Pergamon

Tetrahedron 58 (2002) 10277–10285

TETRAHEDRON

Synthesis of tripodal aza crown ether calix[4]arenes and their supramolecular chemistry with transition-, alkali metal ions and anions

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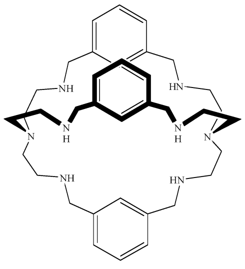
Received 27 August 2002; revised 14 October 2002; accepted 7 November 2002

Abstract—Tripodal aza crown ether calix[4]arenes, **5a**, **5b**, **6a** and **6b**, have been synthesized. The structure of protonated **5a** was elucidated by X-ray crystallography to be a self-threaded rotaxane. Complexation studies of **5a** and **5b** towards anions using Na^+ as countercation were carried out by ^1H NMR titration in dimethylsulfoxide-d_6 and the mixture of chloroform-*d* and methanol-d_4, respectively. Ligands **5a** and **5b** were able to form 1:1 complexes with Br^-, I^- and NO_3^- and the complexation stability varied as follows: $NO_3^- > I^- > Br^-$. The effect of countercation on anion complexation was also investigated. The results showed that the association constants of **5a** towards Br^- in the presence of various cations varied as $K^+ > Bu_4N^+ > Na^+$. The enhancement in anion complexation ability of **5a** may result from the rearrangement of the tripodal ammonium unit in the presence of K^+. The neutral forms, **6a** and **6b**, were able to form complexes with transition metal ions such as Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}. The stability of the complexes followed the sequence: $Ni^{2+} < Co^{2+} \ll Cu^{2+} \gg Zn^{2+}$. Compounds **6a** and **6b** may, therefore, potentially be used as either transition metal ion or anion receptors that can be controlled by pH of the solution. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

During the past decades, supramolecular chemistry has become one of the most popular branches of chemistry due to its versatile applications in environmental and material science. Chemists have synthesized many types of receptors for cations and anions.[1] Lehn and co-workers have synthesized macrobicyclic and macrotricyclic polyamines and found that the protonated forms can bind anions such as F^- and Cl^-.[2] Bowman–James and co-workers employed a bicyclic polyammonium receptor derivatized from tris-(2-amino)ethylamine (tren), **L**, possessing C_3 symmetry to bind nitrate[3] and fluoride[4] ions. They found by X-ray crystallography that such a polyammonium macrocycle was able to include two nitrates in it cavity.[5] In 2000, Nelson and colleague reported the binding properties of the same ligand with the transition metal series Co(II)–Zn(II).[6]

Our group has synthesized hosts for cations,[7] anions[8] and neutral[9] molecules using calix[4]arene as a building block. Recently, derivatives of calixarenes have been employed as receptors for cations, anions and neutral molecules.[10] It is our goal to design and synthesize a versatile receptor for alkali metals, transition metals and anions which can be switched in its function by external stimuli. We chose *p-tert*-butylcalix[4]arene as the building block and combined it with a crown ether and the tren unit to synthesize a compound that has great potential to bind either metal ions or anions. We report herein the synthesis of the tripodal-amine capped benzo crown *p-tert*-butylcalix[4]arenes, **6a** and **6b**. The complexation of **6a** and **6b** with transition metal ions has been studied by potentiometric titration. In addition, the anion complexation studies of the ammonium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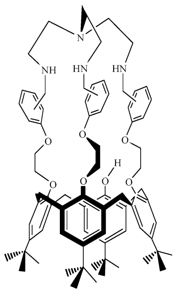
6a, *ortho*
6b, *para*

Keywords: *p-tert*-butylcalix[4]arene; aza crown ether; ammonium groups; anion receptor; metal ion receptor.

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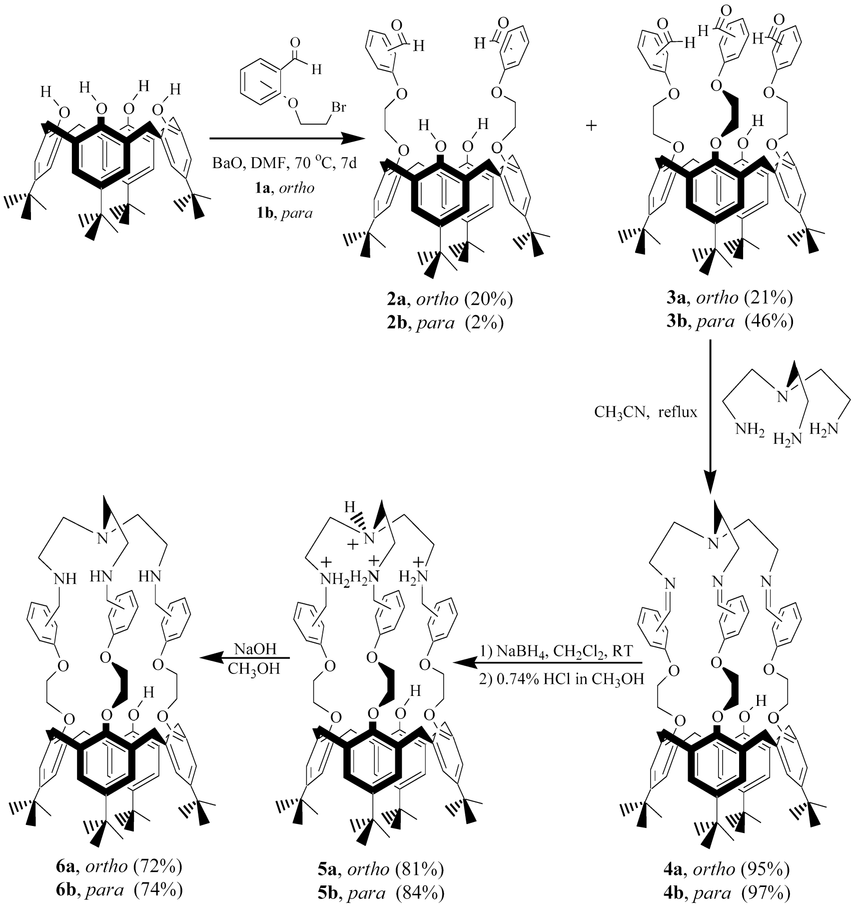
PII: S0040-4020(02)01447-3



Scheme 1.

derivative of **6a** and **6b**, **5a** and **5b**, have been performed in the presence of various countercations in order to understand the role of cations towards anion binding ability.

2. Results and discussion

2.1. Design, synthesis and characterization

Our desired receptors must contain both cation and anion binding sites. Ammonium groups and crown ethers are well-known to bind anions via electrostatic interactions and cations via coordination bonds, respectively. In this paper, we employ *p-tert*-butylcalix[4]arene as a supramolecular building block. Three ethoxy benzaldehyde groups have been attached to the calix[4]arene unit to form a crown ether-like cation ionophore. Condensation reactions of trialdehyde calix[4]arene with tris(2-amino)ethylamine and the subsequent reduction and protonation generate tripodal ammonium receptor unit, **5a** and **5b**. Compounds **5a** and **5b** thus possess both metal ion and anion ionophores next to each other separated by a spacer such as a benzene unit. The neutral forms of **5a** and **5b**, compounds **6a** and **6b**, contain four nitrogen lone pairs and should thus form complexes with transition metal ions.

The synthesis of desired compounds **5a**, **5b**,[11] **6a** and **6b** was carried out as shown in Scheme 1. Substitution reactions of *p-tert*-butylcalix[4]arene with 3.0 equiv. of 2-(2′-bromoethoxy)benzaldehyde, **1a**, and 4-(2′-bromoethoxy)benzaldehyde, **1b**, respectively, were carried out in the presence of a base to produce trialdehyde precursors, **3a** and **3b**, for preparing the tripodal-amine capped calix[4]arene. The synthesis of **3a** was reported previously in acetonitrile using K_2CO_3 as base.[12] This reaction gave only 6% yield of the desired trialdehyde derivative. Furthermore, substitution reactions using K_2CO_3 always gave the dialdehyde derivatives, **2a** and **2b**, in high yields.[7,13] Since then, a number of bases and solvents have been employed to optimize the yields of the desired products. However, it was found that reactions in the presence of strong bases such as KOH underwent Cannizzaro reactions and gave both alcohol and carboxylic acid derivatives instead.[14]Finally, we found that reactions using BaO in DMF gave higher yields of trialdehyde calix[4]arenes, **3a** (21%) and **3b** (46%), than those of dialdehyde calix[4]arenes, **2a** (20%) and **2b** (2%). It should be noted that the yield of **3b** was twice as much as that of **3a** probably due to the lower steric hindrance of the *para* isomer facilitating the substitution reaction. The ^{1}H NMR spectrum of **3a** showed (C=O)*H* at 10.41 and 9.74 ppm and at 9.76 and 9.68 ppm for **3b** in 1:2 integral ratios. FAB MS and elemental analysis results of **3a** and **3b** were in agreement with the proposed structure.

Condensation reactions of **3a** and **3b** with 1.1 equiv. of

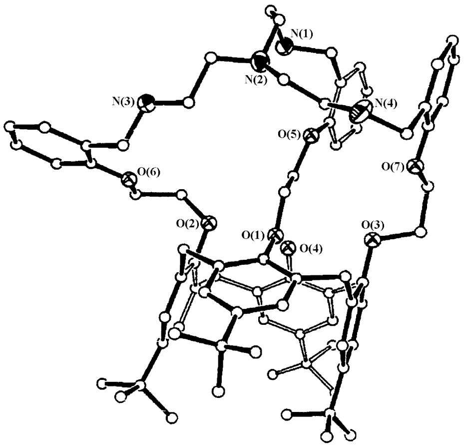


Figure 1. Crystal structure of **5a**. Hydrogen atoms were omitted for clarity.

tris(2-amino)ethylamine in a mixture of CH_3CN and CH_2Cl_2 (high dilution) precipitated imines or Schiff base products, **4a** (95%) and **4b** (97%). The signals due to (C═O)*H* proton disappeared, and the signals due to RN═C*H* protons showed at 8.83 and 8.93 ppm in the ^1H NMR spectrum of **4a** and at 8.07 and 7.68 ppm for **4b**. FAB MS and elemental analysis results were correct for the proposed structures. Reduction of **4a** and **4b** by 20 equiv. of $NaBH_4$ in CH_2Cl_2 and subsequent protonation with HCl/CH_3OH (0.74% v/v) yielded ammonium derivatives, **5a** (81%) and **5b** (84%), which showed very broad signals in the ^1H NMR spectrum due to the effect of positive charges. Signals due to $ArCH_2NH_2^+CH_2-$ appeared at 9.78 and 9.39 ppm with an integral ratio of 2:1 for **5a** and at 8.71 and 8.23 ppm for **5b**. Mass spectra of **5a** and **5b** showed a strong signal at *m*/*z* 1192.1 corresponding to the molecular weight of the neutralized species. Nevertheless, elemental analysis result agreed with the proposed structures. It is interesting that the position of (C═O)*H*, RN═C*H* and $ArCH_2NH_2^+CH_2-$ protons in **3a**–**5a** appear more downfield than those of **3b**–**5b** probably due to the effect of magnetic anisotropy of the adjacent phenyl ring. Neutralization of **5a** and **5b** with NaOH in methanol provided the neutral tripodal-amine capped benzo crown calix[4]arene, **6a** (72%) and **6b** (74%). Spectroscopic and elemental analysis results of **6a** and **6b** agreed well with the proposed structures.

2.2. X-Ray crystallography

The solid state structure of compound **5a** has been determined by X-ray crystallography (Fig. 1). The structure is solvated by one molecule of CH_3OH and two molecules of H_2O. The phenyl rings of the calix[4]arene unit are in a pinched cone conformation. Interestingly, one of the ethoxy benzyl chains connecting to the tren unit threads through the cavity of the other two ethoxy benzyl chains. This structure resembles a self-threaded rotaxane derivatised from two homooxacalix[3]arenes.[15] Recently, Vicens and colleagues have also reported a similar structure of tripodal calix[4]-(azo)crowns.[16] Although suitable crystals of **5b** for X-ray analysis cannot be obtained, the ^1H NMR spectrum of **5b** suggests a more symmetrical orientation of the glycolic chains. The difference in structure and size of the cavity of **5a** and **5b** leads to the different in transition metal ions and anion binding ability, vide infra.

2.3. Anion binding studies and effects of alkali metal ions towards anion binding ability

The charge and geometry of anions were considered in our investigation. Therefore, we chose to investigate spherical anions (F^-, Br^- and I^-), a trigonal planar anion (CO_3^{2-}), an angular anion (AsO_2^-) and tetrahedral anions ($H_2PO_4^-$, HPO_4^{2-}, SO_4^{2-} and PO_4^{3-}). ^1H NMR (200 MHz) titrations were employed in complexation studies of **5a** and **5b** towards anions. NMR titrations for **5a** were carried out in DMSO-d_6 due to the solubility of **5a** and anion salts in that solvent. The compound **5b**, however, was not soluble in DMSO-d_6 but soluble in $CDCl_3$. Anion salts dissolved quite well in CD_3OD. The NMR titrations for **5b** were thus carried out in the mixture of $CDCl_3$ and CD_3OD.

Although excess NaF and Na_2SO_4 was added to solutions of **5a** and **5b**, no chemical shift displacement of any signals in the NMR spectra was observed. Therefore F^- and SO_4^{2-} did not form complexes with **5a** and **5b**. This is probably due to the size of F^- and SO_4^{2-} which is not appropriate for the ligand cavity.

In the case of anions such as AsO_2^-, CO_3^{2-}, PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ (using sodium salts), we observed interesting phenomena when complexation studies of ligand **5a** were performed. Upon increasing the mole ratio of anions, white solids precipitated from the mixture of **5a** and AsO_2^-, CO_3^{2-} and PO_4^{3-}. Therefore, NMR titrations could not be completed with these anions and the association constants cannot be calculated. However, upon addition of HPO_4^{2-} and $H_2PO_4^-$ into the solution of **5a**, moderate upfield shifts of the signal $ArCH_2NH_2^+CH_2-$ at δ 9.39 and 9.78 ppm were observed. When the anion ratio increased the spectrum changed to the same as that of the neutral compound (**6a**) implying that the deprotonation of **5a** took place upon complexing HPO_4^{2-} and $H_2PO_4^-$. Association constants of the complexes of **5a** with HPO_4^{2-} and $H_2PO_4^-$ thus cannot be calculated.

The complexation studies of **5b** towards AsO_2^-, CO_3^{2-} and PO_4^{3-} were also carried out. It was found that complexation occurred along with the deprotonation to give the neutral compound **6b**. Therefore, the association constants for these complexes cannot be calculated. Although addition of Na_2HPO_4 into ligand **5b** caused the displacement of the aromatic signal (at 6.5–8.0 ppm) of **5b**, Na_2HPO_4 did not completely dissolve into solution. The association constant of the complex of **5b** and HPO_4^{2-} cannot be determined correctly. Furthermore, upon addition of excess $NaH_2PO_4 \cdot H_2O$ to a solution of **5b**, no chemical shift displacement in the NMR spectra was observed. Therefore, compound **5b** did not form a complex with $H_2PO_4^-$.

Upon addition of NaBr, NaI and $NaNO_3$ to the solutions of **5a**, moderate upfield shifts of the signal $ArCH_2NH_2^+CH_2-$ at δ 9.39 and 9.78 ppm and slightly shifts of aromatic regions at δ 7.00–8.00 ppm were observed in the ^1H NMR spectra. This indicates that anions form complexes with **5a** in the cavity of the tripodally capped unit using the electrostatic interactions. Job plots indicated that **5a** formed complexes with these anions in a 1:1 fashion. In the case of **5b**, the signal of the $ArCH_2NH_2^+CH_2-$ protons in ligand **5b**

Table 1. Summary of association constants of ligands **5a** and **5b** towards various anions using Na^+ as countercation

Anion	K_{assoc} (M^{-1})	
	5a	**5b**
Br^-	58.6	53.0
I^-	77.2	57.3
NO_3^-	190.2	106.3

All experiments were carried out at 298 K; errors estimated to be less than 15%.

disappeared because the protons on the ammonium group exchanged with CD_3OD. Nevertheless, the moderate downfield shift of the protons in the *para* position of $-CH_2ArH_a$ and $ROArH_b$ was monitored upon addition of various ratios of NaBr, NaI and $NaNO_3$. Job plots indicated that **5b** also formed complexes with anions in a 1:1 ratio. The association constants of **5a** and **5b** towards various anions calculated by the program EQNMR[17] are shown in Table 1. It is found that using Na^+ as countercation **5a** and **5b** form complexes with Br^-, I^- and NO_3^- and the stability of the complexes varies as $NO_3^- > I^- > Br^-$. It should be noted that the interaction of **5a** with NO_3^- is stronger than that of **5b**. The results indicate that **5a** possesses a more appropriate cavity for NO_3^- than **5b** does.

Recently, receptors containing two individual recognition units, one for a cation and one for an anion have attracted attention. Reinhoudt and coworkers have synthesized an elegant calix[4]arene derivative with cation binding ester groups on the lower rim and anion binding urea groups on the upper rim. The compound was able to bind Cl^- efficiently in the presence of Na^+.[18] Beer and co-workers have synthesized a number of ditopic receptors that can undergo selective ion pair recognition. Rhenium(I) bipyridyl amide crown ether receptors were found to complex KCl ion pairs.[19] A tripodal tris(amido benzo-15-crown-5) ligand was found to cooperatively bind chloride, iodide and perrhenate anions via co-bound crown ether complexed sodium cations.[20] Later, a heteroditopic bis-(calix[4]arene) ferrocene receptor was found to give a significant electrochemical response to bromide anions in the presence of Li^+ ion.[21]

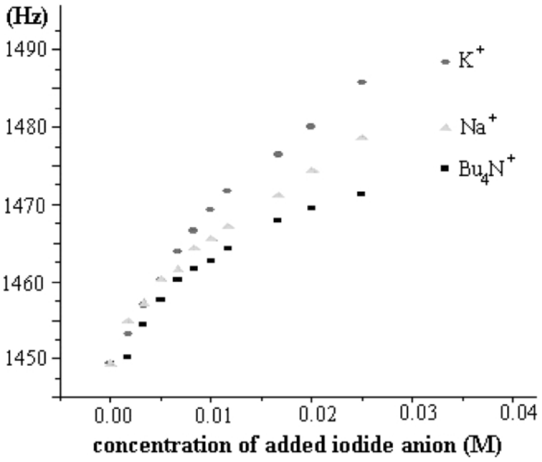


Figure 2. Titration curves of **5b** with I^- in the presence of Bu_4N^+, Na^+ and K^+.

Table 2. Association constants of ligands **5a** and **5b** towards Br^- and I^- in the presence of various countercations

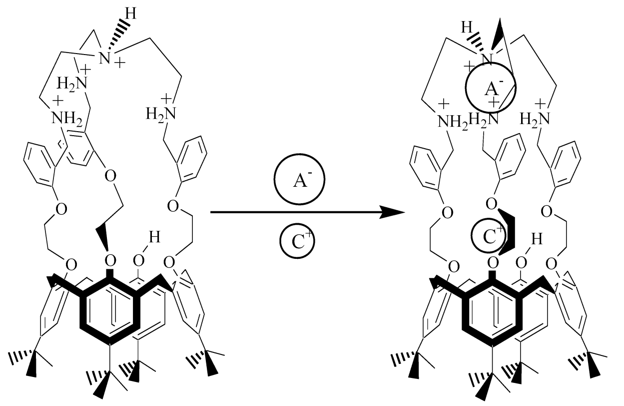
Metal	Anion	K_{assoc} (M^{-1})	
		5a	**5b**
None[a]	Br^-	84.2	76.5
K^+	Br^-	120.1	34.9
None[a]	I^-	108.9	137.9
K^+	I^-	103.3	66.3

All experiments were carried out at 298 K; errors estimated to be less than 15%.

[a] Using Bu_4N^+ as countercation.

We are also interested in the effects of alkali metal ions towards anion binding, especially spherical anions like Br^- and I^-. Upon addition of tetrabutylammonium and potassium salts of Br^- and I^- to **5a** moderate upfield shifts of the signal $ArCH_2NH_2^+CH_2-$ at δ 9.39 and 9.78 ppm and to **5b** strongly downfield shifts of the signal $-CH_2ArH_a$ and $ROArH_b$ at δ 7.38 and 6.93 ppm were observed in the ^1H NMR spectra. The plot showing the relationship between chemical shifts of the signal due to $-OArHCH_2-$ and concentrations of iodide anion in the presence of various countercations are depicted in Fig. 2. Association constants of **5a** and **5b** towards Br^- and I^- in the presence of various countercations such as K^+ and Bu_4N^+ calculated by the program EQNMR are collected in Table 2.

With Bu_4N^+ as countercation, **5a** and **5b** can form more stable complexes with I^-. However, the stability of **5b** towards I^- is higher than **5a**. This signifies that the cavity of **5b** is more suitable for binding a big anion such as I^-. In the presence of K^+, **5a** shows an increase in binding affinity towards Br^- by nearly 1.5-fold. On the other hand, Na^+ does not cause any enhancement in the anion binding ability of **5a**. This result suggests that the crown ether unit of **5a** prefers binding K^+ over Na^+. A similar crown ether cavity found in bis(calix[4]arene) in which two molecules of calix[4]arene linked by four glycolic units has been reported to bind K^+ selectively.[22] From the crystal structure of **5a**, it is also possible that an alkali metal ion can coordinate to the crown ether unit and induces the structural reorganization of **5a** to be more appropriate for binding anions (Scheme 2). Interestingly, the binding ability of **5b** towards Br^- and I^- decreases in the presence of Na^+ and K^+. This observation in which the presence of alkali metal ions



Scheme 2.

Table 3. Stepwise protonation constants of ligands **6a** and **6b** in 1.00×10^{-2} M $Bu_4NCF_3SO_3$ in methanol at 25°C

log K_i	**6a**	**6b**
log K_1	12.03±0.01	10.79±0.04
log K_2	10.17±0.01	9.35±0.04
log K_3	6.95±0.02	7.46±0.04
log K_4	4.44±0.03	5.33±0.04

decreases the anion binding ability of **5a** and **5b** can be rationalized in term of binding competition. Alkali metal ions (Na^+ or K^+) that cannot fit into the cavity size of the crown ether unit in **5a** or **5b** retain cation–anion pairs in selection which can compete in binding with the tripodal ammonium unit of the ligands.

2.4. Transition metal ion binding studies

In order to investigate the complexation ability of compounds **6a** and **6b** towards transition metal ions, compounds **5a** and **5b** were used in potentiometric titrations. Protonation constants and complex stability constants were calculated using the program SUPERQUAD.[23] Protonation constants of **6a** and **6b** in 1.00×10^{-2} M $Bu_4NCF_3SO_3$ in methanol at 25°C are shown in Table 3.

Both compounds **6a** and **6b** can bind up to four protons in the pH range 2–12 and show high basicity in the first two protonation steps, with the first constants log K_1=12.02 and 10.79 for **6a** and **6b**, respectively. Therefore, **6a** and **6b** are more basic than the constitutive subunit tren for which log K_1=10.12.[24] However, it is obvious that the first protonation constant of **6a** is higher than that of **6b**. This outcome may stem from the fact that compound **6a** has nitrogen substituents at the *ortho* position in which the neighboring nitrogen atoms can form intramolecular hydrogen bonding better than in the *para*-position of compound **6b**. This result leads to the more partial negative charge on nitrogen atoms and more positive charge at hydrogen atoms in **6a**. Therefore, the nitrogen donors in **6a** have higher electron density and higher proton affinity than those of **6b**.

Compound **6b** exhibits slightly lower protonation ability for the second proton than its *ortho* analogue. However, for the third and fourth protonation, ligand **6b** shows higher protonation constants than **6a**. These results can be rationalized in term of the electrostatic repulsion. Although both calix[4]arenes have a similar protonation trend in the same pH range, **6b** is less sterically hindered and the binding sites are further apart from each other. Thus, the third and fourth proton bindings of calix[4]arene **6b** are not so difficult and the positive charge repulsion is minimized inducing a higher proton affinity.

Compounds **6a** and **6b** are expected to bind first-row divalent transition metal ions such as Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} to give stable complexes. Nevertheless, ligand **6a** has a different size of binding cavity in comparison with **6b**. Therefore, we aimed to investigate the effects of the size of the binding cavity and flexibility of the ligand on the stability of the complex. The binding ability studies of **6a** and **6b** towards Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} were carried out by means of potentiometric titration using a competitive method with the proton. The stability constants of the complexes between ligand **6a** and **6b** with Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions in 1.00×10^{-2} M $Bu_4NCF_3SO_3$ in methanol are summarized in Table 4.

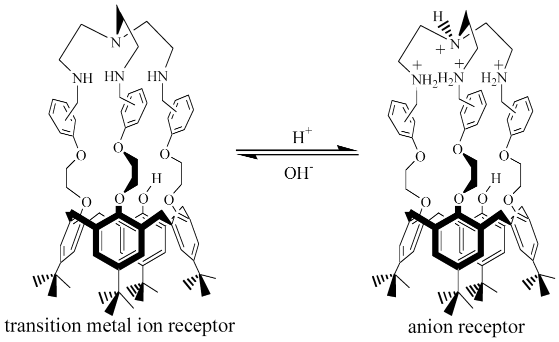
Table 4. Stability constants of complexes of **6a** and **6b** towards Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions in 1.00×10^{-2} M $Bu_4NCF_3SO_3$ in methanol at 25°C

Ligand	Species	log β			
		Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
6a	ML^{2+}	7.52±0.02	6.97±0.03	17.75±0.06	9.97±0.06
	M_2L^{4+}	–	–	–	15.31±0.06
	$ML(OH)^+$	–	–	–	1.17±0.07
6b	ML^{2+}	8.75±0.04	6.08±0.03	17.50±0.07	8.52±0.07
	M_2L^{4+}	–	–	–	14.28±0.05
	$ML(OH)^+$	0.42±0.06	–	–	–

The copper complexes of both **6a** and **6b** are the most stable complexes. Ligand **6a** shows slightly higher stability constants than **6b** with the difference of 0.25 log units. The very high stability constants of compounds **6a** and **6b** with Cu^{2+} are attributed to the suitable geometry of the ligand to accommodate the stable geometry of Cu^{2+} ion. When Cu^{2+} is coordinated to the nitrogen atoms in the tren cavity, the tren unit can arrange itself for the trigonal bipyramidal geometry, which is the most common geometry found in many copper(II) complexes. Another ligand that may occupy the axial position of the metal center is a solvent molecule such as water or methanol in the presence of non-coordinating counteranions (such as ClO_4^- or $CF_3SO_3^-$). X-Ray crystal structures of various copper(II) complexes of symmetric and unsymmetric tripodal tetramine ligands which their structures are similar to the tren unit also possess the trigonal bipyramidal geometry.[25]

Interestingly, the results show that Zn^{2+} forms complexes with ligands **6a** and **6b** in both mononuclear and binuclear fashions. It should be noted that the binding affinity of the second zinc ion for the 1:1 complex of **6b** is slightly higher than that of **6a**. This result can also be rationalized in term of the electronic repulsion. The distance between the tren unit and glycolic ether chains in **6b** is longer than that in **6a**. Therefore, when another zinc ion is included in the position near the lower rim of calix[4]arene, the total electronic repulsion is decreased and leads to greater stability to form a binuclear complex in the case of **6b**. Ligand **6a** also undergoes a hydrolysis reaction and affords $ZnL(OH)^+$, which predominates in an alkaline solution.

Thus far, **6a** possesses higher stability constants towards Ni^{2+}, Cu^{2+} and Zn^{2+} than **6b** does. However, the Co^{2+} complex of **6b** is obviously more stable than that of **6a** (the difference is about 1.25 logarithm units). This may stem from the difference in size of the binding sites of the ligands. Among transition metal ions, both **6a** and **6b** from the least stable complexes with Ni^{2+}. This is probably due to the unsuitable geometry of the ligands. Compounds **6a** and **6b** are too constrained to adjust themselves to accommodate Ni^{2+} in a square planar geometry (the most stable one for Ni^{2+}). Therefore, the stability of the mononuclear



Scheme 3.

complexes of the two ligands follows the sequence: $Ni^{2+} < Co^{2+} \ll Cu^{2+} \gg Zn^{2+}$. This result is in the same trend with the Irving–Williams series of the metal complex stability.[26]

3. Conclusion

In summary, we have synthesized two tripodal aza crown ether calix[4]arenes, **6a** and **6b**, and studied anion complexation with various anions using the acid forms, **5a** and **5b**. Both **5a** and **5b** cannot form complexes with F^- and SO_4^{2-}. In the case of basic anionic guests such as CO_3^{2-}, PO_4^{3-}, AsO_2^-, HPO_4^{2-} and $H_2PO_4^-$, two phenomena, complexation and deprotonation, have occurred concurrently. This is the most crucial defect of anion hosts using ammonium receptors. However, the main advantage of using the electrostatic interaction for anions is that polar and protic solvents can be used, unlike the hydrogen bonding interaction in which the type of solvents employed is limited. For spherical anions like Br^- and I^-, it is found that the presence of K^+ enhances the complexation of **5a** towards anions. Our results thus show the effect of metal ions on anion binding and also demonstrate an example of metal ion-controlled anion receptors. In the mean time, we have shown that compounds **6a** and **6b** can bind transition metal ions such as Co^{2+}, Ni^{2+} and Cu^{2+} in a 1:1 fashion. However, the ligands form the most stable complexes with Cu^{2+} ion. Strikingly, compounds **6a** and **6b** form complexes with Zn^{2+} in both 1:1 and 1:2 ligand to metal ratios. Compounds **6a** and **6b** may thus be used potentially as switchable receptors for metal ions and anions. The binding ability of the receptor can be switched by varying the pH of the solution as illustrated in Scheme 3.

4. Experimental

4.1. Analytical instruments

The ^{1}H NMR spectra were recorded at 200 MHz on a Bruker ACF 200 nuclear magnetic resonance spectrometer, 400 MHz on a Bruker DRX 400 spectrometer and 500 MHz on a GEOL spectrometer. In all cases, samples were dissolved in DMSO-d_6 or in mixed $CDCl_3$ and CD_3OD, and chemical shifts were recorded using a residual proton signal as internal reference.

Elemental analyses were analyzed on a Perkin–Elmer CHON/S analyzer (PE2400 series II). Mass spectra were determined using VG-Analytical ZAB HF Mass Spectrometer. The ESI-TOF mass spectra were obtained from a Micromass LCT Mass Spectrometer and the electrospray ion trap mass spectra were recorded on a Bruker Mass Spectrometer.

4.2. Synthesis

All materials and reagents were standard analytical grade, purchased from BDH, Fluka, J.T. Baker or Merck, and used without further purification. Commercial grade solvents such as acetone, dichloromethane, ethyl acetate, hexane and methanol were distilled and stored over 4 Å molecular sieves. DMF was dried according to the published procedure and distilled before use.[27] Chromatographic separations were performed on silica gel column (kieselgel 60, 0.063–0.200 mm, Merck). Thin layer chromatography (TLC) was carried out using silica gel plates (kieselgel 60 F_{254}, 1 mm, Merck). 2-(2′-Bromoethoxy)benzaldehyde, **1a**,[13] 4-(2′-bromoethoxy)benzaldehyde, **1b**,[7] and *p-tert*-butylcalix[4]arene[28] were prepared according to the literature.

4.2.1. Preparation of 25,26,27-tri((2-ethoxy)benzaldehyde-*p-tert*-butylcalix[4]arene, 3a and 25,26,27-tri((4-ethoxy)benzaldehyde-*p-tert*-butylcalix[4]arene, 3b. In a 250 mL two-necked round bottom flask equipped with a magnetic bar and a reflux condenser, a mixture of *p-tert*-butylcalix[4]arene (6.05 g, 9.34 mmol), barium oxide (5.20 g, 33.90 mmol) and dry DMF (150 mL) was stirred for 1 h. Into this mixture, 2-(2′-bromoethoxy)benzaldehyde, **1a**, (6.56 g, 28.64 mmol) in DMF (50 mL) was then added dropwise through an addition funnel. The mixture was stirred and heated at 70°C under nitrogen atmosphere for 7 days. The reaction was allowed to cool to room temperature, and the solvent was evaporated under reduced pressure to give an orange-brown residue. The residue was dissolved in dichloromethane and it was then added 3 M hydrochloric acid until the pH of the solution reached 1. The organic phase was separated, and the aqueous layer was extracted again with dichloromethane. The combined organic layer was dried over sodium sulfate anhydrous. After filtration of sodium sulfate, the solvent was removed to give an oily orange-brown residue. The residue was redissolved in a minimum amount of dichloromethane. The orange-brown solution was eluted through a silica gel column with dichloromethane as eluent. 25,26,27-Tri((2-ethoxy)benzaldehyde-*p-tert*-butylcalix[4]arene, **3a**, eluted out of the column after 25,27-di((2-ethoxy)benzaldehyde-*p-tert*-butylcalix[4]arene, **2a**. White needle crystals of **3a** can be obtained by adding CH_3OH into its (CH_2Cl_2) solution (2.17 g, 21%).

In a similar manner to **3a**, the reaction between *p-tert*-butylcalix[4]arene (7.03 g, 10.83 mmol) and 4-2(2′-bromoethoxy)benzaldehyde (7.42 g, 32.63 mmol) in dry DMF (50 mL) resulted in compounds **2b** (0.20 g, 2%) and **3b** (5.53 g, 46%) as white solids.

3a: Mp: 239–240°C. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) δ (ppm) 10.41 and 9.74 (s each, 2H and 1H, $-Ar(C{=}O)H$); 7.63–6.32 (m, 20H, aromatic protons); 5.22 (s, 1H, $ArOH$); 4.90, 4.42 and 4.16 (m, 12H, $-OCH_2CH_2O-$); 4.24 and 3.29 (m, 4H each, $ArCH_AH_BAr$); 1.36–0.82 (m, 36H,

$-\mathrm{Ar}\text{-}t\text{-}\mathrm{C_4}H_9$). FAB MS (*m*/*z*): 1092.5. Anal. calcd for **4a** ($\mathrm{C_{71}H_{80}O_{10}}$): C, 77.99; H, 7.37. Found: C, 78.11; H, 7.17.

3b: Mp: 199–200°C. ^{1}H NMR spectrum (500 MHz, $\mathrm{CDCl_3}$) δ (ppm) 9.76 and 9.68 (s each, 2H and 1H, $-\mathrm{Ar(C{=}O)}H$), 7.57 and 7.43 (d each, $J_{\mathrm{H-H}}=8.7$ Hz, 4H and 2H, $-\mathrm{OAr}H_\mathrm{a}$), 7.19 (s, 2H, HOAr*H*), 7.14 (s, 2H, ROAr*H*), 6.70 and 6.63 (d each, $J_{\mathrm{H-H}}=8.7$ Hz, 4H and 2H, $-\mathrm{OAr}H_\mathrm{b}$), 6.54 (s, 4H, ROAr*H*), 5.40 (s, 1H, *H*OAr), 4.86 (m, 2H, $\mathrm{OC}H_2\mathrm{CH_2O}$), 4.45 and 3.32 (d each, $J_{\mathrm{H-H}}=12.4$ Hz, 4H each, $\mathrm{ArC}H_\mathrm{A}H_\mathrm{B}\mathrm{Ar}$), 4.28 (m, 2H, $\mathrm{OCH_2C}H_2\mathrm{O}$), 4.13 (s, 8H, $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}$), 1.36 (s, 18H, $\mathrm{HOAr}\text{-}t\text{-}\mathrm{C_4}H_9$ and $\mathrm{ROAr}\text{-}t\text{-}\mathrm{C_4H_9}$), 0.82 (s, 18H, $\mathrm{ROAr}\text{-}t\text{-}\mathrm{C_4}H_9$). MALDI-TOF MS (*m*/*z*): 1093.6. Anal. calcd for **3b** ($\mathrm{C_{71}H_{80}O_{10}}$): C, 77.99; H, 7.37. Found: C, 77.91; H, 7.52.

4.2.2. Preparation of 25,26,27-*N*,*N*′,*N*″-tri-((2-ethoxy)-benzyl)ethylenetriimine-*p*-*tert*-butylcalix[4]arene, 4a, and 25,26,27-*N*,*N*′,*N*″-tri-((4-ethoxy)benzyl)ethylenetriimine-*p*-*tert*-butylcalix[4]arene, 4b. In a 500 mL two-necked round bottom flask equipped with a magnetic bar and a reflux condenser, a mixture of **3a**, (1.00 g, 0.92 mmol) and acetonitrile (250 mL) was stirred. Tris(2-amino)ethylamine (0.16 g, 1.10 mmol) in dichloromethane (10 mL) and acetonitrile (50 mL) was then added dropwise through an addition funnel in 30 min. The mixture was refluxed under nitrogen atmosphere for 8 h. White solid precipitated from the solution. The mixture was allowed to cool to room temperature and filtered. The white solid **4a** was washed with acetonitrile and dried in vacuo (1.03 g, 95%).

The reaction between **3b** (3.05 g, 2.79 mmol) and tris-(2-aminoethyl)amine (0.50 g, 3.43 mol) in acetonitrile (250 mL) gave compound **4b** as a white solid (3.23 g, 97%).

4a: Mp: 310–312°C (dec.). ^{1}H NMR spectrum (200 MHz, $\mathrm{CDCl_3}$) δ (ppm) 8.93 and 8.83 (s each, 1H and 2H, $-\mathrm{C}H{=}\mathrm{N}-$); 7.91–6.45 (m, 20H, aromatic protons); 5.30 (s, 1H, $-\mathrm{ArO}H$); 5.16, 4.53 and 4.04 (m, 12H, $-\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}$); 2.89 (m, 12H, $-\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}-$); 4.39 and 4.33, 3.39 and 3.32 (d each, 2H each, $J_{\mathrm{H-H}}=13$ Hz, $\mathrm{ArC}H_\mathrm{A}H_\mathrm{B}\mathrm{Ar}$); 1.36, 1.27 and 0.79 (s each, 9H, 9H and 18H, $\mathrm{ROAr}\text{-}t\text{-}\mathrm{C_4}H_9$ and $\mathrm{HOAr}\text{-}t\text{-}\mathrm{C_4}H_9$). FAB MS (*m*/*z*): 1185.7. Anal. calcd for $\mathbf{4a}\cdot\mathrm{H_2O}$ ($\mathrm{C_{77}H_{94}N_4O_8}$): C, 76.84; H, 7.87; N, 4.65. Found: C, 76.70; H, 7.61; N, 4.24.

4b: Mp: 305–307°C (dec.). ^{1}H NMR spectrum (500 MHz, $\mathrm{CDCl_3}$) δ (ppm) 8.07 and 7.86 (s each, 1H and 2H, $-\mathrm{C}H{=}\mathrm{N}$), 7.38 (d, $J_{\mathrm{H-H}}=8.7$ Hz, 4H, $-\mathrm{OAr}H_\mathrm{a}$), 7.20 (s, 2H, HOAr*H*), 7.18 (s, 2H, ROAr*H*), 6.73 (d, $J_{\mathrm{H-H}}=8.7$ Hz, 4H, $-\mathrm{OAr}H_\mathrm{b}$), 6.62 (d, $J_{\mathrm{H-H}}=2.4$ Hz, 2H, $\mathrm{ROAr}H_\mathrm{a}$), 6.52 (d, $J_{\mathrm{H-H}}=2.4$ Hz, 2H, $\mathrm{ROAr}H_\mathrm{b}$), 6.32 (s, 1H, *H*OAr), 6.13 (d, $J_{\mathrm{H-H}}=8.8$ Hz, 2H, ROAr*H*), 6.02 (d, $J_{\mathrm{H-H}}=8.8$ Hz, 2H, ROAr*H*), 4.92 and 3.32 (d each, $J_{\mathrm{H-H}}=13.0$ Hz, 4H, $\mathrm{ArC}H_\mathrm{A}H_\mathrm{B}\mathrm{Ar}$), 4.56 (m, 2H, $\mathrm{OC}H_2\mathrm{CH_2O}$), 4.33 and 3.23 (d each, $J_{\mathrm{H-H}}=13.0$ Hz, 4H, $\mathrm{ArC}H_\mathrm{A}H_\mathrm{B}\mathrm{Ar}$), 4.28–4.02 (m, 10H, $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}$), 3.74 (m, 4H, $\mathrm{CH{=}NC}H_2\mathrm{CH_2N}$), 3.64 (m, 2H, $\mathrm{CH{=}N\ C}H_2\mathrm{CH_2N}$), 2.83 (m, 4H, $\mathrm{CH{=}NCH_2C}H_2\mathrm{N}$), 2.59 (m, 2H, $\mathrm{CH{=}NCH_2\ C}H_2\mathrm{N}$), 1.39 (s, 9H, $\mathrm{HOAr}\text{-}t\text{-}\mathrm{C_4}H_9$), 1.36 (s, 9H, $\mathrm{ROAr}\text{-}t\text{-}\mathrm{C_4}H_9$), 0.83 (s, 18H, $\mathrm{ROAr}\text{-}t\text{-}\mathrm{C_4}H_9$). MALDI-TOF MS (*m*/*z*): 1184.6. Anal. calcd for **4b** ($\mathrm{C_{77}H_{92}N_4O_7}$): C, 78.01; H, 7.82; N, 4.73. Found: C, 77.95; H, 7.66; N, 4.77.

4.2.3. Preparation of 25,26,27-*N*,*N*′,*N*″-tri((2-ethoxy)benzyl)ethylenetetraamine-*p*-*tert*-butylcalix[4]arene·4HCl, 5a and 25,26,27-*N*,*N*′,*N*″-tri((4-ethoxy)benzyl) ethylenetetraamine-*p*-*tert*-butylcalix[4]arene·4HCl, 5b. In a 500 mL one-necked round bottom flask equipped with a magnetic bar and a reflux condenser, **4a** (1.00 g, 0.84 mmol) was dissolved in dry dichloromethane (50 mL). To the solution was added excess sodium borohydride (0.63 g, 0.02 mmol) and the mixture was stirred overnight under nitrogen atmosphere. A copious amount of deionized water was then added to destroy excess sodium borohydride. The organic phase was separated and washed again with deionized water until the pH of the aqueous layer became neutral. The combined organic layer was dried over anhydrous sodium sulfate. After filtration of sodium sulfate, the solvent was evaporated to dryness. The solid residue was dissolved in a minimum amount of methanol and acidified with 0.74% v/v hydrochloric acid in methanol until the pH of the solution reached 1. Upon slow evaporation of the solvent, white crystals of **5a** were precipitated (0.92 g, 81%).

In a similar fashion, the reaction between **4b** (1.52 g, 1.283 mmol) and $\mathrm{NaBH_4}$ (0.92 g, 24.35 mmol) in dry $\mathrm{CH_2Cl_2}$ (300 mL) yielded **5b** as a white solid (1.44 g, 84%).

5a: Mp: 290–292°C (dec.). ^{1}H NMR spectrum (DMSO-d_6) δ (ppm) 9.78 and 9.38 (s each, broad, 4H and 2H, $\mathrm{ArCH_2N}H_2^+\mathrm{Cl^-}$); 7.86, 7.66, 7.57, 7.34 and 7.03 (m, 12H, H_a, H_b, H_c and H_d); 7.17 and 7.11 (s each, 2H each, ROAr*H* and HOAr*H*); 6.54 and 6.46 (s each, 2H each, ROAr*H*); 5.80 (s, 1H, ArO*H*); 5.13 (m, broad, 2H, $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}$); 4.62–4.39 (m, 6H, $\mathrm{H_2N^+C}H_2\mathrm{-Ar}$ and 4H, $\mathrm{ArC}H_2\mathrm{Ar}$); 4.18 (m, broad, 10H, $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}$ and 4H, $\mathrm{ArC}H_2\mathrm{Ar}$); 2.82–2.75 (m, 12H, $\mathrm{^+NHC}H_2\mathrm{C}H_2\mathrm{N^+H_2}$); 1.30, 1.20 and 0.73 (s each, 9H, 9H and 18H, $\mathrm{HOAr}\text{-}t\text{-}\mathrm{C_4}H_9$ and $\mathrm{ROAr}\text{-}t\text{-}\mathrm{C_4}H_9$). ESI-TOF MS (*m*/*z*): 1192.1. Anal. calcd for $\mathbf{5a}\cdot4\mathrm{H_2O}$ ($\mathrm{C_{77}H_{110}N_4O_{11}Cl_4}$): C, 65.69; H, 8.44; N, 3.78. Found: C, 65.61; H, 7.87; N, 3.97.

5b: Mp: 283–285°C (dec.). ^{1}H NMR spectrum (500 MHz, $\mathrm{CDCl_3}$) δ 8.71 and 8.23 (s each, broad, 4H and 2H, $\mathrm{ArCH_2N}H_2^+\mathrm{Cl^-}$), 7.79 (d, $J_{\mathrm{H-H}}=8.6$ Hz, 4H, $-\mathrm{OAr}H_\mathrm{a}$), 7.36 (d, $J_{\mathrm{H-H}}=8.5$ Hz, 2H, $-\mathrm{OAr}H_\mathrm{a}$), 7.14 (s, 2H, HOAr*H*), 7.10 (s, 2H, ROAr*H*), 6.92 (d, $J_{\mathrm{H-H}}=8.7$ Hz, 4H, $-\mathrm{OAr}H_\mathrm{b}$), 6.54 (m, 6H, ROAr*H* and $-\mathrm{OAr}H_\mathrm{b}$), 6.12 (s, 1H, HOAr), 4.56 and 3.30 (d each, $J_{\mathrm{H-H}}=13.3$ Hz, 4H, $\mathrm{ArC}H_\mathrm{A}H_\mathrm{B}\mathrm{Ar}$), 4.55–4.40 (m, 14H, $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}$, $\mathrm{ArC}H_2\mathrm{N}$ and $\mathrm{ArC}H_\mathrm{A}H_\mathrm{B}\mathrm{Ar}$), 4.20–3.98 (m, 6H, $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}$, $\mathrm{ArC}H_2\mathrm{N}$), 3.70 (s, br, 2H, $\mathrm{NCH_2C}H_2\mathrm{N}$), 3.41–3.10 (m, 10H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 3.25 (d, $J_{\mathrm{H-H}}=13.0$ Hz, 2H, $\mathrm{ArC}H_\mathrm{A}H_\mathrm{B}\mathrm{Ar}$), 1.34 (s, 9H, $\mathrm{HOAr}\text{-}t\text{-}\mathrm{C_4H_9}$), 1.32 (s, 9H, $\mathrm{ROAr}\text{-}t\text{-}\mathrm{C_4H_9}$), 0.82 (s, 18H, $\mathrm{ROAr}\text{-}t\text{-}\mathrm{C_4H_9}$). MALDI-TOF MS (*m*/*z*): 1191.8. Anal. calcd for **5b** ($\mathrm{C_{77}H_{102}N_4O_7Cl_4}$): C, 69.15; H, 7.69; N, 4.19. Found: C, 69.19; H, 7.76; N, 4.16.

4.2.4. Preparation of 25,26,27-*N*,*N*′,*N*″-tri((2-ethoxy)benzyl)ethylenetetraamine-*p*-*tert*-butylcalix[4]arene, 6a and 25,26,27-*N*,*N*′,*N*″-tri((4-ethoxy)benzyl)ethylenetetraamine-*p*-*tert*-butylcalix[4]arene, 6b. In a 50 mL round bottom flask equipped with a magnetic bar, 25,26,27-*N*,*N*′,*N*″-tri-((2-ethoxy)benzylethylenetetraamine-*p*-*tert*-butylcalix[4]arene·4HCl, **5a**, (0.10 g, 0.07 mmol) was dissolved in dry methanol (30 mL). NaOH solution (CH_3OH) was then slowly added until the pH of the solution reached 10. The reaction was stirred under nitrogen atmosphere for 1 h. The solvent was subsequently removed under reduced pressure. The residue was redissolved in dichloromethane and extracted with deionized water until the aqueous phase contained no Cl^-. The organic layer was then dried over anhydrous sodium sulfate and concentrated on a rotary evaporator. Upon slow evaporation of the solvent, the white solid of **6a** precipitated (0.064 g, 72 %).

A similar reaction between **5b** (1.69 g, 1.262 mmol) and a solution of NaOH (0.20 g, 5.048 mmol) in methanol (40 mL) yielded **6b** as a white solid (1.12 g, 74%).

6a: Mp: 300–302°C (dec.). ^1H NMR spectrum (400 MHz, $CDCl_3$) δ (ppm) 7.20 and 6.56 (s each, 4H, t-$C(CH_3)_3$-ArHCH$_2$–); 7.47, 7.15, 6.93 and 6.25 (m, 12H, –OArHOCH$_2$–); 5.19 (s, 1H, –ArOH); 4.98, 4.32, 4.03 and 3.86 (m, 12H, –OCH_2CH_2O–); 4.18 and 3.75 (d, 2H and 4H, J_{H-H}=14 Hz, ArCH_2NR); 7.34 (t, 3H, H_c aromatic); 4.85, 4.45, 3.37 and 3.23 (d, 2H each, J_{H-H}=13 Hz, ArCH_ACH_BAr); 2.66–1.99 (m, broad, 12H, RNCH_2CH_2-NR); 1.41, 1.39 and 0.86 (s each, 9H, 9H and 18H, HOAr-t-C$_4H_9$ and ROAr-t-C$_4H_9$). FAB MS (m/z): 1191.7. Anal. calcd for **6a** ($C_{77}H_{98}N_4O_7$): C, 77.61; H, 8.29; N, 4.70. Found: C, 77.57; H, 7.85; N, 4.32.

6b: Mp: 295–298°C (dec.). ^1H NMR spectrum (200 MHz, $CDCl_3$) δ (ppm) 7.18, 7.07, 7.05 and 7.01 (s each, 8H, t-$C(CH_3)_3$ArHCH$_2$–); 6.70–6.30 (m, 12H, –OArHOCH$_2$–); 5.39 (s, 1H, –ArOH); 4.85–4.60 (m, 6H, –OCH_2CH_2O–, ArC$H_A$$H_B$Ar); 3.27 (m, 2H, ArC$H_A$$H_B$Ar); 3.74–3.45 (m, 6H, –OArCH_2N–); 2.86, 2.67, 1.92 (m, broad, 12H, RNCH_2CH_2NR); 1.32 and 0.83 (s each, 18H and 18H, HOAr-t-C$_4H_9$ and ROAr-t-C$_4H_9$). FAB MS (m/z): 1191.7. Anal. calcd for **6b** ($C_{77}H_{98}N_4O_7$): C, 77.61; H, 8.29; N, 4.70. Found: C, 77.58; H, 8.22; N, 4.66.

4.3. X-Ray crystallography

The crystal of **5a** (0.20×0.20×0.10 mm^3) was mounted on the end of a hollow glass fiber approximately parallel to the long dimension of the crystal using cyanoacrylate glue. Preliminary examination and data collection were performed using MoKα X-radiation (λ=0.71073 Å) on Bruker AXS SMART area detector diffractrometer. The collected data were reduced using the program SAINT.[29] Empirical absorption correction was done by the program SADABS.[30] A total of 58283 reflections were measured within the θ range of 0.99–30.46°. The structure was solved by direct methods and refined with anisotropic thermal parameters for all non-hydrogen atoms by full matrix least square using SHELX-97 package.[31] All hydrogen atoms were found in different Fourier maps and were included in the refinement. Due to vibrational disorder of the solvent of crystallization, refinement converged with rather high R and wR values (0.1355 and 0.3402, respectively).[32]

4.4. ^1H NMR titrations

Complexation of **5a** and **5b** towards various anions such as arsenite, bromide, carbonate, fluoride, hydrogen phosphate, dihydrogen phosphate, iodide, nitrate, sulfate and phosphate was studied employing ^1H NMR titrations. For **5a**, typically, a 0.0250 M solution of ligand **5a** (0.0836 g, 0.0625 mmol) in DMSO-d_6 (2.50 mL) was prepared. To 0.20 mL of this solution in NMR tubes were added 0.0–4.0 equiv. of 0.1000 M sodium salts (0.1500 mmol) in DMSO-d_6 (1.50 mL). In each NMR tube, the amount of DMSO-d_6 was then adjusted to the same quantity. For **5b**, typically, a 0.1000 M solution of a sodium salt (0.1500 mmol) in CD_3OD (1.50 mL) was prepared. Ligand **5b** was brought into the NMR tubes and 0.0–4.0 equiv. of 0.1000 M sodium salt were added. In each NMR tube, the amount of the solvents was adjusted to the same quantity. The spectra were recorded every 24 h until the complexation reached the equilibrium. Plots between complex concentration $(1-X)\delta$ and the mole fraction of ligands and anions (X) indicated 1:1 ligand:anion complexes for Br^-, I^- and NO_3^-. The result of the experiment was a plot of displacement in chemical shift as a function of the amount of added anion, which was subjected to analysis by a non-linear curve-fitting method using the program EQNMR.[17]

4.5. Potentiometric titration

All materials and solvents were standard analytical grade purchased from Aldrich, Fluka and Merck, and used without further purification unless otherwise noted. Transition metal salts such as $Co(ClO_4)_2\cdot 6H_2O$, $Ni(CH_3CO_2)_2\cdot 4H_2O$, $Cu(CF_3SO_3)_2$ and $Zn(CF_3SO_3)_2$ were dried under reduced pressure and stored in a desiccator. Compounds **5a** and **5b** were dried under vacuum and kept in a dessicator before use.

Tetrabutylammonium trifluoromethanesulfonate ($Bu_4NCF_3SO_3$) was used as an inert background electrolyte for all experiments. This electrolyte was prepared by dissolving a weighed quantity of $Bu_4NCF_3SO_3$ in methanol. The concentration of the inert background electrolyte was kept constant at 0.01 M. Tetrabutylammonium hydroxide (Bu_4NOH), of concentration 0.05 M, was utilized as a titrant base. Standard solutions of HCl (0.01 M) and $HClO_4$ (0.05 M) in the inert background solution were used to adjust the pH during electrode calibrations[33] and titration experiments. Solutions of metal ions Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} were prepared by dissolution of weighed quantities of metal salts in the inert background solution. The concentration of each metal solution was approximately 0.01 M. Stock solutions of **5a** (0.001 M) and **5b** (0.001 M) were prepared by dissolving weighted quantities of compounds **5a** and **5b** in 0.01 M $Bu_4NCF_3SO_3$.

The stability constants of the complexes were obtained potentiometrically using a competitive method with proton. The concentrations of $[H^+]$ were measured by a combined glass electrode (Mettler DG113-SC) connected to an automatic titrator (Mettler DL25). All titration experiments were performed at 25°C. For complexation constants determination, typically a 10 mL portion of a stock solution of a ligand was added a metal solution under argon atmosphere and subsequently titrated with Bu_4NOH. For each determination at least four experiments were performed with different mole ratios of metal:ligand. The stability constants were calculated using the program

SUPERQUAD.[23] The protonation constants of the free ligands, determined from titrations of ligands in the absence of metal, and metal hydroxide species, MOH^+, were included in the refinement procedures.

Supplementary material

All potentiometric titration plots of **6a** and **6b** towards Co^{2+}, Cu^{2+} and Zn^{2+} are deposited in the editorial office. Crystallographic data for **5a** are available upon request from the Cambridge Crystallographic Data Base (CCDC 165241).

Acknowledgements

This work was financially supported by the Thailand Research Fund (Grant no. PDF4080055). The authors thank Professor Michael J. Hynes for providing the program EQNMR. We also appreciate the National Biotechnology Center for allowing us to use the 400 MHz NMR spectrometer.

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