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Extraction and complexation of alkali and alkaline earth metal cations by lower-rim calix[4]arene diethylene glycol amide derivatives

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The novel calix[4]arene derivatives, 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(N-(2-(2-metoxyetoxy)ethyl)carbamoyl methoxy)calix[4]arene (**1**) and 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetra(N,N-bis(2-(2-metoxyetoxy)ethyl)carbamoyl methoxy)calix[4]arene (**2**), were prepared by introducing diethylene glycol subunits at a lower calixarene rim. Complexation affinities of these compounds towards alkali and alkaline earth metal cations were studied at 25 °C in acetonitrile and methanol by means of spectrophotometric, conductometric, and potentiometric titrations. The stability constants of the corresponding complexes with 1:1 (cation:ligand) stoichiometry were determined (in some cases only estimated), and their values obtained by different methods were in good agreement. Much lower stabilities of the complexes with secondary-amide derivative (**1**) compared to those with tertiary-amide one (**2**) were observed. That was presumably mostly caused by the presence of intramolecular NH···O=C hydrogen bonds in the former case. It was found that solvent significantly affected the stability of the complexes, whereby the prepared calixarenes showed considerably higher affinities for cations in acetonitrile than in methanol. Generally, the ligands studied showed better binding abilities for alkaline earth than for alkali metal cations. The extraction of metal picrates from water to dichloromethane by complexation of metal ions with ligands **1** and **2** was also investigated. In accordance with the complex stabilities, all cations were extracted fairly well (in some cases even excelently) with tertiary-amide derivative, whereas that was not the case in the extraction experiments with the other ligand studied.

Introduction

Complexation properties of calixarene derivatives have been extensively studied due to their ability to selectively bind a wide variety of guest species.[1-3] Numerous macrocyclic receptors have been prepared by functionalization of calixarenes at the lower and/or upper rim. By choosing adequate number of phenolic units and appropriate substituents, it has been possible to prepare selective and efficient calixarene hosts for cations,[4,5], anions,[4,6,7] and neutral species.[4,8–10] The *p*-*tert*-butylcalix[4]arene derivatives containing carbonyl groups at the lower rim (ketones, esters, amides) were reported to possess excellent properties for binding alkali, alkaline earth, and transition metal cations.[5,11] Secondary-[11–13] and tertiary-amide[14–16] calixarene derivatives were shown to have particularly high affinity towards alkali and alkaline earth metal cations. Formation of intramolecular NH···O=C hydrogen bonds in tetrasubstituted secondary-amide derivatives was proven to have strong influence on the binding properties of such ligands.[12,13,17–24] In addition to the above mentioned calixarene size and binding groups nature, its affinity towards metal cations depends strongly on the reaction medium, *i.e.* on the solvent used.[11–14,17,25–31]

Several ethylene glycol-based calixarene derivatives have been reported previously.[1,32–39] The first oxyalkylated *p*-*tert*-butylphenol–formaldehyde oligomers (both linear and cyclic) were developed as demulsifiers for petroleum industry.[1] Calixarene crown ethers with ethylene glycol substituents at the lower rim were shown to selectively bind sodium, potassium, and cesium cations.[32,33] Another interesting group of compounds are *bis*-calixarenes, also known as *calix-tubes*, which possess two calixarene skeletons bridged by ethylene glycol or various polyethylene glycol (PGE) chains.[34] Calixarene derivatives with a large number of attached (poly)ethylene glycol groups have an increased hydrophilic character, and have found application as agents for extraction of metal cations from aqueous to organic phase.[35–37] In order to optimize the structure of calix[4]arene derivatives for metal-ion biphasic extraction and phase-transition catalysis, Shinkai et al.[35] prepared several amphyphilic calix[4]arene derivatives by introducing hydrophobic groups at the upper calixarene rim

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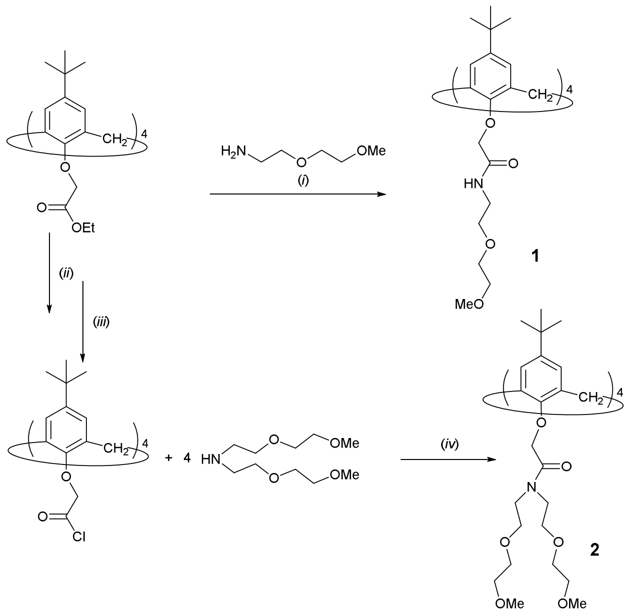
and oligo(ethylene glycol) chains at the lower one. In the course of an extraction process, the latter hydrophilic groups penetrate to the aqueous layer, whereas the hydrophobic calixarene *basket* remains in a non-polar organic layer. In that way such compounds can efficiently bind cations in aqueous phase and transfer them to the organic one. Interestingly, the length of the hydrophilic chains does not significantly affect the ligand extraction and phase-transfer catalysis properties. On the other hand, the receptor can be improved in these respects by increasing its overall lipophilicity, which can be accomplished by appending the larger lipophilic functionalities to the upper calixarene rim.[34] Roundhill et al.[36] synthesized a number of polyethylene glycol functionalized calix[4]arenes by introducing PEG groups at both calixarene rims, and the obtained compounds were envisaged as potential efficient metal-ion host molecules and extracting agents. A larger ethylene glycol-based calix[6]arene derivative[37] was investigated as catalyst and extraction agent for alkali metal cations, whereby the solvent effect on the ligand abilities was proven to be of great importance. Shi and Zhang[38] reported a water-soluble *p-tert*-butycalix[8]arene bearing PGE chains which was capable of efficiently binding organic molecules and ions in its hydrophobic cavity. Most recently, pegylated octopus-shaped calix[4]arenes with different degree of polyoxyethylation of the lower-rim substituents were described as promising supramolecular drug delivery platforms.[39,40] To the best of our knowledge, there is only one calix[4]arene amide derivative bearing diethylene glycol chains bound to the amide nitrogen atoms reported in the literature,[41] which was studied as anion[41] and amino acids[42–44] receptor.

In this work, we present the syntheses of calix[4]arene amide derivatives with diethylene glycol functionalities appended to amide group at the lower rim, and the study of their complexation affinities towards alkali and alkaline earth metal cations in two solvents with different solvation and hydrogen-bonding abilities (methanol, MeOH, and acetonitrile, MeCN). In addition, the efficiencies of the extraction of cations from water to chloroform with both ligands has been investigated and discussed.

Results and discussion

Syntheses

The syntheses of diethylene glycol calixarenes **1** and **2** were performed in several reaction steps, as shown in Scheme 1. Compound **1** was prepared *via* aminolysis (*i*) of the *p-tert*-butylcalix[4]arene tetraethyl ester with 2-(2-methoxyethoxy) ethanamine with 90 % yield, as described in the Experimental section. Compound **2** was synthesized by the modified method described previously, using tetra acid chloride *p-tert*-butylcalix[4]arene,[45] starting from the corresponding tetraester (*cone* conformation) by (*ii*) hydrolysis to the tetraacid, (*iii*) activation to the acid chloride, and (*iv*) amide bond formation (65 % yield). For both compounds an additional purification step was required to ensure that all of the ions were removed, and this was done in a similar manner as described in ref. 46. Details of purification procedure are described in the Experimental section.



Scheme 1 Syntheses of compounds **1** and **2**. Reagents and conditions: (*i*) *tert*-butanol, r.t.; (*ii*); a) NaOH, EtOH/H_2O, Δ; b) HCl (*iii*) $SOCl_2$ Δ; (*iv*) Et_3N, CH_2Cl_2 (Ar), 0 °C → r.t.

Calixarene derivatives **1** and **2** were characterized by spectroscopic methods and mass spectrometry. The ^1H NMR spectra of compounds **1** and **2** ($CDCl_3$) showed the pattern characteristic of *p-tert*-butyl-calix[4]arene in a *cone* conformation and approximately C_4 symmetry of tetrasubstituted calix[4]arene.[19] Two singlets appeared, one corresponding to *tert*-butyl groups (1.10 ppm, 1.09 ppm) and another due to the calixarene aromatic protons (6.79 ppm, 6.77 ppm). In addition, two doublets assigned to the equatorial (3.16 ppm, 3.26 ppm) and axial (4.65 ppm; 5.07 ppm) bridging methylene protons could be found. In the spectrum of compound **1**, a rather high chemical shift of the amide protons (7.94 ppm) indicated the presence of intramolecular NH···O=C hydrogen bonds between the amide groups of the lower-rim substituents.[19,20] The FTIR data were fully in agreement with NMR results. In the spectrum of **1** the NH stretching band at 3373 cm^{-1} corresponded to intramolecular hydrogen-bonds between the amide groups. Positive ESI mass spectra of compounds **1** and **2** were acquired in acetonitrile. The signals of singly- $[M+H]^+$ and doubly- $[M+2H]^{2+}$ protonated ions, as well as that of adducts with alkali metal cations $[M+Na]^+$, $[M+H+Na]^{2+}$, and $[M+H+K]^{2+}$ were observed (see ESI, Figs. S1 and S2). The $[M+H]^+$ ions of the ligands were isolated and MS/MS experiments were performed at different collision energies. Product ion spectra are shown in Figs. S3 and S4 (ESI). The fragmentation of both derivatives was very similar, the loss of substituent(s) on amide nitrogen atom was observed as well as the cleavage of C–O bonds, including phenolic and ether oxygen atoms. The formation of carbocation was noticed in the case of **2**, and the signal at *m/z* 262 was assigned to the fragment ion $C_{12}H_{24}O_3N^+$. The proposed fragmentation pathways of **1** and **2** are shown in Schemes S1 and S2 (ESI).

Cation complexation studies

The hypochromic effect on the UV spectra of the acetonitrile solutions of **1** and **2** was observed upon stepwise addition of $LiClO_4$, $NaClO_4$, $KClO_4$, $RbNO_3$, $CsNO_3$, $Mg(ClO_4)_2$, $Ca(ClO_4)_2$, $Sr(ClO_4)_2$, and $Ba(ClO_4)_2$ (Figs. S5–S18, ESI) solutions. In addition, an isosbestic point at 256 nm appeared in the case of ligand **1** titrations with $Mg(ClO_4)_2$ (Fig. S12, ESI) and $Ba(ClO_4)_2$ (Fig. 1). Isosbestic points were also observed in ligand **2** titrations with Rb^+ (251 nm), Cs^+ (254 nm), and Ba^{2+} (255 nm) (Figs. S10, S11, and S18, ESI).

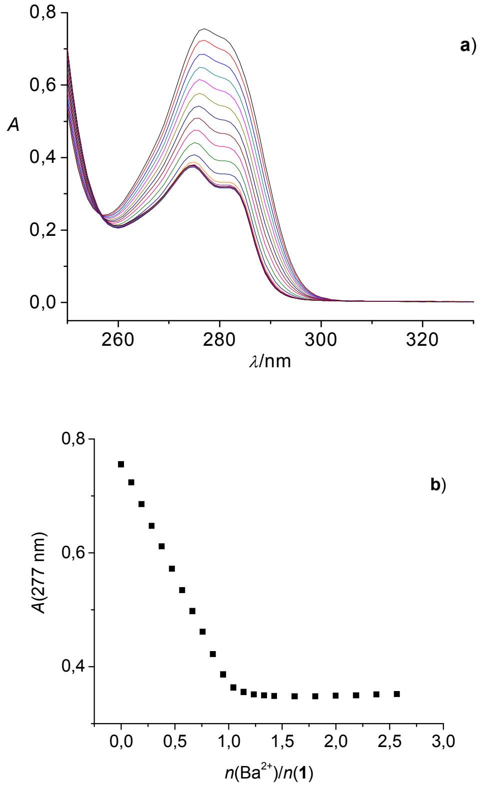


Figure 1. (a) Spectrophotometric titration of **1** ($c = 1.89 \times 10^{-4}$ mol dm^{-3}) with $Ba(ClO_4)_2$ ($c = 1.80 \times 10^{-3}$ mol dm^{-3}) in acetonitrile. l = 1 cm; t = (25.0 ± 0.1) °C; $n(Ba^{2+}) / n(\mathbf{1}) = 0$ (top curve) – 2.57 (bottom curve); the spectra are corrected for dilution. (b) Dependence of absorbance at 277 nm on $n(Ba^{2+}) / n(\mathbf{1})$ ratio.

Linear dependence of absorbance *vs.* the amount of cation added up to the ratio n(cation)/n(ligand) ≈ 1, followed by the break in the titration curve, indicated a strong complexation and formation of 1:1 complexes (Fig. 1; the corresponding stability constants could only be estimated, Table 1). This was observed in all above mentioned titrations, except in that of **1** with $KClO_4$ and $RbNO_3$, and those of both **1** and **2** with $CsNO_3$. In the case of complexes K**1**$^+$ and Cs**2**$^+$, their stability constants could be determined spectrophotometrically (Fig. 2, Fig. S11, ESI, Table 1). Addition of $RbNO_3$ and $CsNO_3$ into the calixarene derivative **1** acetonitrile solution had no significant effect on its UV spectrum, indicating that under the conditions used no observable complexation took place.

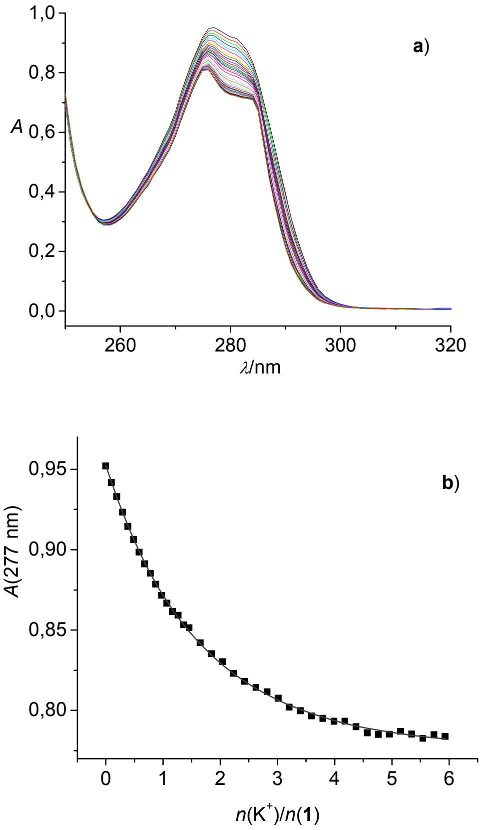


Figure 2. (a) Spectrophotometric titration of **1** ($c = 2.30 \times 10^{-4}$ mol dm^{-3}) with $KClO_4$ ($c = 2.24 \times 10^{-3}$ mol dm^{-3}) in acetonitrile. l = 1 cm; t = (25.0 ± 0.1) °C; $n(K^+) / n(\mathbf{1}) = 0$ (top curve) – 5.93 (bottom curve); the spectra are corrected for dilution. (b) Dependence of absorbance at 277 nm on $n(K^+) / n(\mathbf{1})$ ratio. ■ experimental; – calculated.

To corroborate the findings obtained by spectrophotometry, conductometric titrations of acetonitrile solutions of alkali and alkaline earth cation salts with calixarene derivatives **1** and **2** were carried out (Figs. S19–S33, ESI). In most cases a linear decrease in molar conductivities with the addition of calixarene solutions was recorded up to a break in the titration curve at the molar ratio n(ligand)/n(cation) ≈ 1, indicating, as for spectrophotometric titrations, a strong complexation and formation of 1:1 complexes (example can be seen in Fig. 3). The exceptions were titrations of $KClO_4$ with **1** (Fig. 4) and $CsNO_3$ with **2** (Fig. S25, ESI). By processing the data of these titrations, the stability constants of K**1**$^+$ and Cs**2**$^+$ were determined. In all the above cases, decrease in the molar conductivity was due to the lower electric mobility of the larger complexes compared to the free metal cations. Like with spectrophotometric experiments, during the conductometric titrations of $RbNO_3$

and $CsNO_3$ acetonitrile solutions with ligand **1** no complexation was observed under the experimental titration conditions.

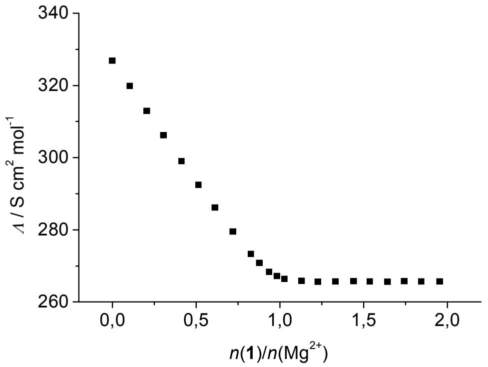


Figure 3. Conductometric titration of $Mg(ClO_4)_2$ ($c = 1.81 \times 10^{-4}$ mol dm^{-3}) with **1** ($c = 1.90 \times 10^{-3}$ mol dm^{-3}) in acetonitrile; $t = (25.0 \pm 0.1)$ °C.

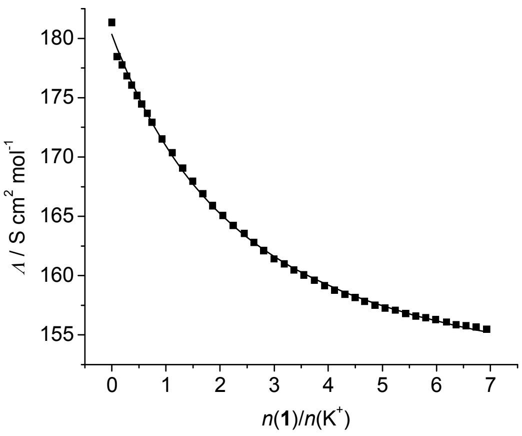


Figure 4. Conductometric titration of $KClO_4$ ($c = 1.09 \times 10^{-4}$ mol dm^{-3}) with **1** ($c = 1.90 \times 10^{-3}$ mol dm^{-3}) in acetonitrile; $t = (25.0 \pm 0.1)$ °C. ■ experimental; – calculated.

The stability constants of the Na**1**$^+$ and Na**2**$^+$ complexes in acetonitrile were too high for spectrophotometric or conductometric determination. For that reason, direct potentiometry using a sodium-selective glass electrode was applied. Potentiometric titration curves for both ligands showed a steep p[Na] jump at the 1:1 *n*(ligand)/*n*(cation) ratio, which is in accordance with the results of previously mentioned methods. However, the p[Na] jump was steeper in the case of titration with tertiary-amide derivative **2**, indicating a higher stability of the corresponding complex. The jump was even too steep (Fig. S34, ESI) to allow accurate calculation of the Na**2**$^+$ complex stability constant so it could only be estimated. On the other hand, stability constant of Na**1**$^+$ complex was determined by processing the corresponding potentiometric titration data (Fig. 5, Table 1).

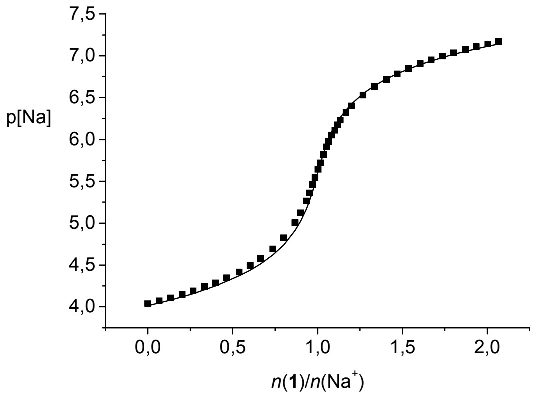


Figure 5. Potentiometric titration of $NaClO_4$ ($c = 9.78 \times 10^{-5}$ mol dm^{-3}) with **1** ($c = 9.97 \times 10^{-4}$ mol dm^{-3}) in acetonitrile. $V_0(NaClO_4) = 30.3$ cm^3 $I_c = 0.01$ mol dm^{-3} ($(C_2H_5)_4NClO_4$); $t = (25.0 \pm 0.1)$ °C. ■ experimental; – calculated.

The spectral changes observed upon the addition of salt solutions to ligand solution in methanol were basically similar to those described above (Figs. S35 – S45, ESI), *i.e.* the spectra exhibited hypochromic effect and in some cases isosbestic points were observed. For secondary-amide derivative **1** linear dependence of absorbance was observed only upon addition of $Ca(ClO_4)_2$ solution (Fig S41, ESI), whereas during titration of tertiary-amide derivative **2** such dependence was observed in titrations with all salt solutions, except with $RbNO_3$ and $CsNO_3$ (Figs. S39 and S40, ESI).

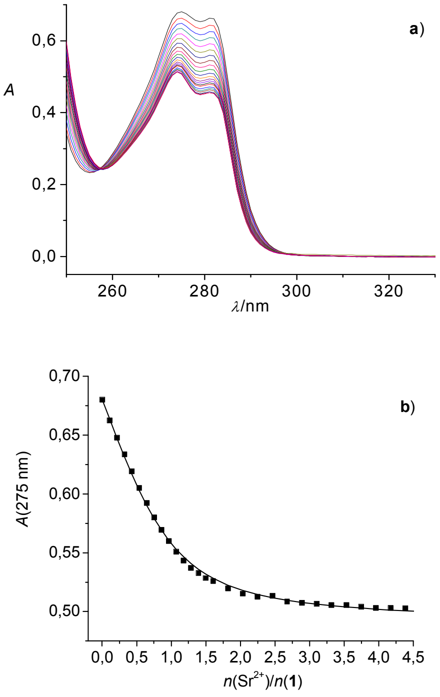


Figure 6. (a) Spectrophotometric titration of **1** ($c = 1.95 \times 10^{-4}$ mol dm^{-3}) with $Sr(ClO_4)_2$ ($c = 2.20 \times 10^{-3}$ mol dm^{-3}) in methanol. $l = 1$ cm; $t = (25.0 \pm 0.1)$ °C; $n(Sr^{2+}) / n(\mathbf{1}) = 0$ (top curve) – 4.38 (bottom curve); the spectra are corrected for dilution. (b) Dependence of absorbance at 275 nm on $n(Sr^{2+}) / n(\mathbf{1})$ ratio. ■ experimental; – calculated.

Apart from a high-stability complex Ca**1**$^{2+}$, spectrophotometric measurements also showed formation of Na**1**$^{+}$, Ba**1**$^{2+}$ (Figs. S36 and S44, ESI) and Sr**1**$^{2+}$ complexes (Fig. 6). The stability constants of these complexes are given in Table 1. As can be concluded from the described experimental results, calixarene derivative **2** in methanol forms high-stability complexes with most of the investigated cations (the exceptions are Rb^{+} and Cs^{+}). The determined stability constant of the Rb**2**$^{+}$ complex is given in Table 1, whereas no observable complexation of cesium cation with ligand **2** took place.

The above results were confirmed by conductometric titrations. By processing of the corresponding data stability constants of the Na**1**$^{+}$, Mg**1**$^{2+}$, Sr**1**$^{2+}$, Ba**1**$^{2+}$, Li**2**$^{+}$, and Rb**2**$^{+}$ complexes given in Table 1 were determined (the corresponding titrations are shown in ESI, Figs. S46 – S51). On the other hand, because of their high values, the equilibrium constants for the reactions of formation of the Ca**1**$^{2+}$, Na**2**$^{+}$, K**2**$^{+}$, Ca**2**$^{2+}$, Sr**2**$^{2+}$, and Ba**2**$^{2+}$ species were only estimated (Table 1; Figs. S52 – S57, ESI). During the conductometric titrations of $LiClO_4$, $NaClO_4$, and $RbNO_3$ with **1** and that of $CsNO_3$ with both ligands in methanol, negligible and irregular changes in molar conductivity were observed indicating that no complexation took place. It should be noted that formation of Mg**1**$^{2+}$ complex was observed conductometrically, although no complexation was detected using spectrophotometry. The stability constant of the Na**2**$^{+}$ complex in methanol was, like in acetonitrile, too high for spectrophotometric and conductometric determinations. For that reason, it was determined by means of direct potentiometric titration (Fig. 7, Table 1). As stability of the sodium complex with **1** was much lower (Table 1), to determine its stability constant potentiometrically considerably higher concentrations of both ligand and sodium perchlorate were needed. Because of the limited solubility of calixarene **1** in methanol these measurements were not conducted.

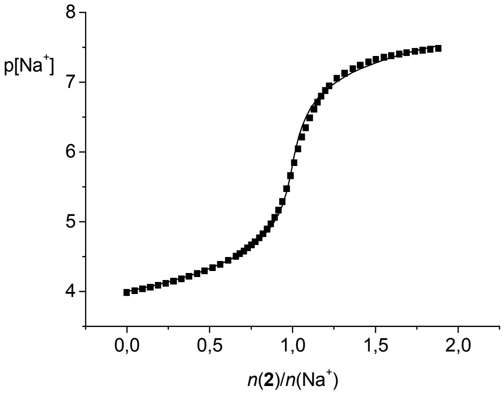


Figure 7. Potentiometric titration of $NaClO_4$ (c = 1.00 × 10^{-4} mol dm^{-3}) with **2** (c = 7.13 × 10^{-4} mol dm^{-3}) in methanol. $V_0(NaClO_4)$ = 30.3 cm^3 I_c = 0.01 mol dm^{-3} ($(C_2H_5)_4NClO_4$); t = (25.0 ± 0.1) °C. ■ experimental; – calculated.

Given the data listed in Table 1, it is evident that the affinity of ligand **2** for alkali and alkaline earth metal cations is much higher than that of ligand **1**. The main reason for the difference can be readily explained by taking into account the presence of N–H···O=C intramolecular hydrogen bonds in the latter case. Namely, in order for a cation to form a complex with **1**, these bonds need to be disrupted to allow reorganization of the amide groups. Amide hydrogen atoms are in fact competing with the cation for the carbonyl oxygen. Tertiary amide derivatives, like **2**, do not have the ability to form the aforementioned hydrogen bonds, so no unfavorable competition between the cation and –NH group could take place. Secondary-amide derivative **1** binds smaller Li^{+} and Na^{+} cations very well. Its affinity for larger K^{+} is lower, whereas Rb^{+} and Cs^{+} are too large to fit into its hydrophilic cavity. On the other hand, this compound binds all alkaline earth metal cations quite strongly in acetonitrile, as expected due to their size and charge. Tertiary-amide derivative **2** forms highly stable complexes with all cations, except with the largest Cs^{+} (even in that case the complex stability is moderate). This size- and charge-dependent selectivity is even more pronounced in methanol. As in MeCN, in MeOH both ligands **1** and **2** showed higher affinity towards alkaline earth compared to alkali metal cations (the only exception is complexation with Ba^{2+} because of its relatively large size). However, the complex stabilities in methanol are considerably lower (Table 1). Such a strong solvent influence can be explained by different solvation of all species taking part in complexation reaction, *i.e.* free cation, free ligand, and the complex. The influence of cation solvation is most pronounced in the case of smallest cations, like Li^{+} and Mg^{2+}. Although they form highly stable complexes with **1** in acetonitrile, the presence of these complexes has been hardly, or not at all, observed in methanol solution. Methanol, as a hydrogen bonding solvent, strongly solvates small cations,[47] thus making substitution of its molecules by ligand binding sites unfavorable. The cation solvation effect is of course present in the complexation of other metal cations, but it is not as dominant as in the cases of Li^{+} and Mg^{2+}. Ligand solvation effect on the studied equilibria should be presumably more pronounced in reactions with **1** than in those with **2**. In both cases methanol molecules compete with the cation for binding sites by forming hydrogen bonds with amide carbonyl oxygen atoms. However, contrary to **2**, in the case of **1**, which is secondary amide derivative, MeCN molecules can (as a proton acceptor) form H-bonds with amide NH groups of the receptor. This in turn leads to disruption of intramolecular N-H···O=C hydrogen bonds and to orientation of carbonyl groups favorable for the complexation of metal ion. Obviously the solvation of the complex also plays an important role in determining its thermodynamic stability. However, on the basis of data presented in this paper we cannot say much about this effect.

It should be also mentioned that the process of solvent molecule inclusion into the hydrophobic cavities of calixarenes **1** and **2** and their complexes could occur. This phenomenon is more pronounced in acetonitrile than in methanol, and could be quite important in determining the equilibria of the complexation reactions.[12,13,28,48–50]

Table 1 Stability constants for alkali and alkaline earth metal complexes of ligands **1** and **2**) in acetonitrile and methanol at 25.0 °C. Uncertainties are given in parentheses as standard errors of the mean (*N* = 3 to 5).

Cation	log *K*			
	MeCN		MeOH	
	1	**2**	**1**	**2**
Li^+	$>5^{a,b}$	$>5^{a,b}$	$–^{d}$	$4.69(2)^{b}$
Na^+	$7.09(3)^{c}$	$>8^{c}$	$3.50(5)^{a}$ $3.84(5)^{b}$	$7.45(1)^{c}$
K^+	$3.59(5)^{a}$ $3.57(7)^{b}$	$>5^{a,b}$	$–^{d}$	$>5^{a,b}$
Rb^+	$–^{d}$	$>5^{a,b}$	$–^{d}$	$4.16(7)^{a}$ $4.02(1)^{b}$
Cs^+	$–^{d}$	$3.9(1)^{a}$ $4.06(1)^{b}$	$–^{d}$	$2.10(1)^{a}$
Mg^{2+}	$>5^{a,b}$	$>5^{a,b}$	$2,9(2)^{b}$	$–^{d}$
Ca^{2+}	$>5^{a,b}$	$>5^{a,b}$	$>5^{a,b}$	$>5^{a,b}$
Sr^{2+}	$>5^{a,b}$	$>5^{a,b}$	$4.44(3)^{a}$ $4.27(3)^{b}$	$>5^{a,b}$
Ba^{2+}	$>5^{a,b}$	$>5^{a,b}$	$3.29(3)^{a}$ $3.0(1)^{b}$	$>5^{a,b}$

[a] Spectrophotometric determinations, [b] Conductometric determinations, [c] Potentiometric determination (I_c = 0.0 1 mol dm^{-3} (Et_4NClO_4)), –[d] no complexation was observed.

Extraction properties

The abilities of compounds **1** and **2** to extract alkali and alkaline earth metal cations from water to dichloromethane were explored according to the procedure described in detail in the Experimental section. As can be seen by inspecting the data in Table 2, secondary-amide derivative **1** moderately extracted sodium, potassium, and calcium picrates from aqueous to organic phase. Other examined picrate salts were extracted poorly (or not at all) by this compound. On the other hand, tertiary-amide derivative **2** was shown to be much better extractant of alkali and alkaline earth metal cations. Most of them were extracted very well (95–100 %) by **2**, the exception being rubidium, cesium, and magnesium ions which were not extracted as efficiently. It is interesting to note that extraction efficiency was 100 % in the case of sodium cation, which was not observed earlier with the other calix[4]arene tertiary-amide derivatives.[16,45] The results described are obviously directly correlated with the stabilities of the corresponding complexes, *i.e.* by the structural features of the compounds studied, and their amphyphilic character.

Conclusion

The diethylene glycol calix[4]arene derivatives **1** and **2** were designed and synthesised as compounds comprising hydrophobic and relatively hydrophilic parts as well as binding site which ensure strong complexation of alkali and alkaline earth metal cations. Hence, due to these properties their strong cation binding associated with high extraction abilities was expected. The complexation of alkali and alkaline earth cations by these ligands was studied by several experimental methods. The solvent effect on the complexation reactions was also examined using two solvents with different solvation and hydrogen-bonding abilities, namely acetonitrile and methanol. In both solvents the affinity for binding alkali and alkaline earth metal cations was found to be much higher in the case of tertiary-amide derivative **2** as compared to compound **1** which comprises secondary-amide subunits. That can be explained mostly by taking into account the presence of intramolecular NH···O=C hydrogen bonds in **1**, which cannot be formed in **2**. In the process of cation complexation, these bonds have to be disrupted, which is energetically quite demanding and therefore significantly reduces the complex stability.

The hydrogen-bonding role is also important for the explanation of the solvent effect on the equilibria of the complexation reactions. Namely, carbonyl-oxygen binding sites of compound **1** are most probably “blocked” by the formation of H-bonds with methanol molecules as a proton donors, whereas such bonds cannot be established with acetonitrile. By considering also the difference in cations solvation in the two solvents, the much higher complex stabilities in MeCN in comparison to MeOH becomes obvious.

In accordance with the above mentioned results, the structural differences between compounds **1** and **2** were shown to be of utmost importance in determining their abilities for extraction of metal cations from water to dichloromethane. Thus, contrary to **1**, calix[4]arene derivative **2** was found to be a very good, even excellent extractant of alkali and alkaline earth metal picrates, with 100 % efficiency in the case of sodium cation. Therefore, it can be concluded that, due to its amphyphilic character and strong cation-binding ability, compound 2 can be considered as a promising reagent for the extraction of metal ions from aqueous to organic phase.

Table 2 Extraction percentage (%E) of alkali and alkaline earth metal picrates from water into CH_2Cl_2 at 25 °C. Uncertainties are given in parentheses as standard errors of the mean (*N* = 3).

	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
1	2.35(2)	10.9(2)	7.8(1)	3.0(1)	3.69(6)	1.7(1)	6.55(9)	2.59(6)	2.3(1)
2	96.0(1)	100.0(1)	96.96(8)	75.6(1)	58.31(8)	68.4(1)	99.6(2)	98.5(2)	93.3 (1)

Experimental

General

All reagents used in the syntheses were of the best grade commercially available and were not further purified. Solvents were purified by standard procedures.[51] Analytical TLC was performed on silica gel plates (SiO_2, Merck 60 F254). Melting points were determined on Kofler hot-bench apparatus and were not corrected. ^1H NMR and ^{13}C NMR spectra were recorded with Bruker Avance 300 or 600 MHz spectrometer (d in ppm relative to $(CH_3)_4Si$ as an internal standard, J values are in Hz). IR spectra were recorded by means of ABB Bomem MB102 FTIR spectrometer. MS measurements were conducted on Agilent 6410 Triple Quadrupole mass spectrometer. The salts used for the investigation of calixarene complexation reactions were $LiClO_4$ (Fluka, p.a. and Sigma Aldrich 99.99 %), $NaClO_4{\cdot}H_2O$ (Fluka p.a.), $NaClO_4$ (Sigma Aldrich 98+ %), $KClO_4$ (Merck, p.a.), $RbNO_3$ (Sigma, 99.7 %), $CsNO_3$ (Sigma, 99.5 %), CsCl (Merck, p.a.), $Mg(ClO_4)_2$ (Aldrich, 99 %), $Ca(ClO_4)_2$ (Aldrich, 99 %), $Sr(ClO_4)_2$ (Aldrich, p.a.), and $Ba(ClO_4)_2$ (Fluka, p.a.). The solvents, acetonitrile (Merck, Uvasol and Baker, HPLC Grade) and methanol (Baker, HPLC Grade and Sigma-Aldrich, 99.9 %, Spectrophotometric Grade) were used without further purification. In all potentiometric titrations the ionic strength was kept constant by addition of Et_4NClO_4 (Fluka, p.a.). Compounds *p*-*tert*-calix[4]arene ethyl ester,[52] tetra acid chloride of *p*-*tert*-calix[4]arene,[15] 2-(2-metoxyetoxy)ethyl amine,[53] and bis(2-(2-methoxyethoxy)ethyl) amine[54] used in the synthesis of **1** and **2** (Scheme 1) were prepared according to the procedures described in the literature.

Synthesis of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetra(N-(2-(2-metoxyetoxy)ethyl)carbamoylmethoxy)calix[4]arene (1)

Preparation of compound **1** by aminolysis: *p*-*tert*-calix[4]arene ethyl ester[52] (1.93 g, 1.5 mmol) and 2-(2-metoxyetoxy)ethylamine[53] (2.63 g, 25 mmol) were added to 10 ml of *i*-butanol. The mixture was kept for several weeks at room temperature. After determining that no calixarene ethyl ester was present in the solution, by means of ^1H NMR spectroscopy, solvent was evaporated and precipitate was dissolved in CH_2Cl_2. The solution was extracted first with HCl (1 mol dm^{-3}) and then with water (mixing of water and dichloromethane solution resulted in emulsion which was separated after 1 hour). The solvent was removed under vacuum, the solid residue was dissolved in methanol, water was added in the solution, and compound **1** was precipitated. The precipitate was separated by suction filtration. After drying, a compound **1** was obtained as a white powder. $R_f = 0.64$ (10 % CH_3OH/CH_2Cl_2); $t_t = 173–174$ °C; yield 90 %. Additional purification step was required to ensure that all of the ions were removed, and that was done in a similar manner as described in ref. 40. Compound **1** was dissolved in methanol followed by addition of deionised water. Subsequently, the solution was heated to evaporate the methanol, leaving a precipitate in the aqueous solution. The precipitated ligand **1** was collected by suction filtration, washed with deionised water, and dried for 12 hours at 110 °C prior to use in physico-chemical experiments.

^1H NMR spectra (600 MHz, $CDCl_3$): δ_H/ppm = 1.10 (36H, s, $(C(CH_3)_3)$), 3.26 (4H, d, $J = 13.3$, $ArCH_{2eq}Ar$), 3.35 (12H, s, OCH_3), 3.52–3.62 (32H, m, OCH_2, NCH_2), 4.62 (8H, s, OCH_2CO), 4.65 (4H, d, $J = 13.3$, $ArCH_{2ax}Ar$), 6.79 (8H, s, ArH), 7.94 (4H, t, $J = 6.3$, NH). ^{13}C NMR spectra (75 MHz, $CDCl_3$): δ_C/ppm = 31.33 $(C(CH_3)_3)$, 31.69 (Ar-CH_2-Ar) 33.83, $(C(CH_3)_3)$, 39.12 ($NHCH_2CH_2$), 58.69 (OCH_3), 69.74 (OCH_2CO), 70.01 (OCH_2CH_2O), 71.88 (NCH_2CH_2O), 74.38 (OCH_2CH_2O), 125.76 (*o*-Ar-C), 132.74 (*m*-Ar-C), 145.53 (Ar-C-*t*-Bu), 153.32 (*p*-Ar-C), 170.03 (CONH). IR (KBr) ν_{max}/cm^{-1} = 3373 (s, NH), 2960 (s, CH), 1674 (s, CO amid I), 1542 (m, NH, amid II), 1479 (m, CH_2), 1198 (s, COC), 1126 (s, COC). HRMS: *m/z* $[M+H]^+$ exact mass, $C_{72}H_{108}N_4O_{16}$: 1285.7839; found: 1285.7852.

Synthesis of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetra(N,N-bis(2-(2-metoxyetoxy)ethyl) carbamoylmethoxy)calix[4]arene (2)

Bis(2-(2-methoxyethoxy)etil)amine[54] (1.4 g, 6.3 mmol) and triethylamine (1.0 mL, 7.2 mmol) were added to the cooled (0 °C) dry CH_2Cl_2 (20 mL) under argon atmosphere. Then, the acid chloride of calix[4]arene tetracetic acid (the *cone* conformer)[15] (1.24 g, 1.3 mmol) in dry CH_2Cl_2 (10 mL) was added at once with a syringe. The reaction mixture was allowed to warm up to room temperature and stirred for 24 h. After filtration of solid, the filtrate was extracted with HCl (1.0 mol dm^{-3}) and water. Dichloromethane was removed under vacuum and the product **2** was obtain as a pale yellow wax. Ligand **2** was additionally purified by continuous liquid-liquid extraction. Dichloromethane solution of **2** was placed in the continuous extractor and extracted with deionised water for 36 hours (the water phase was replaced 3 times) in order to remove ion traces from the product. The resulting CH_2Cl_2 solution was again extracted several times with deionized water. The presence of charged species was checked conductometrically. After evaporating CH_2Cl_2 under vacuum, the compound **2** was obtained as a waxy solid with a yield of 59 %, $R_f = 0.75$ (6 % CH_3OH/CH_2Cl_2). Prior to use, ligand **2** was dried for approximately 12 hours at 110 °C.

^1H NMR (600 MHz, $CDCl_3$): δ_H(ppm) = 1.09 (36H, s, $C(CH_3)_3$), 3.16 (4H, d, J = 12.9, $ArCH_{2eq}Ar$), 3.34 (12H, s, OCH_3), 3.38 (12H, s, OCH_3),3.43–3.66 (64H, m, OCH_2, NCH_2), 5.02 (8H, s, OCH_2CO), 5.07 (4H, d, J = 12.8, $ArCH_{2ax}Ar$), 6.77 (8H, s, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C(ppm) = 31.42 ($C(CH_3)_3$), 32.18 ($Ar\text{-}CH_2\text{-}Ar$), 33.73 ($C(CH_3)_3$), 46.60 (NCH_2CH_2), 47.82 (NCH_2CH_2), 58.96 (OCH_3), 69.74 (OCH_2CO), 69.33 (NCH_2CH_2O), 70.07 (NCH_2CH_2O), 70.23 (OCH_2CH_2O), 70.54 (OCH_2CH_2O), 71.38 (OCH_2CH_2O), 71.91 (OCH_2CH_2O), 125.21 (*o*-Ar-C), 133.58 (*m*-Ar-C), 144.32 (Ar-C-*t*-Bu), 153.70 (*p*-Ar-C), 170.19 (CONH). IR (KBr) ν_{max}(cm^{-1}) = 2953 (s, CH), 2871 (s, CH), 1653 (s, CO), 1482 (s, CH_2),1196 (s, COC), 1120 (s, COC). HRMS: *m/z* [M+Na]$^+$ exact mass, $C_{92}H_{148}N_4O_{24}$: 1716.0381; found: 1716.0386.

Spectrophotometry

UV titrations were performed at (25.0 ± 0.1) °C by means of a Varian Cary 5 double-beam spectrophotometer equipped with a thermostating device. The spectral changes of ligand solution (V_0 = 2.0 cm^3, c_0 = 1.5 × 10^{-4} to 3.0 × 10^{-4} mol dm^{-3}) were recorded upon stepwise addition of an alkali metal salt solution (c = 2.0 × 10^{-3} to 3.5 × 10^{-3} mol dm^{-3}) directly into the measuring cell of 1 cm path length (Hellma, Suprasil QX). Absorbances were sampled at 1 nm intervals, with an integration time of 0.2 s. Titrations for each system were done in triplicate. The obtained spectrophotometric data were processed using the SPECFIT program.[55, 56]

Conductometry

Conductometric titrations were carried out at (25.0 ± 0.1) °C by means of a Metrohm 712 conductometer. The cell constant ((0.861 ± 0.001) cm^{-1}) was determined before each experiment using 0.01 mol dm^{-3} aqueous KCl solution. The alkali metal salt solution (V_0 = 20.0 to 22.0 cm^3, c_0 = 8.0 × 10^{-5} to 2.0 × 10^{-4} mol dm^{-3}) was titrated with a ligand solution (c = 1.0 × 10^{-4} to 2.5 × 10^{-3} mol dm^{-3}) in a thermostated vessel. The measured conductivities were corrected for the conductivity of the solvent. Titrations for each system were done in triplicate. The obtained data were processed by the OriginPro 7.5 program.

Potentiometry

The stability constants of Na**1**$^+$ and Na**2**$^+$ complexes were determined by potentiometric titrations of 30.3 cm^3 $NaClO_4$ solution (c_0 = 1.0 × 10^{-4} mol dm^{-3}) with solution of ligands **1** and **2** (c = 1.0 × 10^{-3} mol dm^{-3}) in a thermostated titration vessel (25.0 ± 0.1) °C. The ionic strength of solutions was set to 0.01 mol dm^{-3} by Et_4NClO_4. The indicator electrode was a sodium-selective glass electrode (Metrohm, 6.0501.100) with Ag/AgCl reference electrode (Metrohm, 6.0733.100) filled with acetonitrile or methanol solution of Et_4NCl (c = 0.01 mol dm^{-3}). The working and reference half-cells were connected with a salt bridge containing 0.01 mol dm^{-3} Et_4NClO_4. A Metrohm 827 pH Lab was used for electromotivity measurements. The cell was calibrated by the incremental addition of $NaClO_4$ solution (c = 1.0 × 10^{-3} mol dm^{-3}) to 30.0 cm^3 solution of Et_4NClO_4 (c = 0.01 mol dm^{-3}). In each calibration experiment a Nernst-like behaviour was observed, with the slope of *E vs.* p[Na] plot being about –58 mV. Each titration was repeated three times, and the obtained potentiometric data were analysed with the HYPERQUAD program.[57]

Picrate extractions

Aqueous solutions of metal picrates (c_0 = 1.5 × 10^{-4} mol dm^{-3}) were prepared *in situ* by dissolving the metal hydroxide (0.001 mol) in picric acid. (c = 1.5 × 10^{-4} mol dm^{-3}, 25 mL). Solutions (c_0 = 2.0 × 10^{-4} mol dm^{-3}) of the calixarene derivatives were prepared in dichloromethane. Equal volumes (5 mL) of the two solutions were shaken vigorously for 20 min in a 100 mL flask. The solutions were left to stand in a thermostated bath at (25.0 ± 0.1) °C for 24 h until phase separation was complete. The concentration of picrate ion in the organic phase was then determined spectrophotometrically as described by Pedersen.[58] Control blank experiments showed that no picrate extraction occurred in the absence of a calixarene. The extraction percentage (%E) has been calculated as %E = [(A_0 – A)/A_0] × 100, where A_0 and A are the initial and final absorbances of the metal picrate at 356 nm before and after the extraction.

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Notes and references

1. C. D. Gutsche, *Calixarenes: An Introduction*, 2nd edn., The Royal Society of Chemistry, Cambridge, 2008.
2. Z. Asfari, V. Böhmer, J. Harrowfield, and J. Vicens, eds. *Calixarenes 2001*, Kluwer Academic Publishers, Dordrecht, 2001.
3. V. Böhmer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 713.
4. B. Mokhtari, K. Pourabdollah and N. Dalali, *J. Inclusion Phenom. Macrocyclic Chem*., 2011, **69,** 1.
5. B. S. Creaven, D. F. Donlon, and J. McGinley, *Coord. Chem. Rev*., 2009, **253**, 893.
6. S. E. Matthews and P. D. Beer, *Supramol. Chem.*, 2005, **17**, 411.
7. P. Lhoták, *Top. Curr. Chem.*, 2005, **255**, 65.
8. P. Cuřínová, M. Pojarová, J. Budka, K. Lang, I. Stibor, I. and P. Lhoták, *Tetrahedron*, 2010, **66**, 8047.
9. S. Smirnov, V. Sidorov, V. Pinkhassik, J. Havlicek and I. Stibor, *Supramol. Chem.*, 1997, **8,** 187.
10. G. Arena, A. Contino, E. Longo, G. Spoto, A. Arduini, A. Pochini, A. Secchi, C. Massera, F. Ugozzolli, *New J. Chem.*, 2004, **28**, 56.
11. F. Arnaud-Neu, M. A. McKervey and M.-J. Schwing-Weill, in *Calixarenes 2001*, ed. Z. Asfari, V. Böhmer, J. Harrowfield and J. Vicens, Kluwer Academic Publishers, Dordrecht, 2001, ch. 21, pp. 385–406.
12. G. Horvat, V. Stilinović, T. Hrenar, B. Kaitner, L .Frkanec and V. Tomišić, *Inorg. Chem.,* 2012, **51**, 6264.
13. G. Horvat, V. Stilinović, B. Kaitner, L. Frkanec and V. Tomišić, *Inorg. Chem*., 2013, **52**, 12702.
14. A. F. Danil de Namor, T. T. Matsufuji-Yasuda, K. Zegarra-Fernandez, O. A. Webb and A. El Gamouz, *Croat. Chem. Acta*, 2013, **86**, 1.
15. F. Arnaud-Neu, G. Barrett, S. Cremin, M. Deasy, G. Ferguson, S. J. Harris, A. J. Lough, L. Guerra, M. A. McKervey,

M. J. Schwing-Weill and P. Schwinte, *J. Chem. Soc. Perkin Trans. 2,* 1992, 1119.

16. F. Arnaud- Neu, S. Barboso, F. Berny, A. Casnati, N. Muzet, A. Pinalli, R. Ungaro, M.-J. Schwing-Weill and G. Wipff, *J. Chem . Soc. Perkin Trans. 2,* 1999, 1727.
17. V. Tomišić, N. Galić, B. Bertoša, L. Frkanec, V. Simeon and M. Žinić, *J. Inclusion Phenom. Macrocyclic Chem.,* 2005, **53**, 263.
18. J. C. Mareque Rivas, C. H. Schwalbe and S. J. Lippard, *Proc. Natl. Acad. Sci. U.S.A.*, 2001, **98***,* 9478.
19. L. Frkanec, A. Višnjevac, B. Kojić-Prodić, and M. Žinić, *Chem. Eur. J.*, 2000, ***6***, 442.
20. E. Nomura, M. Takagaki, C. Nakaoka, M. Uchida and H. J. Taniguchi, *Org. Chem*., 1999, **64**, 3151.
21. N. Galić, N. Burić, R. Tomaš, L. Frkanec and V. Tomišić, *Supramol. Chem.,* 2011, **23**, 389.
22. Y. L. Cho, D. M. Rudkevich, A. Shivanyuk, K. Rissanen and J. Jr. Rebek, *Chem. Eur. J.*, 2000, **6**, 3788.
23. I. Stibor, M. Ružičkova, R. Krátký, M. Vindyš, J. Havlíček, E. Pinkhassik, P. Lhoták, A. R Mustafina,. Y. E. Morozova, E. Kh. Kazakova and V. P. Gubskaya, *Collect. Czech. Chem. Commun.,* 2001, **66**, 641.
24. L. Baldini, F. Sansone, F. Scaravelli, A. Casnati and R. Ungaro, S*upramol. Chem.,* 2010, **22**, 776.
25. A. F. Danil de Namor, R. G. Hutcherson, F. J. Sueros Velarde, M. L. Zapata-Ormachea, L. E. Pulcha Salazar, I. Al Jammaz and N. Al Rawi, *Pure Appl. Chem.,* 1998**, 70***,* 769.
26. A. F. Danil de Namor, R. M. Cleverley and M. L. Zapata-Ormachea, *Chem. Rev.,* 1998, **98**, 2495.
27. A. F. Danil de Namor, in *Calixarenes 2001*, ed. Z. Asfari, V. Böhmer, J. Harrowfield and J. Vicens, Kluwer Academic Publishers, Dordrecht, 2001, ch. 19, pp. 346–364.
28. A. F. Danil de Namor, D. Kowalska, E. E. Castellano, O. E. Piro, F. J. Sueros Velarde and J. Villanueva Salasa, *Phys. Chem. Chem. Phys.,* 2001, **3**, 4010.
29. J. Požar, T. Preočanin, L. Frkanec and V. Tomišić, *J. Solution Chem.*, 2010, **39**, 835.
30. J. Požar, G. Horvat, M. Čalogović, N. Galić, L. Frkanec and V. Tomišić, *Croat. Chem. Acta,* 2012**, 85**, 541.
31. M. Tranfić Bakić, D. Jadreško, T. Hrenar, G. Horvat, J. Požar, N. Galić, V. Sokol, R. Tomaš, S. Alihodžić, M. Žinić, L. Frkanec and V. Tomišić, *RSC Adv.*, 2015, **5**, 23900.
32. L. Baldini, F. Sansone, A. Casnati and R. Ungaro in *Supramolecular Chemistry: From Molecules to Nanomaterials*, ed. G. A. Philip and J. W. Steed, John Wiley & Sons, Chichester, 2012, pp. 863–895.
33. A. Casnati, R. Ungaro, in *Calixarene in Action*, ed. L. Madolini and R. Ungaro, Imperial College Press., London, 2000, pp. 62–84.
34. P. Schmitt, D. P. Beer, M. G. B. Drew and P. D. Sheen, *Angew. Chem. Int. Ed.,* 1997, **36***,* 1840.
35. K. Araki, A. Yanagi and S. Shinkai, *Teaahedron,* 1993, **49**, 6763.
36. J. Shen, H. F. Koch and M. Roundhill, *J. Incl. Phenom. Macrocyclic Chem.,* 2000, **38**, 57.
37. E. Nomura, H. Taniguchi, K. Kawaguchi and Y, Otsujit, *J. Org. Chem*., 1993, **58,** 4709.
38. Y. Shi, and Z. Zhang, *J. Chem. Soc. Chemm. Commun.,* 1994, 375.
39. C. Tu, L. Zhu, P. Li, Y. Chen, Y. Su, D. Yan, X. Zhu, and G. Zhou, *Chem. Commun.,* 2011, **47**, 6063.
40. D. Momekova, D. Budurova, E. Drakalska, S. Shenkov, G. Momekov, B. Trzebicka, N. Lambov, E. Tashev and S. Rangelov, *Int. J. Pharm.,* 2012, **410**, 436.
41. A. Hamdi, R. Abidi and J. Vicens, *J. Inclusion Phenom. Macrocyclic Chem*., 2008, **60**, 193.
42. A. Medvedovici, F. Albu, A. Hamdi, R. Souane, L. Kim, L. Mutihac and J. Vicens, *J. Inclusion Phenom. Macrocyclic Chem*., 2011, **71**, 545.
43. L. Kim, A. Hamdi, A. D. Stancu, R. Souane, L. Mutihac and J. Vicens, *J. Inclusion Phenom. Macrocyclic Chem*., 2010, **66**, 55.
44. A. Hamdi, R. Souane, L. Kim, R. Abidi, L. Mutihac and J. Vicens, *J. Inclusion Phenom. Macrocyclic Chem*., 2009, **64**, 95.
45. F. Arnaud-Neu, G. Barrett, S. Fanni, D. Marrs, W. McGregor, M. A. McKervey, M.-J. Schwing-Weill, V. Vetrogon and S. Wechsler, *J. Chem. Soc. Perkin Trans. 2*, 1995, 453.
46. A. Moser, G. P. A. Yap and D. Detellier, *J. Chem. Soc., Dalton Trans.*, 2002, 428.
47. A. D'Aprano, M. Salomon and V. Mauro, *J. Solution Chem*., 1995, **24**, 685.
48. A. F. Danil de Namor, N. A. de Sueros, M. A. McKervey, G. Barrett, F. A. Neu, M. J. Schwing-Weill, *J. Chem. Soc., Chem. Commun.*, 1991, 1546.
49. A. F. Danil de Namor, S. Chahine, E. E. Castellano and O. E. Piro, *J. Phys. Chem.*, *A* 2005, **109**, 6743.
50. A. F. Danil de Namor, S.; Chahine, D. Kowalska, E. E. Castellano and O. E. Piro, O. E. *J. Am. Chem. Soc.* 2002, **124**, 12824.
51. W. L. F. Armarego and C. L. L. Chai, *Purification of Laboratory Chemicals,* 6th edn., Butterworth-Heinemann (Elsevier): Oxford, UK, 2009.
52. F. Arnaud-Neu, E. M. Collins, M. Deasy, G. Ferguson, S. J. Harris, B. Kaitner, A. J. Lough, M. A. McKervey, E. Marques, B. L. Ruhl, M. J. Schwing-Weill and E. M. Seward, *J. Am. Chem. Soc.,* 1989, **111**, 8681.
53. G. Madhusudhan, G. Ravibabu and G. Reddy, *Indian J. Chem*., 2010, **49B,** 96.
54. A. Jain, S. G. Huang and G. M. Whitesides, *J. Am. Chem. Soc.,* 1994, **116***,* 5057.
55. H. Gamp, M. Maeder, C. J. Meyer and A. D.Zuberbuhler, *Talanta*, 1985, **32**, 95.
56. H. Gamp, M. Maeder, C. J. Meyer and A. D. Zuberbuhler, *Talanta*, 1985, **32**, 257.
57. P. Gans, A. Sabatini, A. Vacca, *Talanta*, 1996, **43**, 1739.
58. C. Pedersen, *J. Fed. Proc.,* 1968, **27**, 1305.