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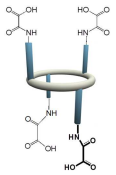

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Synthesis of multivalent oxamate ligands based on calix[4]arene and thiacalix[4]arene backbones in *1,3*-Alternate conformation

Mohamed Habib Noamane[a,b], Sylvie Ferlay[a,*], Rym Abidi[b], Mir Wais Hosseini[a,*]

[a]*Molecular Tectonics Laboratory, Université de Strasbourg, CNRS, CMC UMR 7140, F-67000 Strasbourg, France*
[b]*Université de Carthage, Laboratoire d'Application de la Chimie aux Ressources et Substances Naturelles et à l'Environnement (LACReSNE), unité des interactions moléculaires spécifiques, Faculté des Sciences de Bizerte, 7021 Bizerte, Tunisia*

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ABSTRACT

Five new multivalent ligands based on either *p-tert-butyl*thiacalix[4]arene (TCA) 1 or *p-tert-butyl*calix[4]arene (CA) 2 backbones in *1,3*-Alternate conformation bearing four oxamate coordinating groups at their lower rim were designed and synthesized by a multistep strategy. These ligands differ either by the nature of the calix[4]arene backbone (CA or TCA) or by the nature of the spacer ($(CH_2)_n$) connecting the oxamate binding units to the backbone.

1. Introduction

For the design of multivalent ligands, calixarenes,[1] macrocyclic organic entities based on interconnection of phenolic moieties by CH_2 groups, are of particular interest. Indeed, this class of preorganized backbone offers unlimited design possibilities through functionalization of the lower and/or upper rims. Furthermore, the CH_2 moiety connecting the phenolic units may be replaced by other groups or atoms. Calixarene derivatives have been widely used in the field of supramolecular chemistry[2] for substrate binding, recognition and transport of neutral molecules or ions.[3]

Among the calix[n]arene derivatives, differing by the number of phenolic units (n = 4-12), thiacalix[4]arene (TCA, **1**, Figure 1),[4] for which the four aryl rings are connected by thioether junctions and calix[4]arene (CA, **2**, Figure 1)[1] are of interest owing to their conformational flexibility leading to four limit conformers called cone, partial cone, *1,2*-Alternate and *1,3*-Alternate. This aspect may be exploited for the design of multivalent ligands for which the interaction sites are positioned either on the same face of the backbone (cone conformer) or distributed on both sides of the mean plane of the macrocyclic framework (partial cone, *1,2*-Alternate and *1,3*-Alternate conformers). As stated above, both compounds **1** and **2** may be readily modified allowing thus the design of a large variety of receptors and ligands. Indeed, both backbones may be equipped with interaction sites at both at the lower rim though functionalization of the OH groups or at upper rim by introduction of almost any group at the *para* position. For the thiacalix[4]arene backbone, the thioether junctions may be oxidized to sulfonyl (X = SO)[5] or sulfinyl (X = SO_2).[6] Among the four limit conformations adopted by CA and TCA, the *1,3*-Alternate conformation is of interest for the design of multivalent entities since it allows to position four interactions below and above the macrocyclic backbone in an alternate fashion. We shall focus here on calix based coordinating derivatives. Both calix[4]arene and thiacalix[4]arene have been decorated both at the upper and/or lower rims with a variety of monodentate donor sites (cyano,[7] pyridine,[8] pyrazole,[9] etc..) as well as bidendate (bipyridine,[10] carboxylate,[11], ethylene diamine,[12] etc..) units. These polydentate ligands have been used for the formation of discrete coordination complexes[13] or infinite coordination polymers. Among bis-bidentate N and/or O donor units such as bis-pyrimidine, chloranilate, oxalate and oxamate ligand, the latter has been widely used for the synthesis of a variety of coordination complexes used in catalysis,[14] molecular magnetism[15] and in medicinal chemistry.[16]

To the best of our knowledge, no example of calix[4]arene bearing oxamate coordinating groups has been reported to date. Furthermore, no examples of ligands based on tetrasubstituted CA or TCA *1,3*-Alternate conformation bearing bis-bidentate ligands has been published.

Here, we report on the design, synthesis and characterization of a series of multivalent ligands based on CA or TCA, in *1,3*-Alternate conformation, bearing four oxamate units (compounds **3**-**7**, Figure 1).

2. Results and discussion

The design of the five unprecedented ligands **3**-**7** (Figure 1) is based on either *p*-*tert*-butylthiacalix[4]arene TCA (**3**, **5**, **7**) and *p*-*tert*-butylcalix[4]arene CA (**4**, **6**) backbones in *1,3*-Alternate conformation equipped with four oxamate units. The latter coordinating groups are connected to the macrocyclic backbone by $(CH_2)_n$ spacers (n = 2, 3 or 4).

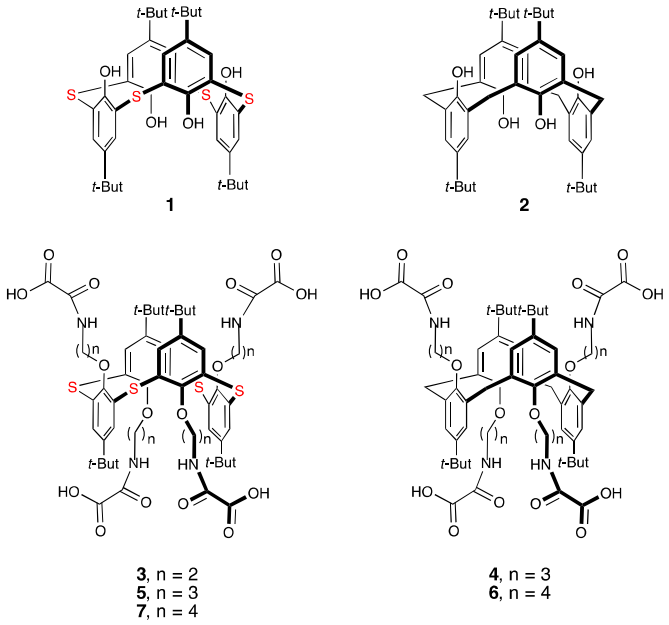

Figure 1: p-tert-butylthiacalix[4]arene TCA 1 and p-tert-butylcalix[4]arene CA 2 in 1,3-Alternate conformation and their derivatives bearing four oxamate units 3-7.

The synthesis of ligands **3**-**7** was achieved following a stepwise strategy. The main intermediate for the synthesis of all five ligands were the phthalimido derivatives **9**-**13** in *1,3*-Alternate conformation (Figure 2).

The synthesis of phthalimido derivatives **10**[17] and **11**[18] (n = 3, TCA and CA respectively) has been previously described. Following the reported procedure, condensation of N-(3-bromopropyl)phthalimide with the parent TCA **1** or CA **2** compounds in the presence of Cs_2CO_3 in DMF or Acetone respectively afforded compounds **10** and **11** in 68 and 55% yields respectively. By applying using the same procedure, compounds **12** and **13** (n = 4, TCA and CA respectively) were obtained in 50% and 29% yields respectively (see experimental section).

Using the same procedure, the condensation of either compound **1** or **2** with (2-bromoethyl)phthalimide in the presence of base, failed to produce intermediates in *1,3*-Alternate conformation, with a shorter spacer (n = 2). It has been previously reported that, the condensation between TCA **1** and (2-bromoethyl)phthalimide in the presence of M_2CO_3 (M = Na, K or Cs) leads to the formation of the mono-substituted derivative in cone conformation.[17a] The same was observed upon increasing the amount of (2-bromoethyl)phthalimide up to 8 equivalents. In order to prepare the tetrasubstituted phthalimido compounds derived from compounds **1** and **2**, another previously reported procedure based on the Mitsunobu reaction was applied. This strategy requires the coupling of a hydroxy derivative **8** with phthalimide **25** in the presence of PPh_3 and DIAD as coupling agent.

Using K_2CO_3 as base, the synthesis of the tetraethylester derivative of CA in cone conformation was reported.[19] We found that the replacement of K_2CO_3 by Cs_2CO_3 upon the condensation of **1** with **24** leads to the formation of the tetraethylester derivative in *1,3*-Alternate conformation. The required compound **8** was the obtained upon reduction of the tetraethyl ester by $LiALH_4$ in THF.[20] Unfortunately, this synthetic approach was only successful with thiacalix[4]arene derivative **8**.

Compound **9**, in *1,3*-Alternate conformation, was prepared in 78% yield upon condensation of **8** with the phthalimide derivative **25** (see experimental section).

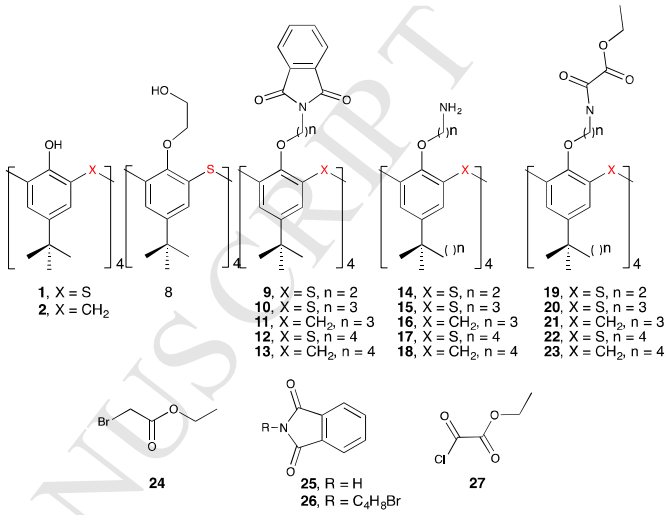

Figure 2: Starting compounds **1** and **2**, precursors **8**-**27** used for the synthesis of ligands **3**-**7**.

The phthalimido derivatives **9**-**13** were converted into their amino derivatives **14**-**18** by hydrazinolysis.[21] The amino compounds **15** and **16** have been already reported[18] and were obtained in 97% and 98% yield respectively. The other three amino derivatives **14**, **17** and **18** were prepared in 98%, 97% and 92% yields respectively (see experimental section).

The ethyloxamate derivatives **19**-**23**, in the *1,3*-Alternate conformation, were obtained upon condensation of the amino derivatives **14**-**18** with ethylchloro(oxo)acetate **27** with yields in the 63-96% range (see table 1 and experimental section). Finally, the targeted ligands **3**-**7** were obtained upon saponification of the ester derivatives **19**-**23**, with yields in the 85-94% range (see table 1 and experimental section).

All intermediates and final compounds **3**-**7**, were fully characterized in solution by ^{1}H- and ^{13}C-NMR spectroscopy, in addition to other usual technics such as elemental analysis, melting point and mass spectrometry.

Table 1: Yields for the condensation of the amino derivatives **14**-**18** with ethyl chloro(oxo)acetate leading to compounds **19**-**23** and their saponification affording the targeted compounds **3**-**7**.

Compound	**19**	**20**	**21**	**22**	**23**
Yield (%)	76	68	67	63	96
Compound	**3**	**4**	**5**	**6**	**7**
Yield (%)	94	92	85	87	83

3. Conclusions

Five new multivalent ligands based on either *p-tert*-butylthiacalix[4]arene **1** or *p-tert*-butylcalix[4]arene **2** backbones in *1,3*-Alternate conformation bearing four oxamate coordinating groups at their lower rim were designed. These ligands differ either by the nature of the calix[4]arene backbone (CA or TCA) or by the nature of the spacer ($(CH_2)_n$) connecting the oxamate binding units to the backbone. Following a multistep synthesis, all targeted compounds were prepared in good yields and fully characterized. The binding propensity of the multivalent ligands **3**-**7** towards transition metal such as Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Cu^{2+} is currently under investigation.

4. Experimental

Materials and methods

^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature on Bruker (300, 400 or 500 MHz) NMR spectrometers.

Mass spectra (ESI) were recorded on a MicroTOF-Q (Bruker) equipped with an electrospray source.

Microanalyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie, Université de Strasbourg, Strasbourg, France.

Melting points were measured in capillary on a Stuart Scientific Melting Point SMP-1 apparatus.

All reagents were purchased from commercial sources (including **2**, **24**-**27**). The synthesis of **1**,[4] **8**,[20] **10**,[17] **11**,[18] **15**,[17b] and **16**[18] has been described in the literature and are not reported here.

All reactions were performed under N_2 atmosphere.

Synthesis

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis (phthalimidoethoxy)thiacalix[4]arene (9)

A mixture of triphenylphosphine (3.80 g, 14.22 mmol) dissolved in 20 mL of THF and diisopropyl azodicarboxylate (DIAD, 2.90 mL, 14.22 mmol) dissolved in 10 mL of THF was stirred at 0 °C for 30 minutes. Phthalimide 25 (2.10 g, 14.22 mmol) was added dropwise and the mixture was further stirred for 15 minutes. 8 (0.88 mmol) dissolved in 20 mL of THF was added dropwise and the mixture was stirred for 48 hours at room temperature. The mixture was evaporated to dryness. Compound **9**, in *1,3*-Alternate conformation, (0.98 g, 78% yield) was obtained as a white powder after washing with MeOH (30 mL). mp = 316 °C

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ(ppm) = 1.35 (36H, s, *t*-Bu), 3.83 (8H, t, Phth-C*H*$_2$), 4.22 (8H, t, C*H*$_2$-O), 7.71 (8H, m, Ar-*H*), 7.79 (8H, s, Ar-*H*), 7.87 (8H, m, Ar-*H*). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): δ(ppm) = 31.3, 34.5, 36.5, 64.9, 123.3, 129, 130.5, 132.2, 133.9, 146.9, 156.9, 167.8.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis (aminoethoxy)thiacalix[4]arene (14)

A mixture of 9 (2.00 g, 1.41 mmol) and hydrazine (14.1 mL, 286 mmol) in 70 mL of EtOH was stirred and refluxed for 24h. After cooling to room temperature, 150 mL of distilled H_2O was added and the reaction mixture was filtered. The white solid thus obtained was washed three times with Et_2O (3x30 mL). The white solid was dried under vacuum at 100 °C during 4 hours affording the pure product **14** in *1,3*-Alternate conformation (1.22 g, 98% yield). mp = 254 °C. ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ(ppm) = 1.27 (36H, s, *t*-Bu), 2.36 (8H, t, NH_2-C*H*$_2$), 3.88 (8H, t, Ar-O-C*H*$_2$), 7.34 (8H, s, Ar-*H*). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): δ = 31.3, 34.3, 41.6, 71.3, 127.8, 128.2, 146.3, 156.7.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(ethyl-2 oxo-2-aminoacetate)ethoxy]thiacalix[4]arene (19)

Compound 14 (0.35 g, 0.39 mmol) was dissolved in 20 mL of $CHCl_3$ and stirred at 0 °C. Triethylamine (270 µL, 1.95 mmol) dissolved in 10 mL of $CHCl_3$ and ethyl chloro(oxo)acetate 27 (210 µL, 1.95 mmol) dissolved in 10 mL of $CHCl_3$ were added dropwise simultaneously and stirred overnight. The solution was washed four times with H_2O (4x40 mL). The organic phase was evaporated to dryness. Compound **19**, in *1,3*-Alternate conformation, (0.38 g, 76% yield) was obtained as a white powder after washing with Et_2O (10 mL). mp = 166 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ(ppm) = 1.19 (36H, s, *t*-Bu), 1.38 (12H, t, C*H*$_3$-CH$_2$), 3.45 (8H, q, NH-C*H*$_2$), 4.33 (8H, t, C*H*$_2$-O), 4.35 (8H, q, CH$_3$-C*H*$_2$), 7.52 (8H, s, Ar-*H*), 8.30 (4H, t, CH$_2$-N*H*-CO). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): δ(ppm) = 14.0, 31.2, 34.2, 39.4, 63.2, 70, 127.3, 132.4, 146.3, 156.7, 157.3, 160.6.

HRMS (ESI): m/z calcd for $C_{66}H_{90}N_5O_{16}S_4^{3+}$ $[M+CH_3CN+(3H)]^{3+}$: 445.87; found: 445.41. Anal. Calcd. for $C_{64}H_{84}N_4O_{16}S_4$: C, 59.42%, H, 6.54%, N, 4.33%. Found: C, 59.64%, H, 6.76%, N, 4.21%.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(2 -oxo-2-aminoacetate)ethoxy]thiacalix[4]arene (3)

KOH (0.105 g, 1.85 mmol) and compound 19 (0.3 g, 0.23 mmol) were dissolved in 20 mL of a THF/H_2O (1/1) mixture. The mixture was stirred at room temperature overnight. HCl (1N) was added until pH = 3 was reached and then THF was evaporated. The solid thus obtained was washed three times with H_2O (3x15 mL), twice with CH_3COCH_3 (2x20 mL) and twice with Et_2O (2x20 mL) and dried under vacuum at 100 °C during 4 hours. Compound **3** (0.255 g; yield = 94%) in *1,3*-Alternate conformation was obtained as a white powder. mp = 262 °C.

^{1}H-NMR (500 MHz, DMSO, 25 °C): δ(ppm) = 1.23 (36H, s, *t*-Bu), 3.17 (8H, q, NH-C*H*$_2$), 3.96 (8H, t, C*H*$_2$-O), 7.57 (8H, s, Ar-*H*), 8.86 (4H, s, CH$_2$-N*H*-CO). ^{13}C-NMR (125 MHz, DMSO, 25 °C): δ(ppm) = 30.9, 34, 37.8, 66.2, 127.8, 130.2, 146, 156.6, 158.7, 161.9.

HRMS (ESI): m/z calcd. for $C_{56}H_{67}N_4O_{16}S_4^-$ $[M-H]^-$: 1180.42; found: 1179.33. Anal. Calcd. for $C_{56}H_{68}N_4O_{16}S_4$: C, 56.93%, H, 5.80%, N, 4.74%. Found: C, 56.60%, H, 5.97%, N, 4.50%.

UV-vis ($CHCl_3$/MeOH (1/1)): λ_{max} (nm) / ε ($mol^{-1}Lcm^{-1}$)= 237 (20912). IR (cm^{-1}): ν_{NH}: 3369, 3012 ; ν_{CO} :1678

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(ethyl-2-oxo-2-aminoacetate)propoxy]thiacalix[4]arene (20)

Compound 15 (0.60 g, 0.63 mmol) was dissolved in 20 mL of $CHCl_3$ and stirred at 0 °C. Triethylamine (450 µL, 3.15 mmol) dissolved in 10 mL of $CHCl_3$ and ethylchloro(oxo)acetate 27

(360 µL, 3.15 mmol) dissolved in 10 mL of $CHCl_3$ were added dropwise simultaneously and the mixture was stirred overnight at room temperature. The solution was washed four times with H_2O (4x40 mL). The organic phase was evaporated to dryness. Compound **20**, in *1,3*-Alternate conformation, (0.58 g; 68% yield) was obtained as a white powder. mp = 242 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ(ppm) = 1.21 (36H, s, *t*-Bu), 1.22 (8H, m, CH_2-C*H*$_2$-CH_2), 1.37 (12H, t, CH_3-C*H*$_2$), 3.05 (8H, q, NH-C*H*$_2$), 3.85 (8H, t, C*H*$_2$-O), 4.43 (8H, q, CH_3-C*H*$_2$), 7.32 (8H, s, Ar-*H*). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): δ(ppm) = 14, 28.8, 31.2, 34.3, 36.3, 63.3, 66, 127.5, 128.1, 146.4, 156.5, 160.7. HRMS (ESI): m/z calcd. for $C_{68}H_{92}N_4O_{16}S_4Na^+$ $[M + Na]^+$: 1372.73; found: 1371.53. Anal. Calcd. for $C_{68}H_{92}N_4O_{16}S_4$: C, 60.51%, H, 6.87%, N, 4.15%. Found: C, 60.17%, H, 7.00%, N, 4.00%.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(2-oxo-2-aminoacetate)propoxy]thiacalix[4]arene (5)

KOH (0.17 g, 2.96 mmol) and compound 20 (0.5 g, 0.37 mmol) were dissolved in 40 mL of a THF/H_2O (1/1) mixture. The mixture was stirred at room temperature overnight. HCl (1N) was added until pH 3 was reached and THF was evaporated. The white precipitate formed was collected and washed three times with H_2O (3x20 mL), twice with CH_3COCH_3 (2x20 mL) and twice with Et_2O (2x20 mL), then dried under vacuum at 100 ° C for 4 hours. Compound **5**, in *1,3*-Alternate conformation, (0.39 g; 85% yield) was obtained as a white powder. mp = 286 °C. ^{1}H-NMR (400 MHz, DMSO, 25 °C): δ(ppm) = 1.20 (36H, s, *t*-Bu), 1.42 (8H, m, CH_2-C*H*$_2$-CH_2), 3.07 (8H, q, NH-C*H*$_2$), 3.80 (8H, t, C*H*$_2$-O), 7.35 (8H, s, Ar-*H*), 8.65 (4H, s, CH_2-N*H*-CO). ^{13}C-NMR (100 MHz, DMSO, 25 °C): δ(ppm) = 28.7, 30.9, 33.8, 36, 67.8, 127.6, 128.8, 145.4, 156.9, 158.1, 162. HRMS (ESI): m/z calcd. for $C_{60}H_{75}N_4O_{16}S_4^-$ $[M-H]^-$: 1236.52; found: 1235.4. Anal. Calcd. for $C_{60}H_{76}N_4O_{16}S_4{\cdot}H_2O$: C, 57.4%, H, 6.26%, N, 4.46%. Found: C, 57.59%, H, 6.32%, N, 4.38%.

UV-vis ($CHCl_3$/MeOH (1/1)): λ_{max} (nm) / ε ($mol^{-1}Lcm^{-1}$)= 265 (21988). IR (cm^{-1}): ν_{NH}: 3391, 2971; ν_{CO}:1664

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis (phthalimidobutoxy)thiacalix[4]arene (12)

1.5 g (2.31 mmol) of compound 1 and 7.5 g (23.11 mmol) of Cs_2CO_3 were dissolved in 80 mL of CH_3COCH_3 and stirred at room temperature for 2h. 5.04 g (23.11 mmol) of *N*-(4-bromobutyl)phthalimide 26 was added and the mixture was stirred for 3 days at 50 °C. After cooling to room temperature, the reaction mixture was filtrated. The solid thus obtained was washed 3 times with $CHCl_3$ (3x20 mL). Filtrates were combined and then evaporated affording a yellow oil which was dissolved in $CHCl_3$ (50 mL) and the solution was washed twice with HCl 1N (2x50 mL). The organic phase was evaporated to dryness leaving a solid which was crystallized from MeOH (100 mL), affording the desired compound **12** in *1,3*-Alternate conformation as a colorless solid (1.75 g, 50 % yield). mp > 320 °C (decomp.). ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ(ppm) = 1.23 (8H, m, Pht-CH_2-C*H*$_2$) 1.28 (36H, s, *t*-Bu), 1.56 (8H, m, CH_2-C*H*$_2$-CH_2), 3.57 (8H, t, Pht-C*H*$_2$), 3.9 (8H, t, Ar-O-C*H*$_2$), 7.34 (8H, s, Ar-*H*), 7.67 (8H, m, Ar-*H*), 7.81 (8H, m, Ar-*H*). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): δ(ppm) = δ = 25.0, 26.3, 31.4, 34.2, 37.7, 68.2, 123.2, 128.3, 132.2, 133.8, 145.8, 157.0, 168.1.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis (aminobutoxy)thiacalix[4]arene (17)

A mixture of compound 12 (2.00 g, 1.31 mmol) and hydrazine (14.1 mL, 286 mmol) in 70 mL of EtOH was stirred and refluxed for 24h. After cooling to room temperature, 150 mL of distilled H_2O was added and the reaction mixture was filtrated. The white solid was washed three times with Et_2O (3x30 mL) and then dried under vacuum at 100 °C during 4 hours, affording the pure product **17** (1.27 g, 97% yield) in *1,3*-Alternate conformation. mp = 206 °C. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ(ppm) = 1.03 (8H, m, NH_2-CH_2-C*H*$_2$), 1.23 (8H, m, O-CH_2-C*H*$_2$), 1.24 (36H, s, *t*-Bu), 2.53 (8H, t, NH_2-C*H*$_2$), 3.81 (8H, t, Ar-O-C*H*$_2$), 7.28 (8H, s, Ar-*H*). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): δ = 26.4, 30.2, 31.3, 34.2, 42.3, 68.4, 127.6, 128.1, 145.4, 157.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(ethyl-2-oxo-2-aminoacetate)butoxy]thiacalix[4]arene (22)

Compound 17 (0.25 g, 0.24 mmol) was dissolved in 20 mL of $CHCl_3$ and stirred at 0 °C. Triethylamine (170 µL, 1.24 mmol) dissolved in 10 mL of $CHCl_3$ and ethyl chloro(oxo)acetate 27 (140 µL, 1.24 mmol) dissolved in 10 mL of $CHCl_3$ were added dropwise simultaneously and stirred overnight. The solution was washed four times with H_2O (4x40 mL). The organic phase was evaporated to dryness. Compound **22** in *1,3*-Alternate conformation (0.22 g; 63% yield) was obtained as a white powder. mp = 242 °C. ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ(ppm) = 1.13 (8H, m, O-CH_2-C*H*$_2$-CH_2-), 1.23 (36H, s, *t*-Bu), 1.35 (12H, t, C*H*$_3$-CH_2), 1.41 (8H, m, NH-C*H*$_2$-CH_2), 3.18 (8H, q, NH-C*H*$_2$), 3.82 (8H, t, C*H*$_2$-O), 4.32 (8H, q, CH_3-C*H*$_2$), 7.15 (8H, s, Ar-*H*), 7.29 (4H, s, CH_2-N*H*-CO). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): δ(ppm) = 14, 25.4, 26.5, 31.4, 34.2, 39.8, 63.2, 68.4, 128, 128.2, 145.7, 156.5, 156.9, 160.7. HRMS (ESI): m/z calcd. for $C_{72}H_{100}N_4O_{16}S_4Na^+$ $[M + Na]^+$: 1428.82; found: 1427.6. Anal. Calcd. for $C_{72}H_{100}N_4O_{16}S_4$: C, 61.51%, H, 7.17%, N, 3.99%. Found: C, 61.21%, H, 7.18%, N, 4.01%.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(2-oxo-2-aminoacetate)butoxy]thiacalix[4]arene (7)

KOH (0.03 g, 0.56 mmol) and compound 22 (0.1 g, 0.07 mmol) were dissolved in 20 mL of a THF/H_2O (1/1) mixture. The mixture was stirred at room temperature overnight. HCl (1N) was added until pH 3 was reached and then THF was evaporated. The solid thus obtained was washed three times with H_2O (3x5 mL), twice with CH_3COCH_3 (2x5 mL) and twice with Et_2O (2x5 mL) and then dried under vacuum at 100 ° C during 4 hours. Compound **7** in *1,3*-Alternate conformation (0.07 g; 83% yield) was obtained as a white powder. mp = 246 °C. ^{1}H-NMR (500 MHz, DMSO, 25 °C): δ(ppm) = 1.00 (8H, m, NH-CH_2-C*H*$_2$), 1.23 (36H, s, t-Bu), 1.31 (8H, m, C*H*$_2$-CH_2-O), 2.98 (8H, q, NH-C*H*$_2$), 3.76 (8H, t, C*H*$_2$-O), 7.31 (8H, s, Ar-*H*), 8.84 (4H, s, CH_2-N*H*-CO). ^{13}C-NMR (125 MHz, DMSO, 25 °C): δ(ppm) = 25.4, 26.2, 31.5, 34.3, 39.2, 68.4, 127.8, 128, 145.9, 156.9, 158.6, 162.6. HRMS (ESI): m/z calcd. for $C_{64}H_{84}N_4O_{16}S_4^+$ $[M]^+$: 1293.63; found: 1293.48.Anal. Calcd. for $C_{64}H_{84}N_4O_{16}S_4$: C, 57.81%, H, 6.67%, N, 4.21%. Found: C, 58.43%, H, 6.56%, N, 4.13%.

UV-vis ($CHCl_3$/MeOH (1/1)): λ_{max} (nm) / ε ($mol^{-1}Lcm^{-1}$)= 237 (22748). IR (cm^{-1}): ν_{NH}: 3399, 2974; ν_{CO}:1668.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(ethyl-2-oxo-2-aminoacetate)propoxy]calix[4]arene (21)

Compound 16 (0.25 g, 0.28mmol) was dissolved in 20 mL of $CHCl_3$ and stirred at 0 °C. Triethylamine (230 µL, 1.7 mmol) dissolved in 10 mL of $CHCl_3$ and ethylchloro(oxo)acetate 27 (190 µL, 1.7 mmol) dissolved in 10 mL of $CHCl_3$ were added dropwise simultaneously and stirred overnight. The solution was washed four times with H_2O (4x20 mL). The organic phase was evaporated to dryness. Compound **21** in *1,3*-Alternate conformation (0.19 g; 67% yield) was obtained as a white powder after purification on a silica column (AcOEt/Cyclohexane, 1/1). mp = 202 °C. ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ(ppm) = 1.21 (8H, m, CH_2-C*H*$_2$-CH_2), 1.24 (36H, s, *t*-Bu), 1.37 (12H, t, C*H*$_3$-CH_2), 3.06 (8H, q, NH-C*H*$_2$), 3.34 (8H, t, C*H*$_2$-O), 3.84 (8H, s, Ar-*CH*$_2$-Ar), 4.34 (8H, q, CH_3-C*H*$_2$), 6.98 (8H, s, Ar-*H*), 7.06 (4H, t, CH_2-N*H*-CO). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): δ(ppm) = 14, 29.3, 31.6, 33.9, 36.9, 39.2, 63.2, 67.5, 125.6, 133.1, 144.4, 154.5, 156.5, 160.7. HRMS (ESI): m/z calcd. for $C_{72}H_{100}N_4O_{16}Na^+$ [M + Na]$^+$: 1300.56; found: 1299.69. Anal. Calcd. for $C_{72}H_{100}N_4O_{16}$: C, 67.69%, H, 7.89%, N, 4.39%. Found: C, 67.41%, H, 7.95%, N, 4.33%.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(2-oxo-2-aminoacetate)propoxy]calix[4]arene (4)

KOH (0.07 g, 1.2 mmol) and compound 21 (0.2 g, 0.15 mmol) were dissolved in 40 mL of a THF/H_2O (1/1) mixture. The mixture was stirred at room temperature overnight. HCl (1N) was added until pH 3 was reached and then THF was evaporated. The solid thus obtained was washed three times with H_2O (3x20 mL), twice with CH_3COCH_3 (2x20 mL) and twice with Et_20 (2x20 mL), then dried under vacuum at 100 ° C during 4 hours. Compound **4** in *1,3*-Alternate conformation (0.16 g; 92% yield) was obtained as a white powder. mp > 320 °C (decomp.). ^{1}H-NMR (300 MHz, DMSO, 25 °C): δ(ppm) = 1.18 (36H, s, *t*-Bu), 1.58 (8H, m, CH_2-C*H*$_2$-CH_2), 3.1 (8H, q, NH-C*H*$_2$), 3.39 (8H, t, C*H*$_2$-O), 3.62 (8H, s, Ar-*CH*$_2$-Ar), 6.95 (8H, s, Ar-*H*), 8.69 (4H, s, CH_2-N*H*-CO). ^{13}C-NMR (125 MHz, DMSO, 25 °C): δ(ppm) = 29.4, 31.4, 33.4, 36.1, 37.6, 69.0, 126.3, 132.5, 142.5, 154.2, 158.5, 162.1. HRMS (ESI): m/z calcd. for $C_{64}H_{86}N_4O_{16}Na$ [M + Na]$^+$: 1187.56; found: 1188.35. Anal. Calcd. for $C_{64}H_{86}N_4O_{16}$: C, 65.85%, H, 7.43%, N, 4.80%. Found: C, 65.23%, H, 7.48%, N, 4.79%.

UV-vis ($CHCl_3$/MeOH (1/1)): λ_{max} (nm) / ε ($mol^{-1}Lcm^{-1}$)= 236 (23640). IR (cm^{-1}): ν_{NH}: 3388, 2973; ν_{CO}:1662.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis (phthalimidobutoxy)calix[4]arene (13)

3 g (4.53 mmol) of compound 2 and 15 g (45.11 mmol) of Cs_2CO_3 were dissolved in 120 mL of DMF and stirred at room temperature for 2h. 13g (45.15 mmol) of *N*-(4-bromobutyl)phthalimide 26 was added and the mixture was stirred at 50 °C for 3 days. After cooling to room temperature, the reaction mixture was filtrated. The solid thus obtained was washed 3 times with $CHCl_3$ (3x20 mL). Filtrates were combined and the evaporated leading to a yellow oil which was dissolved in $CHCl_3$ (100 mL) and the solution was washed twice with HCl 1N (2x100 mL). The organic phase was evaporated to dryness leaving a solid which was crystallized from a $CHCl_3$/MeOH 2/20 mixture (40 mL), affording the desired compound **13** in *1,3*-Alternate conformation as a white powder (1.9 g, 29 % yield). mp > 244 °C (decomp.). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ(ppm) = 1.22 (36H, s, *t*-Bu), 1.38 (8H, m, Pht-CH_2-C*H*$_2$), 1.61 (8H, m, CH_2-C*H*$_2$-O), 3.45 (8H, t, Pht-C*H*$_2$), 3.61 (8H, t, Ar-O-C*H*$_2$), 3.71 (8H, s, Ar-C*H*$_2$-Ar), 6.94 (8H, s, Ar-*H*), 7.7 (8H, m, Ar-*H*), 7.84 (8H, m, Ar-*H*). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C): δ(ppm) = δ = 25.2, 26.9, 31.7, 33.8, 37.7, 38.6, 70.1, 123.2, 126.3, 132.2, 133.2, 133.8, 143.6, 154.4, 168.2.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis (aminobutoxy)calix[4]arene (18)

A mixture of compound 13 (2.00 g, 1.38 mmol) and hydrazine (14.1 mL, 286 mmol) in 70 mL of EtOH was stirred and refluxed for 24h. After cooling to room temperature, 150 mL of distilled H_2O was added and the reaction mixture was filtrated. The white solid was washed three times with Et_20 (3x30 mL). The white solid was dried under vacuum at 100 °C during 4 hours, affording the pure product **18** (1.19 g, 92% yield) in *1,3*-Alternate conformation. mp > 206 °C (decomp.). ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ(ppm) = 1.22 (8H, m, NH_2-CH_2-C*H*$_2$), 1.26 (36H, s, *t*-Bu), 1.3 (8H, m, O-CH_2-C*H*$_2$) 2.60 (8H, t, NH_2-C*H*$_2$), 3.41 (8H, t, Ar-O-C*H*$_2$), 3.73 (8H, s, Ar-C*H*$_2$-Ar), 6.94 (8H, s, Ar-*H*). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): δ = 27.1, 30.4, 31.6, 33.8, 38.9, 42.3, 70.4, 125.9, 133, 143.4, 154.6.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(ethyl-2-oxo-2-aminoacetate)butoxy]calix[4]arene (23)

Compound 18 (0.65 g, 0.69 mmol) was dissolved in 30 mL of $CHCl_3$ and stirred at 0 °C. Triethylamine (500 µL, 3.63 mmol) dissolved in 10 mL of $CHCl_3$ and ethyl chloro(oxo)acetate 27 (400 µL, 3.56 mmol) dissolved in 10 mL of $CHCl_3$ were added dropwise simultaneously and stirred overnight. The solution was washed four times with H_2O (4x30 mL). The organic phase was evaporated to dryness. Compound **23** in *1,3*-Alternate conformation (0.89 g; 96% yield) was obtained as a white powder. mp = 212 °C. ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ(ppm) = 1.22 (8H, m, O-CH_2-C*H*$_2$-CH_2), 1.25 (36H, s, t-Bu), 1.38 (12H, t, C*H*$_3$-CH_2), 1.43 (8H, m, NH-CH_2-C*H*$_2$), 3.24 (8H, q, NH-C*H*$_2$), 3.36 (8H, t, C*H*$_2$-O), 3.75 (8H, s, Ar-C*H*$_2$-Ar), 4.33 (8H, q, CH_3-C*H*$_2$), 6.94 (4H, s, CH_2-N*H*-CO), 7.2 (8H, s, Ar-*H*).^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): δ(ppm) = 14, 25.6, 27, 31.6, 33.8, 38.9, 39.9, 63.2, 70.0, 126.0, 133.1, 143.8, 154.5, 156.6, 160.7. HRMS (ESI): m/z calcd. for $C_{76}H_{108}N_4O_{16}Na^+$ [M + Na]$^+$: 1356.69; found: 1355.77. Anal. Calcd. for $C_{76}H_{108}N_4O_{16}$: C, 68.44%, H, 8.16%, N, 4.20%. Found: C, 68.14%, H, 8.22%, N, 4.11%.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(2-oxo-2-aminoacetate)butoxy]calix[4]arene (6)

KOH (0.14 g, 2.39 mmol) and compound 23 (0.4 g, 0.29 mmol) were dissolved in 40 mL of a THF/H_2O (1/1) mixture. The mixture was stirred at room temperature overnight. HCl (1N) was added until pH 3 was reached and then THF was evaporated. The solid thus obtained was washed three times with H_2O (3x20 mL), twice with CH_3COCH_3 (2x20 mL) and twice with Et_2O (2x20 mL), then dried under vacuum at 100 °C during 4 hours. Compound **6** in *1,3*-Alternate conformation (0.30 g; 87% yield) was obtained as a white powder. mp > 248 °C (decomp.). ^{1}H-NMR (500 MHz, DMSO, 25 °C): δ(ppm) = 1.20 (36H, s, *t*-Bu), 1.22 (8H, m, NH-CH_2-C*H*$_2$), 1.38 (8H, m, C*H*$_2$-CH_2-O), 3.05 (8H, q, NH-C*H*$_2$), 3.33 (8H, t, C*H*$_2$-O), 3.67 (8H, s, Ar-C*H*$_2$-Ar), 6.93 (8H, s, Ar-*H*), 8.78 (4H, s, CH_2-N*H*-CO). ^{13}C-NMR (125 MHz, DMSO, 25 °C): δ(ppm) = 25.1, 26.4, 31.4, 33.4, 37.8, 38.7, 69.8, 125.8, 132.7, 142.5, 154.1, 158.1, 162.1. HRMS (ESI): m/z calcd. for $C_{68}H_{91}N_4O_{16}$ [M-H]$^-$: 1220.48; found: 1219.64. Anal.

Calcd. for $C_{68}H_{92}N_4O_{16}$: C, 66.86%, H, 7.59%, N, 4.59%. Found: C, 66.44%, H, 7.67% N, 4.64%.

UV-vis ($CHCl_3$/MeOH (1/1)): λ_{max} (nm) / ε ($mol^{-1}Lcm^{-1}$)= 236 (20164). IR (cm^{-1}): ν_{NH}: 3393, 2970; ν_{CO}:1671.

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