

New 2-D silver(I) coordination network constructed from thiomethyl group-substituted *p*-tert-butylthiacalix[4]arene

Huriye AKDAŞ-KILIÇ^{1,2,*} , Ernest GRAF³, Mir Wais HOSSEINI³ , Nathalie KYRITSAKAS³ 

¹Department of Chemistry, Yıldız Technical University, İstanbul, Turkey

²Universite de Rennes, CNRS, ISCR-UMR, ISCR-UMR, Rennes, France

³Laboratoire de Tectonique Moléculaire, UMR CNRS, icFRC, Strasbourg University, Strasbourg

Received: 24.02.2022 • Accepted/Published Online: 11.05.2022 • Final Version: 05.10.2022

Abstract: New ligand based on *p*-tert-butyltetrathiacalix[4]arene blocked in 1,3-alternate conformation, was achieved via a multistep synthesis with the introduction of thiomethylpropoxy groups on the lower rim which leads to a neutral tecton. The combination of this *p*-tert-butyltetrathiacalix[4]arene (*p*-TCA-2), in 1, 3-alternate imposed conformation, with tetrahedral Ag(I)SbF₆ salt, leads to the formation of neutral, new 2-D coordination network, which was structurally investigated in the solid state by X-ray diffraction methods on a single crystal.

Key words: Molecular networks, coordination polymer, thiacalix[4]arene, X-ray structure, thioether

1. Introduction

In the field of chemistry, nanotechnology results in the construction of nanometer-sized materials by synthetic means or the interconnection of chemical molecules. Thus, to obtain functional materials, it is necessary to be able to synthesize molecules capable of transferring information through their electronic, optical, or ionic properties. Finally, it is necessary to be able to assemble them in a perfectly controlled way in order to obtain a material having not only the intrinsic properties of the molecules that compose it but also the properties of the material. Obtaining materials with specific properties requires the arrangement of these molecules within the material, in order to take full advantage of their individual properties (alignment of dipole moments, magnetic moments, etc.). The design of molecular architecture in the solid-state is actually a challenging issue of current interest. Molecular tectonics, the research area dealing with the design and generation of such architectures [1] is a powerful strategical approach, which relies on concepts such as molecular recognition, developed in supramolecular chemistry [2] for which the components are assembled by attractive intermolecular interactions. Indeed, molecular tectonics concerns the control, under self-assembly conditions, of connectivity between informed and programmed molecular building blocks or tectons through iterative molecular recognition processes [3–8]. A further step, which remains to be achieved, consists of the incorporation of physical properties within the molecular tectons in order to obtain a functional network. Indeed, the variety of specific features such as coordination geometry, redox, optical, and magnetic properties associated with metallic centers by using extensively coordination bonds and their incorporation within coordination polymers [9, 10] or metal organic frameworks [11] (metals as structural nodes of the network), may lead to new materials, obtained by self-assembly processes, and lead to possible applications [12].

The number of translations of the assembling cores into one, two, or three directions of space respectively will define the dimensionality of the network, i.e. 1-, 2- or 3- D [13-16]. The majority of coordination networks reported are based on the use of cationic metal centers. In order to get neutral networks in the case of neutral organic tectons, the presence, of either an anionic organic tecton or the presence of anions is required. For the latter case, the self-assembly processes taking advantage of the presence of the anion to direct the dimensionality were previously reported [17].

For the design of tectons, *p*-tert-butyltetrathiacalix[4]arene (*p*-TCA), which is a macrocyclic organic platform, composed of four phenol moieties connected by thioether bridges is of interest because of steric reasons, this macrocycle is not planar but adopts four limit conformations (cone, partial cone, 1,2-alternate and 1,3-alternate) [18]. Among the four limit conformations adopted by TCA, the 1,3-alternate conformer is particularly interesting because of four coordinating

* Correspondence: hakdas@yildiz.edu.tr

sites, since the alternate fashion allows to positioning of four interactions below and above the macrocyclic backbone. The *p*-*tert*-butylthiacalix[4]arenes have been decorated both at the upper and/or lower rims with a variety of monodentate donor sites and periodic infinite 1-, 2- and 3-D silver coordination networks based on thiacalix[4]arene or *p*-*tert*-butylthiacalix[4]arene derivatives in 1,3-alternate conformation bearing four nitrile groups [19], carboxylate units [20] or benzonitrile groups [21] have been described. Combinations of thiacalix[4]arenes derivatives bearing carboxylate groups with metal cations and auxiliary ligands lead to infinite architectures [22]. To the best of our knowledge, 2-D network with *p*-*tert*-butylthiacalixarenes bearing pendant thiomethylpropoxy groups has never been reported previously. In the present contribution, we report a new 2-D coordination network from *p*-TCA-2 combined with Ag(I)SbF₆ salt and we demonstrate the influence of the flexibility of the coordinating arm on the dimensionality of the network by X-ray diffraction studies.

2. Material and methods

2.1. Experimental

¹H and ¹³C NMR were obtained on a Bruker WP 200 SY (200 MHz) and Bruker VC 300 (300 MHz) at 298 K. The deuterated solvent was used as purchased. X-ray diffraction data collection was carried out on a Kappa CCD diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using graphite-monochromated Mo-Kα radiation. For all structures, diffraction data were corrected for absorption and analysed using the OpenMolen package [23]. All non-H atoms were refined anisotropically.

2.2. Synthesis

General. All reagents were purchased from commercial sources and used without further purification. *P*-*tert*butylbutylthiacalix[4]arene (*p*-TCA) was prepared by using previously reported procedures [24].

5,11,17,23-Tetrakis(*tert*-butyl)- 25,26,27,28-tetra(3-bromopropoxy) tetrathiacalix[4]arene: A suspension of *p*-*tert*butylthiacalix[4]arene (1 g, 1.3 mmol), acetone (60 ml) and K₂CO₃ (1.5 g, 0.1 mmol) is stirred at 80°C for 3 hours. After adding 10 ml of dibromopropane, the suspension is stirred at the same temperature for 3 days. After filtration, the solvent is evaporated off and the residue is washed with 30 ml of MeOH to give 1.3 g of pure product *p*-TCA-1.

Yield: 92%, Colorless solid. mp: 310 °C. C₅₂H₆₈O₄Br₄S₄·1/2C₅H₁₂ (requires: C, 52.93; H, 6.06; S, 10.28 found: C, 52.74; H, 6.01; S, 10.33 %). ¹H NMR (CDCl₃): δ = 1.32 (s, 36H, C(CH₃)₃), 1.54 (q, *J* = 7.3 Hz, 8H, CH₂), 3.07 (t, *J* = 7.1 Hz, 8H, CH₂), 3.97 (t, *J* = 6.8 Hz, 8H, CH₂), 7.35 (s, 8H, ArH). ¹³C NMR (CDCl₃): δ = 30.4, 31.4, 32.2, 34.4, 67.0, 127.2, 128.2, 146.5, 156.3.

5,11,17,23-Tetrakis(*tert*-butyl)- 25,26,27,28-tetra(3-thiomethylpropoxy) tetrathiacalix[4]arene: A suspension of (3-tetrabromopropoxy)-*p*-*tert*butylthiacalix[4]arene *p*-TCA-1 (0.5 g, 4.14 mmol), in the presence of NaSCH₃ (200 mg, 2.8 mmol) in THF (20 ml) is refluxed overnight. The mixture was then brought to room temperature, the solvent evaporated and the residue triturated with MeOH to give 410 mg of product *p*-TCA-2.

Yield: (93% yield). Colorless solid. mp: 315 °C (decomp). C₅₆H₈₀O₄S₈

¹H NMR (CDCl₃): δ = 1.30 (s + m, 44H, C(CH₃)₃ + CH₂), 2.04 (s, 12H, CH₃), 2.26 (t, *J* = 7.2 Hz, 8H, CH₂), 3.92 (t, *J* = 7.5 Hz, 8H, CH₂), 7.33 (s, 8H, ArH). ¹³C NMR (CDCl₃): δ = 15.9, 28.5, 31.1, 31.3, 34.3, 67.7, 127.5, 128.0, 145.8, 156.7.

2.3. Crystallisation conditions

Procedure for ligand: In a crystallization tube (4 mm diameter, 15 cm height), a solution of compound *p*-TCA-2 (5.5 mmol) in degassed CHCl₃ (1 mL) was layered carefully with a degassed MeOH (1 mL). Slow diffusion at room temperature produced crystals suitable for X-ray diffraction studies after several days.

Procedure for Network: In a crystallisation tube (4 mm diameter, 15 cm height), a solution of compound *p*-TCA-2 (5.5 mmol) in degassed dioxane (1 mL) was layered with a degassed dioxane/MeOH (1/1) mixture (1 mL). A solution of AgSbF₆ (5.5 mmol) in degassed MeOH (1 mL) was carefully added. Slow diffusion at room temperature produced crystals suitable for X-ray diffraction studies after several days.

2.4. Single-crystal XRD data

Table. Crystallographic data for Networks A and B

3. Results and discussion

Metallo-organic frameworks, widely described in the literature, are numerous and the complexes obtained can take the form of linear segments, helicoidal structures, rack structures, ladders, or grids formed by the assembly of rigid tectons or macrocycles via coordination bonds [25]. For the design of this tecton we use the same criteria as for previous works [26] based on *p*-*tert*butyltetrathiacalix[4]arene, namely a ligand presenting two-by-two divergent thioether type coordination sites on the lower rim in a blocked 1,3-alternate conformation. Compound *p*-TCA-2 including all these *ab initio* design information, presented in Figure 1, has been prepared via a multi-step synthesis and characterized.

P-*tert*butyltetrathiacalix[4]arene was initially synthesized according to a known procedure [18]. The synthesis of this type of ligand was carried out in two steps (Figure 1), starting from *p*-*tert*butylthiacalix[4]arene *p*-TCA which was initially

treated with an excess of dibromopropane in acetone under reflux, in the presence of K_2CO_3 to give the tetrabrominated intermediate *p*-TCA-1 in very good yields and in 1,3-alternate conformation (Figure 1). These kinds of compounds carrying four bromopropyl chains can be qualified as precursors. Indeed, bromo groups are very good nucleofuges, they can be replaced by all types of nucleophilic groups and thus may give a very wide variety of thiacalix[4]arenes in 1,3-alternate conformation exclusively, *p*-TCA-1 can be considered as an important intermediate. This intermediate, in the presence of sodium methanethiolate in refluxing THF, yields quantitatively tecton *p*-TCA-2 (93 %) and was identified by NMR and X-ray diffraction (Figure 2). The solid-state X-ray characterization confirms the 1,3-alternate conformation for compound *p*-TCA-2.

The thiacalix[4]arene derivative *p*-TCA-2 adopts the 1,3-alternate conformation positioning, thus two opposite units on the same face of the thiacalix platform, which was confirmed also by 1H NMR spectroscopy. Indeed, the protons in the thiomethyl group are shifted to 1,34 ppm compared to the tables (≈ 2 ppm). These groups, because of the 1,3-alternate conformation, are under the shielding effect of the aromatic wall. The macrocycle presents coordinating sites in two opposite directions which can allow the formation of a coordination network based on the use of the above-mentioned strategy. In the cases when the coordinating arms are rigid and linear, we will observe one-dimensional coordination network. [27]

This intermediate, in the presence of sodium methanethiolate in refluxing THF, yields quantitatively the tecton *p*-TCA-2 which was characterized by X-ray diffraction on a single crystal (Figure 2) obtained by slow diffusion of a MeOH solution into a $CHCl_3$ solution containing product *p*-TCA-2. The X-ray crystal structure shows that the thiacalix[4]arene derivative is blocked in 1,3-alternate conformation. The average distance observed for the C-S bond is 1.76 Å, with a CSC angle of 107.6°. We can also notice an average bond distance for $C_{Ar}-O$ of 1.36 Å and 1.63 Å for S-Me bonds.

Among several trials dealing with the formation of coordination networks using tecton *p*-TCA-2, we attempted the complexation of all these ligands with various metal salts, $AgSbF_6$ salts, so far, have given single crystals of suitable quality

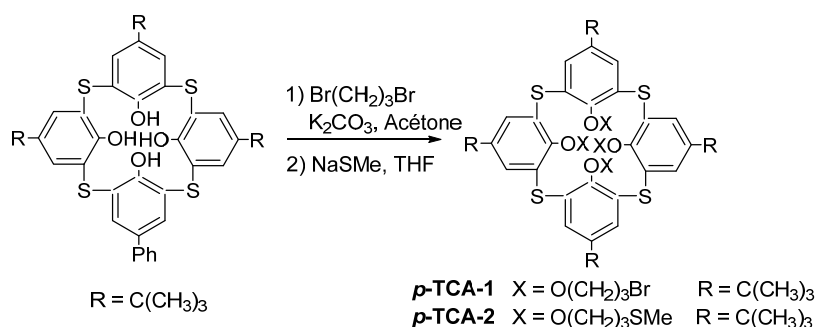


Figure 1. Synthesis of *p*-TCA-1 and *p*-TCA-2 derivatives.

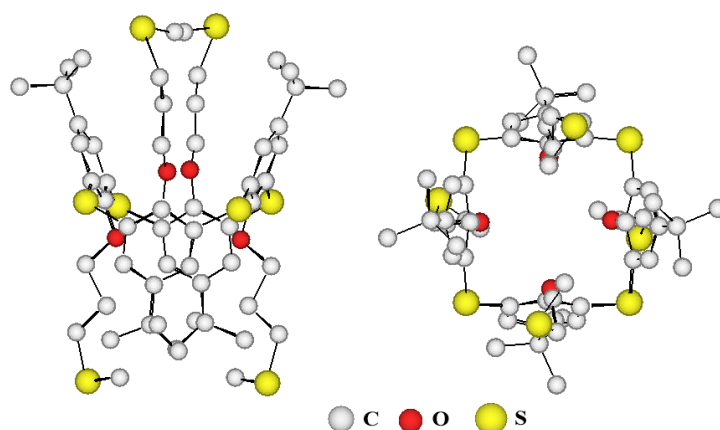


Figure 2. X-ray crystal structure of the ligand *p*-TCA-2 Left: side view; Right: top view.

for X-ray diffraction which was structurally characterized in the solid-state. At room temperature, upon slow diffusion of a dioxane solution of **p-TCA-2** into a MeOH solution of AgSbF_6 , colourless single crystals were obtained respectively after ca. 48 h and were studied by X-ray diffraction. Crystal information data are summarized in the Table.

X-ray crystallographic analysis shows that the crystal is composed of a **p-TCA-2** ligand and Ag(I) atoms and the two-dimensional molecular network can be described by an infinite association of ligands and metals in two directions of the space. The crystal (monoclinic system, space group $P 1 21/n 1$) is composed of charged networks and SbF_6^- anions. The metal Ag(I), which can adopt linear or tetrahedral coordination geometries, in this network adopts a tetrahedral coordination geometry, is bonded to the sulfur atoms of four different thiacalix[4]arenes and this part represents the elementary unit of the coordination network and one thiacalix[4]arene derivative **p-TCA-2** is bonded to four different silver atoms and his center is located at the top of a square of 13.8 Å side, which by translation makes it possible to build the 2-D network (Figure 4). The compensation of the positive charges of the Ag(I) cations is made possible by the presence of SbF_6^- anions in the interstices of the crystal, the latter have been omitted for more clarity.

The tetrahedral coordination geometry of the Ag(I) cation is slightly distorted since the S-Ag-S angles vary from 117.2° to 127.2° and the CSC angles are on average 106.5° whereas it was 107.6° for the free ligand. We observe an average distance for the Ag-S bond is 2.61 Å and an average bond distance for C-S of 1.72 Å and 1.69 Å for S-Me bonds. The four thiacalix[4]arenes derivatives **p-TCA-2** around an Ag(I) cation can be grouped in pairs. Indeed, a front view of the elementary unit (Figure 5) shows that two thiacalix[4]arene derivatives **p-TCA-2** facing each other are symmetrical with respect to a plane and thus form two groups. The ligands of the first group (Blue) are not at the same height and are turned at 90° compared to the second group (Yellow).

The side view in Figure 4 highlights the topology of the polymer. Indeed, the 1,3-alternate conformation of the **p-TCA-2** ligand, and the arrangement in pairs of the thiacalixarenes derivatives which is also given in Figure 6, give a wavy structure to the two-dimensional coordination polymer.

Probably as a result of better packing, the 2-D wavy sheets are stacked in a slightly shifted parallel fashion, generating cavities (Figure 5). Indeed, the first sheet is shifted horizontally from the second, by a unit which represents approximately half a calix. Additionally, the interstices or cavities between these two polymers are filled with SbF_6^- anions. For that reason, we observe no interaction between the different layers since the minimum distance between them is 4.3 Å.

In conclusion, using the thiacalix[4]arene derivative **p-TCA-2**, in the neutral form and in 1,3-alternate conformation, bearing four thiomethyl pendant groups and Ag(I) cations, a 2-D coordination network has been obtained via self-assembly process and structurally characterised in the crystalline phase based on coordination bond type interactions. Thus, we have demonstrated that thiacalixarenes could quite play the role of a rigid skeleton, on which it is quite easy to graft various coordinating units. The effect of the flexible nature of the coordinating arm on the dimensionality was demonstrated: when flexible alkane chains are used, networks with higher dimensions can be obtained.

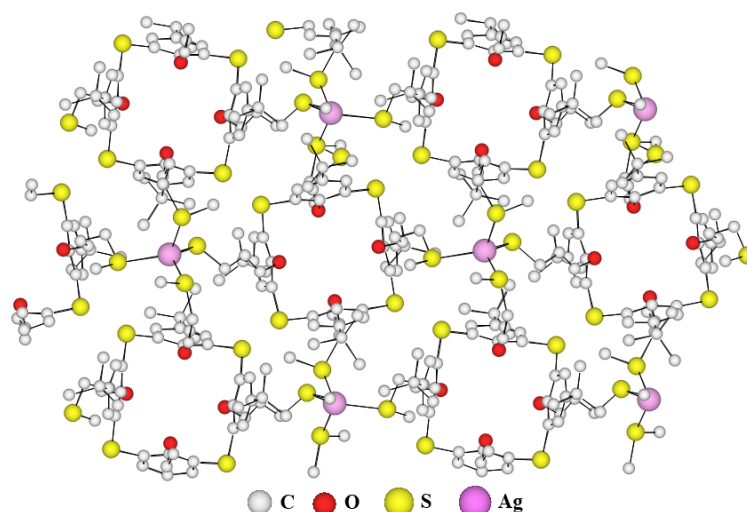


Figure 3. X-ray crystal structure of the 2-D network obtained with ligand **p-TCA-2** and AgSbF_6 . (SbF_6^- anions omitted for clarity).

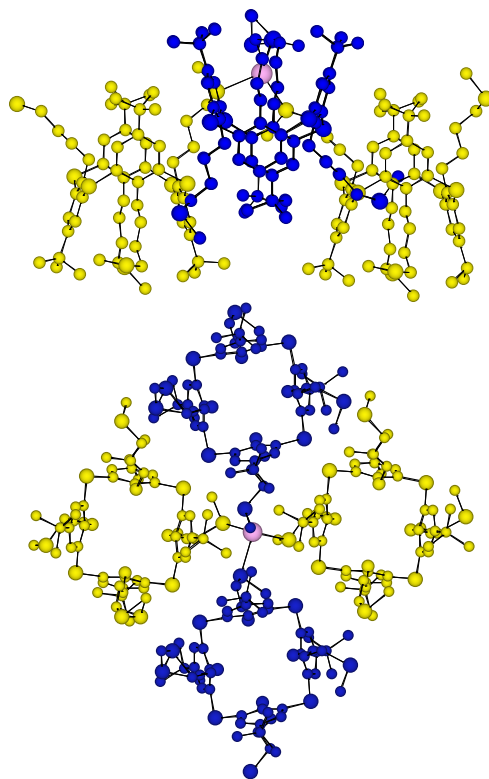


Figure 4. Disposition of the ligands *p*-TCA-2 around the Ag center. Top: side view; Bottom: front view (SbF_6^- anions omitted for clarity).

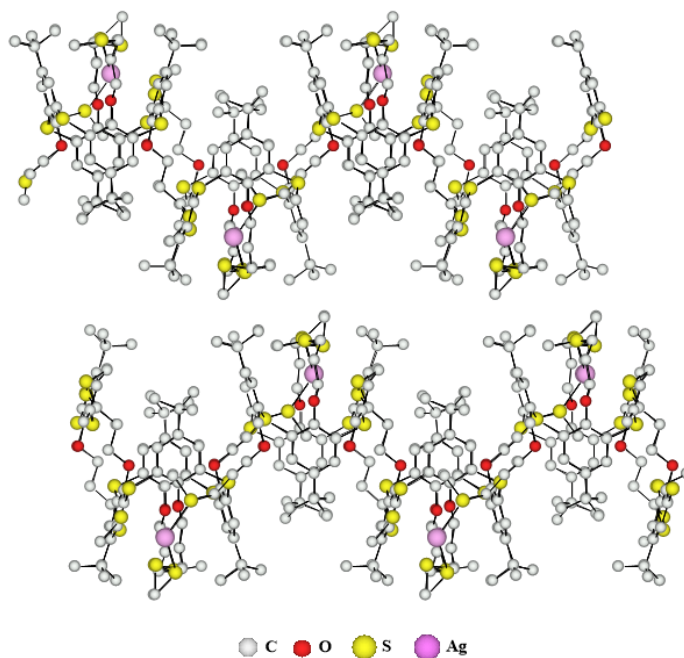


Figure 5. Part of the X-ray crystal structure of the 2-D network obtained with ligand *p*-TCA-2 and AgSbF_6 , stacking of the layers in the crystal (SbF_6^- anions omitted for clarity).

Table. Crystallographic datas for *p*-TCA-2 and the network obtained from *p*-TCA-2 and AgSbF6.

	<i>p</i> -TCA-2	Network
Formula	C ₅₆ H ₈₀ O ₄ S ₈	C ₆₁ H ₉₂ AgF ₆ O ₇ S ₈ Sb :C ₅₆ H ₈₀ Ag.SbF ₆ •C ₄ H ₈ O ₂ •CH ₃ OH
Molecular weight	1073.77	1537.53
Crystal system	tetragonal	monoclinic
Space group	I 4 ₁ /a	P 1 21/n 1
a(Å)	19.3952(8)	14.9907(2)
b(Å)	19.3952(8)	13.8259(2)
c(Å)	15.6769(6)	34.0796(5)
β(deg)		102.489(5)
V(Å ³)	5897.2(4)	6896.2(2)
Z	4	4
Colour	colourless	colourless
Crystal dim(mm)	0.20*0.12*0.10	0.20*0.08*0.04
D _{calc} (gcm ⁻³)	1.21	1.48
F000	2304	3176
m(mm ⁻¹)	0.345	0.982
Trans. min and max	0.932/0.966	0.820/0.961
Temperature(K)	173	173
Wavelength(Å)	0.71073	0.71073
Radiation	MoKα graphite monochromated	MoKα graphite monochromated
Diffractometer	KappaCCD	KappaCCD
Scan mode	'phi scans'	'phi scans'
hkl limits	-25.25/-17.17/-20.15	0.20/0.18/-46.45
Theta limits(deg)	2.5/27.48	2.5/29.10
Number of data meas.	5436	19109
Number of data with I > 3 s(I)	1363	7634
Number of variables	154	703
R	0.107	0.111
Rw	0.117	0.122
GOF	1.017	1.006
Largest peak in final difference (eÅ ⁻³)	0.489	1.053

Acknowledgement and/or disclaimers, if any

We thank Strasbourg University and the Ministry of Research for financial support and the Région Alsace for a scholarship to H. A. K.

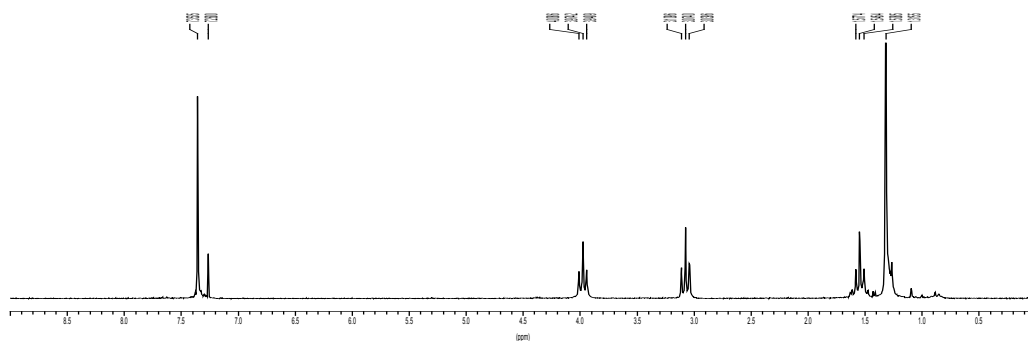
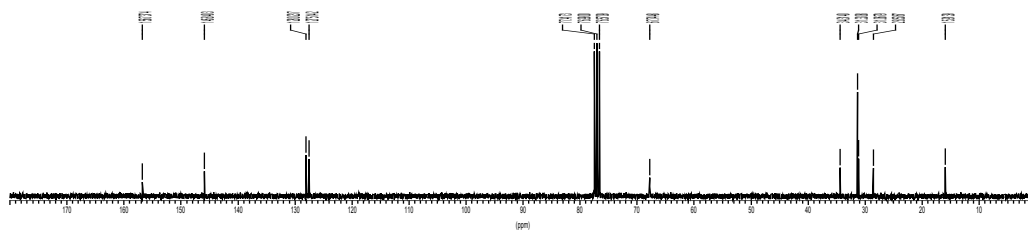
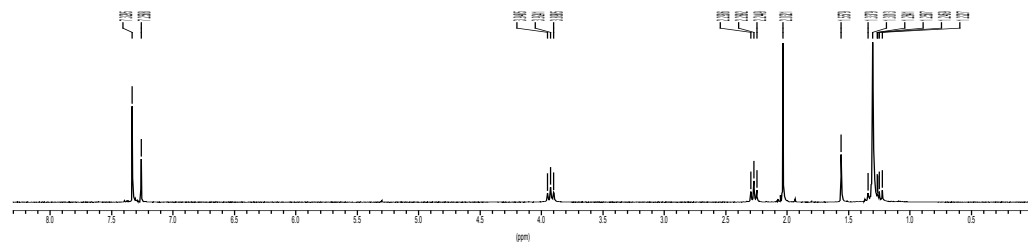
References

1. Mann S. Molecular tectonics in biomineralization and biomimetic materials chemistry. Nature 1993; 365: 499-505. doi: 10.1038/365499a0
2. Hosseini M W. Molecular tectonics: from simple tectons to complex molecular networks. Account Chemical Research 2005; 38: 313-323. doi: 10.1021/ar0401799

3. Kitagawa S, Kitaura R, Noro S. Functional porous coordination polymers. *Angewandte Chemie International Edition* 2004; 43: 2334-2375. doi: 10.1002/anie.200300610
4. Férey G, Mellot-Draznieks C, Serre C, Millange F. Crystallized frameworks with giant pores: are there limits to the possible? *Account Chemical Research* 2005; 38: 217-225. doi: 10.1021/ar040163i
5. Long JR, Yaghi OM. Metal-organic frameworks issue. *Chemical Society Revue* 2009; 38: 1213-1214. doi: 10.1039/b903811f
6. Zhou H-C, Long JR, Yaghi OM. Introduction to metal-organic frameworks. *Chemical Reviews* 2012; 112 (2): 673-674. doi: 10.1021/cr300014x
7. Moulton B, Zaworotko MJ. From molecules to crystal engineering: supramolecular isomerism and polymorphism in network solids. *Chemical Reviews* 2001; 101: 1629-1658. doi: 10.1021/cr9900432
8. Carlucci L, Ciani G, Proserpio DM. A new type of supramolecular entanglement in the silver(I) coordination polymer [Ag₂(bpethy)₅](BF₄)₂ [bpethy = 1,2-bis(4-pyridyl)ethyne]. *Chemical Communications* 1999; 449-450. doi: 10.1039/a809361j
9. Abrahams BF, Hoskins BF, Robson RA. New type of infinite 3D polymeric network containing 4-connected, peripherally-linked metalloporphyrin building blocks. *Journal of the American Chemical Society* 1991; 113: 3606-3607. doi: 10.1021/ja00009a065
10. Hosseini MW. NATO ASI Series, ed. G. Tsoucaris, 1998, vol. C519, 209.
11. Yaghi OM, Li H, Davis C, Richardson D, Groy TL. Synthetic Strategies, Structure Patterns, and Emerging Properties in the Chemistry of Modular Porous Solids, *Account Chemical Research* 1998; 31: 474-484. doi: 10.1021/ar970151f
12. Liu J-Q, Luo Z-D, Pan Y, Singh AK, Trivedi M et al. Recent developments in luminescent coordination polymers: designing strategies, sensing application and theoretical evidences. *Coordination Chemistry Reviews* 2020; 406: 213145-213191. doi: 10.1016/j.ccr.2019.213145
13. Carlucci L, Ciani G, Proserpio DM, Rizzato S. New polymeric networks from the self-assembly of silver(I) salts and the flexible ligand 1,3-bis(4-pyridyl)propane (bpp). A systematic investigation of the effects of the counterions and a survey of the coordination polymers based on bpp, *Crystal Engineering Communications* 2002; 4 (22): 121-129. doi: 10.1039/b201288j
14. Brandys M-C, Puddephatt RJ. Ring, polymer and network structures in silver(I) complexes with dipyriddy and diphosphine ligands. *Chemical Communication* 2001; 1508-1509. doi: 10.1039/b104857k
15. Assoumatinea T, Stoeckli-Evansb H. Silver(I) nitrate two-dimensional coordination polymers of two new pyrazinethiophane ligands: 5,7-dihydro-1H,3H-dithieno[3,4-b:3',4'-e]pyrazine and 3,4,8,10,11,13-hexahydro-1H,6H-bis([1,4]dithiincino)[6,7-b:6',7'-e]pyrazine, *Crystallographic Communications* 2020; 76 (4): 539-546. doi: 10.1107/S205698902000362X
16. Leong WL, <https://pubmed.ncbi.nlm.nih.gov/20804195/> - affiliation-1 Vittal JJ. One-dimensional coordination polymers: complexity and diversity in structures, properties, and applications, *Chemical Revue* 2011; 111 (2): 688-764. doi: 10.1021/cr100160e
17. Grosshans P, Jouaiti A, Hosseini MW, Kyritsakas N. Molecular tectonics: structural and magnetic properties of a discrete copper binuclear complex and a 1-D coordination network. *New Journal of Chemistry* 2003; 27: 1801-1805. doi: 10.1039/B308944B
18. Akdas H, Bringel L, Graf E, Hosseini MW, Mislin G et al. Thiocalixarenes: Synthesis and structural analysis of thiocalix[4]arene and of p-tert-butylthiocalix[4]arene, *Tetrahedron Letters* 1998; 39: 2311-2314. doi: 10.1016/S0040-4039(98)00067-7
19. Kozlova M N, Ferlay S, Solovieva S E, Antipin IS, Kononov AI et al. Molecular tectonics: on the formation of 1-D silver coordination networks by thiocalixarenes bearing nitrile groups. *Dalton Transactions* 2007; 5126-5131. doi: 10.1039/b902267h
20. Kozlova MNK, Ferlay S, Kyritsakas N, Hosseini MW, Solovieva SE et al. Molecular tectonics: 3-D organisation of decanuclear silver nanoclusters, *Chemical Communications* 2009; 2514-2516. doi: 10.1039/b902267h
21. Kim K, Park S, Park K-M, Lee SS. Thiocalix[4]arene-based three-dimensional coordination polymers incorporating neutral bridging coligands. *Crystal Growth and Design* 2011; 11: 4059-4067. doi: 10.1021/cg4014703
22. Akdas H, Graf E, Hosseini MW, De Cian A, Harrowfield JM. Design, synthesis and structural investigation of a 2-D coordination network based on the self-assembly of the tetracarboxylate derivative of tetrathiocalix[4]arene and silver cation. *Chemical Communications* 2000; 2219-2220. doi: 10.1039/b007761p
23. Nonius BV. OpenMolenN, Interactive Structure Solution, Delft, The Netherlands, 1997.
24. Kumagai H, Hasegawa M, Miyanari S, Sugawa Y, Sato Y et al. Facile synthesis of p-tert-butylthiocalix[4]arene by the reaction of p-tert-butylphenol with elemental sulfur in the presence of a base. *Tetrahedron Letters* 1997; 38: 3971-3972. doi: 10.1016/S0040-4039(97)00792-2
25. Cook TR, Zheng Y-R, Stang PJ. Metal-organic frameworks and self-assembled supramolecular coordination complexes: comparing and contrasting the design. *Synthesis and Functionality of Metal-Organic Materials*, *Chemical Revue* 2013; 113 (1): 734-777. doi: 10.1021/cr3002824
26. Akdas H, Mislin G, Graf E, Hosseini MW, De Cian A et al. Synthesis and solid state structural analysis of conformers of tetrakis((ethoxycarbonyl)methoxy) tetrathiocalix[4]arene. *Tetrahedron Letters* 1999; 40 (11): 2113-2116. doi: 10.1016/S0040-4039(99)00143-4
27. Baklouti L, Harrowfield J, Pulpoka B, Vicens J. 1,3-Alternate, the Smart Conformation of Calix[4]arenes, *Mini-Reviews in Organic Chemistry* 2006; 3 (4): 355-384. doi: 10.2174/157019306778742850

Electronic supporting information

NMR characterizations

Figure S1. ^1H NMR of *p*-TCA-1 in CDCl_3 .Figure S2. ^{13}C NMR of *p*-TCA-1 in CDCl_3 .Figure S3. ^1H NMR of *p*-TCA-2 in CDCl_3 .

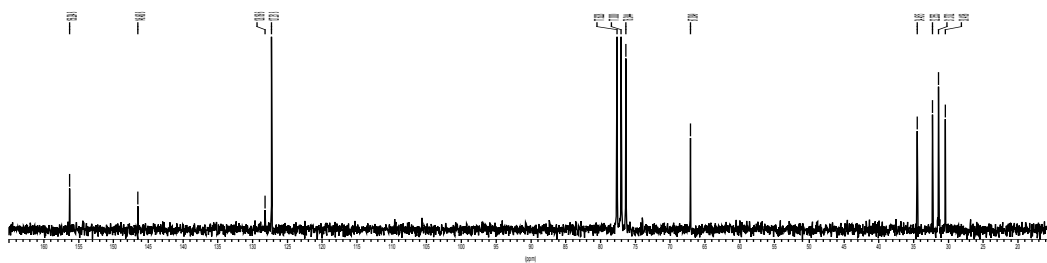


Figure S4. ^{13}C NMR of *p*-TCA-2 in CDCl_3 .