

Unique self-assembly patterns based on thiacalix[4]arene–silver interactions

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Abstract—Novel self-assembled supramolecular networks were prepared by the interactions of thiacalix[4]arenes bearing simple alkyl groups on the lower rim ($4\times\text{MeO-}$, $4\times n\text{-PrO-}$) with silver triflate. Contrary to the classical calix[4]arenes (with CH_2 bridges between the aromatic moieties), the presence of four sulfur atoms enables the formation of S–Ag–S connections between the individual molecules leading to the coordination topology so far unknown in calixarene chemistry. These systems form infinite 1-D coordination polymeric structures in the solid state, where the thiacalixarene moieties are preorganized in a side-by-side arrangement. Interestingly, the linear coordination polymers were obtained using both the conformational immobilised ($4\times n\text{-PrO}$, *cone*, *1,3-alternate* conformers) and the conformational mobile ($4\times\text{MeO}$) thiacalix[4]arenes, which indicates the generality of this behaviour in thiacalixarene series.

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1. Introduction

Calixarenes,¹ a well-known family of macrocyclic compounds, represent readily available three-dimensional structures widely used as starting materials and/or useful building blocks in the design of more sophisticated supramolecular systems. The easy derivatization of calix[4]arene together with controllable shape of its cavity make this molecule a very attractive candidate for various applications in supramolecular chemistry. Due to their excellent complexation and inclusion properties, calix[4]arenes are very popular for the design of receptors and self-assembled systems. Depending on the substitution pattern and the conformation of the parent calixarene, they can interact via many non-covalent interactions including hydrogen bonds, cation– π interactions, π – π interactions, electrostatic interactions, van der Waals interactions, coordination bonds, etc.

Crystal engineering or molecular tectonics² deal with the design and intentional formation of a molecular network in a macroscopic scale (crystals). The strategy is based on the fact that the building blocks (tectons) used for the crystal generation possess the corresponding functions with recognition abilities (self-recognition or recognition of suitable guest molecules) leading to the targeted self-assembly process during the crystal growth. Using their inclusion

properties, the concave cavities of calixarenes immobilised in the *cone* conformation were successfully applied as the tectons (here called koilands)³ in crystal design. This strategy enables the formation of an infinite 1-D solid-state structures exploring the interactions between the calixarenes (koilands) and the guest molecules (connectors). The above approach leads to a self-assembled system where individual building blocks adopt head-to-head mutual positions (Fig. 1). Similarly, calix[4]arenes in a *1,3-alternate* conformation

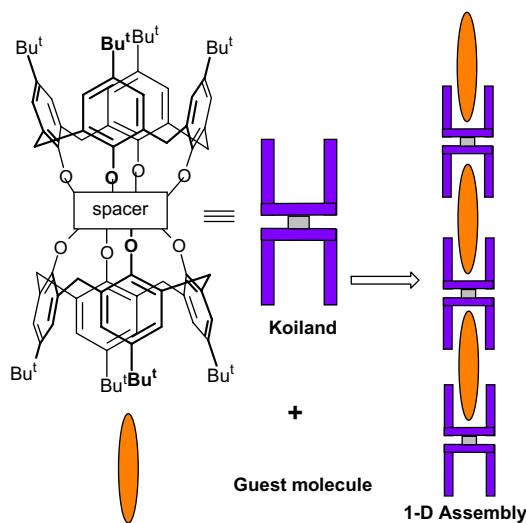


Figure 1. The formation of 1-D self-assembly using inclusion phenomenon in classical calix[4]arene series.

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formed 1-D polymer based on coordination chemistry of Ag^+ , possessing a similar topology.⁴ On the other hand, the formation of supramolecular assembly with a side-by-side architecture of calixarenes is impossible by this method.

Thiacalixarenes have recently emerged⁵ as new members of the calixarene family. The incorporation of four sulfur atoms instead of common CH_2 bridges makes thiacalix[4]arenes very interesting molecules with many new features when compared with the chemistry of ‘classical’ calixarenes. Among them, novel possibilities arising from the combination of the classical skeleton with sulfur atoms, such as different conformational preferences and special complexation properties, are now obvious and promise many potential applications.⁶ In this paper we demonstrate the utilisation of simple thiacalix[4]arene derivatives for the generation of 1-D supramolecular self-assembled systems with so far unknown topology, where the individual molecules of the macrocycle are in a side-by-side orientation (Fig. 2).

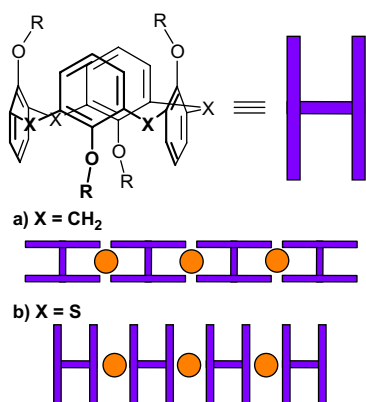


Figure 2. The comparison of 1-D coordination polymer in calix[4]arene and thiacalix[4]arene series.

2. Results and discussion

Thiacalixarenes **1–3** selected for the crystallographic study (Fig. 3) were chosen to cover three different types of thiacalixarene conformations. Thus, tetra-*n*-propoxythiacalixarenes **1** and **2** represent immobilised structures with the cone and the 1,3-alternate conformations, respectively. On the other hand, tetramethoxy derivative **3** is an example of conformationally mobile structure. Single crystals suitable for the structure determination were obtained by a slow evaporation of thiacalixarene solution ($\text{CHCl}_3/\text{AcOEt}/\text{CH}_3\text{CN}=2:1:2$) in the presence of 2.5 equiv of silver triflate.

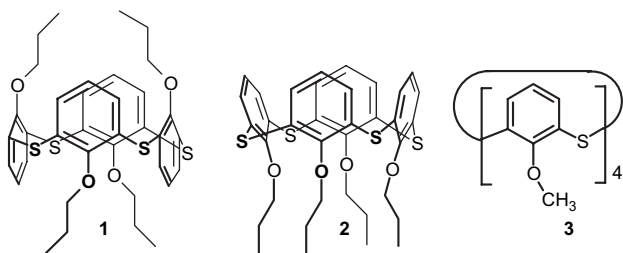


Figure 3. Thiacalix[4]arenes studied.

In our previous paper⁴ we have shown that under these conditions 25,26,27,28-tetrapropoxythiacalix[4]arene 1,3-alternate creates infinite channel-like structures (1-D-coordination polymer), where two silver cations are held by cation- π interactions with both sides of calixarene cavities. X-ray crystallographic analysis shows that the overall self-assembly (schematically depicted in Fig. 2a) is held together by triflate anions playing the role of the bridges between the individual silver complexes.

As expected, the situation in the thiacalixarene series is completely different. Thiacalix[4]arene **1** does not interact with silver triflate via cation- π interactions, but rather via electrostatic interactions with sulfur atoms.¹³ As a consequence, thiacalix[4]arene forms *exo*-complexes with silver being coordinated to the all four sulfur atoms. Interestingly, silver cations are trapped between thiacalix[4]arene units in such a way, that thiacalixarene cavities are mutually oriented side by side. Thiacalix[4]arene neighbours are connected via two S-Ag-S bridges on both sides forming along the X-axis a 1-D polymeric chain with the final ratio thiacalixarene/silver triflate=1:2. All thiacalix[4]arene units within a polymeric chain are oriented to the same direction (Fig. 4). The rest of the silver coordination sphere (trigonal/distorted tetrahedral) is occupied by triflate oxygen atoms providing the interconnection of individual chains in the perpendicular Y-direction resulting in 2-D sheet-like structure. Sheets are layered in the Z-direction in such a way that the thiacalix[4]arene moieties create an infinite channel network, well known from the free thiacalix[4]arene¹⁴ or classical calixarene¹⁵ molecular packing (Fig. 5).

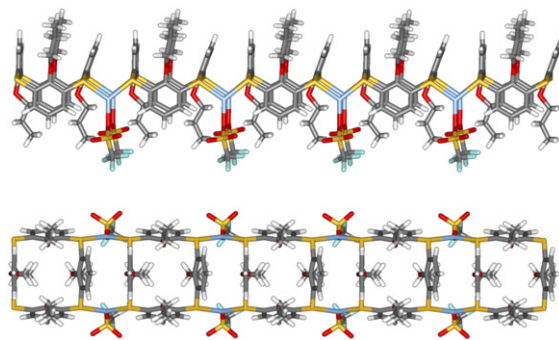


Figure 4. Side-by-side self-assembly of AgTfI and thiacalixarene **1**.

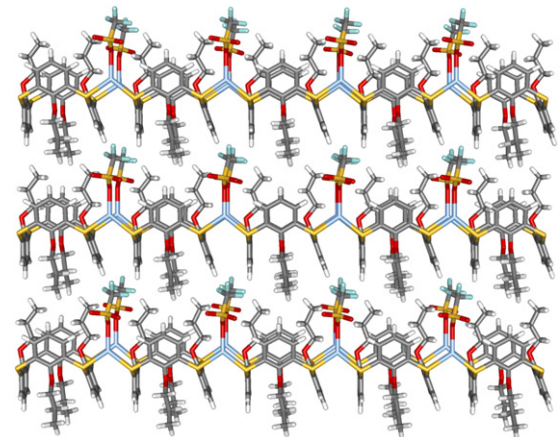


Figure 5. The interconnection of individual chains in **1**/ AgTfI system.

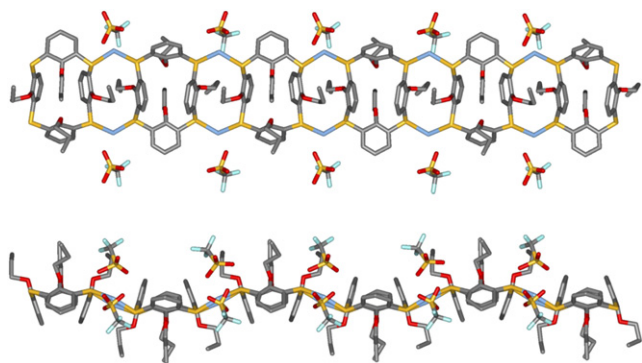


Figure 6. Side-by-side self-assembly of AgTfI and thiacalixarene **2**.

Similar silver coordination pattern and the same intermolecular interactions also take place in the *cone* tetrapropoxythiacalix[4]arene **2**. Obviously, due to the different molecular geometry (if compared with a *1,3-alternate*) a different self-assembly arrangement in the crystal lattice emerged. Again, 1-D polymeric chains along the [011] direction are formed, but this time, the thiacalix[4]arene units alternate the mutual orientations (Fig. 6) within the chains (up-down). Due to the intermolecular CH- π interactions (the O-CH₂ group in the propoxy substituent interacts with the aromatic subunit of neighbour thiacalix[4]arene; 2.8 Å distance indicates strong CH- π interaction), thiacalix[4]arenes are not so close to each other within the 1-D chain as it was in the *1,3-alternate* structure. Thus, the intermolecular S-S distances for the *cone* complex **2** (4.6 Å) are longer than those in compound **1** (4.0 Å). As described for compound **1**, the individual 1-D chains of complex **2** are again interconnected via triflate anions in the X-direction and 2-D sheets are formed. As these sheets are layered in the third direction, the thiacalix[4]arene units are alternatively oriented head-to-head and/or tail-to-tail. When the head-to-head (upper rim-upper rim) orientation occurs in the structure some cavities or channels are formed. To clearly demonstrate the size of this free space the spheres of 3 Å radius were placed there (Fig. 7). This free space was treated with the SQUEEZE¹² procedure. It corresponds to 364 Å³ and is well reflected in the material density: 1.54 g/cm³ for the *cone* complex **2** versus 1.70 g/cm³ for *1,3-alternate* complex **1**.

It was shown that free ligand **3** adopts a complicated solid-state structure where the *cone* and the *1,3-alternate*

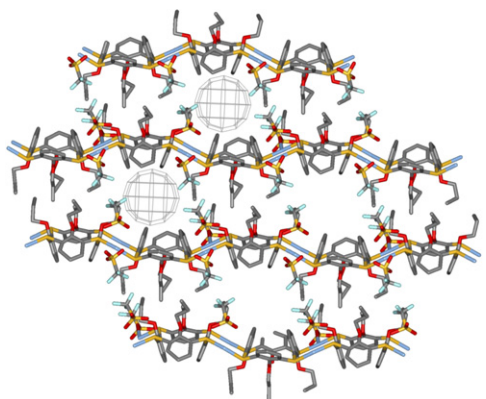


Figure 7. Voids in **2**/AgTfI complex.

conformations coexist in a 3:1 ratio within the crystal lattice.⁹ On the other hand, the **3**/AgTfI complex prefers the *cone* conformation in the solid state. The way of interactions and the molecular packing within a 2-D sheet is fully identical with that in the *cone* complex **2**, including the strong CH- π intermolecular interaction of the methoxy group with the aromatic unit (CH- π distance=2.8 Å). The structures **2** and **3** could be isostructural as the cell parameters indicate, but the sheets are mutually slightly shifted in 3-D packing of **3** if compared with the structure of complex **2**. Nevertheless, similar voids located between the individual sheets were found also in this structure. In this case it was possible from the low temperature data to localise three ethyl acetate molecules per unit cell. Trapped solvent thus significantly increases the material density to 1.73 g/cm³ (Fig. 8).

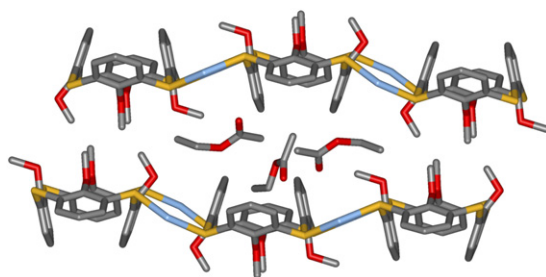


Figure 8. Voids in **3**/AgTfI complex filled with ethyl acetate molecules.

3. Conclusions

We have demonstrated that simple thiacalixarene derivatives form well-defined self-assembly with silver triflate. The coordination of Ag⁺ via sulfur atoms of parent thiacalixarenes enables unique preorganisation of the calixarene cavities in a side-by-side manner. To the best of our knowledge, this type of preorganisation has never been described in classical calixarene series, and makes thiacalixarenes suitable candidates for the crystal engineering and design of new materials.

4. Experimental

4.1. General

Compounds **1** (4×*n*-PrO, *1,3-alternate*),⁷ **2** (4×*n*-PrO, *cone*)⁸ and **3** (4×MeO)⁹ were prepared according to the methods reported in the literature.

4.1.1. 25,26,27,28-Tetrapropoxy-2,8,16,22-tetrathiacalix[4]arene (1,3-alternate)/2AgTfI complex. The complex was obtained as white needles by a slow evaporation of thiacalixarene solution (CHCl₃/AcOEt/CH₃CN=2:1:2) in the presence of 2.5 equiv of AgTf, mp: >250 °C (dec). ¹H NMR (CDCl₃/CD₃OD=3:2 v/v, 300 MHz, 298 K) δ 0.68 (t, 12H, -CH₃, *J*=7.6 Hz), 1.21 (m, 8H, -CH₂-), 3.84 (t, 8H, -O-CH₂-, *J*=7.8 Hz), 6.88 (t, 4H, H-arom, *J*=7.5 Hz), 7.41 (d, 8H, H-arom, *J*=7.5 Hz). EA calcd for 2CF₃SO₃Ag·C₃₆H₄₀O₄S₄: C, 38.72; H, 3.42; S, 16.32%. Found C, 38.47; H, 3.35; S, 16.28%. MS ESI+ *m/z* 773.26, 771.24 [3+Ag⁺] (100%).

4.1.1.1. Crystallographic data. $2\text{AgCF}_3\text{SO}_3 \cdot \text{C}_{36}\text{H}_{40}\text{O}_4\text{S}_4$, $M=1178.85$ g/mol, monoclinic system, space group $P2_1/m$, $a=9.522(2)$, $b=21.290(2)$, $c=11.338(2)$ Å, $\beta=90.36(1)$, $Z=2$, $V=2305.8(7)$ Å³, $D_c=1.70$ g/cm³, $\mu(\text{Cu K}\alpha)=10.04$ mm⁻¹, crystal dimensions of $0.1 \times 0.1 \times 0.3$ mm. Data were collected at 293 K on an Enraf–Nonius CAD4 diffractometer with graphite monochromated Cu K α radiation. The structure was solved by direct methods.¹⁰ Only minor geometrical restraints were applied to correct the distances within propoxy groups. The whole structure was refined by full matrix least squares on F values¹¹ to final $R=0.0887$ and $R_w=0.0624$ using 2621 independent reflections ($\theta_{\text{max}}=60^\circ$). All heavy atoms were refined anisotropically. Hydrogen atoms were located from expected geometry and were not refined. CCDC number 178410.

4.1.2. 25,26,27,28-Tetrapropoxy-2,8,16,22-tetrathiacalix[4]arene (cone)/2AgTf complex. The complex was obtained as white glossy needles by a slow evaporation of thiacalixarene solution ($\text{CHCl}_3/\text{AcOEt}/\text{CH}_3\text{CN}=2:1:2$) in the presence of 2.5 equiv of AgTf, mp: >250 °C (dec). ¹H NMR ($\text{CDCl}_3/\text{CD}_3\text{OD}=3:2$ v/v, 300 MHz, 298 K) δ 1.02 (t, 12H, $-\text{CH}_3$, $J=7.5$ Hz), 1.89 (m, 8H, $-\text{CH}_2-$), 4.10 (br s, 8H, $-\text{O}-\text{CH}_2-$), 6.72 (br s, 4H, H-arom), 7.05 (br s, 8H, H-arom). EA calcd for $2\text{CF}_3\text{SO}_3\text{Ag} \cdot \text{C}_{36}\text{H}_{40}\text{O}_4\text{S}_4$: C, 38.72; H, 3.42; S, 16.32%. Found C, 38.51; H, 3.25; S, 16.15%. MS ESI+ m/z 773.09, 771.09 [$2+\text{Ag}^+$] (100%).

4.1.2.1. Crystallographic data. $2\text{AgCF}_3\text{SO}_3 \cdot \text{C}_{36}\text{H}_{40}\text{O}_4\text{S}_4$, $M=1178.85$ g/mol, triclinic system, space group $P-1$, $a=12.622(1)$, $b=13.438(1)$, $c=16.793(1)$ Å, $\alpha=76.90(1)$, $\beta=73.62(1)$, $\gamma=70.16(1)$, $Z=2$, $V=2543.3(4)$ Å³, $D_c=1.54$ g/cm³, $\mu(\text{Cu K}\alpha)=9.10$ mm⁻¹, crystal dimensions of $0.1 \times 0.1 \times 0.2$ mm. Data were collected at 293 K on an Enraf–Nonius CAD4 diffractometer with graphite monochromated Cu K α radiation. The structure was initially solved by direct methods¹⁰ in the space group $P-1$ showing almost perfect inner symmetry. Nevertheless all attempts in solving the structure in the space group $P-1$ totally failed. We started the refinement only with silver and sulfur atoms then we located the rest of the complex molecule from the difference electron density maps. The whole structure was then refined by full matrix least squares on F values.¹¹ This leads to much more accurate results. Disorder of two propoxy groups was modelled and it was necessary to apply geometrical restraints to these groups. All heavy atoms with full occupancy were refined anisotropically. Hydrogen atoms were located from expected geometry and were not refined. Additionally, the free space in the structure was treated by the SQUEEZE procedure¹² to eliminate the contribution of the electron density in this region to intensity data. This strategy leads to further improvement of the refinement results. In the solvent accessible void of 364 Å³ 133 electrons were found; that might correspond to two ethyl acetate molecules (the same solvent was found in the similar structure of **3**; see below). The escape of the solvent molecules from the crystal is probably responsible for the 31.5% decay of the intensity standards during data collection. The model converged to final $R=0.0909$ and $R_w=0.0987$ using free solvent reflection data (4327 independent reflections, $\theta_{\text{max}}=60^\circ$). CCDC number 178411.

4.1.3. 25,26,27,28-Tetramethoxy-2,8,16,22-tetrathiacalix[4]arene/2AgTf complex. The complex was obtained as white needles by a slow evaporation of thiacalixarene solution ($\text{CHCl}_3/\text{AcOEt}/\text{CH}_3\text{CN}=2:1:2$) in the presence of 2.5 equiv of silver triflate, mp: >250 °C (dec). ¹H NMR ($\text{CDCl}_3/\text{CD}_3\text{OD}=3:2$ v/v, 300 MHz, 298 K) δ 3.87 (br s, 12H, $-\text{OCH}_3$), 6.83 (br s, 4H, H-arom), 7.24 (br s, 8H, H-arom). EA calcd for $2\text{CF}_3\text{SO}_3\text{Ag} \cdot \text{C}_{28}\text{H}_{24}\text{O}_4\text{S}_4 \cdot 1/4\text{EtOAc}$: C, 34.20; H, 2.41; S, 17.67%. Found C, 33.89; H, 2.54; S, 17.55%. MS ESI+ m/z 660.96, 658.96 [$1+\text{Ag}^+$] (100%).

4.1.3.1. Crystallographic data. $2\text{AgCF}_3\text{SO}_3 \cdot \text{C}_{28}\text{H}_{24}\text{O}_4\text{S}_4 \cdot 1/2\text{CH}_3\text{COOCH}_2\text{CH}_3$, $M=1198.79$ g/mol, triclinic system, space group $P-1$, $a=12.6050(4)$, $b=13.3580(4)$, $c=16.5559(5)$ Å, $\alpha=83.177(2)$, $\beta=67.664(2)$, $\gamma=63.347(2)$, $Z=2$, $V=2300.0(1)$ Å³, $D_c=1.73$ g/cm³, $\mu(\text{Mo K}\alpha)=1.21$ mm⁻¹, crystal dimensions of $0.1 \times 0.1 \times 0.3$ mm. Data were collected at 150 K on a Nonius KappaCCD diffractometer with graphite monochromated Mo K α radiation. The structure was solved by direct methods.¹⁰ The whole structure was refined by full matrix least squares on F values.¹¹ All heavy atoms were refined anisotropically. Disorder of one triflate anion molecule and propoxy group was modelled. Geometrical restraints were applied to correct the distances in the disordered triflate molecule and these atoms were refined only isotropically. Hydrogen atoms were located from expected geometry and were not refined. As the solvent molecule with 1/2 occupancy is disordered and additionally sits on the symmetry element no hydrogen atoms were included into calculated structure. This model converged to final $R=0.0432$ and $R_w=0.0379$ using 6909 independent reflections ($\theta_{\text{max}}=27.1^\circ$). CCDC number 178412.

Acknowledgements

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