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O-Phosphorylated calix[4]arenes as Li^+-selective receptors[†]

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ABSTRACT: Phosphorylation of *p-tert*-butylcalix[4]arene **9** or calix[4]arene **10**, having two diethoxyphosphoryl groups at distal positions on their narrow rim (phenolic oxygen atoms), by dibutyloxophosphinechloride or alkylation of **10** by methyl bromoacetate led to the corresponding tetrasubstituted calix[4]arenes **8b–d** fixed in a cone conformation. The latter compounds and the similar derivative of calix[4]arene **8a** with four diethoxyphosphoryl groups were found to exhibit lithium cation selectivity, which was supported by UV–Vis spectra of THF solutions of the alkali metal picrates and their water–chloroform extraction in the presence of ligands **8a–d**. Calculated $K_{a_{Li+}}/K_{a_{Na+}}$ selectivities range from 2.9 (**8d**) to 9.5 (**8a**), which are among the highest values for the calixarene-based Li^+-selective receptors reported to date. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: calixarenes; extraction; lithium selectivity; phosphorylation; NMR; UV–Vis

INTRODUCTION

Calixarenes[1] belong to the most intensively studied macrocycles during the last 10 years. They can be readily prepared by one-pot procedures from *para*-substituted phenols and formaldehyde. These macrocycles proved their utility in the design and synthesis of artificial receptors for cations,[2] anions and neutral organic molecules.[3] Receptors with high selectivities for sodium,[4] potassium,[5] cesium[6] and calcium[7] cations have been reported.

An ample possibility in the design of receptors can be provided by the functionalization of calixarenes with phosphoryl (P=O)-containing groups which are capable of binding effectively different cations and organic molecules with hydrogen bond donors. For instance, the calixarenes **1–3** bearing phosphine oxide[8] and carbamoylmethylphosphine oxide (CMPO) groups[9] (for CMPO derivatives of conformationally rigidified bis-crown-3 calix[4]arenes see Ref. 10) at the narrow (phenolic oxygen atoms) or wide rims of the macrocycle show effective and selective extraction of transition metal, lanthanide and actinide ions. The calix[6]arenes with one, two, four or five thionphosphoryl groups (P=S) at the narrow rim have been used in the design of ion-selective electrodes for the determination of Pb^{2+} cation concentrations in aqueous solutions in the presence of Ca^{2+} or Cd^{2+}.[11] Cavitand **4**[12] with four phosphoryl groups oriented into the center of the cavity forms complexes with alkali and alkaline earth metal and alkylammonium cations. *O*-Phosphorylated derivatives of calix[4]arenes, calix[8]arenes and resorcarenes form complexes with benzene derivatives in acetonitrile–water (70:30) solutions.[13]

Recently, during the progress of our research on lithium-selective ionophores,[14] several laboratories reported on calix[4]- and -[6]arene-based lithium-selective ionophores **5**[15] and **6**[16] (the synthesis of **6** was reported in Ref. 16b) containing P=O groups at the narrow rim. Li^+/Na^+ selectivity calculated from the percentage extraction of these metals from their aqueous solutions into CH_2Cl_2 or 1,2-dichloroethane, are 0.91–1.05[15] (**5**) and 1.11[16] (**6**), respectively. Interestingly, recent molecular dynamics calculations and variable-temperature ^1H NMR experiments[17] show that only three arms of ligand **6** bind the lithium cation. Another approach has been demonstrated on a single example of calix[6]crown-4 **7**[18] bearing four ester groups. The Li^+/Na^+ selectivity for this ionophore derived from the percentage extraction of metal picrates from aqueous solutions into chloroform is 26.54. (Unexpectedly, the ester derivative similar to **7** but with ethoxy instead of methoxy groups has demonstrated Li^+/Na^+ = 1.38 selectivity[18]).

In many of these cases the origin of lithium selectivity

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[†] Dedicated to Professor Dr Hans-Jörg Schneider on the occasion of his 65th birthday.

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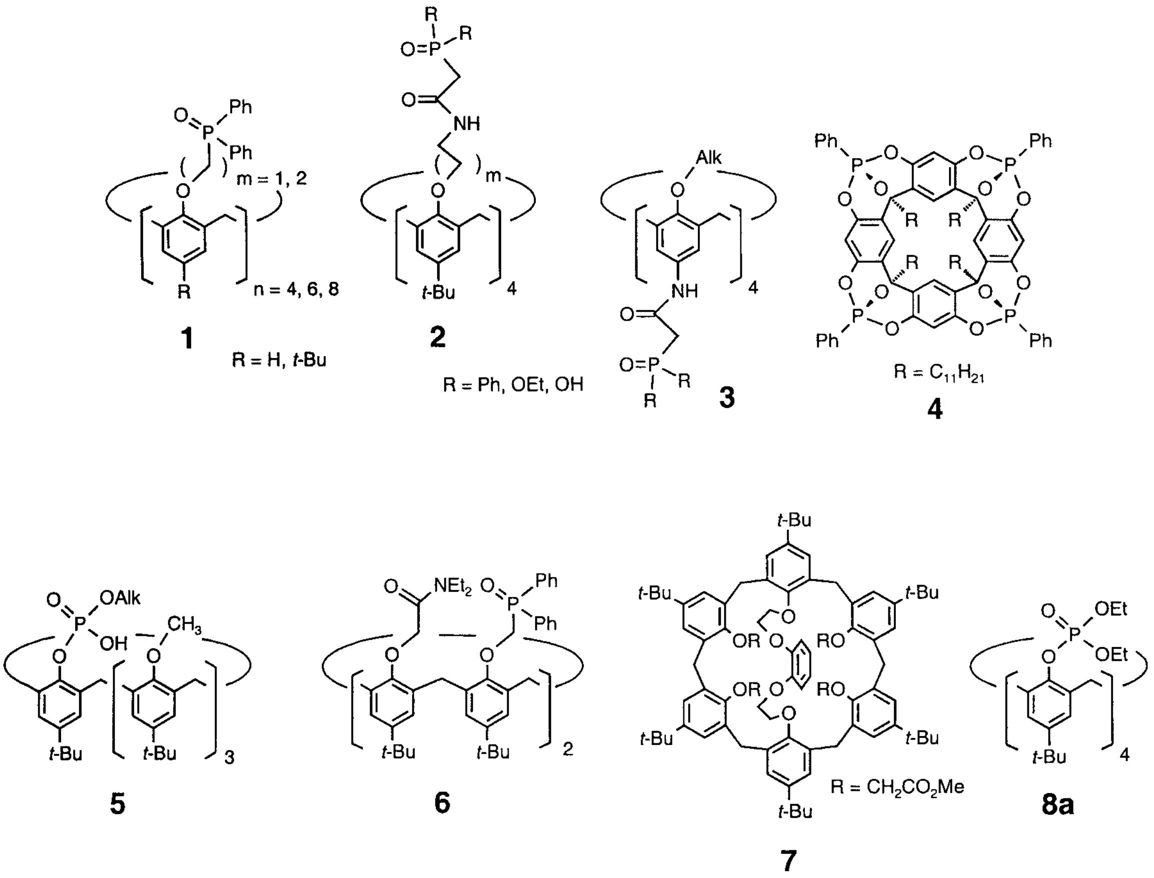


Chart 1

is not completely understood and our design idea for achieving lithium selectivity is based on the shortening of the distances between phosphoryl (carbonyl) oxygen atoms and phenolic oxygen atoms of the narrow rim of calix[4]arene receptor **6**, which would significantly decrease the dimensions of the binding pocket. We have examined ligand **8a** by molecular mechanics calculations and found that its narrow rim is adapted very well to binding of lithium cation (the diameter of Li$^+$ is ca 1.20 Å). Despite the fact that **8a** has been described in the literature,[19] it has never been tested for binding alkali and alkaline earth metal cations. To our knowledge, only rare earth cation extraction by **8a** has been reported.[20]

In this paper, we report studies on alkali metal cation complexation by tetra-substituted calix[4]arenes with two or four phosphoryl groups directly attached at the narrow rim.

RESULTS AND DISCUSSION

Synthesis

The tetraphosphate **8a** was synthesized as described elsewhere.[19] Syntheses of the ligands **8b–d** is depicted in Scheme 1. Calix[4]arene **8b** with four dibutyloxophosphine groups was obtained via deprotonation of hydroxyl groups of the parent calix[4]arene **9** with *n*-butyllithium (THF, 0 °C, Scheme 1) followed by phosphorylation (0–20 °C, 24 h). In a similar way but using NaH as a base, ligands **8c**[20] and **8d** were obtained from corresponding distally diphosphorylated calix[4]arene **10** [in this case we assume that *para* substituent (*tert*-butyl group or hydrogen) does not influence the binding strength of this type of ligand].

All the newly synthesized ligands **8b–d** have the cone conformation, which is readily seen from the characteristic difference in the chemical shifts of the methylene bridge protons $\Delta\delta \geq 1.50$ ppm.[1b]

Complexation with alkali metal cations

The binding properties of ligands **8** with alkali metal cations were studied by the following methods:

(a) UV–Vis spectral changes of alkali metal picrates in THF solutions with a 10-fold excess ligand concentration;
(b) ^{1}H and ^{31}P NMR spectral changes of ligands upon extraction of alkali metal picrates from the solid phase into chloroform-*d* solutions;

(c) extraction of alkali metal picrates from their aqueous solutions into chloroform solutions of ligands monitored by UV–Vis measurements.

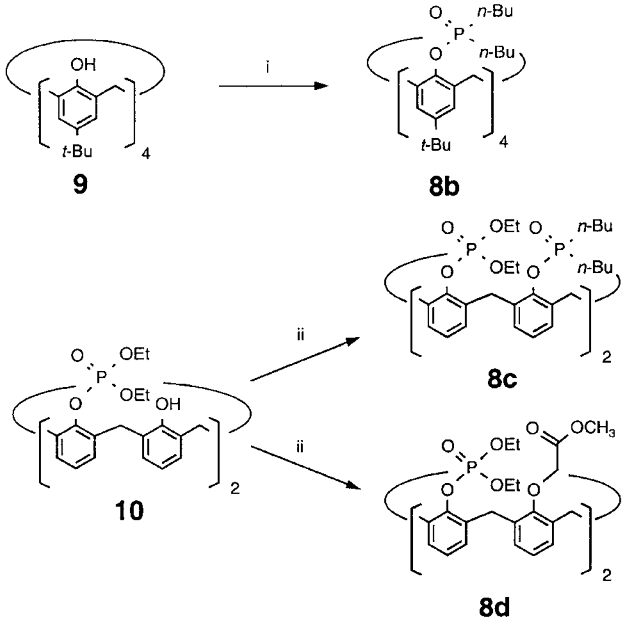
The bathochromic shift of a picrate salt band in the UV–Vis spectra is caused by the separation of a tight ion pair due to the complexation of a cation with a suitable ligand in weakly polar media. Therefore, the higher the bathochromic shift, the stronger is the cation complexation expected. In our studies (Table 1), the highest bathochromic shifts were observed for lithium picrate. Thus, ligands **8a–c** having four phosphoryl groups at the narrow rim, give shifts of 34 –36 nm, whereas ligand **8d** with two phosphoryl groups and two methoxycarbonyl methyl moieties shows a 6 nm shift.

The 1:1 stoichiometry of the Li^+:**8a** and Na^+:**8a** complexes in THF was supported by the titration of lithium picrate solution with **8a**, showing only one breakpoint at a 1:1 ratio. The association constants for complexes of **8a** with Li^+ and Na^+ calculated from the titration isotherms in THF solution are 2.7×10^5 and 2.5×10^4 M^{-1}, respectively.

During one day, only one molar equivalent of the lithium picrate is extracted from the crystalline phase into chloroform-*d* solutions of **8a** and **8b**, as supported by the integral intensities of the picrate anion signal in the ^{1}H NMR spectra. At Li^+:**8a** and Li^+:**8b** ratios lower than one equivalent, only one set of calixarene signals is observed in $CDCl_3$ due to fast exchange between complexed and free ligand on the NMR time-scale (whereas in the case of tetraalkoxycarbonyl-substituted calix[4]arenes, known as sodium-selective ligands, the complexes with Na^+ and K^+ are kinetically stable on the NMR time-scale[4]). Variable-temperature ^{1}H NMR experiments were performed in these cases (down to −55 °C), but only broadening of the signals was observed (compare also the behavior of the lithium complex with **6**, which at low temperature shows C_s symmetry[17]). In the Li^+:**8a** complex the difference $\Delta\delta$ in chemical shifts between signals of the axial and the equatorial protons of the methylene bridges ($ArCH_2Ar$) is decreased by only 0.13 ppm in comparison with the same value in the free ligand **8a**, which probably reflects a high degree of preorganization of the binding groups in the ligand. The positions of the other signals are not changed by more than 0.02–0.05 ppm, whereas in the ^{31}P NMR spectra the signal of the phosphorus atoms shifts from δ −3.68 ppm to −6.13 ppm, which indicates strong interactions of phosphoryl oxygen atoms with lithium cation.

The extraction of alkali metal picrates from their aqueous solutions into chloroform solutions of the ligands **8a–d** gave us the possibility of calculating the association constants and the binding free energies (Table 2) using the method developed by Moor *et al.*[22]

In these cases all ligands exhibit lithium cation selectivity. The most effective and selective ionophore is **8a** (The Li^+/Na^+ selectivity calculated from the K_a value is 9.5). It is difficult to explain the lower binding constants (by a magnitude of 10) and the lower selectivity of the ligand **8b** having similar binding units in its structure. In the series **8a** to **8d** the Li^+/Na^+ selectivity also decreases. It should be noted that the binding parameters determined by Moor *et al.*'s method exhibit some differences from the parameters determined by the UV–Vis titration method in THF solution for complexation of **8a** with Li^+ and Na^+ (Table 2), while the Li^+/Na^+ selectivity remains similar.



Scheme 1. i, *n*-BuLi, Bu_2 P(O)Cl, THF; ii, NaH, Bu_2 P(O)Cl, benzene; iii, N_a H, $C_3H_5O_2$ Br, benzene

Molecular Mechanics (MMX force field[23]) calculations of the ligand **8a** with lithium cation show binding of the cation by eight oxygen atoms (four of the phenolic narrow rim and four of the phosphoryl oxygen P═O atoms). A plausible structure of the complex is shown in Fig. 1.

The $Li^+/Na^+ = 5$ selectivity found for the best crown ether Li^+ binder,[24] e.g. 14-crown-4 **11**, calculated from $\log K_a^{Li}$ (2.34) and $\log K_a^{Na}$ (1.63) in CH_3OH solution,[25] is half that exhibited by the calixarene **8a** (Table 2). The

Table 1. Complexation-induced bathochromic shifts $\Delta\lambda$ (nm) of alkali metal picrates in their THF solutions in the presence of **8a–d**[a]

Ligand	Li^+	Na^+	K^+	Cs^+
8a	34	9	5	3
8b	35	3	0	0
8c	36	5	1	0
8d	6	1	0	0

[a] Spectra were recorded at 25 °C at a 2×10^{-4} M concentration of picrates and a 1:10 ratio of M^+Pic to ligand.

Table 2. Association constants K_a (M^{-1}), free energies of binding [$-\Delta G$] (kJ mol^{-1}) of alkali metal cations by ligands **8a–d** and their Li$^+$/Na$^+$ selectivities[a]

Ligand	Li$^+$	Na$^+$	K$^+$	Cs$^+$	Ka_{Li^+}/Ka_{Na^+}
8a	4.2×10^6 [37.7] (2.7×10^5)[b]	4.4×10^5 [32.3] (2.5×10^4)[b]	8.7×10^4 [28.1]	$6.1\ 10^4$ [27.2]	9.5 10.9
8b	4.6×10^5 [32.3]	9.9×10^4 [28.5]	1.0×10^4 [22.8]	–[c]	4.6
8c	6.7×10^5 [33.2]	1.7×10^5 [29.8]	3.0×10^4 [25.5]	–[c]	3.9
8d	3.8×10^4 [26.1]	1.3×10^4 [23.4]	1.0×10^4 [22.8]	–[c]	2.9

[a] At 25 °C, the extraction of alkali metal picrates from their aqueous solutions into chloroform, is used.
[b] UV–Vis titration in THF solution at 25 °C.
[c] The amount extracted lies within limit of error of the method applied.

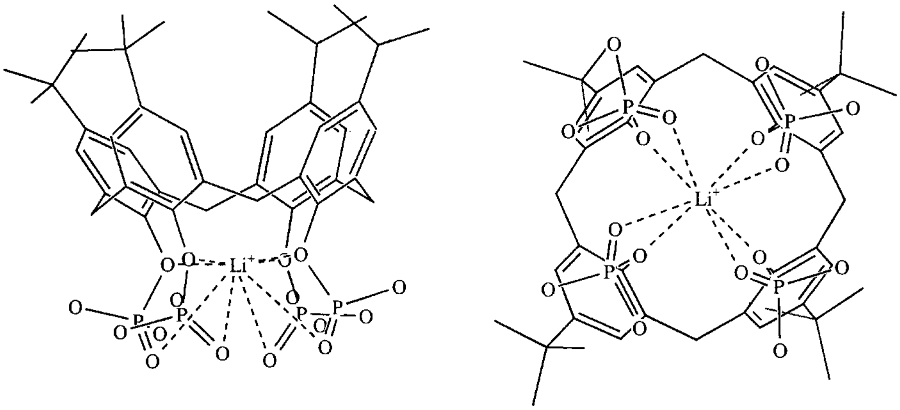
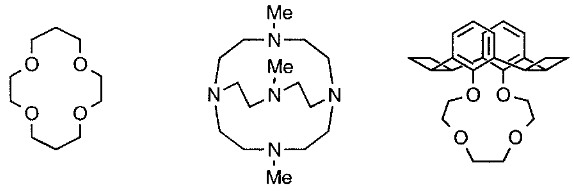


Figure 1. Two projections of a plausible structure of the complex between **8a** and Li$^+$ in accordance with MM calculations (MMX force field, ethyl groups and hydrogen atoms are omitted for clarity). The calixarene oxygen atoms and phosphoryl P=O oxygen atoms form the shortest distances to the lithium cation, as indicated by dashed lines



11 **12** **13**

Chart 2

observed selectivity is explained by the very similar sizes of the binding cavity of the 14-crown-4 and the diameter of Li$^+$, as shown by the examination of CPK molecular models. The best Li$^+$ binder found among the aza cryptands, e.g. **12**, shows high log K_a^{Li} value of 5.5 (measured in water) as a result of the regular coordination geometry adapted for inclusion of the cation.[26] Unfortunately, no Li$^+$/Na$^+$ selectivity was reported in this case. Another interesting macrocyclic receptor, 'crownopaddlane' **13**, should also be mentioned here[27] (for Li$^+$-selective ion transport by similar calix[4]arene analogs with cyclobutane bridges, see Ref. 28) This compound exhibits an Li$^+$/Na$^+$ = 610 selectivity, derived from the percentage extraction of the metal thiocyanates from the solid phase into dichloromethane solutions of **13**, and unfortunately can hardly be compared with other selectivity data calculated from parameters determined in liquid–liquid extraction experiments.

In conclusion, we have demonstrated that calix[4]-arenes with four phosphoryl groups on their narrow rim exhibit high lithium efficiency and selectivity in complexation of alkali metal cations, similarly to other lithium selective binders found among crown ethers and cryptands.

EXPERIMENTAL

^{1}H and ^{31}P NMR spectra were recorded in chloroform-*d* solutions (if not stated otherwise) on Gemini VXR-200 (200 MHz) and Bruker WP-200 (82 MHz) instruments. UV–Vis spectra were recorded on a Specord M-80 instrument. Melting-points have not been corrected. The starting compounds **9**[29] and **10**[21] and phosphate **8a**[19] were obtained in accordance with the literature.

*25,26,27,28-Tetrakis(dibutyloxyphosphine)-p-tert-butylcalix[4]arene (**8b**).* An 8.5 ml (11.4 mmol) amount of a 1.36 N solution of *n*-BuLi in *n*-hexane was added dropwise to a suspension of 2 g (2.7 mmol) of the toluene complex of **9** in 20 ml of THF. The reaction mixture was cooled to 0 °C and 2.5 g (11.7 mmol) of $Bu_2P(O)Cl$ were added during 1 h. The mixture was then stirred for 24 h at room temperature. The solvent was evaporated under reduced pressure and the residue (yellowish oil) was purified on silica gel [chloroform–acetone (5 :1)] to give 0.9 g (26%) of **8b**, m.p. 100–105 °C. ^{1}H NMR: δ (ppm) 6.91 (s, 8 H, ArH-*m*), 4.95 and 3.28 [two d, 8 H, ^2J(H,H) = 13 Hz, $ArCH_2Ar$], 2.20–1.30 [m, 48 H, $P(CH_2)_3CH_3$], 1.09 (s, 36 H, CCH_3), 0.85 [t, 24 H, ^3J(H,H) = 7 Hz, $P(CH_2)_3CH_3$]. ^{31}P NMR: δ (ppm) 58.88. Anal. Found: C 70.52, H 9.53, P 9.60 Calc. for $C_{76}H_{124}O_8P_4$: C 70.78, H 9.69, P 9.61%.

*25,27-Bis(diethoxyphosphoryloxy)-26,28-bis(dibutyloxyphosphine)calix[4]arene (**8c**).* A hot solution of 1.4 g (2.1 mmol) of phosphate **10** in benzene (30 ml) was added to 0.124 g (5.2 mmol) of sodium hydride and heated to reflux. Then 1.24 g (6.3 mmol) of $Bu_2P(O)Cl$ were added and the reaction mixture was refluxed for 0.5 h. After cooling to room temperature, the reaction mixture was separated from the salt by centrifugation and evaporated under reduced pressure to a volume of approximately 10 ml, and 50 ml of light petroleum were added. After 3 days at 3 °C, the white solid that formed was filtered off, washed with light petroleum and dried to give 0.627 g (31%) of **8c**, m.p. 97–99 °C. ^{1}H NMR: δ (ppm) 6.82 (m, 8 H, ArH-*m*), 6.67 (m, 4 H, ArH-*p*), 4.81 and 3.31 [two d, 8 H, ^2J(H,H) = 14 Hz, $ArCH_2Ar$], 4.24 [sep, 8 H, ^3J(H,H) = ^3J(H,P) = 6.9 Hz, OCH_2CH_3], 2.10 [m, 8 H, $PCH_2(CH_2)_2CH_3$], 1.60–1.20 [m, 16 H, $PCH_2(CH_2)_2CH_3$], 1.28 [t, 12 H, ^3J(H,H) = 7 Hz, OCH_2CH_3], 0.90 [t, 12 H, ^3J(H,H) = 7 Hz, $P(CH_2)_3CH_3$]. ^{31}P NMR: δ (ppm) −4.62, 60.05. Anal. Found: C 61.44, H 7.53, P 12.20. Calc. for $C_{52}H_{76}O_{12}P_4$: C 61.41, H 7.53, P 12.18%.

*25,27-Bis(diethoxyphosphoryloxy)-26,28-di(methoxycarbonylmethoxy)calix[4]arene (**8d**).* A hot solution of 1.0 g (1.4 mmol) of phosphate **10** in benzene (25 ml) was added to 0.100 g (4.2 mmol) of sodium hydride and heated to reflux. Then 0.64 g (4.2 mmol) of methyl bromoacetate was added and the reaction mixture was refluxed for 0.5 h. After cooling to room temperature, the reaction mixture was filtered off and evaporated under reduced pressure. After recrystallization from *n*-pentane, 0.608 g (51%) of **8d** was obtained, m.p. 133–135 °C. ^{1}H NMR: δ (ppm) 7.16 [d, 4 H, ^3J(H,H) = 7 Hz, ArH-*m*], 6.99 [t, 2 H, ^3J (H,H) = 7 Hz, ArH-*p*], 6.30 [t, 2 H, ^3J(H,H) = 7 Hz, ArH-*p*], 6.07 [d, 4 H, ^3J(H,H) = 7 Hz, ArH-*m*], 4.79 (s, 4 H, OCH_2CO), 4.72 and 3.33 [two d, 8 H, ^2J(H,H) = 15 Hz, $ArCH_2Ar$], 4.24 (m, 8 H, OCH_2CH_3), 3.76 (s, 6 H, OCH_3), 1.32 [d t, 12 H, ^3J(H,H) = 7 Hz, ^4J(H,P) = 0.6 Hz, OCH_2CH_3]. ^{31}P NMR: δ (ppm) −4.74. Anal. Found: C 58.96, H 5.97, P 7.65. Calc. for $C_{40}H_{50}O_{12}P_2$: C 58.82, H 6.17, P 7.58%.

*UV–Vis titration of metal picrates with calixarene **8a**.* A sample of a metal picrate was dissolved in dry THF (a concentration of 0.0002 M was used). The solution was separated into two portions. One portion was used as a metal picrate guest sample, and the rest was used to dissolve and to dilute the sample of the calixarene host, so that the concentrations of a metal picrate remained constant during the titration. Successive aliquots of the host solution were added to a guest sample, and UV–Vis spectra were recorded after each addition. The metal picrate:calixarene ratio was varied in the range from 1:0.5 to 1:12 during the titration. The changes in absorption maximum as a function of the host concentration were then analyzed with the Benesi–Hildebrand method.[30]

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