



**HAL**  
open science

## **Molecular tectonics: tetracarboxythiacalix[4]arene derivatives as tectons for the formation of hydrogen-bonded networks**

Alexander Ovsyannikov, Marina N. Lang, Sylvie Ferlay, Svetlana Solovieva, Igor Antipin, A. Konovalov, Nathalie Kyritsakas, Mir Wais Hosseini

### ► To cite this version:

Alexander Ovsyannikov, Marina N. Lang, Sylvie Ferlay, Svetlana Solovieva, Igor Antipin, et al.. Molecular tectonics: tetracarboxythiacalix[4]arene derivatives as tectons for the formation of hydrogen-bonded networks. *CrystEngComm*, 2016, 18 (44), pp.8622-8630. <10.1039/c6ce02026g>. <hal-02301783>

**HAL Id: hal-02301783**

**<https://hal.science/hal-02301783v1>**

Submitted on 3 Oct 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

## Molecular tectonics: tetracarboxythiacalix[4]arene derivatives as tectons for the formation of hydrogen-bonded networks

A.S. Ovsyannikov,<sup>b,c</sup> M. N. Lang,<sup>a</sup> S. Ferlay,<sup>\*a</sup> S. E. Solovieva,<sup>\*b,c</sup> I. S. Antipin,<sup>\*b,c</sup> A. I. Konovalov,<sup>b,c</sup> N. Kyritsakas,<sup>a</sup> M. W. Hosseini<sup>\*a</sup>

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

**Abstract:** A series of thiacalix[4]arene derivatives blocked in 1,3-alternate conformation and bearing four carboxylic acids has been designed and synthesized. These compounds, owing to the H-bond donor (OH moiety) and acceptor (C=O group) nature of the carboxylic acid moieties behave as self-complementary tectons and lead to the formation of tubular 1D H-bonded networks in the crystalline phase. Upon deprotonation of the self-complementary neutral compounds, *i.e.* transformation of the carboxylic moieties into carboxylates, anionic tectons are generated. Their propensity to form H-bonded networks in the presence of the dicationic H-bond donor tecton of the cyclic bis-amidium type, designed to behave as a molecular staple interconnecting two carboxylates moieties, 1- and 2-D H-bonded networks are formed under self-assembly conditions.

### Introduction

Tubular architectures<sup>1,2,3</sup> are of interest as they form channels that may lead to the transport of neutral or charged species. Such an entity may be either discrete or infinite networks displaying translational symmetry. For the latter category, they may be formed by self-assembly processes upon interconnection of cyclic entities using either hydrogen or coordination-bonds.<sup>4,5,6,7</sup> Tubular architectures may also be helical assemblies.<sup>8</sup> Organisation of cyclic units into tubular architectures using liquid crystalline phases<sup>9</sup> or polymeric backbones<sup>10</sup> have been also reported.

Following the concepts developed in *molecular tectonics*<sup>11</sup> for the design and formation by self-assembly processes of infinite molecular networks in the crystalline phase, we are interested in tubular architecture based on H-bonds between macrocyclic entities behaving as tectons.<sup>12</sup> Owing to their cyclic nature, calix[4]arene,<sup>13</sup> and thiacalix[4]arene **1-3**<sup>14,15</sup> (Fig. 1) in their 1,3-alternate conformation are interesting backbones for the design of such tectons. Indeed the 1,3-alternate conformation of these two platforms allows to position up to 4 interaction

sites in a divergent fashion, *i.e.* two above and two below the main plane of the calixarene. We have previously exploited this feature and designed metallatubulanes based on calix[4]arene derivatives<sup>16</sup> or on [1,1,1,1]-metacyclophane in 1,3-alternation fixed conformation, an analogous backbone to calix[4]arene.<sup>17</sup>

Here we report on the design, synthesis and characterization of thiacalixarene based derivatives **4-8**, in their 1,3-alternate conformation, bearing four carboxylic acid groups and thus behaving as self-complementary tectons. We describe their self-assembly in the crystalline phase into 1D tubular H-bonded networks as well as their combinations of their deprotonated derivatives as anionic tectons with a dicationic tecton **A**<sup>2+</sup>, behaving as a molecular staple, capable of bridging consecutive anionic units, leading to extended H bonded networks.

Compounds **4-7**, and **8** are based on *p*-tert-butylthiacalix[4]arene and on *H*-thiacalix[4]arene backbone in its 1,3-alternate conformation respectively (Fig. 1). They are analogous derivatives bearing four carboxylic acid moieties and differ by the nature of the spacer connecting the carboxyl groups to the backbone. They have been designed in order to investigate the role played by the spacer on their ability to form tubular H-bonded networks (Fig. 2a) based on the formation of H-bonded dimeric nodes (Fig. 2b) between carboxylic acid belonging to consecutive self-complementary tectons. Owing to the acidic nature of compounds **4-8**, upon their deprotonation leading to anionic species, they offer another possibility for the design of tubular H-bond networks.

<sup>a</sup> Molecular Tectonics Laboratory, UMR Uds-CNRS 7140, University of Strasbourg, Institut Le Bel, 4, rue Blaise Pascal, F-67000 Strasbourg, France.

<sup>b</sup> Kazan Federal University, Kremlevskaya str. 18, Kazan 420008, Russian Federation

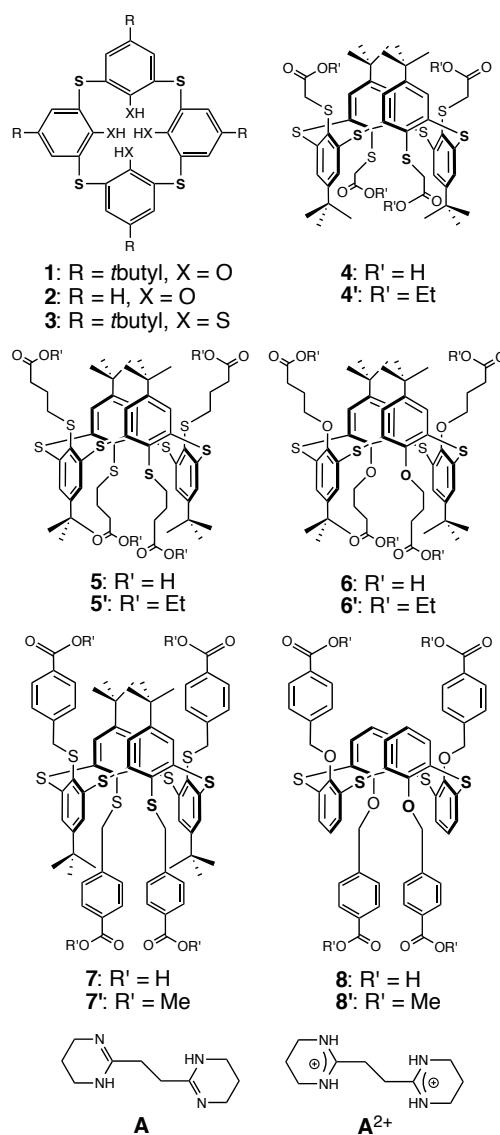
<sup>c</sup> A. E. Arbusov Institute of Organic and Physical Chemistry, Russian Academy of Science, Arbuzov str. 8, Kazan 420088, Russian Federation

† Electronic supplementary information (ESI) available: X-ray diffraction data, tables of selected bonds and angles. See DOI: 10.1039/x0xx00000x. ESI

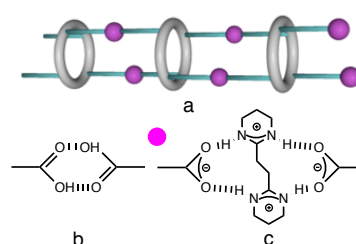
Indeed these anionic tectons bearing carboxylate moieties may be combined with the dicationic organic tecton  $A^{2+}$  (Fig. 1) designed to bridge two carboxylates, one on each of its faces, and thus behave as a molecular staple (Fig. 2c) connecting consecutive carboxylate bearing components.<sup>18,19</sup> Depending on the deprotonation degree of neutral compounds **4-8** and the nature of the spacer connecting the calix backbone to the carboxylate units, one may expect the formation of 1D tubular H-bonded networks (Fig. 2a). The driving force for the formation of such extended architectures is the establishment of charge-assisted H-bonds.<sup>20</sup>

Although few tetra-acid derivatives based on calix[4]arene<sup>21</sup> (CA) and thiacalix[4]arene<sup>22</sup> (TCA) backbones have been reported, to the best of our knowledge, no example of tetramercaptothiacalixarene (TMTCA) **3** (Fig. 1) based derivative has been documented to date.

Few examples of H-bonded nanotubular assemblies based on *p*-*tert*-butylthiacalix[4]arene **3** bearing carboxylic acid and/or urea have been reported.<sup>23</sup> An interesting investigation dealing with photoisomerization of a H-bonded network based on *p*-*tert*-butylthiacalix[4]arene derivative bearing carboxylic acid moieties combined with bipyridylethene has been also reported.<sup>24</sup>



**Figure 1:** Tetrathia- and tetrathiatetramercapto- calix[4]arene precursors **1**, **2** and **3**, and tetraakis carboxyl derivatives **4-8** in 1,3-A conformation.



**Figure 2:** Recognition patterns through H bonds between tectons a) schematic view of tetrasubstituted macrocyclic species leading to 1D tubular systems b) a dimeric nod involving two carboxylic moieties and c) in dihapto mode between carboxylate and amidinium moieties, behaving as molecular staples.

## Experimental

### Characterization techniques

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded at room temperature on a Bruker 300 MHz and 500 MHz.

FT-IR spectra were recorded on a Perkin Elmer ATR spectrometer.

Mass spectra (MS (ES+)) were recorded on a Bruker MicroTOF spectrometer.

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

Elemental analyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie of the University de Strasbourg.

### Single-Crystal Studies

Data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid  $\text{N}_2$  device, using graphite-monochromated Mo- $\text{K}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. For all structures, diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on  $F^2$  using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model).<sup>25</sup> They can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/datarequest/cif](http://www.ccdc.cam.ac.uk/datarequest/cif). CCDC: 1504484-1504490 and 1505426 (see tables S4 and S5, ESI).

### Powder X-ray Diffraction

Powder diffraction studies (PXRD) diagrams were collected on a Bruker D8 diffractometer using monochromatic Cu- $\text{K}\alpha$  radiation with a scanning range between 3.8 and 40° using a scan step size of 2°/mn.

As already demonstrated and currently admitted, for all the compounds, discrepancies in intensity between the observed and simulated patterns are due to preferential orientations of the microcrystalline powders.

### Synthesis

General: All reagents were purchased from commercial sources and used without further purification. The synthesis of **1**,<sup>14a</sup>, **2**,<sup>26</sup> and **3**,<sup>27</sup> and **8**,<sup>28</sup> has been previously reported. The synthesis of **4-7** was adapted from previously reported procedures.<sup>22,29</sup>

The bisamidinium compound **A**<sup>2+</sup>, used as its distosylate salt (**A**<sup>2+</sup>·2TsO<sup>-</sup>), has been prepared using an already reported procedure.<sup>18b</sup>

### Synthesis of the tetraester derivative **4'** in **1,3-A** conformation

Under argon, a mixture of TMTCA **3** (0.3 g, 0.38 mmol) and  $\text{Cs}_2\text{CO}_3$  (2.47 g, 7.6 mmol) in dry and degassed acetone (60 ml) was refluxed for 2 hours before  $\text{BrCH}_2\text{COOEt}$  (0.85 ml, 7.6 mmol) was added. The reaction mixture was refluxed during 50 hours under argon. After cooling, the solid was filtrated and the filtrate evaporated. The residue was treated with MeOH (50 ml) affording the desired compound **4'** (0.2 g, 46% yield) in **1,3-A** conformation as a white powder.

Mp: 310 °C (decomp.); MALDI TOF:  $m/z = 1129.3$  [ $\text{M}$ ]<sup>+</sup> (calculated 1129.69); Elemental Analysis: % *calculated*: C, 59.54%; H, 6.42%; % *found*: C, 59.45 %; H, 6.48 %;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz, 25 °C):  $\delta(\text{ppm}) = 1.18$  (12H, t,  $-\text{CH}_3$ ), 1.26 (36H, s, *t*Bu); 3.61 (8H, s,  $\text{ArSCH}_2$ ), 4.12 (8H, q,  $-\text{C}(\text{O})\text{CH}_2-$ ), 7.76 (8H, s, *Ar-H*);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125 MHz, 25 °C):  $\delta(\text{ppm}) = 14.4$ ; 31.1; 34.8; 37.7; 61.5; 136.1; 139.9; 143.2; 150.9; 170.0.

### Synthesis of the tetraester derivative **5'** in **1,3-A** conformation

Under argon, a mixture of **3** (0.5 g, 0.63 mmol) and  $\text{Cs}_2\text{CO}_3$  (4.12 g, 12.6 mmol) in dry and degassed acetone (60 ml) was refluxed for 2 hours before  $\text{Br}(\text{CH}_2)_3\text{COOEt}$  (1.8 ml, 12.6 mmol) was added. The reaction mixture was refluxed during 50 hours under argon. After cooling, the mixture was filtrated and the solvent was evaporated. The residue was treated with 2M HCl (40 ml) and extracted with  $\text{CHCl}_3$  (2x50 ml). The organic layers were combined, washed with water (100 ml) and dried over  $\text{MgSO}_4$ . After filtration, the organic solvent was evaporated and addition of MeOH (100 ml) to the oily residue afforded the compound **5'** (0.43g, 60% yield) as a white precipitate.

Mp: 320 °C (decomp.) MALDI TOF:  $m/z: 1241.5$  [ $\text{M}$ ]<sup>+</sup> (calculated 1241.88); Elemental Analysis: % *calculated*: C, 61.90%; H, 7.14%; % *found*: C, 61.68 %; H, 7.10 %;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz, 25 °C):  $\delta(\text{ppm}) = 1,24$  (12H, t,  $-\text{CH}_3$ ), 1,26 (36H, s, *t*Bu); 1,75 (8H, p,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ); 2,56 (8H, t,  $-\text{CH}_2\text{C}(\text{O})-$ ); 2,93 (8H, t,  $-\text{SCH}_2-$ ); 4,14 (8H, q,  $-\text{C}(\text{O})\text{O}-\text{CH}_2-$ ); 7,71 (8H, s, *Ar-H*).

### Synthesis of the tetraester derivative **6'** in **1,3-A** conformation

A mixture of **2** (3.00 g, 4.17 mmol),  $\text{Br}(\text{CH}_2)_3\text{C}(\text{O})\text{OEt}$  (6.55 g, 33.3 mmol) and  $\text{Cs}_2\text{CO}_3$  (8.16 g, 25 mmol) was refluxed under argon in acetone (100 mL) for 3 days. The reaction mixture was filtered. The filtrate was concentrated in vacuum. The residue was treated with MeOH (50 ml) affording the desired compound **6'** (2.25 g, 46% yield) in **1,3-A** conformation as a white powder.

Mp: 315-317 °C; MALDI TOF:  $m/z: 1176,85$  [ $\text{M}$ ]<sup>+</sup> (calculated 1177,64); Elemental Analysis: % *calculated*: C, 65.28%; H, 7.53%; % *found*: C, 65.33 %; H, 7.51 %;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 600 MHz, 25 °C):  $\delta(\text{ppm}) = 1.25$  (s, 36H, *t*Bu), 1.25 (t, 12H,  $-\text{CH}_3$ ), 1.41 (m, 8H,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ), 2.11 (t, 8H,  $-\text{CH}_2\text{C}(\text{O})-$ ), 3.91 (t, 12H,  $-\text{O}-\text{CH}_2-$ ), 4.09 (q, 8H,  $-\text{OCH}_2\text{CH}_3$ ), 7.36 (s, 8H, *Ar-H*);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125 MHz, 25°C):  $\delta\text{ppm} = 14.3, 24.3, 30.9, 31.2, 34.3, 60.1, 67.9, 127.8, 128.2, 145.9, 156.8, 172.8$ .

### Synthesis of the tetraester derivative **7'** in **1,3-A** conformation

Under argon, a mixture of **3** (0.5 g, 0.63 mmol) and  $\text{Cs}_2\text{CO}_3$  (1.3 g, 4 mmol) and methyl-(4-bromomethyl)benzoate (2.05 g, 9 mmol) in dry and degassed DMF (60 ml) was stirred during 40 hours at 80°C. After cooling, the solvent was evaporated under reduced pressure. The residue was treated with 2M HCl (40 ml) and extracted with  $\text{CH}_2\text{Cl}_2$  (2x50 ml). The organic layers were combined and dried over  $\text{MgSO}_4$ . After filtration, the solvent was evaporated. The residue was treated with MeOH (200 ml) affording the desired compound **7'** (0.43g, 60% yield) in **1,3-A** conformation as a white powder.

Mp: 300 °C (decomp.) MALDI TOF:  $m/z$ : 1377.15 [M]<sup>+</sup> (calculated 1377.95); Elemental Analysis: % *calculated*: C, 66.25%; H, 5.85%; % *found*: C, 66.18%; H, 5.86%; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, 25 °C):  $\delta$ (ppm) = 1.06 (36H, s, tBu); 3.92 (12H, s, -C(O)O-CH<sub>3</sub>); 4.05 (8H, s, -SCH<sub>2</sub>-); 7.28 (8H, d, Ar-H); 7.61 (8H, s, Ar-H); 7.90 (8H, d, Ar-H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz, 25 °C):  $\delta$ (ppm) = 30.7; 34.4; 51.0; 52.2; 128.7; 129.1; 129.7; 134.9; 140.0; 143.4; 143.6; 150.4; 167.2.

#### Synthesis of the tetraester derivative 8' in 1,3-A conformation

Compound 8' was prepared using the reported procedure (63 % yield).<sup>23</sup>

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, 25 °C):  $\delta$ (ppm) = 4.05 (12H, s, -C(O)O-CH<sub>3</sub>); 5.29 (8H, s, -OCH<sub>2</sub>-); 6.44 (4H, t, Ar-H); 7.01 (8H, d, Ar-H); 7.13 (8H, d, Ar-H); 8.1 (8H, d, Ar-H).

#### Synthesis of the tetracarboxyl derivative 4 in 1,3-A conformation

Compound 4' (0.3 g, 0.26 mmol) was mixed with LiOH (0.15 g, 6.25 mmol) in a THF-H<sub>2</sub>O mixture (5/1 100 ml) and refluxed during 48 hours. After cooling, an aqueous 2M HCl aqueous solution (20 ml) was added. The precipitate was filtrated and washed with water (50 ml). Compound 4 was obtained as a white solid (0.23 g, 92 % yield).

Mp: 312 °C (decomp.) MALDI TOF:  $m/z$ : 1039.19 [M+Na]<sup>+</sup> (calculated 1040.47); Elemental Analysis: % *calculated*: C, 56.66%; H, 5.55%; % *found*: C, 56.40%; H, 5.50%; <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 300 MHz, 25 °C):  $\delta$ (ppm) = 1.21 (s, 36H, tBu); 3.56 (s, 8H, ArSCH<sub>2</sub>), 7.76 (s, 8H, Ar-H); <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 125 MHz, 25 °C):  $\delta$ (ppm) = 30.3; 34.1; 37.7; 135.7; 140.2; 141.9; 149.8; 170.5.

#### Synthesis of the tetracarboxyl derivative 5 in 1,3-A conformation

To a dispersion of the compound 5' (0.5 g, 0.4 mmol) in EtOH (80 ml), an aqueous NaOH solution (20 ml, 0.16 g, 4 mmol) was added and the mixture was refluxed during 48 hours. After cooling to 0 °C, an aqueous 2M HCl solution (40 ml) was added. The precipitate was filtrated and washed by water (3x50 ml) affording the compound 5 as a white solid (0.43 g, 95 % yield).

Mp: 315 °C (decomp.) MALDI TOF:  $m/z$  = 1167.31 [M+K]<sup>+</sup> (calculated 1168.76); Elemental Analysis: % *calculated*: C, 59.54%; H, 6.42%; % *found*: C, 59.40%; H, 6.46%; <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 300 MHz, 25 °C):  $\delta$ (ppm) = 1.23 (36H, s, tBu); 1.60 (8H, m, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-); 2.46 (8H, t, -SCH<sub>2</sub>-); 2.88 (8H, t, -CH<sub>2</sub>-C(O)-); 7.71 (8H, s, Ar-H); <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 125 MHz, 25 °C):  $\delta$ (ppm) = 24.2; 30.5; 32.6; 34.0; 34.6; 133.9; 140.0; 141.9; 149.4; 174.1.

#### Synthesis of the tetracarboxyl derivative 6 in 1,3-A conformation

Compound 6' (0.75 g, 0.64 mmol), KOH (0.72 g, 12.86 mmol), EtOH (125 mL) and water (31 mL) were stirred at 100 °C during 3 hours. The reaction mixture was cooled in an ice-water bath

before 2M aqueous HCl solution (12 mL) was added. The final product 6 was isolated as a white powder (0.65 g, 95 %).

Mp: 330 °C (decomp.) MALDI TOF:  $m/z$  = 1087.41 [M+Na]<sup>+</sup> (calculated 1088.41); Elemental Analysis: % *calculated*: C, 61.09%; H, 6.90%; % *found*: C, 61.25%; H, 6.83%; <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 300 MHz, 25 °C):  $\delta$ (ppm) = 1.21 (36H, s, tBu); 1.21 (8H, m, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-); 1.99 (8H, t, -CH<sub>2</sub>-C(O)-); 3.80 (8H, t, -OCH<sub>2</sub>-); 7.34 (8H, s, Ar-H); 11.92 (4H, s, -COOH); <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 125 MHz, 25 °C):  $\delta$ (ppm) = 23.7; 30.0; 30.9; 34.0; 67.3; 127.0; 127.3; 145.6; 156.2; 174.0.

#### Synthesis of the tetracarboxyl derivative 7 in 1,3-A conformation

To a dispersion of the compound 7' (0.4 g, 0.29 mmol) in EtOH (80 ml), an aqueous NaOH (0.1 g, 2.5 mmol) solution (20 ml) was added and the mixture was stirred during 48 hours at 70 °C. After cooling to 0 °C, an aqueous 2M HCl solution (40 ml) was added. The precipitate was filtrated and washed with water (3x50 ml), affording the compound 7 as a white solid (0.35 g, 92 % yield).

Mp: 330 °C (decomp.) MALDI TOF:  $m/z$  = 1343.47 [M+Na]<sup>+</sup> (calculated 1344.83); Elemental Analysis: % *calculated*: C, 65.42%; H, 5.49%; % *found*: C, 65.38%; H, 5.52%; <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 300 MHz, 25 °C):  $\delta$ (ppm) = 0.98 (36H, s, tBu); 4.07 (8H, s, -SCH<sub>2</sub>-); 7.37 (8H, d, Ar-H); 7.65 (8H, s, Ar-H); 7.81 (8H, d, Ar-H); <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 125 MHz, 25 °C):  $\delta$ (ppm) = 30.1; 33.9; 129.0; 129.2; 134.9; 140.3; 142.7; 142.7; 167.1.

#### Synthesis of the tetracarboxyl derivative 8 in 1,3-A conformation

Compound 8 was prepared following a reported procedure (yield 94%).<sup>23</sup>

<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 300 MHz, 25 °C):  $\delta$ (ppm) = 5.20 (8H, s, -OCH<sub>2</sub>-); 6.44 (4H, t, Ar-H); 6.98 (8H, d, Ar-H); 7.15 (8H, d, Ar-H); 7.95 (8H, d, Ar-H).

#### Crystallisation conditions

**4:** In a crystallization tube (length 20 cm, diameter 4 mm), a DMF solution (0.5 ml) containing the compound 4 (3 mg, 0.003 mmol) was carefully added on a water layer (0.5 ml). Upon slow diffusion at the room temperature, colourless crystals, suitable for X-ray analysis, were obtained after several days. Formula C<sub>48</sub>H<sub>56</sub>O<sub>8</sub>S<sub>8</sub>. 4DMF (see ESI, table S4).

**5:** In a crystallization tube (length 20 cm, diameter 4 mm), a DMF solution (0.5 ml) containing the compound 5 (5 mg, 0.0044 mmol) was carefully added on a water layer (0.5 ml). Upon slow diffusion at the room temperature, colourless crystals, suitable for X-ray analysis, were obtained after several days. Formula C<sub>56</sub>H<sub>72</sub>O<sub>8</sub>S<sub>8</sub> (see ESI, table S4).

**6:** The colourless crystals suitable for X-ray diffraction were obtained by slow evaporation of a CHCl<sub>3</sub>-MeOH mixture (5 ml, 5/1) containing the compound 6 (3 mg, 0.0027 mmol). Formula C<sub>56</sub>H<sub>72</sub>O<sub>12</sub>S<sub>4</sub>. CHCl<sub>3</sub> (see ESI, table S4).

**7:** In a crystallization tube (length 20 cm, diameter 4 mm), a DMF-CH<sub>2</sub>Cl<sub>2</sub> mixture (0.5 ml, 3/2) containing the compound 7

(5 mg, 0.0037 mmol) was carefully layered by DMF (0.1 ml) before a H<sub>2</sub>O-CH<sub>3</sub>CN mixture (0.5 ml) was added. Upon slow diffusion at the room temperature, colourless crystals, suitable for X-ray analysis, were obtained after several days. Formula: (C<sub>72</sub>H<sub>72</sub>O<sub>8</sub>S<sub>8</sub>)<sub>2</sub> · CH<sub>2</sub>Cl<sub>2</sub> · 2H<sub>2</sub>O (see ESI, table S4).

[(4<sup>3-</sup>)<sub>2</sub>-(A<sup>2+</sup>)<sub>3</sub>]: In a crystallization tube (length 20 cm, diameter 4 mm), a DMF solution (2 ml) of **4** (3 mg, 0.003 mmol) and 0.24 ml of 0.05 M solution of NEt<sub>3</sub> (0.012 mmol) in DMF was carefully layered by a DMF/MeOH mixture (1 ml, 1/1). Then a MeOH-H<sub>2</sub>O solution (2 ml, 4/1) containing (A<sup>2+</sup>, 2TsO<sup>-</sup>) (3.2 mg, 0.006 mmol) was added. Upon slow diffusion at the room temperature, colourless crystals suitable for X-ray analysis were obtained after several days. Formula: [(4)<sub>2</sub>(A)<sub>3</sub>].4 DMF. H<sub>2</sub>O (see ESI, table S5) Anal. Calcd.: C, 56.61%; H, 6.75%; N, 7.65%; Found: C, 56.81%; H, 6.69%; N, 7.72%.

[5<sup>2-</sup>-A<sup>2+</sup>]: In a crystallization tube (length 20 cm, diameter 4 mm), a DMF solution (2 ml) containing **5** (3 mg, 0.0026 mmol) and 0.22 ml of 0.05 M solution of NEt<sub>3</sub> (0.01 mmol) in DMF was carefully layered by a DMF/MeOH mixture (1 ml, 1/1). Then a MeOH-H<sub>2</sub>O solution (2 ml, 4/1) containing (A<sup>2+</sup>, 2TsO<sup>-</sup>) (2.8 mg, 0.0052 mmol) was added. Upon slow diffusion at the room temperature, colourless crystals suitable for X-ray analysis were obtained after one week. Formula: [5-A]. 0.5 CH<sub>3</sub>OH · 0.5 H<sub>2</sub>O (see ESI, table S5). Anal. Calcd.: C, 59.12%; H, 7.09%; N, 4.15%; Found: C, 59.35%; H, 6.92%; N, 4.21%.

[7<sup>4-</sup>-(A<sup>2+</sup>)<sub>2</sub>]: In a crystallization tube (length 20 cm, diameter 4 mm), a DMF solution (2 ml) containing the compound **7** (3 mg, 0.0023 mmol) and 0.18 ml of 0.05 M solution of NEt<sub>3</sub> (0.0092 mmol) in DMF was carefully layered by DMF/MeOH mixture (1 ml, 1/1). Then a MeOH-H<sub>2</sub>O solution (2 ml, 4/1) containing (A<sup>2+</sup>, 2TsO<sup>-</sup>) (2.4 mg, 0.0046 mmol) was added. Upon slow diffusion at the room temperature, colourless crystals suitable for X-ray analysis were obtained after one week. Formula: [7-(A)<sub>2</sub>]. 2H<sub>2</sub>O (see ESI, table S5). Anal. Calcd.: C, 63.27%; H, 6.46%; N, 6.42%; Found: C, 63.18%; H, 6.56%; N, 6.49%.

[8<sup>4-</sup>-(A<sup>2+</sup>)<sub>2</sub>]: In a crystallization tube (length 20 cm, diameter 4 mm), a DMF solution (2 ml) containing the compound **8** (3 mg, 0.003 mmol) and 0.24 ml of 0.05 M solution of NEt<sub>3</sub> (0.012 mmol) in DMF was carefully layered by DMF/MeOH mixture (1 ml, 1/1). Then a MeOH-H<sub>2</sub>O solution (2 ml, 4/1) containing (A<sup>2+</sup>, 2TsO<sup>-</sup>) (3.2 mg, 0.006 mmol) was added. Upon slow diffusion at the room temperature, colourless crystals suitable for X-ray analysis were obtained after one week. Formula: [8-(A)<sub>2</sub>] (see ESI, table S5) Anal. Calcd.: C, 64.21%; H, 5.39%; N, 7.88%; Found: C, 64.24%; H, 5.45%; N, 7.85%.

## Results and discussion

### Synthesis and solid state characterization of the tectons.

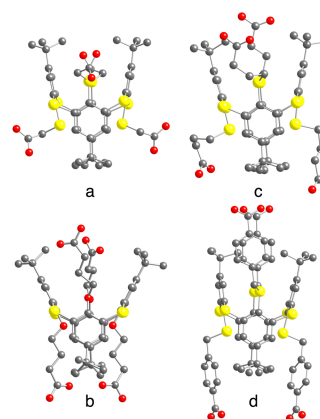
The synthesis of thiacalix[4]arene derivatives **4-8** was achieved using reported procedures (see experimental section). Compounds **4-8** bearing four carboxylic moieties were

obtained in 46-95 % yield upon hydrolysis of the tetraester derivatives **4'-8'** (see ESI, table S1).

In solution, all four compounds **4-8** were characterized by both <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy which showed sharp signals indicating the presence of conformationally blocked 1,3-alternate isomers (see experimental section). Furthermore, among the five new compounds **4-8**, four (compounds **4-7**) have been also characterized in the solid state by X-ray diffraction methods on single crystals obtained upon slow diffusion or slow evaporation techniques (see experimental part and table S4, ESI). As expected, all compounds adopt the 1,3-A conformation (Figure 4). As indicated by the C-O distances (see ESI, table S2), the carboxyl moieties are fully protonated.

Compound **4** crystallises in presence of DMF molecules which are found to be disordered. Crystals of **5** are exclusively composed of the tecton. Tectons **6** crystallises with CHCl<sub>3</sub> solvent molecules whereas compound **7** crystallize with both H<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub> molecules.

For compounds **4-7**, the metrics for the macrocyclic backbone is close to the one observed for the parent compound **1**,<sup>15</sup> **2**<sup>15a</sup> and **3**<sup>27</sup> (see table S2, ESI). In the case of **5**, one of the four tertibutyl groups is found to be disordered.



**Figure 3:** Crystal structures of tectons **4(a)**, **5(b)**, **6(c)** and **7(d)** in a 1,3-alternate conformation. H atoms, disordered tertibutyl groups (**5**) and solvent molecules are not presented for clarity. For bond distances and angles see text and ESI, table S2.

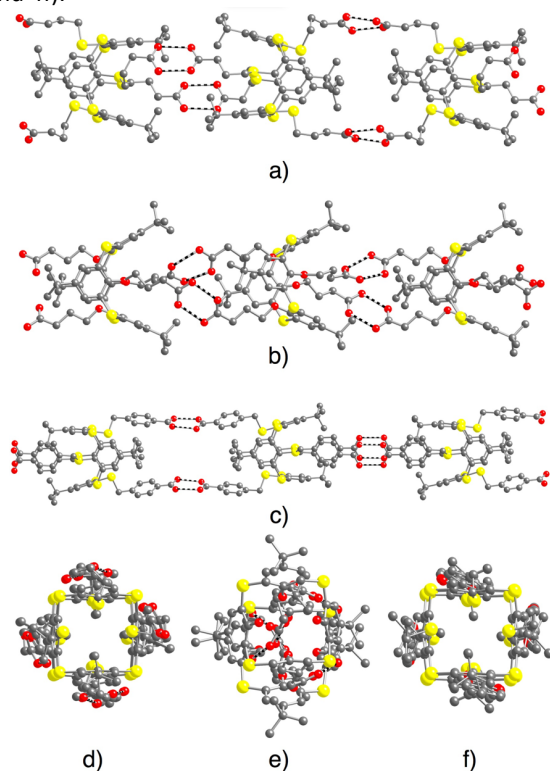
### Formation of extended 1D tubular architectures by self-complementary tectons **4-8**.

Owing to the propensity of carboxylic acids to form a H-bonded dimeric complex (Fig. 2b) and due to the 1,3-A conformation adopted by the tetracarboxyl compounds **4-8**, the latter might behave as self-complementary tectons and self-assemble into 1D H-bonded tubular networks (Fig. 2a).

In the case of **4**, the presence of disordered DMF molecules interacting with the carboxyl groups (O-O distances of 2.552(4) 2.806(7) Å) prevents the formation of dimeric H-bonded motives (Fig. 2b) and consequently, the generation of the extended 1D architecture. In this case, the isolated species is observed in the crystals.

For tectons **5-7**, the tubular arrangement was observed. All three self-complementary tectons display the dimeric recognition pattern (Fig. 2b) and self-assemble into analogous 1D H-bonded networks (Fig. 2a) with O-O bond distance in the

2.579(4) - 2.686(5) Å range (Fig. 4) (see ESI, table S2). Whereas tubular architectures formed by tectons **5** (Fig. 4a and 4d) and **7** (Fig. 4c and 4f) are linear, for tecton **6** (Fig. 4b and 4e) a slightly *zig-zag* type arrangement is observed. Consequently, the diameter of the tubular networks formed by **5** and **7** of ca 5 Å, is substantially larger than the one observed for **6** (Fig. 4d, 4e and 4f).

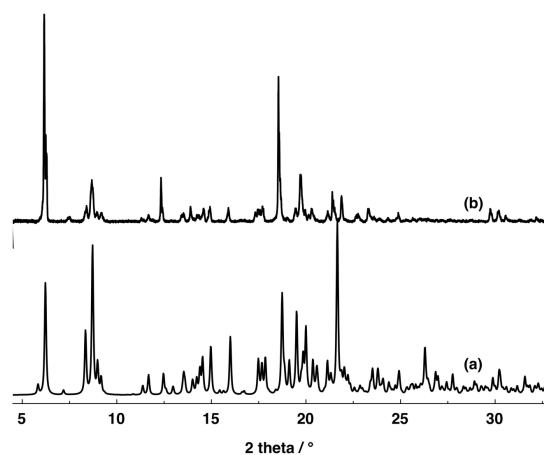


**Figure 4:** Solid state structures of 1D tubular H bonded networks formed by self-complementary tectons **5-7**. Views along the 1D network (a-c respectively) and perpendicular views (d-f respectively). H atoms, disordered *tert*butyl groups (in the case of tecton **5**) and solvent molecules are not presented for clarity. For bond distances and angles see text and ESI, table S2.

For all three cases, the 1D tubular architectures are packed in a parallel fashion.

For tecton **6**, no specific interactions between  $\text{CHCl}_3$  solvent molecules and the network are found. For **7**, however, whereas no interactions between  $\text{CH}_2\text{Cl}_2$  solvent molecules and the network could be spotted, the water molecules do form H-bonds with the carboxylic moieties of the tecton (O-O distance of 3.197(6) Å).

Owing to the instability of crystals of **4**, **5** and **7** outside the crystallization mother liquor, no PXRD powder patterns could be recorded on the corresponding microcrystalline powder. In marked contrast, the microcrystalline powder of **6** was found to be stable and thus it could be investigated by PXRD. The study revealed a good match between the simulated and observed patterns (Fig. 5).



**Figure 5:** Simulated (a) and observed (b) PXRD powder patterns for compound **6**. Discrepancies in peak intensity are due to preferential orientation of the microcrystalline powder.

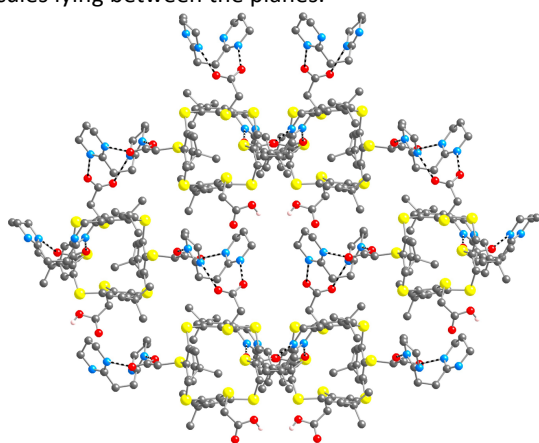
#### Formation of extended networks by combinations of deprotonated compounds **4-8** and the dicationic H-bond donor tecton $\mathbf{A}^{2+}$ .

As stated in the introduction, the dicationic organic tecton  $\mathbf{A}^{2+}$  (Fig. 1) is well suited to recognize two carboxylate moieties, through a dihapto mode of interaction (Fig. 2c). In other terms, tecton  $\mathbf{A}^{2+}$  may be regarded as a molecular staple interconnecting two consecutive carboxylate groups by charge assisted H-bonds. This particular mode of interaction may be considered as a structural node of extended H-bonded networks (Fig. 2a) resulting from mutual bridging between deprotonated anionic tectons **4-8** bearing divergently oriented carboxylate moieties as H-bond acceptors and the H-bond donor cationic tecton  $\mathbf{A}^{2+}$ .

The role played by the spacer connecting the four carboxylic acid moieties to the calixarene backbone in compounds **4-8** was systematically investigated. Furthermore, combinations of their deprotonated analogues, generated using 4 eq. of  $\text{NEt}_3$ , as base, with tecton  $\mathbf{A}^{2+}$  (2 eq.) were also studied (see experimental section). Among several attempts, the following crystalline materials  $[(\mathbf{4}^{3-})_2-(\mathbf{A}^{2+})_3]$ ,  $[\mathbf{5}^{2-}-\mathbf{A}^{2+}]$ ,  $[(\mathbf{7}^{4-})-(\mathbf{A}^{2+})_2]$  and  $[\mathbf{8}^{4-}-(\mathbf{A}^{2+})_2]$  were obtained and analysed by X-ray diffraction on single crystals (see table S5, ESI).

For the combination of **4** with  $\mathbf{A}^{2+}$  in presence of 4 eq. of  $\text{NEt}_3$ , probably because of the short nature of the spacer ( $-\text{CH}_2-$ ) and the presence of *tert*butyl groups, the expected tubular architecture (Fig. 2a) was not observed in the obtained crystals under the crystallization conditions used (see experimental section). Indeed, instead of the projected 1/2 stoichiometry  $[(\mathbf{4}^{4-})-(\mathbf{A}^{2+})_2]$ , the calixarene derivative was partially deprotonated and found to be in its trianionic form. This was substantiated by C-O distances ranging from 1.187(9) to 1.291(8) Å (see table S3 in ESI). In the crystal, a 2/3 stoichiometry between the trianionic compound  $\mathbf{4}^{3-}$  and the dicationic tecton  $\mathbf{A}^{2+}$ , leading to  $[(\mathbf{4}^{3-})_2-(\mathbf{A}^{2+})_3]$ , is observed. The metrics observed for  $\mathbf{4}^{3-}$  is close to the one observed for **4** and the structural parameters observed for  $\mathbf{A}^{2+}$  are close to those already reported.<sup>29</sup>

$[(4^{3-})_2-(A^{2+})_3]$  crystallises in the presence of DMF and water solvent molecules. Interestingly, the interaction between all three carboxylate moieties of  $4^3$  and the dicationic tecton  $A^{2+}$ , as expected from the design of  $A^{2+}$ , takes place through a dihapto mode of H-bonding with N...O distances in the range of 2.669(10) and 2.818(10) Å (see ESI, table S3). Owing to the 3/2 anion/cation ratio, the overall architecture is a deformed honeycomb 2D H-bonded network in the xOy plane (Fig. 6). The four DMF and the H<sub>2</sub>O molecules interact with each other and with the H-bonded network. The DMF molecule is H-bonded with the water molecule with a O...O distance of 2.786(15) Å. Furthermore, the water molecule interacts with a carboxylate group (O...O distance of 2.784(22) Å). Consecutive 2D H-bonded planes are packed along the *c* axis with solvent molecules lying between the planes.



**Figure 6:** Solid state structures of the 2D honeycomb type H bonded  $[(4^{3-})_2-(A^{2+})_3]$  network formed by complementary tectons  $4^3$  and  $A^{2+}$ . H atoms, DMF and water solvent molecules are not presented for clarity. For bond distances and angles see text and ESI, table S3.

Owing to the decomposition of crystals of  $[(4^{3-})_2-(A^{2+})_3]$  in air, no PXRD measurements could be performed.

For the combination of **5** with  $A^{2+}$  in presence of 4 eq. of NEt<sub>3</sub>, again the formation of the tubular architecture (Fig. 2a) was not observed under the crystallization conditions used (see experimental section). The calixarene based tecton was in its dianionic state ( $5^{2-}$ ) resulting from the partial deprotonation of two out of the four carboxylic acid moieties. This was reflected by C-O distances ranging from 1.204(9) to 1.316(8) Å (see ESI, table S3).

Again, the metrics observed for  $5^{2-}$  is close to the one observed for **5** and structural parameters for  $A^{2+}$  are similar to those reported.<sup>29</sup> In the crystal, a 1/1 stoichiometry between the dianionic compound  $5^{2-}$  and the dicationic tecton  $A^{2+}$  leading to  $[5^{2-}-A^{2+}]$  is observed. The latter crystallises in presence of 1 MeOH and 1 H<sub>2</sub>O solvent molecules. The two deprotonated carboxyl groups are in *trans* disposition, thus divergently oriented, and located above and under the main plane of the calix backbone.

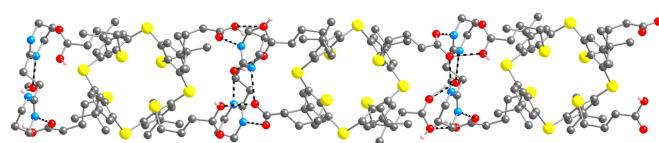
The overall structure is a 1D H-bonded network (Fig. 7). The connectivity pattern between the components (tectons  $5^{2-}$ ,  $A^{2+}$  and H<sub>2</sub>O and MeOH solvent molecules) is rather complex.

In marked contrast with the above mentioned combination of  $4^{3-}$  with  $A^{2+}$ , for  $[5^{2-}-A^{2+}]$ , interactions between carboxylate

groups and the dicationic tecton takes place through a monohapto mode of H-bonding ( $d_{ON}$  of 2.725(8) and 2.815(10) Å) (see ESI, table S3). Further more, the tecton  $A^{2+}$  forms also H-bonds of NHO type with the carboxylic groups of  $5^{2-}$  ( $d_{ON}$  of 2.791(7) Å). The cationic tecton  $A^{2+}$  is also connected MeOH by H bond ( $d_{ON}$  of 2.780(11) Å). Owing to the presence of both carboxylic and carboxylate moieties, several H-bonded patterns are observed between them: carboxylic - carboxylate ( $d_{OO}$  of 2.508(7) Å), carboxylic - carboxylic ( $d_{OO}$  of 2.481(9) Å). Furthermore, MeOH molecule, in addition to the  $A^{2+}$  is also H bonded to a carboxylate group ( $d_{OO}$  of 2.685(10) Å).

The 1D arrangements are packed in a parallel fashion along the *a* and *b* axis. Water molecules are located between 1D networks without specific interactions with them.

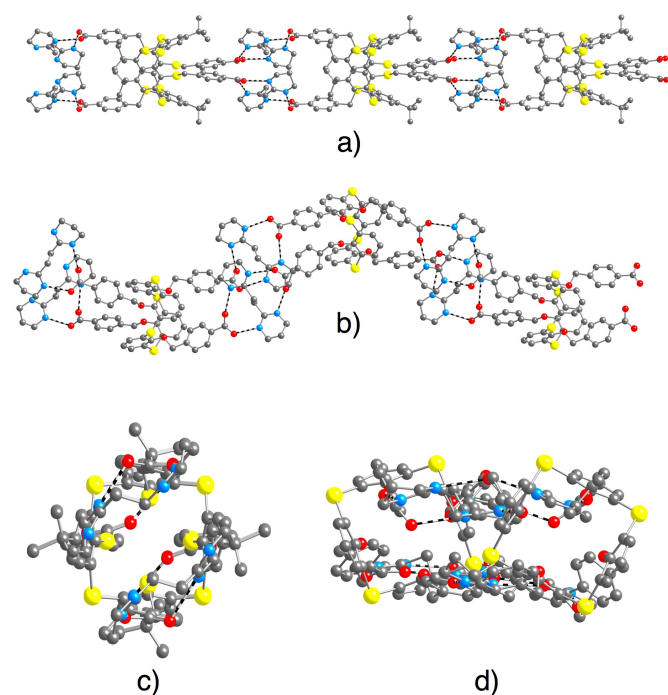
Again, due to the decomposition of crystals of  $[5^{2-}-A^{2+}]$  in air, no PXRD measurements could be performed.



**Figure 7:** Solid state structures of the 1D H bonded  $[5^{2-}-A^{2+}]$  network formed by complementary tectons  $5^{2-}$  and  $A^{2+}$ . H atoms, MeOH and H<sub>2</sub>O solvent molecules are not presented for clarity. For bond distances and angles see the text and ESI, table S3.

The combination of  $A^{2+}$  in presence of 4 eq. of NEt<sub>3</sub>, with either **7** or **8**, afforded crystals which were investigated by X-ray diffraction on single crystals. The structural study revealed that both **7** or **8** are fully deprotonated and behave as tetra anionic tectons ( $7^{4-}$  and  $8^{4-}$ ) (see ESI, table S3). The anion/cation stoichiometry is  $\frac{1}{2}$ , leading to  $[X^{4-}-(A^{2+})_2]$  ( $X = 7$  or **8**). The metrics observed for  $7^{4-}$  and for  $8^{4-}$  is similar to those for **7** and reported for **8**.<sup>27</sup> Structural parameters for the dicationic tecton  $A^{2+}$  within the networks are close to the one reported.<sup>29</sup> For  $[7^{4-}-(A^{2+})_2]$ , the crystal, in addition to the cationic and anionic tectons, contains two water molecule. For the anionic partner  $7^{4-}$ , two out of the four phenyl groups bearing the carboxylate moieties are found to be disordered.

In both cases, as result of the design of the complementary anionic and cationic tectons behaving as H-bond acceptor and donor sites respectively, a dihapto mode of H-bonding with N...O distance in the of 2.625(15) - 2.816(13) Å range is observed (Fig. 8) (see ESI, table S3). Consequently, the mutual interconnection of the anionic tectons  $7^{4-}$  or  $8^{4-}$  and the cationic tecton  $A^{2+}$  leads to the formation of 1D tubular H-bonded networks (Fig. 2a). For  $[7^{4-}-(A^{2+})_2]$ , the 1D network runs along the *b* axis (Fig. 8a and 8c). For  $[8^{4-}-(A^{2+})_2]$ , the 1D network running along the *a* axis is not linear but corrugated (Fig. 8b and 8d).

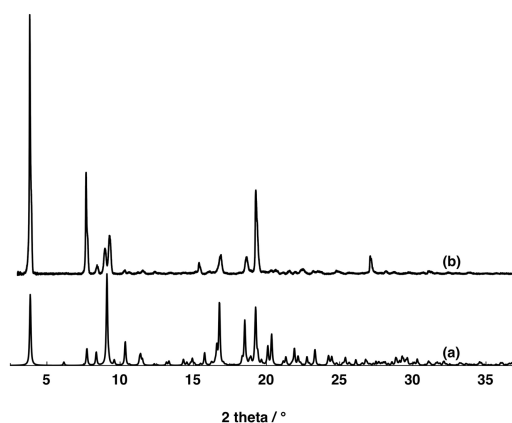


**Figure 8:** Solid state structures of 1D H-bonded networks formed by  $[7^4-(A^{2+})_2]$  (perpendicular (a) and parallel (c) views of the extended arrangement) and by  $[8^4-(A^{2+})_2]$  (perpendicular (b) and parallel (d) views of the extended arrangement). For  $[7^4-(A^{2+})_2]$  disordered Phenyl groups and  $H_2O$  solvent molecules and H atoms are not presented for clarity. For bond distances and angles see the text and ESI, table S3.

The 1D networks are packed in a parallel fashion along the other two space directions ( $a$  and  $c$  for  $[7^4-(A^{2+})_2]$  and  $b$  and  $c$  for  $[8^4-(A^{2+})_2]$ ).

For  $[7^4-(A^{2+})_2]$ , the water molecules are located between the 1D chains and interact with the carboxylate groups of the tecton  $7^4$  through H bonds with O-O distances of 2.138(15), 2.844(14) and 2.914(11) Å (see ESI, table S3).

The PXRD analysis of the microcrystalline powder of  $[7^4-(A^{2+})_2]$  revealed a good match between simulated and experimental diffractograms (Fig. 9). For  $[8^4-(A^{2+})_2]$ , unfortunately due to the instability of crystals in air, no PXRD investigation could be carried out.



**Figure 9:** Simulated (a) and observed (b) PXRD powder patterns for compound  $[7^4-(A^{2+})_2]$ . Discrepancies in peak intensity are due to preferential orientation of the microcrystalline powder.

## Conclusions

The aim of this systematic study was to investigate the formation of tubular 1D H-bonded networks in the crystalline phase. For that purpose, a series of thiacalix[4]arene derivatives blocked in 1,3-alternate conformation and bearing four carboxylic acids has been designed and studied in the solid state. Owing to the presence of divergently oriented carboxylic acid groups, compounds **4-8** may, in principle, behave as self-complementary H-bond donor (OH moiety) and acceptor (C=O group) tectons. Under used crystallization conditions, among the five compounds investigated, only tectons **5-7** afforded crystals which were investigated by X-ray diffraction on single crystals. For all three cases, as expected from their self-complementary nature, 1D H-bonded tubular architectures were obtained (Fig. 2a). These arrangements result from mutual bridging of consecutive tectons through COOH-COOH H-bonded nodes (Fig. 2b).

Upon deprotonation of the self-complementary neutral tectons **4-8** with  $NEt_3$ , *i.e.* transformation of the carboxylic moieties into carboxylates, anionic tectons were generated *in situ*. Their propensity to form H-bonded networks in the presence of the dicationic H-bond donor  $A^{2+}$ , designed to behave as a molecular staple interconnecting two carboxylates moieties (Fig. 2c), was studied. Under used conditions, *i.e.* combinations of compounds **4-8** as tetraacids with 4 eq. of  $NEt_3$  and  $(A^{2+}, 2TsO^-)$ , depending on the nature of the spacer connecting the carboxylate unit to the calix backbone, different deprotonated species are obtained. Indeed, whereas in the case compound **4** the latter was in its  $4^{3-}$ , for compound **5**, the dianionic form  $5^{2-}$  was obtained. The other two compounds **7** and **8** were fully deprotonated in  $X^4$  ( $X=7$  or **8**). The combination of  $4^{3-}$  and  $A^{2+}$ , the network  $[(4^{3-})_2-(A^{2+})_3]$  is a deformed honeycomb 2D H-bonded network (Fig. 6). On the other hand, the combination of  $5^{2-}$  and  $A^{2+}$ , leads to a non tubular 1D H-bonded network  $[5^{2-}-A^{2+}]$  (Fig. 7). Finally, for  $7^4$ , and  $8^4$ , their combinations with  $A^{2+}$  leads to a 1/2 stoichiometry and the formation of the expected (Fig. 2a) 1D tubular H-bonded networks  $[7^4-(A^{2+})_2]$ , and  $[8^4-(A^{2+})_2]$  (Fig. 8).

## Acknowledgements

The Russian Science Foundation (grant N° 15-13-30006), the University of Strasbourg, the International Centre for Frontier Research in Chemistry (icFRC), the Labex CSC (ANR-10-LABX-0026 CSC) within the Investissement d'Avenir program ANR-10-IDEX-0002-02, the Institut Universitaire de France and the CNRS are acknowledged for financial support.

## References

- 1 a) P. De Santis, S. Morosetti, R. Rizzo, *Macromolecules*, 1974, **7**, 52; b) J. D. Lear, Z. R. Wasserman and W. F. DeGrado, *Science*, 1988, **240**, 117; c) M. R. Ghadiri, J. R. Granja, R. A. Milligan, D. E. McRee, N. Khazanovich, *Nature*, 1993, **366**, 324; d) D. H. Lee and M. R. Ghadiri, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. Macnicol and F. Vögtle, Pergamon, vol. 9 (ed. J.-P. Sauvage and M. W. Hosseini), 1996, p. 451.
- 2 a) V. Semetey, D. Rognan, C. Hemmerlin, R. Graff, J.-P. Briand, M. Marraud, G. Guichard, *Angew. Chem. Intl. Ed.*, 2002, **41**, 1893; b) N. Sakai, S. Matile, *Chem. Commun.*, 2003, 2514.
- 3 T. Shimizu, M. Masuda and H. Minamikawa, *Chem. Rev.*, 2005, **105**, 1401.
- 4 C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton and A. White, *Angew. Chem. Intl. Ed.*, 1998, **37**, 920.
- 5 a) O. J. Gelling, F. van Bolhuis and B. L. Feringa, *J. Chem. Soc., Chem. Commun.*, 1991, 917; b) Y. Dai, T. J. Katz and D. A. Nichols, *Angew. Chem., Intl. Ed. Engl.*, 1996, **35**, 2109; c) B. Wu, W.-J. Zhang, S.-Y. Yu and X.-T. Wu, *Chem. Commun.*, 1997, 1795.
- 6 M. J. Hannon, C. L. Painting and W. Errington, *Chem. Commun.*, 1997, 1805.
- 7 M. Løi, M. W. Hosseini, A. Jouaiti, A. De Cian and J. Fischer, *Eur. J. Inorg. Chem.*, 1999, 1981.
- 8 W. L. Leong and J. J. Vittal, *Chem. Rev.*, 2011, **111**, 688.
- 9 a) J.-M. Lehn, J. Malthête and A.-M. Levelut, *J. Chem. Soc., Chem. Commun.*, 1985, 1794; b) C. Mertesdorf and H. Ringsdorf, *Mol. Cryst. Liq. Cryst.*, 1989, **5**, 1757; c) V. Percec, G. Johansson, J. A. Heck, G. Ungar and S. V. Betty, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1411; d) T. Komori and S. Shinkai, *Chem. Lett.*, 1993, 1455.
- 10 U. F. Kragten, M. F. M. Roks and R. J. M. Nolte, *J. Chem. Soc., Chem. Commun.*, 1985, 1275.
- 11 a) S. Mann *Nature*, 1993, **365**, 499; b) M. W. Hosseini, *Acc. Chem. Res.*, 2005, **38**, 313.
- 12 a) M. Simard, D. Su, and J. D. Wuest *J. Am. Chem. Soc.*, 1991, **113**, 4696; b) M. W. Hosseini *CrystEngComm.*, 2004, **6**, 318; c) M. W. Hosseini *Chem. Commun.*, 2005, 582.
- 13 a) C. D. Gutsche "Calixarenes revisited", Monographs in Supramolecular Chemistry, Ed. J. F. Stoddart, R.S.C., London, 1998; b) "Calixarenes 2001", Eds J. Vicens, Z. Asfari, J. M. Harrowfield, V. Böhmer, Kluwer, 2001.
- 14 a) H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama, S. Miyano, *Tetrahedron Lett.*, 1997, **38**, 3971; b) T. Sone, Y. Ohba, K. Moriya, H. Kumada, K. Ito, *Tetrahedron* 1997, **53**, 10689.
- 15 a) H. Akdas, L. Bringel, E. Graf, M. W. Hosseini, G. Mislin, J. Pansanel, A. De Cian, J. Fischer *Tetrahedron Lett.*, 1998, **39**, 2311; b) M. W. Hosseini, ACS Series, "Calixarene Molecules for Separation", Eds. G. J. Lumetta, R. D. Rogers, A. S. Gopalan, 2000, **557**, 296.
- 16 G. Mislin, E. Graf, M. W. Hosseini, A. De cian, N. Kyritsakas, J. Fischer, *Chem. Commun.*, 1998, 2545; b) G. Laugel, E. Graf, M. W. Hosseini, J.-M. Planeix, N. Kyritsakas, *New J. Chem.*, 2006, **30**, 1340.
- 17 C. Klein, E. Graf, M. W. Hosseini, A. De Cian, J. Fischer, *Chem. Commun.*, 2000, 239.
- 18 a) M. W. Hosseini, R. Ruppert, P. Schaeffer, A. De Cian, N. Kyritsakas, J. Fischer, *Chem. Commun.* 1994, 2135; b) O. Félix, M. W. Hosseini, A. De Cian, J. Fischer, *New. J. Chem.*, 1998, **22**, 1389; c) O. Félix, M. W. Hosseini, A. De Cian and J. Fischer, *New J. Chem.*, 1998, **22**, 1389.
- 19 M. W. Hosseini, *Coord. Chem. Rev.* 2003, **240**, 157.
- 20 a) K. T. Holman, S. M. Martin, D. P. Parker and M. D. Ward *J. Am. Chem. Soc.* 2001, **123**, 4421; b) K. T. Holman, A. M. Pivovar and M. D. Ward *Science* 2001, **294**, 1907; c) S. A. Dalrymple and G. K. H. Shimizu, *J. Am. Chem. Soc.*, 2007, **129**, 12114.
- 21 K.-M. Park, E. Lee, C. S. Park, and S. S. Lee *Inorg. Chem.*, 2011, **50**, 12085.
- 22 H. Akdas, W. Jaunky, E. Graf, M. W. Hosseini, A. De Cian and J. Fischer, *Tetrahedron Lett.*, 2000, **41**, 3601.
- 23 a) X. Li, S. L. Gong, W. P. Yang, Y. Y. Chen and X. G. Meng, *Tetrahedron*, 2008, **64**, 6230; b) Y. Li, W. Yang, Y. Chen and S. Gong *CrystEngComm*, 2011, **13**, 259; c) Y. Li, W. Yang, R. Guo, Y. Chen and S. Gong *CrystEngComm*, 2012, **14**, 1455.
- 24 E. Lee, H. Ju, S. Sung Lee, and K.-M. Park *Cryst. Growth Des.* 2013, **13**, 992.
- 25 G. M. Sheldrick: *Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.
- 26 H. Akdas, E. Graf, M. W. Hosseini, A. De Cian and N. Kyritsakas-Gruber, *C. R. Chim.*, 2003, **6**, 565.
- 27 P. Rao, M. W. Hosseini, A. De Cian and J. Fischer, *Chem. Commun.*, 1999, 2169.
- 28 D. Appelhans, V. Stastny, H. Komber, D. Voigt, B. Voit, P. Lhotak, I. Stibor, *Tetrahedron Letters*, 2004, **45**, 7145.
- 29 G. Brand, M.; W. Hosseini, R. Ruppert, A. De Cian, J. Fischer, N. Kyritsakas, *New J. Chem.*, 1995, **19**, 9.

Journal Name

ARTICLE

## Graphical Abstract

Thiacalix[4]arene derivatives in *1,3*-alternate conformation bearing four carboxylic acids behaves as self-complementary tectons and lead to the formation of tubular 1D H-bonded networks. Combinations of their deprotonated analogues, behaving as anionic H-bond acceptor tectons, with a dicationic H-bond donor tecton, behaving as a molecular staple, also lead to the formation of 1- and 2-D H-bonded networks.

