indicated that calix[4]-crowns-4 **2a** with 6-methoxy-2-naphthoylmethyl pendant groups shows remarkable Ca^{2+} cation-induced photophysical effects, which could be utilized as a selective photophysical sensor for Ca^{2+}.

EXPERIMENTAL

Melting points were determined on a Yanaco micro melting point apparatus. Samples for elemental analysis were dried *in vacuo* at 60°C. Elemental analyses were carried out using Perkin Elmer 240C. ^{1}H NMR and ^{13}C NMR were recorded on Inova 600 MHz or Bruker 300 MHz. MS spectra were recorded by electrospray mass spectrometer (LCQ, Finnigan) in negative or positive mode. IR spectra were recorded on Bruker IFS 66v. Preparative column chromatography separations were performed on G60 silica gel, while precoated silica gel plates (GF_{254}) were used for analytical TLC. All the solvents were purified by standard procedures. 6-Methoxy-2-bromoacetylnaphthalene **4** and 2-methoxy-1-aminomethylnaphthalene were synthesized according to literature procedures, respectively [36,37]. All other chemicals were purchased from Sigma or Aldrich.

Synthesis of Calix[4]crown with Two Pendant Groups

2-Methoxy-1-bromoacetylaminomethylnaphthalene 5

2-Methoxy-1-aminomethylnaphthalene (2.0 g, 10.7 mmol) was added to a solution of bromoacetyl bromide (6.0 g, 30 mmol) in anhydrous acetonitrile (20 cm^3) with stirring at 0–5°C. After stirring for 1.0 h, $NaHCO_3$ (1.0 g, 11.7 mmol) was added, stirring was continued for another hour at room temperature. The reaction mixture was poured into cold water (150 cm^3). The white precipitate was collected by filtration, washed with cold water, and then recrystallized from acetonitrile to give **5** (1.4 g, 42.5%), mp: 180–182°C. $R_f = 0.80$ (CH_2Cl_2:$CH_3COOC_2H_5 = 4:1$, v/v). *m/z* (EI): 307 (M^+, 43.21%), 309 ($[M+2]^+$, 41.22) and 228 ($M^+ - Br$, 100); ν_{max} (KBr)/cm^{-1}: 3284.7 (–NH–), 1634.7 (–C=O); δ_H (300 MHz, $CDCl_3$, 25°C): 8.12 (d, 1H, $J = 8.1$ Hz, Naph–H), 7.82 (d, 1H, $J = 8.1$ Hz, Naph–H), 7.88 (d, 1H, $J = 9.0$ Hz, Naph–H), 7.32 (d, 1H, $J = 9.0$ Hz, Naph–H), 7.56 (m, 1H, Naph–H), 7.40 (m, 1H, Naph–H), 6.87 (br, 1H, –NHC=O), 4.98 (d, $J = 5.4$ Hz, 2H, $ArCH_2NH$–), 4.03 (s, 3H, $-OCH_3$), 3.89 (s, 2H, $-COCH_2Br$). Found: C, 54.46; H, 4.58; N, 4.55. Calcd for $C_{14}H_{14}BrNO_2$: C, 54.58; H, 4.64; N, 4.57.

2,4-Bis[(6-methoxy-2-naphthoylmethyl)oxy]-(1,3)-p-tert-butylcalix[4]crown-4 (2a)

Anhydrous Na_2CO_3 (320 mg, 3.0 mmol) was added to a solution of *p-tert*-butylcalix[4]crown-4 **2** (230 mg, 0.3 mmol) in anhydrous acetonitrile (40 cm^3). After stirring for 30 min. at 50°C, compound **4** (167 mg, 0.6 mmol) was added. The mixture was refluxed for 5 days. After cooling, a small amount of precipitate was removed by filtration. The filtrate was evaporated *in vacuo* to leave a residue, which was redissolved in chloroform (60 cm^3), washed with 0.5 M HCl solution ($2 \times 30\,cm^3$) and water ($3 \times 30\,cm^3$) successively, and then dried ($MgSO_4$). The solvent was evaporated *in vacuo*, the residue was purified by column chromatography (CH_2Cl_2:CH_3COOCH_3, 1:2, V/V) and then recrystallized from $CHCl_3$–CH_3OH to give **2a** (94 mg, 27.2 %), mp: 194–196°C, $R_f = 0.42$ (CH_2Cl_2:$CH_3COOC_2H_5 = 1{:}2$, v/v). *m/z* (ESIMS): 1157.7 ($[M - H]^-$, calcd 1157.6); ν_{max} (KBr)/cm^{-1}: 1715.7 (–C=O); δ_H (300 MHz, $CDCl_3$, 25°C): 8.49 (s, 2H, Naph–H), 8.08 (d, 2H, $J = 8.6$ Hz, Naph–H), 7.88 (d, 2H, $J = 8.6$ Hz, Naph–H), 7.84 (d, 2H, $J = 8.6$ Hz, Naph–H), 7.21 (d, 2H, $J = 8.6$ Hz, Naph–H), 7.19 (s, 2H, Naph–H), 7.12 (s, 4H, ArH), 6.51 (s, 4H, ArH), 5.26 (s, 4H, 2 × $-COCH_2O-$), 3.95 (s, 6H, 2 × $-OCH_3$), 4.52 (d, 4H, $J = 12.6$ Hz, 2 × $ArCH_2Ar$), 3.17 (d, 4H, $J = 12.6$ Hz, 2 × $ArCH_2Ar$), 4.45 and 4.12 (m, 12H, 3 × $-OCH_2CH_2O-$), 1.33 (s, 18H, 2 × $-C(CH_3)_3$), 0.83 (s, 18H, 2 × $-C(CH_3)_3$). δ_C (300 MHz, $CDCl_3$, 25°C): 197.8 (C=O), 154.1, 149.8, 149.1, 148.4, 145.3, 143.2, 135.3, 134.6, 134.1, 132.9, 131.7, 128.2, 127.5, 126.6, 126.1, 125.8, 124.7, 121.9, 120.8, 106.1, 102.9 (aromatic C), 80.8 ($-COCH_2O$), 69.8, 69.3, 68.4, 68.0 ($-OCH_2CH_2O-$), 56.0 ($-OCH_3$), 40.3, 34.5, 34.3, 32.8, 31.8, 31.4 ($C(CH_3)_3$, $ArCH_2Ar$). Found: C, 78.62; H, 7.35. Calcd for $C_{76}H_{86}O_{10}$:C, 78.73; H, 7.48.

2,4-Bis[(2-methoxy-1-naphthylmethylaminocarbonylmethyl)oxy]-(1,3)-p-tert-butylcalix[4]crown-4 (2b)

Anhydrous Na_2CO_3 (320 mg, 3.0 mmol) was added to a solution of *p-tert*-butylcalix[4]crown-4 **2** (230 mg, 0.3 mmol) in anhydrous acetonitrile (40 cm^3). After stirring for 30 min at 50°C, compound **5** (185 mg, 0.6 mmol) was added. The mixture was refluxed for 5 days. After cooling, a small amount of precipitate was removed by filtration. The filtrate was evaporated *in vacuo* to leave a residue, which was redissolved in chloroform (60 cm^3), washed with 0.5 M HCl solution ($2 \times 30\,cm^3$) and water ($3 \times 30\,cm^3$) successively, and then dried ($MgSO_4$). The solvent was evaporated *in vacuo*, the residue was purified by column chromatography (CH_2Cl_2: CH_3COOCH_3, 1:2, v/v) and then recrystallized from $CHCl_3$–CH_3OH to give **2b** (118 mg, 32.0%), mp: 174–176°C, $R_f = 0.52$ (CH_2Cl_2:$CH_3COOC_2H_5 = 1{:}2$, v/v). *m/z* (ESIMS): 1215.5 ($[M - H]^-$, Calcd 1215.7); ν_{max} (KBr)/cm^{-1}: 3359.2 (–NH–), 1657.6 (–NHC=O); δ_H (300 MHz, $CDCl_3$, 25°C): 8.05 (d, 2H, $J = 8.6$ Hz, Naph–H), 7.22 (d, 2H, $J = 8.6$ Hz, Naph–H), 7.80 (m, 4H, Naph–H), 7.50 (m, 2H, Naph–H), 7.37 (m, 2H, Naph–H), 7.64 (bs, 2H,–NHC=O), 7.02 (s, 4H, ArH), 6.31 (s, 4H, ArH), 5.02 (d, $J = 5.0$ Hz, 4H, 2 × $-COCH_2O-$), 4.32 (s, 4H, 2 × $ArCH_2NH-$), 3.89 (s, 6H, 2 × $-OCH_3$), 3.99 (d, $J = 12.6$ Hz, 4H, 2 × $ArCH_2Ar$), 2.97 (d, $J = 12.6$ Hz, 4H, 2 × $ArCH_2Ar$), 3.26 and 3.43 (m, 12H, 3 × $-OCH_2CH_2O-$), 1.32 (s, 18H, 2 × $-C(CH_3)_3$), 0.75 (s, 18H, 2 × $-C(CH_3)_3$). δ_C (300 MHz, $CDCl_3$, 25°C): 168.8 (–NHC=O), 158.2, 148.7, 148.1, 147.8, 145.3, 143.1, 136.3, 133.8, 129.8, 128.5, 128.0, 127.7, 126.4, 126.1, 125.9, 122.7, 121.7, 120.8, 119.4, 111.7, 103.7 (aromatic C), 76.6 ($-NHCOCH_2O$), 69.6, 68.7, 68.1, 67.4 ($-OCH_2CH_2O-$), 56.3 ($-OCH_3$), 39.3, 34.4, 34.0, 32.5, 31.8, 31.3, 31.0 ($C(CH_3)_3$, $ArCH_2Ar$, $ArCH_2$-NHCO). Found: C, 76.76; H, 7.61; N, 2.03. Calcd for $C_{78}H_{92}\,N_2O_{10}$: C, 76.94; H, 7.62; N, 2.30.

2,4-Bis[(6-methoxy-2-naphthoylmethyl)oxy]-(1,3)-p-tert-butylcalix[4]crown-5 (3a)

Anhydrous K_2CO_3 (420 mg, 3.0 mmol) was added to a solution of *p-tert*-butylcalix[4]crown-5 **3** (242 mg, 0.3 mmol) in anhydrous acetonitrile (40 cm^3). After stirring for 30 min at 50°C, compound **4** (167 mg, 0.6 mmol) was added. The mixture was refluxed for 3 days. After cooling, a small amount of precipitate was removed by filtration. The filtrate was evaporated *in vacuo* to leave a residue, which was redissolved in chloroform (60 cm^3), washed with 0.5 M HCl solution ($2 \times 30\,cm^3$) and water ($3 \times 30\,cm^3$) successively, and then dried ($MgSO_4$). The solvent was evaporated *in vacuo*, the residue was purified by column chromatography (CH_3COOCH_3) and then recrystallized from $CHCl_3$–CH_3OH to give **3a** (158 mg, 43.0%), mp: 122–124°C, $R_f = 0.38$ ($CH_3COOC_2H_5$). *m/z* (ESIMS): 1201.5 ($[M - H]^-$, calcd 1201.6); ν_{max} (KBr)/cm^{-1}: 1699.6 (–C=O); δ_H (300 MHz, $CDCl_3$, 25°C): 8.45 (s, 2H, Naph–H), 8.05 (d, 2H, $J = 8.6$ Hz, Naph–H), 7.85 (d, 2H, $J = 8.6$ Hz, Naph–H), 7.78 (d, 2H, $J = 8.6$ Hz, Naph–H), 7.20 (d, 2H, $J = 8.6$ Hz, Naph–H), 7.17 (s, 2H, Naph–H), 7.04 (s, 4H, ArH), 6.57 (s, 4H, ArH), 5.42 (s, 4H, 2 × $-COCH_2-$), 3.94 (s, 6H, 2 × $-OCH_3$), 4.62 (d, $J = 12.6$ Hz, 4H, 2 × $ArCH_2Ar$), 3.18 (d, $J = 12.6$ Hz, 4H, 2 × $ArCH_2Ar$), 4.36, 3.76 and 3.67 (m, 16H, 4 × $-OCH_2CH_2O-$), 1.27 (s, 18H, 2 × $-C(CH_3)_3$). 0.90 (s, 18H, 2 × $-C(CH_3)_3$). δ_C (300 MHz, $CDCl_3$, 25°C): 196.5 (C=O), 152.0, 148.8, 148.2, 147.5, 145.1, 143.5, 136.0, 135.8, 134.8, 133.6, 131.8, 129.7, 127.8, 127.9, 126.5, 125.4, 124.1, 122.7, 121.8, 106.8, 103.2 (aromatic C), 79.8 ($-COCH_2O$), 68.9, 68.4, 68.0, 67.7 ($-OCH_2CH_2O-$), 56.5 ($-OCH_3$), 41.0, 35.1, 33.8, 32.5, 31.7, 31.2 ($C(CH_3)_3$, $ArCH_2Ar$). Found: C, 77.67; H, 7.48. Calcd for $C_{78}H_{90}O_{11}$: C, 77.84; H, 7.54.

2,4-Bis[(2-methoxy-1-naphthylmethylamino-carbonylmethyl)oxy]-(1,3)-p-tert-butylcalix[4]crown-5 (3b)

Anhydrous K_2CO_3 (420 mg, 3.0 mmol) was added to a solution of *p-tert*-butylcalix[4]crown-5 **3** (242 mg, 0.3 mmol) in anhydrous acetonitrile (40 cm^3). After stirring for 30 min at 50°C, compound **5** (185 mg, 0.6 mmol) was added. The mixture was refluxed for 3 days. After cooling, a small amount of precipitate was removed by filtration. The filtrate was evaporated *in vacuo* to leave a residue, which was redissolved in chloroform (60 cm^3), washed with 0.5 M HCl solution ($2 \times 30\,cm^3$) and water ($3 \times 30\,cm^3$) successively, and then dried ($MgSO_4$). The solvent was evaporated *in vacuo*, the residue was purified by column chromatography ($CHCl_3$–CH_3COOCH_3, 10:1, v/v) and then recrystallized from $CHCl_3$–CH_3OH to give **3b** (198 mg, 57.2%), mp: 136–138°C, $R_f = 0.42$ ($CHCl_3$–$CH_3COOC_2H_5 = 10{:}\ 1$, v/v). *m/z* (ESIMS): 1260.6 ($[M-H]^-$, calcd 1260.3); ν_{max} (KBr)/cm^{-1}: 3329.9 (–NH–), 1671.6 (–NHC=O); δ_H (300 MHz, $CDCl_3$, 25°C): 7.97 (d, 2H, $J = 8.4$ Hz, Naph–H), 7.23 (d, 2H, $J = 8.4$ Hz, Naph–H), 7.79 (m, 4H, Naph–H), 7.36 (m, 4H, Naph–H), 6.93 (s, 4H, ArH), 6.49 (s, 4H, ArH), 4.94 (s, 4H, $2 \times$ –$COCH_2$–), 4.88 (d, 4H, $J = 5.2$ Hz, $2 \times ArCH_2NH$–), 3.88 (s, 6H, $2 \times$ –OCH_3), 4.21 (d, 4H, $J = 12.6$ Hz, $2 \times ArCH_2Ar$), 2.92 (d, 4H, $J = 12.6$ Hz, $2 \times ArCH_2Ar$), 3.69 and 3.45 (m, 16H, $4 \times$ –OCH_2CH_2O–), 1.26 (s, 18H, $2 \times$ –$C(CH_3)_3$), 0.82 (s, 18H, $2 \times$ –$C(CH_3)_3$). δ_C (300 MHz, $CDCl_3$, 25°C): 168.3 (–NHC=O), 158.9, 148.3, 148.0, 147.6, 145.9, 144.0, 135.7, 132.6, 129.8, 128.8, 128.3, 127.5, 126.8, 126.1, 125.2, 122.3, 121.8, 121.0, 119.5, 110.8, 102.9 (aromatic C), 75.8 (–$NHCOCH_2O$), 68.8, 68.5, 67.9, 67.3 (–OCH_2CH_2O–), 56.8 (–OCH_3), 38.9, 35.7, 34.6, 32.8, 31.9, 31.4, 31.2 ($C(CH_3)_3$, $ArCH_2Ar$, $ArCH_2NHCO$). Found: C, 76.01; H, 7.60; N, 2.34. Calcd for $C_{80}H_{96}N_2O_{11}$: C, 76.16; H, 7.67; N, 2.22.

ESIMS Experiments

ESIMS spectra of the solutions of chloroform and methanol (v/v, 5:1) of calix[4]crown with two pendant groups (5×10^{-5} M) and alkali metal salt (NaSCN or KSCN at 5×10^{-4} M) were recorded by electro spray mass spectrometer (LCQ, Finnegan) in the positive mode.

^{1}H NMR Titration Experiments

^{1}H NMR spectra in the titration experiments were recorded by Inova 600 MHz. The solvent $CDCl_3$–CD_3OD (1:1 v/v) was used. The concentration of the host was fixed in 4×10^{-6} M and the concentration of the potassium or sodium thiocyanate was chaged in the range of 1.0×10^{-6}–1.2×10^{-5} M.

Determinations of UV and Fluorescent Spectra

UV absorption spectra of hosts and their complexes with perchlorate salts in acetonitrile solution were recorded by UVPC-3000 spectrophotometer. The concentrations of the hosts and perchlorate salts were 2.0×10^{-5} M. Fluorescence spectra of hosts and their complexes with perchlorate salts in acetonitrile solution were recorded on a SIM.AMINCO fluorescence spectrophotometer. The concentrations of the hosts and perchlorate salts were 2.0×10^{-5} M and excitation wavelength was 308 nm.

Extraction Experiments

The experiments of picrate extraction from water to chloroform were performed according to the procedures given in reference [43]. An aqueous solution (10 cm^3) of alkaline metal picrate (4.0×10^{-5} M) and a solution of host in chloroform (10 cm^3, 4.0×10^{-5}–2.0×10^{-4} M) were mixed in a centrifuge tube, shaken mechanically for 30 min at 25°C, then centrifuged for 10 min. The amount of picrate ion extracted into the organic phase was then determined from its absorption in the UV spectrum (355 nm) and from subtraction of the original aqueous phase. The blank extraction without adding the host was also done under the same conditions.

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