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

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A series of thiacalix[4]arene derivatives blocked in the 1,3-alternate conformation and bearing four carboxylic acids have 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 carboxylic acid moieties into carboxylates, anionic tectons are generated. Due to their propensity to form H-bonded networks in the presence of a dicationic H-bond donor tecton of the cyclic bis-amidinium 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.

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Introduction

Tubular architectures^{1–3} are of interest as they form channels that may lead to the transport of neutral or charged species. Such entities 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.^{4–7} Tubular architectures may also be helical assemblies.⁸ Organisation of cyclic units into tubular architectures using liquid crystalline phases⁹ or polymeric backbones¹⁰ has been also reported.

Following the concepts developed in *molecular tectonics*¹¹ for the design and formation by self-assembly processes of infinite molecular networks in the crystalline phase, we are interested in tubular architectures based on H-bonds between macrocyclic entities behaving as tectons.¹² Owing to their cyclic nature, calix[4]arene¹³ and thiacalix[4]arene 1–3^{14,15} (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 up to 4 interaction sites to be positioned 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 derivatives¹⁶ or on [1]-metacyclophane in the 1,3-alternate fixed conformation, an analogous backbone to calix[4]arene.¹⁷

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 combinations of their deprotonated derivatives as anionic tectons with a dicationic tecton A²⁺, 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 the 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 in their ability to form tubular H-bonded networks (Fig. 2a) based on the formation of H-bonded dimeric nodes (Fig. 2b) between carboxylic acids 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

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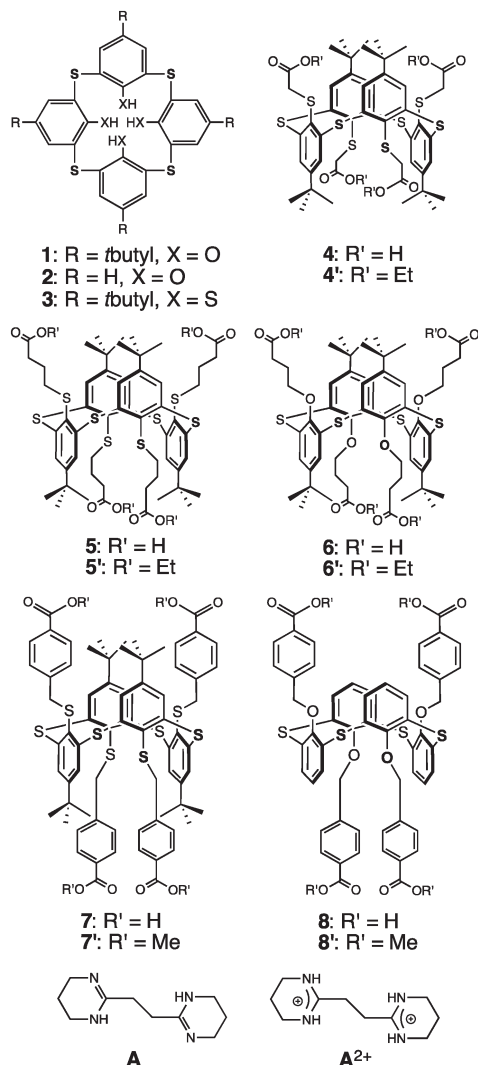


Fig. 1 Tetrathia- and tetrathiathetramercaptocalix[4]arene precursors **1**, **2** and **3**, and tetrakis carboxyl derivatives **4–8** in the 1,3-A conformation.

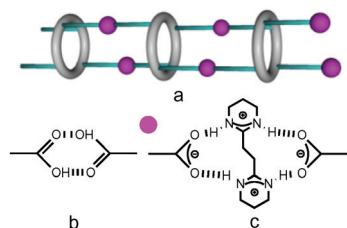


Fig. 2 Recognition patterns through H bonds between tectons: a) schematic view of tetra-substituted macrocyclic species leading to 1D tubular systems, b) a dimeric node involving two carboxylic acid moieties and c) dihapto mode between carboxylate and amidinium moieties, behaving as molecular staples.

H-bonded networks. Indeed these anionic tectons bearing carboxylate moieties may be combined with the dicationic organic tecton **A²⁺** (Fig. 1) designed to bridge two carboxylates, one on each of its faces, and thus behave as a molecular sta-

ple (Fig. 2c) connecting consecutive carboxylate-bearing components.^{18,19} Depending on the degree of deprotonation 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.²⁰

Although few tetra-acid derivatives based on calix[4]arene²¹ (CA) and thiacalix[4]arene²² (TCA) backbones have been reported, to the best of our knowledge, no example of tetramercaptocalixarene (TMTCA) **3** (Fig. 1) based derivatives 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.²³ An interesting investigation dealing with the photoisomerization of a H-bonded network based on a *p*-*tert*-butylthiacalix[4]arene derivative bearing carboxylic acid moieties combined with bipyridylethene has been also reported.²⁴

Experimental

Characterization techniques

¹H-NMR and ¹³C-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 Micro-TOF spectrometer.

Melting points were measured in capillary tubes 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 Université de Strasbourg.

Single-crystal studies

Data were collected at 173(2) K on a Bruker APEX8 CCD diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) 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).²⁵ CCDC: 1504484–1504490 and 1505426 (see Tables S4 and S5, ESI[†]).

Powder X-ray diffraction

Powder diffraction (PXRD) diagrams were collected on a Bruker D8 diffractometer using monochromatic Cu-K α radiation in a scanning range between 3.8 and 40° using a scan step size of 2° mn⁻¹.

As already demonstrated and currently admitted, for all the compounds, discrepancies in intensity between the



observed and simulated patterns are due to the preferential orientations of the microcrystalline powders.

Synthesis

General: all reagents were purchased from commercial sources and used without further purification. The synthesis of 1,^{14a} 2,²⁶ 3²⁷ and 8²⁸ has been previously reported. The synthesis of 4–7 was adapted from previously reported procedures.^{22,29}

The bisamidinium compound A²⁺, used as its ditosylate salt (A²⁺, 2TsO⁻), has been prepared using an already reported procedure.^{18b}

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 Cs₂CO₃ (2.47 g, 7.6 mmol) in dry and degassed acetone (60 ml) was refluxed for 2 hours before BrCH₂COOEt (0.85 ml, 7.6 mmol) was added. The reaction mixture was refluxed for 50 hours under argon. After cooling, the solid was filtered and the filtrate was evaporated. The residue was treated with MeOH (50 ml) affording the desired compound 4' (0.2 g, 46% yield) in the 1,3-A conformation as a white powder.

Mp: 310 °C (decomp.); MALDI TOF: *m/z* = 1129.3 [M]⁺ (calculated 1129.69); elemental analysis: % *calculated*: C, 59.54%; H, 6.42%; % *found*: C, 59.45%; H, 6.48%; ¹H-NMR (CDCl₃, 300 MHz, 25 °C): δ(ppm) = 1.18 (12H, t, -CH₃), 1.26 (36H, s, *t*Bu); 3.61 (8H, s, ArSCH₂), 4.12 (8H, q, -C(O)CH₂-), 7.76 (8H, s, Ar-H); ¹³C-NMR (CDCl₃, 125 MHz, 25 °C): δ(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 Cs₂CO₃ (4.12 g, 12.6 mmol) in dry and degassed acetone (60 ml) was refluxed for 2 hours before Br(CH₂)₃COOEt (1.8 ml, 12.6 mmol) was added. The reaction mixture was refluxed for 50 hours under argon. After cooling, the mixture was filtered and the solvent was evaporated. The residue was treated with 2 M HCl (40 ml) and extracted with CHCl₃ (2 × 50 ml). The organic layers were combined, washed with water (100 ml) and dried over MgSO₄. After filtration, the organic solvent was evaporated and addition of MeOH (100 ml) to the oily residue afforded compound 5' (0.43 g, 60% yield) as a white precipitate.

Mp: 320 °C (decomp.) MALDI TOF: *m/z*: 1241.5 [M]⁺ (calculated 1241.88); elemental analysis: % *calculated*: C, 61.90%; H, 7.14%; % *found*: C, 61.68%; H, 7.10%; ¹H-NMR (CDCl₃, 400 MHz, 25 °C): δ(ppm) = 1.24 (12H, t, -CH₃), 1.26 (36H, s, *t*Bu); 1.75 (8H, p, -CH₂CH₂CH₂-); 2.56 (8H, t, -CH₂C(O)-); 2.93 (8H, t, -SCH₂-); 4.14 (8H, q, -C(O)O-CH₂-); 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), Br(CH₂)₃C(O)OEt (6.55 g, 33.3 mmol) and Cs₂CO₃ (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 under vacuum. The residue was treated with MeOH (50 ml) affording the desired compound 6' (2.25 g, 46% yield) in the 1,3-A conformation as a white powder.

Mp: 315–317 °C; MALDI TOF: *m/z*: 1176,85 [M]⁺ (calculated 1177,64); elemental analysis: % *calculated*: C, 65.28%; H, 7.53%; % *found*: C, 65.33%; H, 7.51%; ¹H-NMR (CDCl₃, 600 MHz, 25 °C): δ(ppm) = 1.25 (s, 36H, *t*Bu), 1.25 (t, 12H, -CH₃), 1.41 (m, 8H, -CH₂CH₂CH₂-), 2.11 (t, 8H, -CH₂C(O)-), 3.91 (t, 12H, -O-CH₂-), 4.09 (q, 8H, -OCH₂CH₃), 7.36 (s, 8H, Ar-H); ¹³C-NMR (CDCl₃, 125 MHz, 25 °C): δ 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), Cs₂CO₃ (1.3 g, 4 mmol) and methyl-(4-bromomethyl)benzoate (2.05 g, 9 mmol) in dry and degassed DMF (60 ml) was stirred for 40 hours at 80 °C. After cooling, the solvent was evaporated under reduced pressure. The residue was treated with 2 M HCl (40 ml) and extracted with CH₂Cl₂ (2 × 50 ml). The organic layers were combined and dried over MgSO₄. After filtration, the solvent was evaporated. The residue was treated with MeOH (200 ml) affording the desired compound 7' (0.43 g, 60% yield) in the 1,3-A conformation as a white powder.

Mp: 300 °C (decomp.) MALDI TOF: *m/z*: 1377,15 [M]⁺ (calculated 1377,95); elemental analysis: % *calculated*: C, 66.25%; H, 5.85%; % *found*: C, 66.18%; H, 5.86%; ¹H-NMR (CDCl₃, 300 MHz, 25 °C): δ(ppm) = 1.06 (36H, s, *t*Bu); 3.92 (12H, s, -C(O)O-CH₃); 4.05 (8H, s, -SCH₂-); 7.28 (8H, d, Ar-H); 7.61 (8H, s, Ar-H); 7.90 (8H, d, Ar-H); ¹³C-NMR (CDCl₃, 125 MHz, 25 °C): δ(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 a reported procedure (63% yield).²³

¹H-NMR (CDCl₃, 300 MHz, 25 °C): δ(ppm) = 4.05 (12H, s, -C(O)O-CH₃); 5.29 (8H, s, -OCH₂-); 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-H₂O mixture (5/1100 ml) and refluxed for 48 hours. After cooling, an aqueous 2 M HCl aqueous solution (20 ml) was added. The precipitate was filtered 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]⁺ (calculated 1040.47); elemental analysis: % *calculated*: C, 56.66%; H, 5.55%; % *found*: C, 56.40%; H, 5.50%; ¹H-NMR (DMSO-*d*₆, 300 MHz, 25 °C): δ(ppm) = 1.21 (s, 36H, *t*Bu); 3.56 (s, 8H, ArSCH₂), 7.76 (s, 8H, Ar-H); ¹³C-NMR (DMSO-*d*₆, 125 MHz, 25 °C): δ(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 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 for 48 hours. After cooling to 0 °C, an aqueous 2 M HCl solution (40 ml) was added. The precipitate was filtered and washed with water (3 × 50 ml) affording compound 5 as a white solid (0.43 g, 95% yield).



Mp: 315 °C (decomp.) MALDI TOF: $m/z = 1167.31 [M + K]^+$ (calculated 1168.76); elemental analysis: % *calculated*: C, 59.54%; H, 6.42%; % *found*: C, 59.40%; H, 6.46%; $^1\text{H-NMR}$ (DMSO- d_6 , 300 MHz, 25 °C): $\delta(\text{ppm}) = 1,23$ (36H, s, *t*Bu); 1,60 (8H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2-$); 2,46 (8H, t, $-\text{SCH}_2-$); 2,88 (8H, t, $-\text{CH}_2-\text{C}(\text{O})-$); 7,71 (8H, s, Ar-*H*); $^{13}\text{C-NMR}$ (DMSO- d_6 , 125 MHz, 25 °C): $\delta(\text{ppm}) = 24.2$; 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 for 3 hours. The reaction mixture was cooled in an ice-water bath before 2 M 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: $m/z = 1087.41 [M + \text{Na}]^+$ (calculated 1088.41); elemental analysis: % *calculated*: C, 61.09%; H, 6.90%; % *found*: C, 61.25%; H, 6.83%; $^1\text{H-NMR}$ (DMSO- d_6 , 300 MHz, 25 °C): $\delta(\text{ppm}) = 1,21$ (36H, s, *t*Bu); 1,21 (8H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2-$); 1,99 (8H, t, $-\text{CH}_2-\text{C}(\text{O})-$); 3,80 (8H, t, $-\text{OCH}_2-$); 7,34 (8H, s, Ar-*H*); 11,92 (4H, s, $-\text{COOH}$); $^{13}\text{C-NMR}$ (DMSO- d_6 , 125 MHz, 25 °C): $\delta(\text{ppm}) = 23.7$; 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 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 for 48 hours at 70 °C. After cooling to 0 °C, an aqueous 2 M HCl solution (40 ml) was added. The precipitate was filtered and washed with water (3 × 50 ml), affording compound 7 as a white solid (0.35 g, 92% yield).

Mp: 330 °C (decomp.) MALDI TOF: $m/z = 1343.47 [M + \text{Na}]^+$ (calculated 1344.83); elemental analysis: % *calculated*: C, 65.42%; H, 5.49%; % *found*: C, 65.38%; H, 5.52%; $^1\text{H-NMR}$ (DMSO- d_6 , 300 MHz, 25 °C): $\delta(\text{ppm}) = 0.98$ (36H, s, *t*Bu); 4,07 (8H, s, $-\text{SCH}_2-$); 7,37 (8H, d, Ar-*H*); 7,65 (8H, s, Ar-*H*); 7,81 (8H, d, Ar-*H*); $^{13}\text{C-NMR}$ (DMSO- d_6 , 125 MHz, 25 °C): $\delta(\text{ppm}) = 30.1$; 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%).²³

$^1\text{H-NMR}$ (DMSO- d_6 , 300 MHz, 25 °C): $\delta(\text{ppm}) = 5.20$ (8H, s, $-\text{OCH}_2-$); 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 compound 4 (3 mg, 0.003 mmol) was carefully added onto a water layer (0.5 ml). Upon slow diffusion at room temperature, colourless crystals, suitable for X-ray analysis, were obtained after several days. Formula: $\text{C}_{48}\text{H}_{56}\text{O}_8\text{S}_8 \cdot 4\text{DMF}$ (see ESI,† Table S4).

5. In a crystallization tube (length 20 cm, diameter 4 mm), a DMF solution (0.5 ml) containing compound 5 (5 mg, 0.0044 mmol) was carefully added onto a water layer (0.5 ml). Upon slow diffusion at room temperature, colourless crystals,

suitable for X-ray analysis, were obtained after several days. Formula: $\text{C}_{56}\text{H}_{72}\text{O}_8\text{S}_8$ (see ESI,† Table S4).

6. Colourless crystals suitable for X-ray diffraction were obtained by slow evaporation of a CHCl_3 -MeOH mixture (5 ml, 5/1) containing compound 6 (3 mg, 0.0027 mmol). Formula: $\text{C}_{56}\text{H}_{72}\text{O}_{12}\text{S}_4 \cdot \text{CHCl}_3$ (see ESI,† Table S4).

7. In a crystallization tube (length 20 cm, diameter 4 mm), a DMF- CH_2Cl_2 mixture (0.5 ml, 3/2) containing compound 7 (5 mg, 0.0037 mmol) was carefully layered with DMF (0.1 ml) before a H_2O - CH_3CN mixture (0.5 ml) was added. Upon slow diffusion at room temperature, colourless crystals, suitable for X-ray analysis, were obtained after several days. Formula: $(\text{C}_{72}\text{H}_{72}\text{O}_8\text{S}_8)_2 \cdot \text{CH}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (see ESI,† Table S4).

$[(4^{3-})_2 \cdot (A^{2+})_3]$. 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_3 (0.012 mmol) in DMF were carefully layered with a DMF/MeOH mixture (1 ml, 1/1). Then a MeOH- H_2O solution (2 ml, 4/1) containing $(A^{2+}, 2\text{TsO}^-)$ (3.2 mg, 0.006 mmol) was added. Upon slow diffusion at room temperature, colourless crystals suitable for X-ray analysis were obtained after several days. Formula: $[(4)_2(A)_3] \cdot 4 \text{DMF} \cdot \text{H}_2\text{O}$ (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%.

$[5^{2-} \cdot A^{2+}]$. 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_3 (0.012 mmol) in DMF were carefully layered with a DMF/MeOH mixture (1 ml, 1/1). Then a MeOH- H_2O solution (2 ml, 4/1) containing $(A^{2+}, 2\text{TsO}^-)$ (2.8 mg, 0.0052 mmol) was added. Upon slow diffusion at room temperature, colourless crystals suitable for X-ray analysis were obtained after one week. Formula: $[5-A] \cdot 0.5\text{CH}_3\text{OH} \cdot 0.5\text{H}_2\text{O}$ (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%.

$[7^{4-} \cdot (A^{2+})_2]$. In a crystallization tube (length 20 cm, diameter 4 mm), a DMF solution (2 ml) containing compound 7 (3 mg, 0.0023 mmol) and 0.18 ml of 0.05 M solution of NEt_3 (0.0092 mmol) in DMF were carefully layered with a DMF/MeOH mixture (1 ml, 1/1). Then a MeOH- H_2O solution (2 ml, 4/1) containing $(A^{2+}, 2\text{TsO}^-)$ (2.4 mg, 0.0046 mmol) was added. Upon slow diffusion at room temperature, colourless crystals suitable for X-ray analysis were obtained after one week. Formula: $[7-(A)_2] \cdot 2\text{H}_2\text{O}$ (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%.

$[8^{4-} \cdot (A^{2+})_2]$. In a crystallization tube (length 20 cm, diameter 4 mm), a DMF solution (2 ml) containing compound 8 (3 mg, 0.003 mmol) and 0.24 ml of 0.05 M solution of NEt_3 (0.012 mmol) in DMF were carefully layered with a DMF/MeOH mixture (1 ml, 1/1). Then a MeOH- H_2O solution (2 ml, 4/1) containing $(A^{2+}, 2\text{TsO}^-)$ (3.2 mg, 0.006 mmol) was added. Upon slow diffusion at room temperature, colourless crystals suitable for X-ray analysis were obtained after one week. Formula: $[8-(A)_2]$ (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 thiocalix[4]arene derivatives 4–8 was achieved using reported procedures (see the Experimental section). Compounds 4–8 bearing four carboxylic acid 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 ^1H - and ^{13}C -NMR spectroscopy which showed sharp signals indicating the presence of conformationally blocked 1,3-alternate isomers (see the 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 the Experimental part and Table S4, ESI†). As expected, all compounds adopt the 1,3-A conformation (Fig. 4). As indicated by the C–O distances (see ESI†, Table S2), the carboxyl moieties are fully protonated.

Compound 4 crystallises in the presence of DMF molecules which are found to be disordered. Crystals of 5 are exclusively composed of the tecton. Tecton 6 crystallises with CHCl_3 solvent molecules, whereas compound 7 crystallizes with both H_2O and CH_2Cl_2 molecules.

For compounds 4–7, the metrics for the macrocyclic backbone is close to the one observed for the parent compounds 1,¹⁵ 2 (ref. 15a) and 3 (ref. 27) (see Table S2, ESI†). In the case of 5, one of the four tertibutyl groups is found to be disordered (Fig. 3).

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).

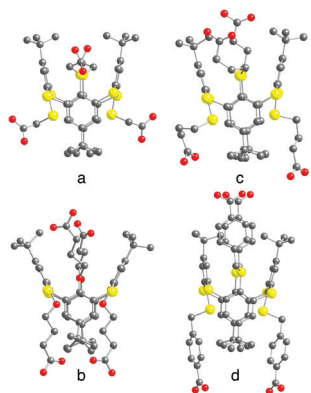


Fig. 3 Crystal structures of tectons 4 (a), 5 (b), 6 (c) and 7 (d) in the 1,3-alternate conformation. H atoms, disordered tertibutyl groups (5) and solvent molecules are not presented for clarity. For bond distances and angles, see the text and ESI†, Table S2.

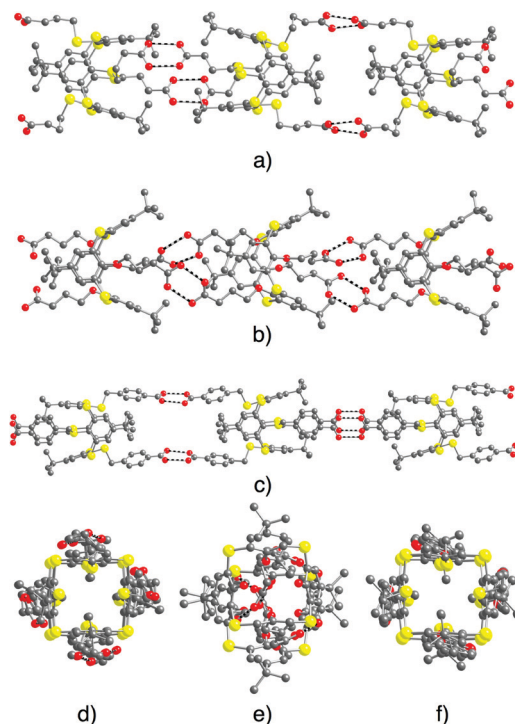


Fig. 4 Solid state structures of 1D tubular H-bonded networks formed by self-complementary tectons 5–7. Views along the 1D network (a–c, respectively) and perpendicular views (d–f, respectively). H atoms, disordered tertibutyl groups (in the case of tecton 5) and solvent molecules are not presented for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

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 the 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 d) and 7 (Fig. 4c and f) are linear, for tecton 6 (Fig. 4b and e) 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–f).

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

For tecton 6, no specific interactions between CHCl_3 solvent molecules and the network are found. For 7, however, whereas no interactions between CH_2Cl_2 solvent molecules and the network could be spotted, the water molecules do form H-bonds with the carboxylic acid moieties of the tecton (O–O distance of 3.197(6) Å).



Owing to the instability of the 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).

Formation of extended networks by combinations of deprotonated compounds 4–8 and the dicationic H-bond donor tecton A^{2+}

As stated in the introduction, the dicationic organic tecton A^{2+} (Fig. 1) is well suited to recognize two carboxylate moieties, through a dihapto mode of interaction (Fig. 2c). In other terms, tecton 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 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 NEt_3 , as base, with tecton A^{2+} (2 eq.) were also studied (see the Experimental section). Among several attempts, the following crystalline materials $[(4^{3-})_2-(A^{2+})_3]$, $[5^{2-}-A^{2+}]$, $[(7^{4-})-(A^{2+})_2]$ and $[8^{4-}-(A^{2+})_2]$ were obtained and analysed by X-ray diffraction on single crystals (see Table S5, ESI†).

For the combination of 4 with A^{2+} in the presence of 4 eq. of NEt_3 , probably because of the short nature of the spacer ($-CH_2-$) and the presence of tertibutyl groups, the expected tubular architecture (Fig. 2a) was not observed in the obtained crystals under the crystallization conditions used (see the Experimental section). Indeed, instead of the

projected 1/2 stoichiometry $[(4^{4-})-(A^{2+})_2]$, 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 the ESI†). In the crystal, a 2/3 stoichiometry between the trianionic compound 4^{3-} and the dicationic tecton A^{2+} , leading to $[(4^{3-})_2-(A^{2+})_3]$, is observed. The metrics observed for 4^{3-} is close to the one observed for 4 and the structural parameters observed for A^{2+} are close to those already reported.²⁹

$[(4^{3-})_2-(A^{2+})_3]$ 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 $N\cdots O$ distances in the range of 2.669(10) to 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_2O molecules interact with each other and with the H-bonded network. The DMF molecule is H-bonded with the water molecule with a $O\cdots O$ distance of 2.786(15) Å. Furthermore, the water molecule interacts with a carboxylate group ($O\cdots O$ distance of 2.784(22) Å). Consecutive 2D H-bonded planes are packed along the c axis with solvent molecules lying between the planes.

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 the presence of 4 eq. of NEt_3 , again the formation of the tubular architecture (Fig. 2a) was not observed under the crystallization conditions used (see the 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.²⁹ In the crystal, a 1/1 stoichiometry between

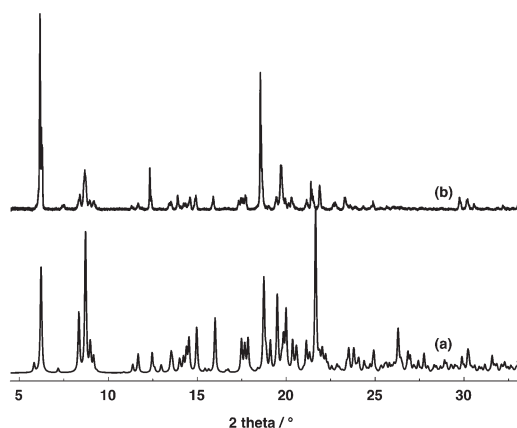


Fig. 5 Simulated (a) and observed (b) PXRD powder patterns for compound 6. Discrepancies in peak intensity are due to the preferential orientation of the microcrystalline powder.

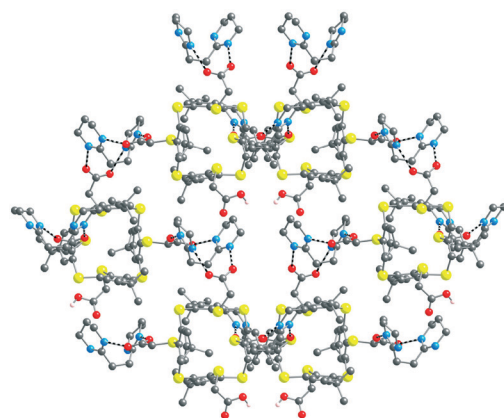


Fig. 6 Solid state structures of the 2D honeycomb type H-bonded $[(4^{3-})_2-(A^{2+})_3]$ network formed by complementary tectons 4^{3-} and A^{2+} . H atoms, DMF and water solvent molecules are not presented for clarity. For bond distances and angles, see the text and ESI†, Table S3.



the dianionic compound 5^{2-} and the dicationic tecton A^{2+} leading to $[5^{2-}\text{-}A^{2+}]$ is observed. The latter crystallises in the presence of 1 MeOH and 1 H_2O solvent molecule. 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_2O and MeOH solvent molecules) is rather complex.

In marked contrast with the abovementioned combination of 4^{3-} with A^{2+} , for $[5^{2-}\text{-}A^{2+}]$, 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). Furthermore, tecton A^{2+} also forms H-bonds of NHO type with the carboxylic acid groups of 5^{2-} (d_{ON} of 2.791(7) Å). The cationic tecton A^{2+} is also connected with MeOH by a H bond (d_{ON} of 2.780(11) Å). Owing to the presence of both carboxylic acid 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, the MeOH molecule, in addition to 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* axes. Water molecules are located between 1D networks without specific interactions with them.

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

The combination of A^{2+} in the presence of 4 eq. of NEt_3 , with either 7 or 8, afforded crystals which were investigated by X-ray diffraction on single crystals. The structural study revealed that both 7 and 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 $[X^{4-}\text{-}(A^{2+})_2]$ ($X = 7$ or 8). The metrics observed for 7^{4-} and for 8^{4-} is similar to those for 7 and reported for 8.²⁷ Structural parameters for the dicationic tecton A^{2+} within the networks are close to the one reported.²⁹

For $[7^{4-}\text{-}(A^{2+})_2]$, the crystal, in addition to the cationic and anionic tectons, contains two water molecules. 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 a result of the design of the complementary anionic and cationic tectons behaving as H-bond acceptor and donor sites, respectively, a dihapto mode of

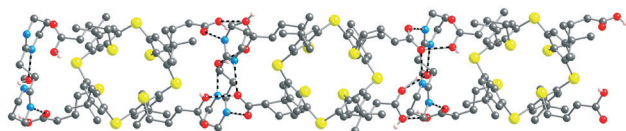


Fig. 7 Solid state structures of the 1D H-bonded $[5^{2-}\text{-}A^{2+}]$ network formed by complementary tectons 5^{2-} and A^{2+} . H atoms, MeOH and H_2O solvent molecules are not presented for clarity. For bond distances and angles, see the text and ESI,† Table S3.

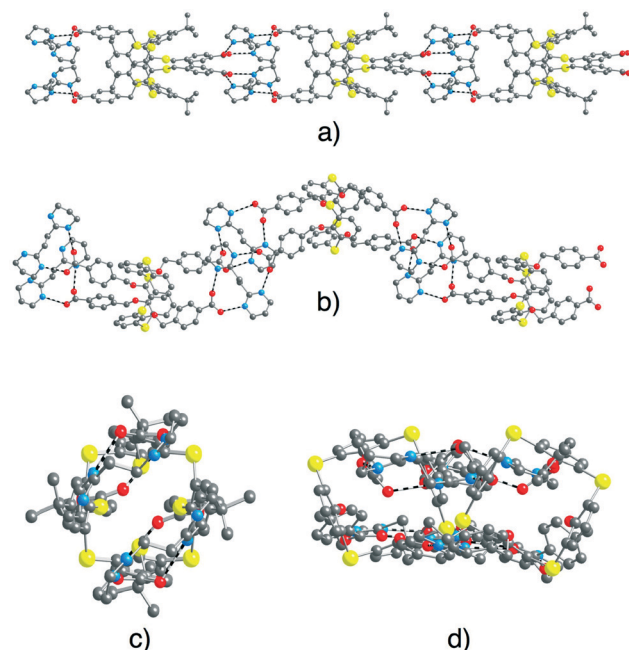


Fig. 8 Solid state structures of 1D H-bonded networks formed by $[7^{4-}\text{-}(A^{2+})_2]$ (perpendicular (a) and parallel (c) views of the extended arrangement) and by $[8^{4-}\text{-}(A^{2+})_2]$ (perpendicular (b) and parallel (d) views of the extended arrangement). For $[7^{4-}\text{-}(A^{2+})_2]$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

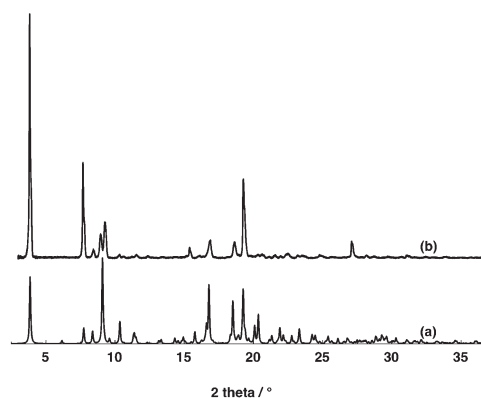


Fig. 9 Simulated (a) and observed (b) PXRD powder patterns for compound $[7^{4-}\text{-}(A^{2+})_2]$. Discrepancies in peak intensity are due to the preferential orientation of the microcrystalline powder.

H-bonding with the $N\cdots O$ distance in the range of 2.625(15)–2.816(13) Å is observed (Fig. 8) (see ESI,† Table S3). Consequently, the mutual interconnection of the anionic tectons 7^{4-} and 8^{4-} and the cationic tecton A^{2+} leads to the formation of 1D tubular H-bonded networks (Fig. 2a). For $[7^{4-}\text{-}(A^{2+})_2]$, the 1D network runs along the *b* axis (Fig. 8a and c). For $[8^{4-}\text{-}(A^{2+})_2]$, the 1D network running along the *a* axis is not linear but corrugated (Fig. 8b and d).

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



For $[7^{4-}-(A^{2+})_2]$, the water molecules are located between the 1D chains and interact with the carboxylate groups of 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 the 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.

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 the 1,3-alternate conformation and bearing four carboxylic acids have 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 acid 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 tetra-acids 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-} form, 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+} lead 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).

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