

Molecular tectonics: on the formation of 1-D silver coordination networks by thiacalixarenes bearing nitrile groups

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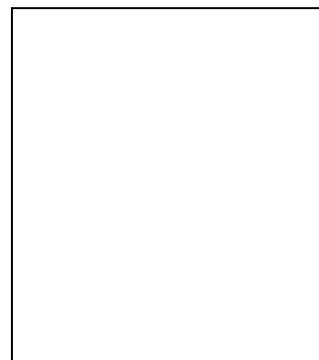
Two new *p-tert*-butylthiacalix[4]arene derivatives **2** and **3** decorated at the lower rim with four nitrile groups have been prepared and structurally characterised in the crystalline phase. The two ligands, differing by the length of the spacer between the calix moiety and the nitrile group, adopt the 1,3-alternate conformation in the solid state. The ligand **3** bearing four (CH₂)₃CN fragments behaves as a tecton in the presence of silver salts (AgX, X = BF₄, PF₆ or SbF₆) and leads to the formation of analogous 1-D linear coordination networks. The tecton **3** acts as a bis chelate unit and bridges consecutive silver cations adopting a tetrahedral coordination geometry. Anions and solvent molecules occupy the free space between networks and exhibit no specific interactions with the cationic architecture.

Introduction

The design, formation and characterisation of coordination networks, infinite periodic architectures formed upon mutual interconnection between organic units and metal centres or metal complexes are areas of current interest.¹ Molecular tectonics is an efficient and operational approach in this area.²⁻⁷ It is based on two main principles which are specific coordination events taking place between organic and metallic construction units called tectons⁶ leading to an assembling pattern and the iteration of the process transforming the latter into the nodes of the network. Thus, for coordination networks, the organic tecton must offer coordinating sites (often donor hetero elements) and the metal centre or metal complex must possess free coordination sites. The formation of coordination networks occurs under self-assembly processes (for crystalline materials during the crystallisation event) and one of the driving forces is the establishment of coordination bonds between the donor sites located on the organic tecton and available coordination sites on the metal centre. Since almost two decades, considerable effort has been invested in obtaining coordination networks and a large variety of examples have been reported.⁸⁻¹⁶

Molecular networks are defined by their dimensionality (1-, 2- or 3-D) which results from the number of translations in different directions of space operating on the assembling pattern. Within each dimensional category, these networks are defined by their geometry. For example, within 1-D networks, several types of arrangements (linear, stair type, zigzag type, helical, tubular etc.) may be formed. The geometry of the final assembly is obviously governed by both the structural and coordination features of the organic tecton and the metal centre. Dealing with linear and tubular coordination networks (Fig. 1), one may design an organic tecton offering four

coordinating sites located in an alternate fashion above and below a cyclic unit (*S*₄ symmetry). Using a metal connector adopting linear coordination geometry, one may envisage the formation of a tubular network (Fig. 1 top) in which the tecton behaves as tetrakis monodentate unit towards metal centres. We have previously demonstrated this possibility by combining [1,1,1,1]-*metacyclophane* derivatives in 1,3-alternate conformation bearing either four nitrile groups¹⁷ or four pyridyl units.¹⁸ with silver cation. In the case of tectons offering the proper orientation and an appropriate distance between the coordinating sites on the same face allowing the two sites to bind to the same metal centre infinite 1-D non-tubular architectures may be generated in the presence of metal centres adopting the tetrahedral coordination geometry (Fig. 1 bottom). We have also reported such a case using a calix[4]arene derivative in 1,3-alternate blocked conformation bearing four nitrile groups at the upper rim.¹⁹



70 **Fig. 1** Schematic representation of the formation of a tubular (top) or non-tubular (bottom) 1-D networks based on the self-assembly of a tecton bearing four coordinating sites occupying the apices of a tetrahedron and metal centres offering either linear or tetrahedral coordination geometries.

75 In this contribution, we report on the formation of three homometallic 1-D coordination networks based on combinations of AgX salts (X = BF₄⁻, PF₆⁻ and SbF₆⁻) and the *p-tert*-butylthiacalix[4]arene derivative **3** in 1,3-alternate conformation bearing four butyronitrile groups at the lower

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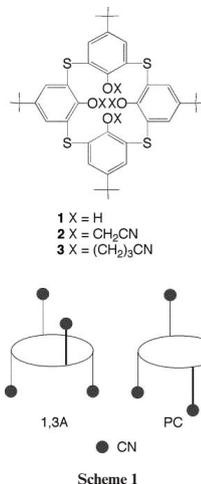
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† Electronic Supplementary Information (ESI) available: [Crystallographic data in cif format]. See <http://dx.doi.org/10.1039/b000000x/>

rim (Scheme). The free ligand **3** and its analogue **2** bearing shorter spacers as well as the networks have been characterised in the crystalline phase by X-ray diffraction on single crystals.

85 For the design principle of 1-D networks discussed above, the calix[4] arene²⁰⁻²¹ and thiacalix[4] arene²²⁻²⁷ derivatives are interesting backbones. However, when unsubstituted at the lower rim, these tetraphenolic macrocycles are flexible entities and exist in solution as a mixture of four conformers (cone (C), partial cone (CP), 1,2-alternate (1,2-A) and 1,3-alternate (1,3-A)). In the solid state, both *p*-*tert*butylcalix[4]arene²⁸ and *p*-*tert*butylthiacalix[4]arene **1**²³ adopt the cone conformation. Among the four conformers, only the 1,3-A one fulfils the orientation requirement discussed above. Based on the calix[4]arene backbone, using the functionalisation of both the lower rim to impose the 1,3-A conformation and the upper rim to introduce coordination sites, we have demonstrated the viability of the approach by generating 1-D silver coordination networks.¹⁹ One may also envisage another strategy which consists of imposing the 1,3-A conformation by functionalising only the lower rim with a fragment bearing at its extremity a monodentate coordination site. This was applied using the *p*-*tert*butylthiacalix[4]arene for which only few examples of infinite coordination has been reported.²⁹⁻³⁰

100 The design of compounds **2** and **3** (Scheme) is based on *p*-*tert*butylthiacalix[4]arene **1** in 1,3-A conformation as a backbone, four nitrile groups as coordinating sites and alkyl spacer connecting the two parts. The junction between the calix and the spacer occurs at the lower rim and is ensured by an ether link. The two ligands **2** and **3** differ by the length of the spacer (CH₂ for **2** and (CH₂)₃ for **3**) connecting the nitrile group to the calix moiety. The length of the spacer was varied in order to explore its role on the conformational mobility of the calix backbone. Indeed, as previously reported for calix[4]arene derivatives,²⁰⁻²¹ whereas for **2** one would expect interconvertible conformers, for **3** blocked conformers should be obtained. Furthermore, for the 1,3-A conformer, the length of the spacer would allow to control the positioning and distance of the nitrile groups with respect to the *p*-*tert*butyl



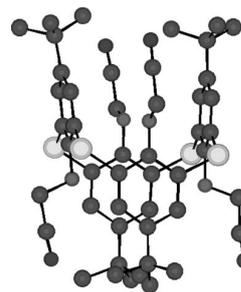
Results and discussion

125 The synthesis of **2** and **3** was rather straightforward (see experimental part). The starting material for the preparation of

2 and **3** was *p*-*tert*butylthiacalix[4]arene **1**.²² Both compounds **2** and **3** were obtained upon condensation of **1** with a ω -halonitriles under basic conditions (K₂CO₃) in refluxing dry acetone. Whereas for the synthesis of **2** the condensation was performed between **1** and bromoacetonitrile, for the preparation of the compound **3**, 4-chlorobutyronitrile was reacted with **1**. For the compound **2**, although overall yield was 76%, in solution (CDCl₃) ¹H-NMR investigations revealed the simultaneous presence of the partial cone (PC) and 1,3-alternate (1,3-A) conformers in 1/1.5 ratio at room temperature. The equilibrium between the two conformers could be shifted to 1/2 by heating the solution to 50 °C for 30 minutes. Based on the nature of the spacer connecting the nitrile group to the calix oxygen atom (CH₂), this conformational mobility is expected. In marked contrast, compound **3** was isolated in 67% yield under experimental conditions used, as a pure 1,3-A conformer. No interconversion between conformers was observed by NMR in CDCl₃.

145 The solid state structure of both ligands **2** and **3** were investigated using X-ray diffraction on single crystal (see experimental part).

Although in CDCl₃ solution, the compound **2** presents conformational mobility with the PC and 1,3-A conformers as dominant species, upon crystallisation, only the 1,3-A conformer was obtained under the conditions used (see experimental part) (Figure 2). Compound **2** crystallises in the trigonal system (Space group *P*321). No solvent molecule is present in the lattice. The observed C-S distance, in the range of 1.76-1.80 Å, is in agreement with the one observed for the parent compound **1** (1.79 Å).²³ For the ether junction between the calix and the pendent arms, the carbon to oxygen distances are in the range of 1.38 - 1.39 Å for O-C(Ph)) and 1.42 - 1.43 Å for C-O. The four nitrile groups (C≡N distance of 1.10 Å and 1.14 Å) are located in an alternate fashion below and above the main plane of the thiacalixarene. The CH₂CN fragments are almost linear with NCC angle of 173.3 and 178.5°. The pendent arms bearing the nitrile groups are oriented almost parallel to the calix long axis (CCO angle in the range of 106.4° and 109.0°, COC angle in the range of 110.2° and 111.7°). The aromatic moieties on the same face of the molecule are almost parallel. It is worth noting that because of the short nature of the spacer connecting the nitrile group to the calix, the CN groups are in close proximity with the *t*-butyl moieties located on the same face (distance in the range of *ca* 3.6 - 4.6 Å).



175 **Fig. 2** The solid state structure of **2** showing the adopted 1,3-alternate conformation. H atoms and solvent molecules are not presented for sake of clarity. For bond distances and angles see text.

180 The packing of calix units **2** is rather peculiar as shown on
figure 3. Indeed, among the three thiacalixarene moieties in the
unit cell, two present short N-N distances of 3.88 Å between
nitrile groups belonging to two different calix **2**. (see below
for comparison with the packing of free ligands **3**).

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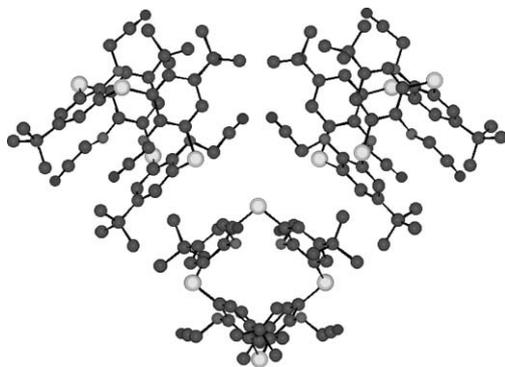


Fig. 3 Packing of three consecutive units **2** in the solid state
(projection of the (001) plane). H atoms and solvent
molecules are not presented for sake of clarity. For bond
distances and angles see text.

The solid state structure of the ligand **3** was also investigated
by X-ray diffraction on single crystal (see experimental part).
As in solution (CDCl₃), compound **3** adopts the 1,3-A
conformation (Figure 4). Compound **3** crystallises in the
orthorhombic system (Space group *P*222) with one CHCl₃
solvent molecule. The latter occupies the empty space with no
specific interactions with calix unit. The C-S distance, in the
range of 1.76 - 1.79 Å, is again in agreement with the one
observed for **2** and for the parent compound **1** (1.79 Å).²³ For
the ether junction between the calix and fragments bearing the
nitrile groups, the carbon to oxygen distances are in the range
of 1.38 - 1.39 Å for O-C(Ph) and 1.43 - 1.47 Å for C-O. The
four nitrile groups (C≡N distance in the range of 1.10 - 1.14
Å, NCC Angle in the range of 175.9 - 179.0°) are also located
in an alternate fashion below and above the main plane of the
thiacalixarene. However, in marked contrast with **2**, among
the four (CH₂)₃CN groups (CCO angle in the range of 106.5°
and 110.0°, COC angle in the range of 111.0° and 114.0°),
three of them are oriented towards the exterior whereas one is
pointing towards the interior. Again in contrast with **2**, the
aromatic rings on the same face of the molecule are not almost
parallel but tilted leading to a flattened 1,3-A conformation.

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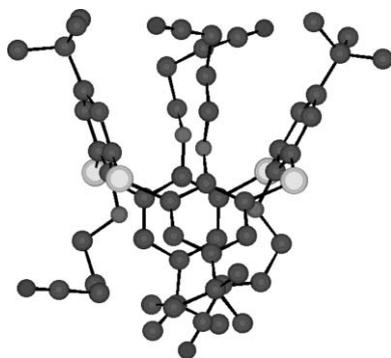


Fig. 4 The solid state structure of **3** showing the adopted 1,3-
alternate conformation. Among the four arms bearing the
nitrile groups, one is oriented outwardly. H atoms and solvent
molecules are not presented for sake of clarity. For bond
distances and angles see text.

Interestingly, in terms of packing, compounds **3** are arranged
in a linear fashion along the *c* axis thus placing the nitrile
groups in ideal dispositions for binding of metal centres
adopting the tetrahedral coordination geometry (Fig. 5).

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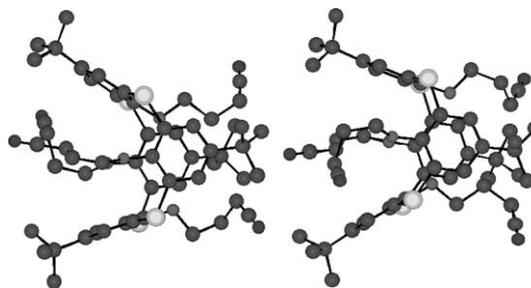


Fig. 5: Packing of consecutive calix units **3** in the solid state
along the *c* axis showing the linear arrangement of ligands and
the disposition of nitrile groups. H atoms and solvent
molecules are not presented for sake of clarity. For bond
distances and angles see text.

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The propensity of both ligands **2** and **3** to behave as a tecton
by forming infinite coordination networks was tested in the
presence of silver cation. In order to study the possible role
played by the anion, BF₄⁻ and XF₆⁻ (X = P or Sb) anions
possessing tetrahedral and octahedral coordination geometries
respectively were used.

For the compound **2**, although we have made several attempts
based on many combinations of solvent and crystallisation
conditions, unfortunately, we were unable to produce
crystalline material for structural investigations by X-ray
diffraction methods. Based on the solid structure of **2**
mentioned above (Fig. 2), this could have been anticipated
for steric reasons. Indeed, because of the short nature of the
spacer (CH₂) connecting the calix backbone to the nitrile
group, the formation of a 1-D network upon connection of
consecutive units by silver cation must generate severe steric
interactions, in particular between *t*-butyl groups belonging to
consecutive calix units.

On the other hand, the inspection of the packing of compound
3 in the crystalline phase (Fig. 5) clearly shows the proper
predisposition of the units and thus the possibility of behaving
as a coordinating tecton by bridging consecutive metal
centres. This was indeed achieved by combining the tecton **3**
with AgX (X = BF₄⁻, SbF₆⁻ and PF₆⁻). In all three cases,
suitable crystals for X-ray diffraction on single crystal have
been obtained upon slow liquid-liquid diffusion at room
temperature using either CH₂Cl₂ or CHCl₃ to solubilize the
tecton **3** and a *i*PrOH or EtOH solution of the silver salt (see
experimental section). Since, independent of the nature of the
anion used, almost identical polycationic silver 1-D networks
were obtained, here, we shall only discuss in detail the
combination of **3** with AgBF₄. In all three cases, the crystal is
composed of neutral tecton **3**, Ag⁺ cation, anion (BF₄⁻, PF₆⁻ or
SbF₆⁻) and solvent molecules (CHCl₃ and *i*PrOH for AgBF₄,
CHCl₃ for AgSbF₆ and CH₂Cl₂ for AgPF₆). In none of the

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three studied structures specific interactions between the Ag^+ cation and anions could be observed. The solvent molecules present in the lattice occupy the empty space again with no specific interactions with **3** or Ag^+ cation. For all three crystals, the $\text{3}/\text{Ag}^+$ stoichiometry is 1/1. When considering the interactions between organic tectons **3** and silver cations, the crystal may be described as 1-D cationic silver coordination networks separated by anions and solvent molecules. The cationic part of the crystal is generated by mutual interconnection of organic moieties and metallic centres through nitrile silver interactions (Fig. 6). The other heteroatoms (O and S) are not involved in bonding interactions with the cation.

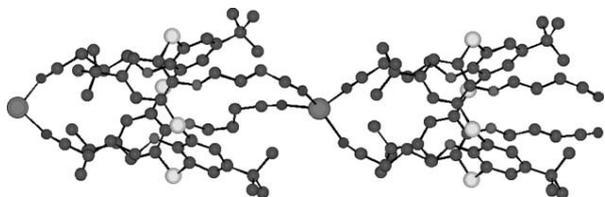


Fig. 6: A portion of the solid state structure obtained upon combining compound **3** with AgBF_4 showing the mutual bridging between the organic tecton **3** and Ag^+ cations leading to the formation of a cationic 1-D coordination network. H atoms, anions and solvent molecules are not presented for sake of clarity. For bond distances and angles see text.

For the organic tecton **3**, as for its free form, it adopts the 1,3-A conformation with the four nitrile groups ($\text{C}\equiv\text{N}$ distance in the range of 1.03 - 1.15 Å, NCC Angle in the range of 171.0 - 177.2°) located in an alternate fashion below and above the main plane of the thiacalixarene. The C-S distances, in the range of 1.76 - 1.79 Å, are close to those observed for the free tecton **3**. For the ether junction, the carbon to oxygen distances are in the range of 1.34 Å - 1.37 Å for O-C(Ph) and 1.41 Å - 1.46 Å for C-O. In marked contrast with the free ligand **3**, all four $(\text{CH}_2)_3\text{CN}$ groups (CCO angle in the range of 100.9° and 107.5°, COC angle in the range of 113.0° and 115.4° and OCCO dihedral angle in the range of -179.2 - 179.9) are almost fully stretched. As for the free ligand **3**, the aromatic rings on the same face of the molecule are tilted leading to a flattened 1,3-A conformation.

The Ag^+ cation (two crystallographically non equivalent) connecting consecutive tectons **3** is tetra coordinated. Its coordination sphere is composed of four N atoms belonging to two consecutive tectons **3** (Ag-N distance in the range of 2.19 - 2.33 Å). The coordination geometry around the cation is a distorted tetrahedron (NAgN angle varying between 93° and 124°). Due to the length and flexible nature of the spacer connecting the calix moiety to the nitrile group, tecton **3** behaves as a bischelating unit. Indeed, on each face of the molecule, two nitriles bind to the same silver cation.

The distances between consecutive Ag^+ cations within the 1-D network are *ca* 16.20 and 16.46 Å. The shortest distances between Ag^+ cations belonging to two consecutive networks along the a and b axis are 15.00 Å and 11.75 Å respectively.

In terms of packing (Fig. 7), the 1-D networks are arranged in parallel (along the a axis) and antiparallel (along the b axis) fashions.

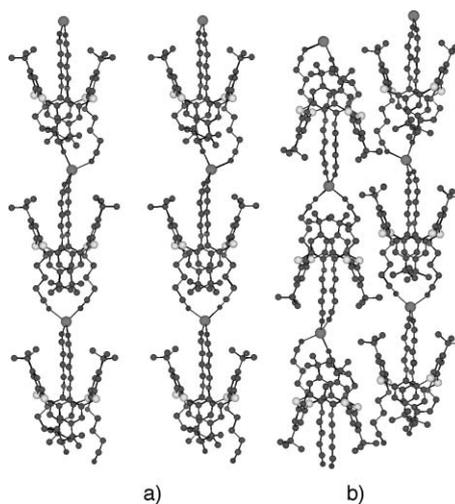


Fig. 7: Packing of 1-D silver coordination networks generated upon combining the tecton **3** with AgBF_4 showing the parallel arrangement along the a axis (a) and the antiparallel disposition along the b axis (b) of consecutive 1-D networks in the crystal. H atoms, anions and solvent molecules are not presented for sake of clarity. For bond distances and angles see text.

Conclusions

Both ligands **2** and **3** in the 1,3-alternate conformation offer four nitrile coordinating sites occupying the apices of a pseudo tetrahedron. However, in the case of ligand **2** bearing four CH_2CN groups, so far we have not been able to generate silver coordination networks. This may be due to the length of the spacer, a methylene groups, connecting the thiacalix backbone to the nitrile moiety which would generate steric interactions between the *t*-butyl groups and the silver cation. On the other hand, for the ligand **3**, the propyl spacer, connecting the nitrile to the oxygen atoms of the thiacalix, is long enough to avoid such a steric interactions and thus, allows the formation of linear 1-D silver coordination networks in the presence of different silver salts. The ligand **3** behaves as a bischelating tecton, *i.e.* on each face of the unit the two nitrile groups coordinate to the same metal cation. Consequently, the formation of the network results from bridging of consecutive silver cations adopting tetrahedral coordination geometry. Interestingly, the generation of the network is robust and independent of the nature of the anion. The combination of ligands reported here and longer analogues with other metal centres is currently under investigation.

Experimental

General: All reagents were purchased from commercial sources and used without further purification. *p*-tert-Butylthiacalix[4]arene **1** was prepared according to the literature.²² ^1H NMR spectra were recorded at room temperature on a Bruker (300 MHz) NMR spectrometer. FT-IR spectrum were recorded on a Perkin Elmer spectrometer. Mass spectra ($\text{MS}(\text{ES}^+)$) were obtained on a MALDI-TOF Dynamo Finnigan mass spectrometer using 1,8,9-

370 Trihydroxyanthracene or p-nitroaniline as matrix. Microanalyses were performed by the Service de Microanalyses de la Fédération de Recherche de Chimie, Université Louis Pasteur, Strasbourg.

Synthesis

375 **25,26,27,28-tetrakis(O-cyanomethoxy)-5,11,17,23-tetra-p-tert-butyl-2,8,14,20-tetrathiacalix[4]arene (2)**

A mixture of p-tert-butylthiacalix[4]arene **1** (1.00 g, 1.39 mmol), K₂CO₃ (3.84 g, 27.78 mmol) and bromoacetonitrile (1.94 mL, 27.78 mmol) in dry acetone (30 mL) was refluxed under argon 380 for 48 hours. After cooling, the reaction mixture was evaporated to dryness, treated with 2M HCl (60 mL) and extracted with dichloromethane. The organic layer was dried over MgSO₄, and the solvent removed. The residue was precipitated from a CHCl₃-pentane mixture and washed with methanol affording a white 385 solid ((0.92 g, 76%). NMR study revealed that the powder was composed of the compound **2** in PC and 1,3-A conformations in 1:1.5 ratio at room temperature. mp = 335-337 °C. ¹H NMR (CDCl₃): δ = 1.12 (s, 18H, PC); 1.32 (s, 36H, 1,3-A); 1.34 (s, 9H, PC); 1.46 (s, 9H, PC); 4.31 (s, 2H, PC); 4.78 (d, 2H, J = 15.6 Hz, PC); 4.79 (s, 8H, 1,3-A); 4.92 (s, 2H, PC); 5.01 (d, 2H, J = 15.3 Hz, PC); 7.13 (d, 2H, J = 2.7 Hz, PC); 7.59 (s, 8H, 1,3-A); 7.60 390 (d, 2H, J = 2.7 Hz, PC); 7.93 (s, 2H, PC). ¹³C NMR (CDCl₃): δ = 149.3, 135.2, 134.7, 133.6, 132.8, 132.1, 128.3, 115.4, 58.7, 54.8, 34.5, 31.3, 31.2, 31.0, 29.7. FTIR (KBr): ν = 2019 cm⁻¹ (C≡N). 395 MS(ES⁺), m/z: 915 (M⁺K⁺) and 899 (M⁺Na⁺). Anal.Calcd.: C, 65.75%; H, 5.94%; N, 6.39%. Found: C, 64.67%; H, 5.92%; N, 6.02%.

395 **25,26,27,28-tetrakis[O-(3-cyano)propoxy]-5,11,17,23-tetra-p-tert-butyl-2,8,14,20-tetrathiacalix[4]arene (3)**

400 A mixture of p-tert-butylthiacalix[4]arene **1** (2.50 g, 3.47 mmol), K₂CO₃ (9.60 g, 69.46 mmol), 4-chlorobutyronitrile (5.2 mL, 58.15 mmol), KI (catalytic quantity) in dry acetone (65 mL) was refluxed under argon for 56 hours. After cooling, the reaction mixture was evaporated to dryness, treated with 2M HCl and 405 extracted with dichloromethane. The organic layer was separated, dried over MgSO₄, and the solvent was removed. The solid residue was precipitated from a CHCl₃-pentane mixture affording the pure compound **3** in the 1,3-A conformation as a white powder (1.75 g, 67%). mp = 367-370 °C. ¹H NMR (CDCl₃): δ = 410 1.33 (s, 36H); 1.42 (m, 8H); 1.97 (t, 8H, J = 7.8 Hz); 3.97 (t, 8H, J = 6.6 Hz); 7.38 (s, 8H). ¹³C NMR (CDCl₃): δ = 156.1; 147.1; 128.3; 127.6; 119.3; 66.6; 34.5; 31.4; 25.2; 13.8. FTIR (KBr): ν = 2243 cm⁻¹ (C≡N). MS(ES⁺): 1027 m/z (M⁺K⁺). Anal.Calcd.: C, 68.02%; H, 6.88%; N, 5.67%. Found: C, 67.94%; H, 7.12%; N, 415 5.56%.

Crystallisation conditions:

Crystallisation of **2**: A mixture of chloroform (1.0 mL) and 420 ethanol (5.0 mL) containing the ligand **2** (20.0 mg) was refluxed for 6 hours. Upon cooling to room temperature, suitable colourless crystals for X-ray diffraction study were obtained after 2 days.

Crystallisation of **3**: A mixture of chloroform (3.0 mL) and 425 ethanol (1.0 mL) containing the ligand **3** (16.6 mg) was refluxed for 1 hour. Upon cooling to room temperature and slow evaporation, suitable colourless crystals for X-ray diffraction study were obtained after several days.

Crystallisation of (3-AgBF₄)_n: In a crystallising tube, a 430 solution of **3** (3.0 mg) in CHCl₃ (1 mL) was layered with a CHCl₃-i-PrOH 1/1 mixture (0.25 mL). A solution of AgBF₄ (7.8 mg) in i-propanol (1 mL) was carefully added. The slow

diffusion at room temperature and in the dark produced colourless crystals after several days.

435 Crystallisation of (3-AgPF₆)_n: In a crystallising tube, a solution of **3** (3.0 mg) in CH₂Cl₂ (1 mL) was carefully layered with THF (0.25 mL) and then a solution of AgPF₆ (7.7 mg) in EtOH (1 mL) was added. Upon slow diffusion at room temperature and in the dark, colourless crystals were obtained 440 after several days.

Crystallisation of (3-AgSbF₆)_n: In a crystallising tube, a solution of **3** (4.0 mg) in CHCl₃ (1 mL) was layered with a solution of AgSbF₆ (13.7 mg) in i-propanol (1 mL). The slow diffusion at room temperature and in the dark produced 445 colourless crystals after several days.

X-Ray Crystallography

Data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid 450 N₂ device, using graphite-monochromated Mo-Kα (λ = 0.71073) radiation. For all structures, diffraction data were corrected for absorption and structural determination was achieved using the APEX (1.022) package. All hydrogen atoms have been calculated except those connected to 455 disordered atoms. CCDC ????-???? contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic data Centre, 12 Union Road, 460 Cambridge CB2 1EZ, UK; Fax: (Internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

Crystallographic data for 2: C₄₈H₅₂N₄O₄S₄, M = 877.18, Trigonal, a = b = 18.5910(6) Å, c = 11.7442(7) Å, α = β = 465 90°, γ = 120°, U = 3515.3(3) Å³, Space group P321, Z = 3, μ = 0.249 mm⁻¹, Refls measured: 21748, Independent Refls: 5390, Final R indices [I > 2σ(I)]: R1 = 0.0815, wR2 = 0.2107, GOF = 1.035.

Crystallographic data for 3: C₅₆H₆₈N₄O₄S₄.CHCl₃, M = 470 1108.75, Orthorhombic, a = 14.8603(8), b = 15.2097(8) Å, c = 25.1404(15) Å, α = β = γ = 90°, U = 5682.3(5) Å³, Space group P222, Z = 4, μ = 0.357 mm⁻¹, Refls measured: 34181, Independent Refls: 12247, Final R indices [I > 2σ(I)]: R1 = 0.0695, wR2 = 0.1422, GOF = 1.039.

475 **Crystallographic data for (3-AgBF₄)_n:** (C₅₆H₆₈N₄O₄S₄Ag)₄, (BF₄)₄.(C₃H₈O)₃.(CHCl₃)₈, M = 5871.48, monoclinic, a = 20.780(2), b = 15.006(3) Å, c = 23.042(2) Å, β = 96.081(4)°, U = 7144.9(17) Å³, Space group P2, Z = 1, μ = 0.680 mm⁻¹, Refls measured: 74628, Independent Refls: 30720, Final R 480 indices [I > 2σ(I)]: R1 = 0.1057, wR2 = 0.2830, GOF = 1.038.

Crystallographic data for (3-AgSbF₆)_n: (C₅₆H₆₈N₄O₄S₄Ag)₄, (SbF₆)₄.(CHCl₃)₁₄, M = 6286.96, monoclinic, a = 16.4840(3) 485 Å, b = 15.0260(4) Å, c = 28.9440(6) Å, β = 94.169(2)°, U = 7150.1(3) Å³, Space group P21/c, Z = 1, μ = 1.052 mm⁻¹, Refls measured: 30216, Independent Refls: 17018, Final R indices [I > 2σ(I)]: R1 = 0.0952, wR2 = 0.2798, GOF = 1.038.

Crystallographic data for (3-AgPF₆)_n: (C₅₆H₆₈N₄O₄S₄Ag)₄, (PF₆)₄.(CH₂Cl₂)₈, M = 1412.08, monoclinic, a = 13.7751(4) Å, 490 b = 15.2061(6) Å, c = 16.6762(4) Å, β = 94.453(3)°, U = 3482.45(19) Å³, Space group P2, Z = 2, μ = 0.645 mm⁻¹, Refls measured: 17806, Independent Refls: 17706, Final R indices [I > 2σ(I)]: R1 = 0.0779, wR2 = 0.2174, GOF = 1.002.

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Notes and references

- 1 S. R. Batten and R. Robson, *Angew. Chem. Int. Ed.*, 1998, **37**, 1460.
- 2 S. Mann, *Nature*, 1993, **365**, 499.
- 505 3 J. D. Wuest, *Chem. Comm.*, 2005, 5830
- 4 M. W. Hosseini, *Acc. Chem. Res.*, 2005, **38**, 313.
- 5 M. W. Hosseini, *Cryst. Eng. Comm.*, 2004, **6**, 318.
- 6 M. Simard, D. Su and J. D. Wuest, *J. Am. Chem. Soc.*, 1991, **113**, 4696.
- 510 7 M. W. Hosseini, in *NATO ASI Series*, Eds. D. Braga, F. Grepiono, G. Orpen, Serie C, Kluwer, Dordrecht, Netherlands, 1999, **538**, 181.
- 8 B. Moulton and M.J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
- 9 C. Janiak, *Dalton Trans.*, 2003, 2781.
- 10 A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **193**, 117.
- 515 11 G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483.
- 12 M. Eddaoui, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keefe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319.
- 13 L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247.
- 520 14 S. Kitagawa, *Angew. Chem. Int. Ed.*, 2004, **43**, 2434.
- 15 G. Férey, C. Mellot-Draznieks, C. Serre and F. Millange, *Acc. Chem. Res.*, 2005, **38**, 218.
- 16 D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273.
- 525 17 C. Klein, E. Graf, M. W. Hosseini, A. De Cian, J. Fischer, *Chem. Commun.*, 2000, 239.
- 18 G. Laugel, E. Graf, M. W. Hosseini, J.-M. Planeix, N. Kyritsakas, *New J. Chem.*, 2006, **30**, 1340.
- 530 19 G. Mislin, E. Graf, M. W. Hosseini, A. De Cian, N. Kyritsakas, J. Fischer, *Chem Commun.*, 1998, 2545.
- 20 C.D. Gutsche in *Calixarenes Revised: Monographs in Supramolecular Chemistry Vol. 6*, The Royal Society of Chemistry, Cambridge, **1998**.
- 535 21 Z. Asfari, V. Böhmer, J. Harrowfield and J. Vicens in *Calixarenes 2001*, (Eds. Z. Asfari, V. Böhmer, J. Harrowfield and J. Vicens) Kluwer Academic, Dordrecht, **2001**.
- 22 H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama and S. Miyano, *Tetrahedron Lett.*, 1997, **38**, 3971.
- 540 23 H. Akdas, L. Bringel, E. Graf, M. W. Hosseini, G. Mislin, J. Pansanel, A. De Cian, J. Fischer, *Tetrahedron Lett.*, 1998, **39**, 2311.
- 24 M. W. Hosseini, ACS Series, Eds G. J. Lumetta, R. D. Rogers, A. S. Gopalan, 2000, **557**, 296.
- 545 25 M.W. Hosseini in *Calixarenes 2001*, (Eds. Z. Asfari, V. Böhmer, J. Harrowfield and J. Vicens) Kluwer Academic, Dordrecht, **2001**, pp.110.
- 550 26 P. Lhoták, *Eur. J. Org. Chem.*, 2004, 1675.
- 27 N. Morohashi, F. Narumi, N. Iki, T. Hattori, S. Miyano, *Chem. Rev.*, 2006, **106**, 5291.
- 28 G. D. Andreetti, R. Ungaro, A. Pochini, *Chem. Commun.*, 1979, 1005.
- 555 29 H. Akdas, E. Graf, M.W. Hosseini, A. De Cian, J.M. Harrowfield, *Chem. Commun.*, 2000, 2219.
- 30 J. Sykora, M. Himl, I. Stobor, I. Cisarova, P. Lhotak, *Tetrahedron.*, 2007, **63**, 1675.

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Graphical abstract

The combination of a thiacalix[4]arene in 1,3-alternate conformation bearing four nitrile groups at the lower rim with silver cation leads, independent of the nature of the anion used, to the formation of 1-D coordination networks in the crystalline phase.

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