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## Synthesis and Complexation Properties Towards Metal Ions of New Tri-substituted Thiocalix[4]arenes

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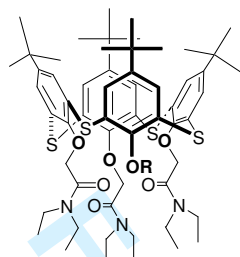
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### Synthesis and Complexation Properties Towards Metal Ions of New Tri-substituted Thiacalix[4]arenes

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Keywords:	thiacalix[4]arenes, synthesis, conformation, metal complexation



**Synthesis and Complexation Properties Towards Metal Ions of New Tri-substituted Thiacalix[4]arenes**S. Ben Maamar<sup>a,b</sup>, N. Jadambaa<sup>a</sup>, F. Vocanson<sup>a,c\*</sup>, F. Meganem<sup>b</sup>, C. Felix<sup>a</sup>, I. Bonnamour<sup>a</sup>

TC1 R = H  
TC2 R = nPropyl  
TC3 R = Etylacetate

New thiacalix[4]arenes appended with three amide functions have been prepared. The complexation ability of these ligands towards various metal ions ( $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Pd}^{2+}$ ;  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Hg}^+$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ ) has been investigated by UV-vis absorption.

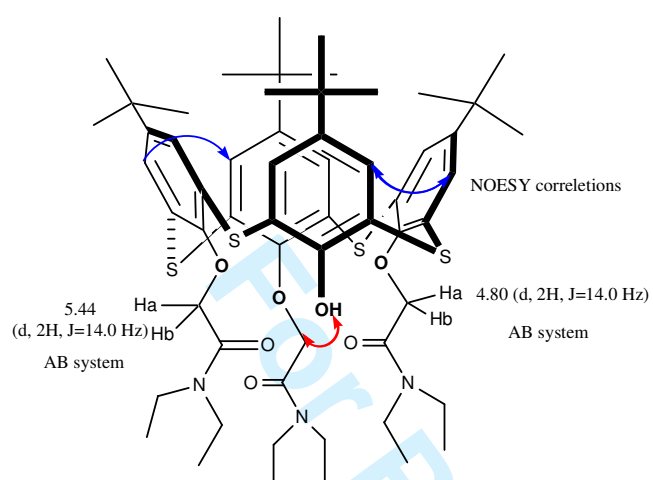


Figure 1. Conformational analysis of TC1.

$\text{CH}_3\text{CN}$  resulting from additions of  $\text{Pb}(\text{NO}_3)_2$  ( $5 \cdot 10^{-4}$  M in acetonitrile/water, 3v/v).

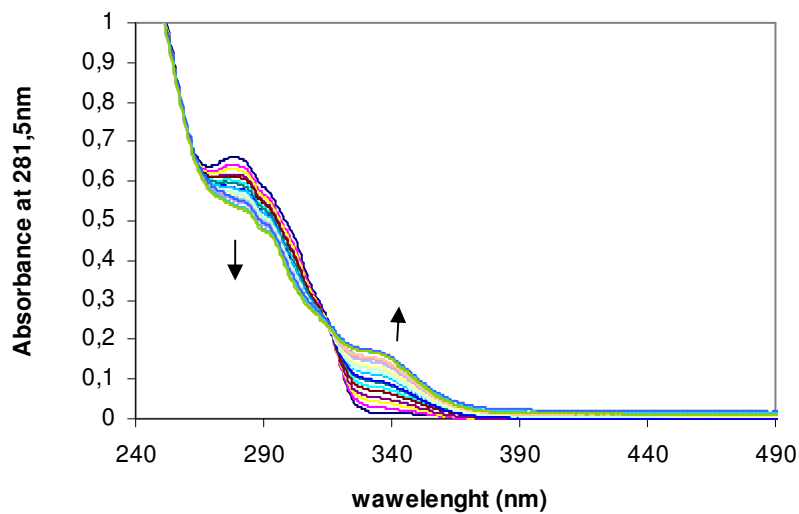
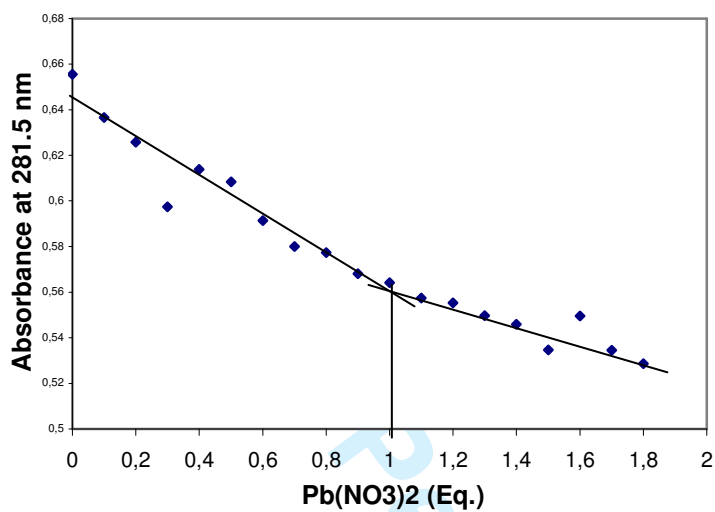
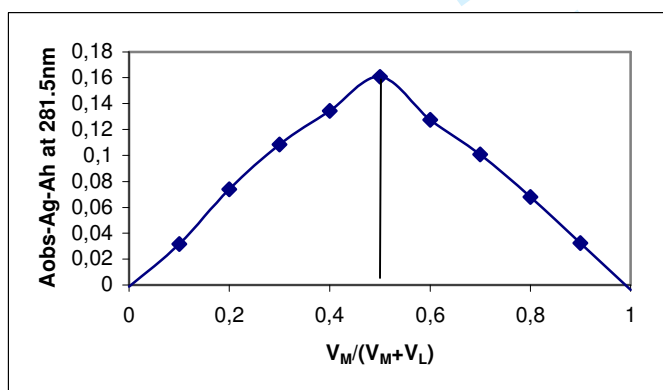


Figure 2. Changes in the absorbance spectrum of a  $5.10^{-5}$  M solution of ligand **TC1** in  $\text{CH}_3\text{CN}$  resulting from additions of  $\text{Pb}(\text{NO}_3)_2$  ( $5.10^{-4}$  M in acetonitrile/water, 3v/v).

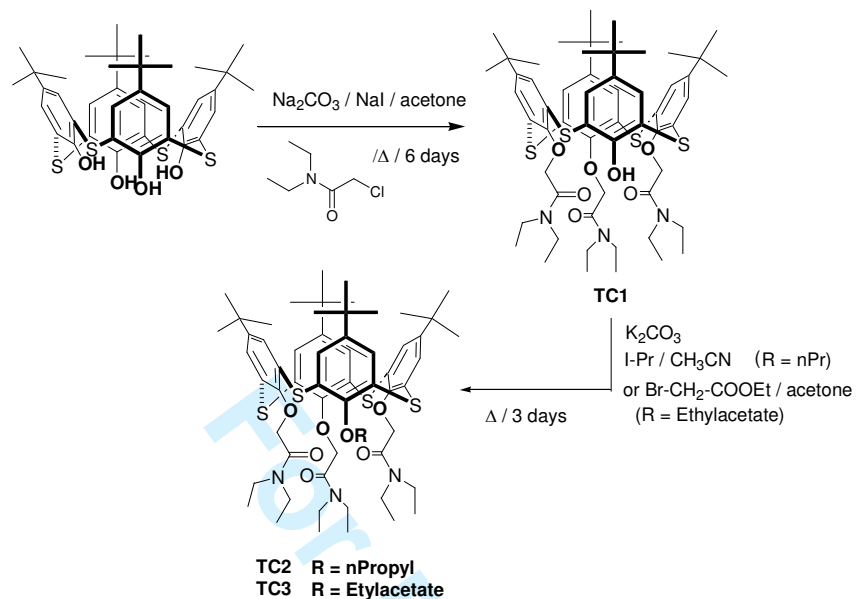


27 (a) Mole ratio method of  $\text{Pb}^{2+}$ -TC1 mixture



43 (b) Job plot of the titration of  $\text{Pb}^{2+}$  with TC1.

44  
45  
46  
47 Figure 3. Determination of the stoichiometry of Pb-ligand Complex



Scheme 1. Synthesis of triamide ligand derivatives.

*Supramolecular Chemistry***Synthesis and Complexation Properties Towards Metal Ions of New Tri-substituted  
Thiacalix[4]arenes**

**Abstract.** New thiacalix[4]arenes appended with three amide functions have been prepared. Their conformations have been solved thanks to  $^1\text{H}$  NMR 2D COSY and NOESY. The complexation ability of these ligands towards various metal ions ( $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Pd}^{2+}$ ;  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Hg}^+$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ ) has been investigated by UV-vis absorption and the stoichiometry of the metal-ligand complexes was determined.

**Keywords:** thiacalix[4]arene, synthesis, conformation, metal complexation.

**Introduction**

Toxic heavy metals like copper, mercury, lead, nickel or cadmium can have a serious impact on the aqueous environment. So, detection and treatment of these toxic metal ions still remain an important topic. In this field, calixarenes, the well known cyclic oligomers of *p*-substituted phenols and formaldehyde, have attracted increased interest. Since the conventional



1  
2  
3 calix[4]arenes have poor coordination ability towards metal ions, chemical modifications have  
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5 taken place by introducing functional groups having metal-binding ability. Recently, a new  
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7 class of macrocycles named thiacalixarenes has emerged. The presence of sulphur atoms  
8  
9 (which possess lone pairs and vacant 3d orbitals) instead of methylene bridges opens new  
10  
11 possibilities, especially in the field of metal complexation. The parent thiacalix[4]arene was  
12  
13 found to extract a wide range of transition metal ions from water, in contrast to classical  
14  
15 calix[4]arene (1). From many years, our group was interested in metal ions complexation and  
16  
17 extraction (2-4). Hence, we have previously reported the synthesis of a thiacalix[4]arene with  
18  
19 tetra-amide functions at the lower rim (4). Extraction experiments have evidenced a remark-  
20  
21 able binding ability of this ligand towards a wide range of metal cations.  
22  
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27 With the aim of supplementing this study, we wondered about the role of the number of  
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29 chelating groups. The lower rim functionalization of thiacalix[4]arene is becoming better  
30  
31 understood following the work of Lhotak (5,6) and Yamamoto (7). A few articles reports the  
32  
33 odd functionalisation of thiacalixarenes. Among them, for example the trimethylation of the  
34  
35 hydroxyls of thiacalix[4]arene (5) was described (5) using  $K_2CO_3$  in acetonitrile.  
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37

38  
39 In this paper, we describe the preparation of thiacalix[4]arenes substituted with tri-amide  
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41 functions at the lower rim. The complexation ability of these new ligands towards various  
42  
43 metal ions has been investigated by UV-vis titration. The goal of this work is to dispose of a  
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45 macrocycle which could be grafted on a surface without losing its complexation properties.  
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49

### 50 51 **Preparation and characterization of the ligands**

52  
53 The synthetic route for the ligands **TC1-3** is depicted in Scheme 1. The O-alkylation of the  
54  
55 lower rim of the parent *p-tert*-butylthiacalix[4]arene was achieved by action of  $Na_2CO_3$  (3eq.)  
56  
57 in acetone in presence of NaI, followed by 2-chloro-*N,N*-diethylacetamide. The reaction was  
58  
59 refluxed three days and the crude product was purified by chromatography on silica gel to  
60

1  
2  
3 afford the pure **TC1**.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **TC1** in  $\text{CDCl}_3$  showed the presence of the  
4 expected tri-amide derivative. However, it was difficult to determine the conformation of  
5  
6  
7  
8 **TC1**. To complete the structural analysis, 2D COSY and NOESY experiments were  
9  
10 performed. The  $^1\text{H}$  NMR shows two doublets and one singlet for the  $\text{O-CH}_2\text{-C=O}$  signal. The  
11  
12 2D COSY confirms the presence of an AB system for two  $\text{O-CH}_2\text{-C=O}$  groups and a singlet  
13  
14 for the third one (Figure 1). This AB system results from the rigidity of the calixarene  
15  
16 conformation and of the prochirality of two of the  $\text{CH}_2$  groups. The 2D NOESY shows  
17  
18 correlation spots between the aromatic hydrogens of neighboring phenyl moieties. A  
19  
20 correlation spot is also present between one  $\text{O-CH}_2\text{-C=O}$  group (corresponding to the singlet  
21  
22 signal) and the *OH* function (Figure 1). With the sight of these results, we can conclude that  
23  
24 the tri-substituted thiacalix[4]arene **TC1** adopts a cone conformation in solution. Then the  
25  
26 derivatization of the thiacalixarene **TC1** was researched to establish the influence of the  
27  
28 substitution of the phenolic group on the complexation of metallic cations. At first **TC1** was  
29  
30 alkylated with 1-iodopropane in refluxing acetonitrile in the presence of  $\text{K}_2\text{CO}_3$  as a base. The  
31  
32 desired product **TC2** bearing three amide group and one propyl group was obtained after  
33  
34 chromatographic separation. **TC1** was also alkylated with ethylbromoacetate in refluxing  
35  
36 acetone in the presence of  $\text{K}_2\text{CO}_3$  as a base. The desired product **TC3** bearing three amide  
37  
38 group and one ethylacetate group was also obtained after chromatographic separation. The  
39  
40 compounds **TC2** and **TC3** were identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and, ES-MS. The NMR  
41  
42 analysis showed that the cone conformation was conserved for the two macrocyclic  
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44 derivatives.  
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### 55 **Complexation study**

56  
57 The UV-vis spectra of **TC1-3** show characteristic bands between 290 and 340 nm in  $\text{CH}_3\text{CN}$  /  
58  
59  $\text{H}_2\text{O}$  (3v/v). Complexation properties of **TC1-3** were studied towards various metal salts  
60

(Cd<sup>2+</sup>, Pb<sup>2+</sup>, Pd<sup>2+</sup>, Ni<sup>2+</sup>, Hg<sup>2+</sup>, Hg<sup>+</sup>, Ag<sup>+</sup>, Zn<sup>2+</sup> and Cu<sup>2+</sup>) by UV-vis titrations. In all cases, upon addition of metal cations solutions to a solution of **TC1-3**, spectra undergo clear changes and show the presence of isobestic points indicating the existence of complex species. The addition of aliquots of Pb<sup>2+</sup> (from 0.2 to 1 equivalent) to a solution of **TC1** in a mixture of acetonitrile and water (3v/v) led to a decrease in the absorption bands at 280 nm and to the appearance of a new absorption band centred at 335.5 nm that is characteristic of a MLCT (Metal-Ligand Charge Transfer) band between Pb<sup>2+</sup> and the nitrogen and oxygen atoms of the amide functions on the macrocycle (Figure 2). The isobestic point centred at 315.5 nm shows the formation of a new complex. Similar effects were observed upon addition of Ag<sup>+</sup>, Cd<sup>2+</sup>, Hg<sup>+</sup>, Zn<sup>2+</sup>, Pd<sup>2+</sup> and Cu<sup>2+</sup>. Upon addition of cations solutions, we can observe in all cases a hypsochromic effect of the band at 285 nm and MLCT bands.

The stoichiometry of metal-ligand (M-L) complexes was determined both by the molar ratio (8) and the Job plot (9) methods (Figure 3). The results are given in Table 1. They indicate a 1:1 stoichiometry for five complexes (Ag<sup>+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, Pd<sup>2+</sup>) in accordance with the literature data (10). We observed the formation of M<sub>x</sub>-L<sub>y</sub> complexes with Hg<sup>+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup>. It should be outlined that no complexation was observed for **TC1** with Hg<sup>2+</sup>. For comparison, the complexation of mercury salts by the tetra-amide-thiacalix[4]arene derivative was studied: this macrocycle does not retain Hg<sup>+</sup> (11) ions but a complex is obtained between Hg<sup>2+</sup> ions and the receptor in acetonitrile as solvent (5). Complexation properties of **TC2** are reported in Table 1. ML type complexes are obtained for Ag<sup>+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup> and Pd<sup>2+</sup>. Compared with the ligand **TC1**, we can highlight the formation of a monovalent complex with Zn<sup>2+</sup>. No complexation occurs with Hg<sup>+</sup> whereas the addition of Hg<sup>2+</sup> ions in a solution of **TC2** leads to the formation of a multivalent complex. The ligand **TC3**, bearing an ester group instead of a propyl chain, affords ML type complexes with Cd<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Hg<sup>2+</sup> and Pd<sup>2+</sup>. A ML<sub>2</sub> type complex is observed with Ag<sup>+</sup>.

The stability constants  $K$  are defined as the concentration ratio [Eq. (1)] :

$$(1) \quad K = \frac{[ML]}{[M][L]}$$

$K$  can be correlated to the change in absorbance due to the formation of the  $ML$  complex.

Further modifications of the Benesi –Hildebrand method (12) result in an equation where a double reciprocal plot can be made with  $1/\Delta A$  as a function of  $1/[M]$  [Eq.(2)] :

$$(2) \quad \frac{1}{\Delta A} = \left[ \frac{1}{\Delta \varepsilon [L]_0 K} \right] \left[ \frac{1}{[M]} \right] + \frac{1}{\Delta \varepsilon [L]_0}$$

The logarithms of the stability constants (Log  $K$ ) are collected in Table 2. Values of the stability constants seem to indicate that the cation  $Cd^{2+}$  is strongly complexed with ligand **TC1** undoubtedly because of its great affinity for N and O atoms. **TC2** and **TC3** ligands exhibit affinity in the same range for all metal cations. This indicates that the introduction of an ester function instead of a propyl chain does not affect their binding ability. These results also show that it will be possible to introduce on the ligand **TC1**, a spacer with a terminal function as silane or thiol allowing the grafting on a surface without loss of recognition. On this way **TC1** is more interesting than the thiacalixarene with the four tetra-amide functions.

## Conclusion

New thiacalix[4]arene derivatives appended with three amide functions have been prepared and their conformation described. The complexation ability of these ligands towards various metal ions has been investigated by UV-vis absorption. These receptors exhibit similar

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3 complexation ability and selectivity except for  $\text{Cd}^{2+}$ . The main difference is observed for  
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5 mercury salts. **TC1** binds selectively  $\text{Hg}^+$  (*versus*  $\text{Hg}^{2+}$ ), whereas **TC2** forms selectively a  
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7 multivalent complex with  $\text{Hg}^{2+}$  (*versus*  $\text{Hg}^+$ ) and **TC3** gives only a ML type complex with  
8  
9  $\text{Hg}^{2+}$ . It seems that the number of amide groups doesn't play a crucial role (4), but the  
10  
11 presence of an OH function directs the selectivity towards the complexation of  $\text{Hg}^+$ . The  
12  
13 extraction ability of **TC1** derivative for noble metals such as  $\text{Pd}^{2+}$  and  $\text{Au}^{3+}$  has been  
14  
15 investigated by means of liquid-liquid extraction experiments (13). It has been observed that a  
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17 similar behaviour is exhibited in the case of gold for the ligand **TC1** and for the  
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19 thiocalix[4]arene tetra-amide. In the case of palladium, the extraction efficiency increases  
20  
21 with **TC1** ligand. Moreover, the new **TC1** derivative has been successfully used as carrier for  
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23  $\text{Pd}^{2+}$  and  $\text{Au}^{3+}$  transport in a SLM (supported liquid membrane).  
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## 32 **Experimental section**

33  
34 **General methods.** Solvents were purified and dried by standard methods prior to use. All  
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36 reactions were carried out under nitrogen. Column chromatography was performed with silica  
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38 gel 60 (0.040-0.063 nm). Melting points are uncorrected.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were  
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40 obtained at 300.13 and 75 MHz ( $\text{CDCl}_3$ , TMS as internal standard, chemical shifts in ppm, J  
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42 in Hertz). Mass spectra were obtained by electrospray technique (positive mode).  
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### 48 **5,11,17,23-tetra-*p*-*tert*-butyl-25,26,27-*N,N*-diethylaminocarbonyl-28-hydroxythia-**

49  
50 **calix[4]arene **TC1**** (cone conformer). To a solution of 0.4g ( $5.55 \cdot 10^{-4}$  mol) of *p*-*tert*-  
51  
52 butylthiocalix[4]arene and 0.176g ( $1.66 \cdot 10^{-3}$  mol) of  $\text{Na}_2\text{CO}_3$  in acetone (60 mL), under  
53  
54 nitrogen flux, was added 0.25g ( $1.66 \cdot 10^{-3}$  mol) of NaI and 0.24 mL ( $1.66 \cdot 10^{-3}$  mol) of 2-  
55  
56 chloro-*N,N*-diethylacetamide. The mixture was refluxed for three days. The solvent was re-  
57  
58 moved under vacuum. To the residue was added  $\text{CHCl}_3$  (40 mL). The organic layer was sepa-  
59  
60

rated, washed with water ( $2 \times 20$  mL) and dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the residue was purified by chromatography on silica gel (0.04-0.063 mm from Merck; eluted with heptane /  $\text{CHCl}_3$  1:1) to afford pure **TC1** (286 mg, 48 %).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) :  $\delta = 9.18$  (s, H, Ar-OH), 7.53 (s, 2H, Ar-H), 7.38 (s, 2H, Ar-H), 7.12 (s, 4H, Ar-H), 5.54 (s, 2H, Ar-O- $\text{CH}_2$ -CO-), 5.44 (d, 2H (AB system),  $^2J = 14.0$ , Ar-O- $\text{CH}_2$ -CO-), 4.82 (d, 2H (AB system),  $^2J = 14.0$ , Ar-O- $\text{CH}_2$ -CO-), 3.51-3.34 (m, 12H, -CO-N( $\text{CH}_2$ - $\text{CH}_3$ ) $_2$ ), 1.32-0.94 (m, 54H, Ar-C( $\text{CH}_3$ ) $_3$ , -CO-N( $\text{CH}_2$ - $\text{CH}_3$ ) $_2$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) :  $\delta = 168.70$  and  $167.72$  (- $\text{CH}_2$ -CO-N-), 157.28 and 157.83 (ArC-O), 147.12, 145.57 et 142.03 (Ar-C( $\text{CH}_3$ ) $_3$ ), 135.53, 134.48 and 133.37 (ArC-H), 129.42 and 122.14 (ArC-S), 72.71 and 69.39 (Ar-O- $\text{CH}_2$ -CO-), 41.37 and 40.17 (-CO-N( $\text{CH}_2$ - $\text{CH}_3$ ) $_2$ ), 34.39 (Ar-C( $\text{CH}_3$ ) $_3$ ), 31.67 (Ar-C( $\text{CH}_3$ ) $_3$ ), 14.82 and 13.56 (CO-N( $\text{CH}_2$ - $\text{CH}_3$ ) $_2$ ). ES-MS. (positive mode) : mass (m/z) = 1060  $[\text{M}+\text{H}]^+$ , 1082.4  $[\text{M}+\text{Na}]^+$ . Mp = 138 °C.

**5,11,17,23-tetra-*p*-tert-butyl-25,26,27-27-N,N-diethylaminocarbonyl-28-propyloxythiacalix[4]arene TC2** (cone conformer). To a solution of 0.1 g (0.094 mmol) of **TC1** and 0.065 g (0.471 mmol) of  $\text{K}_2\text{CO}_3$  in acetonitrile (5 mL), under nitrogen flux, was added 0.092 mL (0.943 mmol) of 1-iodopropane. The mixture was refluxed for three days. The solvent was removed under vacuum. To the residue was added  $\text{CHCl}_3$  (10 mL) and an aqueous solution of HCl 1N (10 mL). The organic layer was separated, washed with water ( $3 \times 10$  mL) and dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the residue was purified by chromatography on silica gel (0.04-0.063 mm from Merck; eluted with heptane /  $\text{CHCl}_3$  60:40) to afford pure **TC2** (23 mg; 22 %) as white powder.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) :  $\delta = 7.43$  and  $7.45$  (d, 4H, Ar-H), 7.11 (s, 4H, Ar-H), 5.45 (s, 2H, O- $\text{CH}_2$ -CO-N( $\text{CH}_2$ - $\text{CH}_3$ ) $_2$ ), 5.04 (s, 4H, 2 -O- $\text{CH}_2$ -CO-N( $\text{CH}_2$ - $\text{CH}_3$ ) $_2$ ), 4.28 (t, 2H,  $^3J = 7.72$ , O- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_3$ ), 3.36-3.54 (m, 12H, 3 O- $\text{CH}_2$ -CO-N( $\text{CH}_2$ - $\text{CH}_3$ ) $_2$ ), 1.94-1.97 (m, 2H, O- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_3$ ), 1.04, 1.16 and 1.25 (m, 57 H, O-

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2  
3 CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, 3 O-CH<sub>2</sub>-CO-N(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub> and Ar-C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) : δ  
4  
5 = 167.52 (Ar-O-CH<sub>2</sub>-CO-), 158.01 (ArC-O), 146.92 (ArC-C(CH<sub>3</sub>)<sub>3</sub>), 134.85, 135.57 and  
6  
7 135.96 (ArC-H), 128.50, 129.17 and 130.96 (ArC-S-), 70.28 and 72.69 (Ar-O-CH<sub>2</sub>-), 40.26,  
8  
9 41.56 and 41.78 (O-CH<sub>2</sub>-CO-N(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>), 34.41 and 34.57 (Ar-C(CH<sub>3</sub>)<sub>3</sub>), 31.48, 31.67 and  
10  
11 31.83 (Ar-C(CH<sub>3</sub>)<sub>3</sub>), 24.23 (O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 14.52 and 14.89 (O-CH<sub>2</sub>-CO-N(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>),  
12  
13 13.44 (O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>). ES-MS. (positive mode): mass (m/z) = 1102.5 [M+H]<sup>+</sup>, 1124.5  
14  
15 [M+Na]<sup>+</sup>. Mp = 200 °C.  
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22 **5,11,17,23-tetra-*p*-*tert*-butyl-25,26,27-*N,N*-diethylaminocarbonyl-28-ethoxycarbonylthia-**  
23 **calix[4]arene TC3** (cone conformer). To a solution of 0.15 g (0.141 mmol) of **TC1** and 0.011  
24  
25 g (0.08 mmol) of K<sub>2</sub>CO<sub>3</sub> in acetone (5 mL), under nitrogen flux, was added 0.031 mL (0.283  
26  
27 mmol) of ethylbromoacetate. The mixture was refluxed for three days. The solvent was  
28  
29 removed under vacuum. To the residue was added CHCl<sub>3</sub> (20 mL) and an aqueous solution of  
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31 HCl 1N (10 mL). The organic layer was separated, washed with water (3 × 10 mL) and dried  
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33 over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the residue was purified by chromatography on  
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35 silica gel (0.04-0.063 mm from Merck; eluted with heptane / CHCl<sub>3</sub> 60:40) to afford pure  
36  
37 **TC3** (81 mg; 50 %) as white powder. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) : δ = 7.36, 7.52 and 7.64  
38  
39 (m, 6H, Ar-*H*), 7 (s, 2H, Ar-*H*), 4.73, 4.98 and 5.37 (m, 8H, 3 O-CH<sub>2</sub>-CO-N(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub> and  
40  
41 O-CH<sub>2</sub>-CO-O-CH<sub>2</sub>-CH<sub>3</sub>), 4.21 (q, 2H, <sup>3</sup>J = 7.32, O-CH<sub>2</sub>-CO-O-CH<sub>2</sub>-CH<sub>3</sub>), 3.21 and 3.41 (m,  
42  
43 12H, 3 O-CH<sub>2</sub>-CO-N(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>), 1.10, 1.18, 1.25, 1.28 and 1.31 (m, 57H, 3 O-CH<sub>2</sub>-CO-  
44  
45 N(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>, Ar-C(CH<sub>3</sub>)<sub>3</sub> and O-CH<sub>2</sub>-CO-O-CH<sub>2</sub>-CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) : δ =  
46  
47 166.43 and 167.29 (Ar-O-CH<sub>2</sub>-CO-), 156.03 and 158.44 (ArC-O), 149.82 (Ar-C(CH<sub>3</sub>)<sub>3</sub>),  
48  
49 136.80, 136.99 and 137.02 (ArC-H), 128.32, 130.43 and 130.94 (ArC-S-), 71.74 and 75 (Ar-  
50  
51 O-CH<sub>2</sub>-), 61.74 (O-CH<sub>2</sub>-CO-O-CH<sub>2</sub>-CH<sub>3</sub>), 40.44, 41.44 and 41.92 (O-CH<sub>2</sub>-CO-N(CH<sub>2</sub>-  
52  
53 CH<sub>3</sub>)<sub>2</sub>), 34.83 (Ar-C(CH<sub>3</sub>)<sub>3</sub>), 31.32 and 31.52 (Ar-C(CH<sub>3</sub>)<sub>3</sub>), 14.72 (O-CH<sub>2</sub>-CO-O-CH<sub>2</sub>-CH<sub>3</sub>),  
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3 13.40 and 14.57 (3 O-CH<sub>2</sub>-CO-N(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>). ES-MS. (positive mode): mass (m/z) = 1146,4  
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5 [M+H]<sup>+</sup>, 1168,4 [M+Na]<sup>+</sup>. Mp = 215 °C.  
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10 **Complexation.** The stability constants K defined as the concentration ratio [ML] / ([M][L])  
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12 (where M = cation and L = ligand) were determined at 18 °C, in acetonitrile or a mixture of  
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14 acetonitrile/water (3v/v) by UV absorption spectrophotometry. The spectra were recorded on  
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16 a Shimadzu UV-2401-PC. The procedure consisted in adding increasing amounts of metallic  
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18 salts (5.10<sup>-4</sup> M) to a solution of **PC1-3** ([**PC1-3**] = 5.10<sup>-5</sup> M). The metal salts used were  
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20 chlorides, perchlorates, nitrates or trifluoroacetates according to their solubility in the solvents  
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22 used. The following salts were used in pure acetonitrile : Cd(ClO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O, CF<sub>3</sub>COOAg,  
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24 Zn(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O, Cu(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O, PdCl<sub>2</sub>, (CF<sub>3</sub>COO)<sub>2</sub>Hg. In a mixture of acetonitrile/water  
25  
26 (3v/v) the following salts were used : Pb(NO<sub>3</sub>)<sub>2</sub>, NiCl<sub>2</sub>.6H<sub>2</sub>O, Hg(ClO<sub>4</sub>)<sub>2</sub>.4H<sub>2</sub>O.  
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Table 1. Stoichiometry of Metal-Ligand complexes.

	Cd <sup>2+</sup>	Pd <sup>2+</sup>	Pb <sup>2+</sup>	Hg <sup>+</sup>	Hg <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Ni <sup>2+</sup>	Ag <sup>+</sup>
<b>TC1</b>	ML	ML	ML	<i>a</i>	<i>b</i>	<i>a</i>	<i>a</i>	ML	ML
<b>TC2</b>	<i>a</i>	ML	ML	<i>b</i>	<i>a</i>	ML	<i>a</i>	ML	ML
<b>TC3</b>	ML	ML	ML	<i>b</i>	ML	ML	<i>a</i>	<i>a</i>	ML <sub>2</sub>

(a) M<sub>x</sub>-L<sub>y</sub> complexes are observed. (b) no complexation was observed.

Table 2. Stability constants of (1:1) Metal-Ligand complexes. LogK ( $\lambda(\text{nm})$ ).

	$\text{Cd}^{2+}$	$\text{Pd}^{2+}$	$\text{Pb}^{2+}$	$\text{Hg}^{2+}$	$\text{Zn}^{2+}$	$\text{Ni}^{2+}$	$\text{Ag}^+$
<b>TC1</b>	8.04 (281.5)	2.69 (244.5)	4.51 (281.5)	-	-	4.42 (278)	4.14 (281)
<b>TC2</b>	-	3.21 (242.5)	4.76 (294.5)	-	4.28 (236)	4.07 (284)	3.78 (294)
<b>TC3</b>	4.20 (283)	3.21 (242.5)	2.82 (284.5)	4.61 (282.5)	2.28 (292)	-	-

It should be noted that these values are approximations of the ligand affinity. Indeed, error in our calculations due to the uncertainties involved in  $\epsilon$  determination and concentration of the solutions cannot be neglected.