

Abstract: The four new multivalent ligands 5-8 derived from calix[4]arene and thiacalix[4]arene backbones in 1,3-Alternate conformation bearing ortho-imino- and ortho-amino-methylpyridine chelating sites have been designed, prepared and characterized. Owing to the imposed 1,3-Alternate conformation of the backbone, ligands 5-8 offer two coordinating pockets composed of two sets of chelates located above and below the mean plane of the macrocyclic framework. Ligands 6-8, independent of the nature of the anion associated with Ag⁺ cation, form tetranuclear silver complexes (AgX, X = BF₄⁻, PF₆⁻, SbF₆⁻, AsF₆⁻, NO₃⁻) in solution and in the solid state. Ligand 7, in the presence of an excess of Ag⁺, also forms tetranuclear silver complexes 7-{AgBF₄}₄ and 7-{AgNO₃}₄ in presence of two different auxiliary ligands (H₂O or NO₃⁻) that have been characterized in the solid state. Due to a rather short Ag–Ag distance of ca. 2.89 Å, the tetranuclear complex 7-{AgBF₄}₄ is emissive in the solid state, at 298 K (λ_exc = 295 nm, λ_em = 425 nm) resulting from argentophilic interactions between the closely positioned silver cations.

Introduction

Multivalent ligands are of interest for the formation of multinuclear metal complexes. For the design of such complexing agents, calix[4]arene (CA, 1, X = CH₃, Z = OH),¹ thiacalix[4]arene (TCA, 2, X = S, Z = OH),² and its sulfonyl (Z = OH, X = SO₂)³ or sulfinyl (Z = OH, X = SO₃)⁴ derivatives are backbones of interest (Scheme 1). Indeed, for sterical reasons this class of molecule can not be planar and adopts four limit conformations (cone, partial cone, 1,2-Alternate and 1,3-Alternate). For all conformers, the nature of the substituent Y in the para position of the phenolic rings (Scheme 1) may be varied.

Finally, using the reactivity of the phenolic OH group under basic conditions towards electrophiles, the backbone may be functionalized with a variety of groups. Over the past three decades, calix[4]arene and thiacalix[4]arene derivatives have been widely exploited in several areas of supramolecular chemistry⁵,⁶ or catalysis,⁷ for example.

Examples of nanometric multinuclear metal complexes based on calix[4]arene or thiacalix[4]arene derivatives in different conformations, have been well documented⁸,⁹,¹⁰ Among the four possible conformations adopted by calix[4]arene backbone, the 1,3-Alternate conformer is particularly well suited for the design of multivalent ligands. Indeed, the latter allows to position in an alternate fashion up to four interaction sites forming two distinct coordinating pockets above and below the mean plane of the macrocyclic unit. Multinuclear silver complexes with short AgAg distances are of particular interest since, owing to argentophilic interactions, they emit light upon excitation, in the solid state and also in solution.¹¹

Here we report on a series of four new ligands 5-8 based on either p-tert-butylcalix[4]arene 1 or p-tert-butylthiacalix[4]arene 2 in 1,3-Alternate conformation (Scheme 1) bearing four ortho-imino (ligands 5 and 6) or ortho-amino (ligands 7 and 8) chelating units and their propensity to form binuclear or tetranuclear silver complexes (Figures 1 and 2).

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Supporting information for this article is given via a link at the end of the document: ¹H-NMR spectra for 5-8 and Crystallographic tables for 6, 7, 6-{AgX}² (X = SbF₆⁻, BF₄⁻, AsF₆⁻ and NO₃⁻), 8-{AgX}² (X = AsF₆⁻ and PF₆⁻), 7-{AgBF₄}² and 7-{AgNO₃}².

Scheme 1: Generic representation of calix[4]arene derivatives 1-4 showing all possible modification sites (Y (upper rim), Z (lower rim) and X (bridge)).
not been reported. Interactions within each coordinating pocket is unusual and has classical and previously described, to the best of our knowledge, coordination mode for the binucle
the macrocyclic backbone (Figure 2c and 2d). Although the

Figure 1: Ortho-imino- and ortho-amino ligands 5-8 based on either p-tert-
butylcalix[4]arene 1 or p-tert-butylthiacalix[4]arene 2 in 1,3-Alternate
conformation.

Results and Discussion

Design of ligands 5-8

With aim of preparing binuclear (Figure 2a and 2b) and
tetranuclear silver complexes (Figure 2c and 2d) with short Ag’-
Ag’ distance, ligands 5-8 based on calix[4]arene CA (compounds 5 and 6) and thiacalix[4]arene TCA (compounds 7 and 8) macrocyclic backbones in 1,3-Alternate conformation were designed (Figure 1). The backbone is equipped with four ortho-imino-methylpyridyl (ligands 5 and 6) or ortho-amino-

Figure 2: Schematic representations of possible binuclear (a and b) and
tetranuclear (c and d) silver complexes by ligands 5-8.

Synthesis of ligands 5-8

The synthesis of the ligands 5-8 (Figure 1) was achieved using a
stepwise strategy. Starting with either calix[4]arene derivative 1
or thiacalix[4]arene derivative 2, their condensation with N-(3-
bronopropyl)phthalimide 13 (Scheme 2) in the presence of 
CsCO3 afforded the amino-protected compounds 9 and 10 in
1,3-A conformation respectively (see experimental section).

Scheme 2: Starting compounds 1 and 2 and precursors 9-14 used for the
synthesis of ligands 5-8.

The synthesis of 9 has been previously investigated.15 It was
reported that the formation of the cone conformer in high yield
(83%) was favoured by the stepwise use of (i) K2CO3/acetonitrile
for disubstitution and NaH/DMF for tetrasubstitution15c or (ii) NaH/DMF (yield 55 %).15c,16 In our hand, the combination 
Cs2CO3 and DMF afforded the intermediate 9 in 1,3-A
conformation in a relatively good yield (55%). The phthalimido
derivative 10 in cone and 1,3-A conformation 17,18 was also
reported with 68% yield for the latter. The deprotection of
phthalimido derivatives 9 and 10 was achieved by treatment with
hydrazine.19 The amino compounds 11 and 12 were obtained in
98% and 97% yields respectively.
The imino compounds 5 and 6 were obtained in 63% and 78% yields respectively upon condensation of 2-Pyridinecarboxaldehyde 14 with the amino derivatives 11 and 12 in DMF/ EtOH (scheme 2). Compounds 5 and 6 are unstable under acidic conditions. Finally, the ortho-aminomethylpyridine ligands 7 and 8 were obtained in 84% and 85% yields respectively upon reduction of compounds 5 and 6 using NaBH4 in MeOH (or EtoH).

All four ligands (5-8), in addition to usual characterisation methods, were studied in solution by 1H- and 13C-NMR spectroscopy. As expected, the 1H-NMR study revealed that the imino N=CH group signals were downfield shifted (8.23 and 3.78 ppm for 5 and 6 respectively) with respect to signals corresponding to the amino HN-CH2 unit (3.83 and 7.8 ppm for 7 and 8 respectively) (see figure S1 in Supporting Information).

The imino ligands 6 based on the TCA backbone and the amino ligand 7 based on the CA platform have been also characterized in the solid state by X-ray diffraction on single crystals.

**Solid-state description of ligands 6 and 7**

After many attempts, we were only able to grow single crystals for compounds 6 and 7. Crystals of compounds 6 were obtained upon CH3CN vapours diffusion into CHCl3 solutions of 6, whereas crystals of 7 were obtained upon Hexane vapours diffusion into a CHCl3 solution of 7. The structural investigations of ligands 6 and 7 were carried out by X-ray diffraction methods on single crystals (Crystallographic table S1 (Supporting Information) and Figure 3).

In agreement with solution NMR studies, both compounds 6 and 7 adopt the expected 1,3-A conformation in the crystalline phase. Compound 6 and 7 crystallise in the P21/n and P212121 space groups respectively. Whereas crystals of compound 6 contain CHCl3 molecules with no specific interactions with the ligand, for ligand 7, no solvent molecule is found in the crystal.

For both compounds 6 and 7, metrics for the macrocyclic part are close to those observed for the parent CA and TCA and will not be detailed here. Relevant distances and angles are gathered in Table 1. For compounds 6, one of the four tert-butyl groups was found to be disordered, the same holds for one of the four imino-pyridyl appended group.

For the imino derivative 6, the C=N distances are in the 1.203(7) - 1.340(10) Å range (see table 1) with the CNC angles ranging from 108.0(7)° to 119.2(5)°. For the amino derivative 7, the HC-NH distances are in the 1.409(5)Å -1.435(6)Å range with CNC angles ranging from 111.8(6)° to 113.3(4)°. These bond distances and angles confirm the presence of sp3 nitrogen atoms.

<table>
<thead>
<tr>
<th>6</th>
<th>7</th>
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<tbody>
<tr>
<td>d(C=C)</td>
<td>1.760(5)</td>
</tr>
<tr>
<td>S</td>
<td></td>
</tr>
<tr>
<td>d(C=C-N)</td>
<td>1.511(5)</td>
</tr>
<tr>
<td>C</td>
<td></td>
</tr>
<tr>
<td>d(O-C)</td>
<td>1.360(5)</td>
</tr>
</tbody>
</table>

Owing to the presence of propyl linker connecting the imino- or amino-pyridyl units to the macrocyclic calix[4]arene backbone, no rational trend could be spotted for the position and orientation of pyridyl groups (see Figure 3).

![Figure 3: The solid-state structures of 6 (left) and 7 (right) showing the 1,3-A conformation of both ligands.](image)

The binding propensity of all four multivalent ligands 5-8 towards silver cation, in particular the formation of tetranuclear species, was investigated both in the solid state and in solution.

**Silver complexes in the solid state**

After many attempts to prepare crystalline species upon combining ligands 5-8, with different silver salts (AgX, X = BF4-, PF6-, SbF6-, AsF6-, AsF5O-, NO3-), only for ligands 6, 7 and 8 crystalline complexes have been obtained (see experimental section). All three ligands 6, 7 and 8, when combined with Ag+ cation with Metal/Ligand (M/L) ratio of 2 or 3, form, independent of the nature of the anion, binuclear complexes (M2L, L = 6, 7 or 8) in the solid state.

Interestingly, in the case of ligand 7, for M/L ratio greater than 4, tetranuclear species have been observed in the solid-state with two different counter-anions (BF4- or NO3-).
For all ligands 5-8, owing to the remote position of S atoms, the latter do not participate in the binding of silver cation.

Since metrics associated with the calix backbones for the binuclear and tetrarnuclear complexes was found to be close to those observed for the parent compounds 6 and 7, they will not be discussed in detail here.

**Binuclear silver complexes**

As stated above, the role played by the anion on the formation of binuclear complexes was studied by using different Ag⁺ salts with weakly (BF₆⁻, AsF₆⁻, SbF₆⁻, PF₆⁻) to strongly (NO₃⁻) coordinating anions. Furthermore, the role of the M/L ratio (2:1 or 3:1) on the stoichiometry of the complex was also investigated.

*Ortho-*iminopyridine TCA based binuclear complexes 6-(AgSbF₆)₂, 6-(AgAsF₆)₂, 6-(AgBF₆)₂ and 6-(AgNO₃)₂ were obtained at room temperature as single crystals (see table 4) upon slow diffusion of a MeOH solution containing the silver salt into a CHCl₃ solution of 6, through an iso-ProOH/CHCl₃ layer with a 3:1 or 2:1 M/L ratio (see experimental part). Using *Ortho-*iminopyridine TCA based ligand 7 or TCA based compound 8, single crystals of 7-(AgBF₆)₂ and 7-(AgPF₆)₂ and 8-(AgAsF₆)₂, 8-(AgPF₆)₂ (table S2, Supporting Information) were obtained upon either vapour diffusion into a MeOH/CHCl₃ mixture containing 7 (or 8) and the silver salt with a 3:1 or 2:1 M/L ratio (see experimental part).

The unit cell of all binuclear compounds 6-(AgX)₂ (X = BF₆⁻, AsF₆⁻, SbF₆⁻ and NO₃⁻) are isometric and crystallise in the orthorhombic space group Pccn for X = BF₆⁻, AsF₆⁻ and NO₃⁻ and Pna₂ for SbF₆⁻ (table S2, Supporting Information). 7-(AgX)₂ (X = BF₆⁻ and PF₆⁻) are isometric and crystallise in the monoclinic system in the space group P2/c, P2/c or C2/c. (see crystallographic table 4). 8-(AgPF₆)₂ is also isometric to the above mentioned series and crystallise in the Pccn space group. Binuclear complexes 8-(AgAsF₆)₂ and 6-(AgSbF₆)₂ crystallise with CHCl₃ solvent molecules, 6-(AgAsF₆)₂ with H₂O molecules, 7-(AgPF₆)₂ with MeOH molecules, 6-(AgNO₃)₂ with MeOH and H₂O molecules and 7-(AgBF₆)₂ with CHCl₃ solvent molecules. Owing to the presence of disorder, structures of 6-(AgBF₆)₂, 6-(AgNO₃)₂, 8-(AgAsF₆)₂ and 8-(AgPF₆)₂ were refined using the SQUEEZE software.

For the imino binuclear compounds 6-(AgX)₂ (X = BF₆⁻, AsF₆⁻, SbF₆⁻ and NO₃⁻), the C-N distances are in the 1.241(16) - 1.334(10) Å range with the CNC angles varying between 114.9(6)° and 120.1(13)° (table 2).

For the amino binuclear compounds 8-(AgX)₂ (X = AsF₆⁻ and PF₆⁻), 7-(AgX)₂ (X = BF₆⁻ and PF₆⁻), C-N distances are in the 1.443(13) - 1.537(19) Å range with CNC angles varying between 107.8(4)° and 115.8(9)° (table 3).

<table>
<thead>
<tr>
<th>6-(AgSbF₆)₂</th>
<th>6-(AgAsF₆)₂</th>
<th>6-(AgBF₆)₂</th>
<th>6-(AgNO₃)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-N (imino)</td>
<td>1.241(16)</td>
<td>1.255(7)</td>
<td>1.249(7)</td>
</tr>
<tr>
<td></td>
<td>1.258(12)</td>
<td>1.275(9)</td>
<td>1.259(8)</td>
</tr>
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<td></td>
<td>1.294(13)</td>
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</table>

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<tr>
<th>CNC</th>
<th>117.7(9)</th>
<th>118.2(10)</th>
<th>119.1(10)</th>
<th>120.2(9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(im)</td>
<td>117.9(7)</td>
<td>117.7(9)</td>
<td>117.4(5)</td>
<td>118.4(6)</td>
</tr>
</tbody>
</table>

For all the binuclear complexes 6-(AgX)₂ (X = BF₆⁻, AsF₆⁻, SbF₆⁻ and NO₃⁻), 7-(AgX)₂ (X = BF₆⁻ and PF₆⁻) and 8-(AgX)₂ (X = AsF₆⁻ and PF₆⁻), the metal centre is tetra-coordinated and the environment around the silver cations is similar and composed of 4 nitrogen atoms, two of them belonging to the amino (imino) coordinating groups and two of the pyridyl type (Figure 3), for relevant distances see tables 2 and 3. The θ(NO₃) varies between 2.197(6) and 2.499(4) Å and the θ(NAgN) angles are in the 68.5(8)° - 169.6(4)° range showing a strong deformed...
tetrahedral environment around the silver cations (Figures 4). In all cases (except for 7-(AgBF₄)₄), the Ag-N₄ distances are always longer than Ag-N₃ or Ag-N₂ (see tables 2 and 3). It is worth noting that for all binuclear complexes, owing to the tetrahedral coordination geometry around the silver cation, for each metallic centre one expects either a R or a S configuration. For the binuclear species, one thus expects (RR), (SS) and (RS) = (SR) (meso form due to the symmetry of the ligand). For 7 out of the 8 binuclear complexes, the crystal contains both (RR) and (SS) enantiomers thus forming an internal racemate. Interestingly, only for the 8-(AgAsF₆)₂, within the complex both R and S configuration for the two silver cation leading thus to an achiral meso form.

In all cases, no specific interactions between anions and the binuclear complexes could be spotted. Only short van der Waals contacts with C-F distance of ca 3.1Å for 6-(AgX)₂ (X = BF₄⁻ or AsF₆⁻ and SbF₆⁻), 7-(AgX)₂ (X = BF₄⁻ or PF₆⁻) and 8-(AgX)₂ (X = AsF₆⁻ and PF₆⁻) are observed.

![Solid state structures of binuclear complexes 6-(AgAsF₆)₂, 7-(AgBF₄)₂ and 8-(AgPF₆)₂.](image)

**Figure 4:** Solid state structures of binuclear complexes 6-(AgAsF₆)₂, 7-(AgBF₄)₂ and 8-(AgPF₆)₂, formed by combination of the organic tectons 6, 7 and 8 with AgX salts. H atoms, anions and solvent molecules, when present, are not presented for clarity. For bond angles and distances see text and tables.

### Tetranuclear silver complexes

The tetranuclear complexes 7-(AgNO₃)₄ and 7-(AgBF₄)₄ were also obtained by either vapour diffusion into a CH₃CN solution (or H₂O/CH₃CN mixture) of 7 and the silver salt AgX (X = BF₄⁻ or NO₃⁻) with the M/L ratio of 4:1 (see experimental part). 7-(AgBF₄)₄ crystallizes in the tetragonal system (I₄₁/a space group), whereas 7-(AgNO₃)₄ crystallizes in the monoclinic system (C2 space group) (see crystallographic table S3, Supporting Information). Whereas crystals of 7-(AgBF₄)₄ contain H₂O molecules in the unit cell, those of 7-(AgNO₃)₄ contain both H₂O and CHCl₃ molecules.

C-N distances of (1.484(7) and 1.489(8) Å) and 1.484(6) Å are observed for 7-(AgNO₃)₄ and 7-(AgBF₄)₄ respectively. The CNC angles vary between 110.5(5) and 112.1(5)° (table 4).

<table>
<thead>
<tr>
<th></th>
<th>7-(AgNO₃)₄</th>
<th>7-(AgBF₄)₄</th>
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<tbody>
<tr>
<td>C-N (amino)</td>
<td>1.484(7)</td>
<td>1.484(6)</td>
</tr>
<tr>
<td>Cyclam (amino)</td>
<td>1.105(5)</td>
<td>1.119(3)</td>
</tr>
</tbody>
</table>

**Table 4:** Useful angles and distances for the tetranuclear species. 7-(AgX)₄ (X = BF₄⁻ or NO₃⁻), am and py indicate the localization of the N atom on either amino or pyridyl units.

Owing to the distance between the two binding pockets composed of a N4 set of coordinating sites located above and below the mean plane of the ligand and the absence of electronic communication between them, they behave independently and each binds two silver cations leading thus to the tetranuclear silver complex 7-(AgBF₄)₄ and 7-(AgNO₃)₄ differing by the nature of the anion (BF₄⁻ or NO₃⁻) (Figure 5). For the tetranuclear species, the set of two Ag⁺ cations, located on the same side of the backbone, may be described as internal...
and external metal centres (Figures 1 and 5). Interestingly, due to the proper positioning of the two chelating ortho-aminomethylpyridine units on each side of the macrocyclic backbone, a rather short Ag-Ag distance of 2.8928(7) Å and 2.8775(5) Å (table 4) are obtained for 7-(AgBF₄)₄ and 7-(AgNO₃)₄ respectively. Dealing with the surrounding of silver cations, for 7-(AgBF₄)₄ among the water molecules present in the crystal, two of them are located within the coordination sphere of the external silver cation, whereas for 7-(AgNO₃)₄, then external metal centre interacts with two nitrate anions through Ag-O bonds.

As stated above, for the tetranuclear silver complex, two types of silver cations are present on each side of the ligand. The internal cation is di-coordinated and its coordination sphere is composed of two N atoms belonging to two amino units located on the same side of the backbone. The Ag-N distances are 2.173(3) Å for 7-(AgBF₄)₄ and in the 2.161(5)-2.269(6) range for 7-(AgNO₃)₄. The NAgN angles are 177.80(19)° and 175.4(17)° and NAgAg angles are 91.10(10)°, 90.90(13)° and 93.64(12)° (table 4) showing a slightly distorted linear coordination geometry around the internal silver cation.

The external silver cation is tetracoordinated adopting a distorted tetrahedral coordination geometry and is surrounded by a N₂O₂ set of coordinating atoms. The environment around the cation is composed of two nitrogen atoms belonging to two pyridyl units located on the same face of the ligand and two oxygen atoms either belonging to two H₂O molecules in 7-(AgBF₄)₄ or to two nitrate anions in 7-(AgNO₃)₄ (Figure 5). For distances and angles see table 4.

**Solid state emission**

The rather short Ag-Ag distance of 2.8928(7) Å in 7-(AgBF₄)₄ leads to strong d¹⁰-δ¹⁰ interactions between vicinal silver atoms on each face of the complex. The emission due to argentophilic interaction was investigated using polycrystalline samples (Figure 6).

The solid-state reflectance spectra recorded at 298K displays two major bands at ca 295 nm and 450 nm (Figure 6 left). Upon excitation at λ_exc = 295 nm, a dominant emission peak at λ_em = 425 nm is observed (Figure 6 right). The latter is attributed to Ag-Ag argentophilic interactions. It is worth noting that no such an emission is observed for the binuclear complexes discussed above.

**Behaviour in solution**

The binding of silver cation by the ligand 7 in solution was investigated. The complexation process was monitored by ¹H-NMR spectroscopy. Upon addition of AgBF₄ in CD₃CN, to a CD₃CN solution of the ligand 7 at C = 8.05 10⁻³ mol.L⁻¹ signals corresponding to the pyridyl moieties, CH₂NH and the CH₂ bridging the aryl groups of the calix backbone were found to be shifted (Figure 7). The titration experiment in CD₃CN consisting in addition of increasing amounts of the silver salt to a solution of 7 clearly showed the formation of the binuclear complex 7-(AgBF₄)₂. Indeed, after reaching the 2:1 M/L ratio, further addition of the silver salt had no effect on the displacement of signals. In marked contrast with the solid state structural investigations discussed above, the solution study revealed that, even in the presence of 5 equivalents of silver cation, no trace of the tetranuclear silver complex could be detected.
Figure 7: Pyr-H, Ar-CH₂Ar and CH₂-Pyr proton shift changes of the ¹H-NMR spectra (bottom) of 7 (top) with upon addition of increasing amount of AgBF₄. (*RMS = Concentration of metal/concentration of ligand) C = 8.05 10⁻² mol L⁻¹.

Conclusions

Four new multivalent ligands 5-8 derived from calix[4]arene and thiacalix[4]arene backbones in 1,3-Alternate bearing ortho-amino- and ortho-imino-pyridine chelating sites have been prepared and two of them (ligands 6 and 7) have been structurally characterized in the solid state by X-ray diffraction methods. Owing to the imposed 1,3-Alternate conformation of the backbone, they offer two coordinating pockets composed of two sets of chelates located above and below the mean plane of the macrocyclic framework. Among the four unprecedented ligands, for compounds 6-8, the two coordinating pockets behave independently and form binuclear silver complexes independent on the nature of the anion associated with Ag⁺ cation. This propensity was established both in the solid state and in solution using ¹H-NMR spectroscopy. Interestingly, ligand 7, based on four ortho-amino-pyridyl units, in addition to binuclear silver complexes, forms in the solid state tetranuclear silver complexes 7-[AgBF₄]₄ and 7-[AgNO₃]₄ in presence of two different auxiliary ligands (H₂O or NO₃⁻). In the solid state, the tetranuclear complex 7-[AgBF₄]₄, due to a rather short Ag-Ag distance of ca 2.89 Å, displays argentophilic interactions leading, at 298 K, to an emission band at ca 425 nm (λₐmm = 295 nm). No such an emission was detected for the binuclear silver complexes in solution (CH₃CN). No further purification. p-tert-butylcalix[4]arene 1 is commercial product and p-tert-butylthiacalix[4]arene 2 was prepared according to the literature procedures. The synthesis of 10 has already been reported.¹⁷

All the reactions were performed under a N₂ atmosphere.

Experimental Section

Materials and methods

¹H-NMR and ¹³C-NMR spectra were recorded at room temperature on a Bruker (300, 400 or 500 MHz) NMR spectrometer.

Mass spectra (ESI) were obtained on a MicroTOF-Q (BRÜKER) equipped with an electrospray source.

Microanalyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie, Université de Strasbourg, Strasbourg, France.

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

Reflectance spectra in the solid state were recorded on a Perkin-Elmer Lambda 650 spectrometer.

Luminescence spectra in the solid state were recorded on a Perkin-Elmer LS55 spectrophotometer.

Single-Crystal Studies

Data were collected at 173(2) K on a Bruker Apex-II CCD Diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. For all the structures, diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on F² using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model).²¹ They can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.CCDC: 1538265-1538276.

Synthetic procedures

A mixture of p-tert-butylcalix[4]arene 1 (1.50 g, 2.31 mmol) and Cs₂CO₃ (7.5 g, 23.11 mmol) in DMF (80 mL) was stirred at R.T. for 2 hours. N-(3-bromopropyl)phthalimide 13 (6.19 g, 23.11 mmol) was added to the mixture and stirring was further continued for 3 days at 50 °C during. After cooling to R.T., the reaction mixture was filtrated. The filtrate was washed three times with CHCl₃ (3x50 mL). Washes were combined and evaporated. The yellow oil thus obtained was dissolved in 50 mL of CHCl₃ and washed twice with HCl (1N, 2x50 mL). After evaporation, the residue was recrystallised twice from MeOH (50 mL) affording the pure product 9 in 1,3-Alternation as a white solid (1.77 g, 55%). mp = 256 °C. ¹H-NMR (500 MHz, CDCl₃, 25 °C): δ(ppm) = 1.17 (36H, s, -CH₂(CH₃)₂), 1.69 (8H, m, -CH₂-CH₂-CH₂-), 3.47 (8H, t, -Ph₂CH₂-), 3.63 (8H, t, -Ar-O-CH₂), 3.69 (8H, s, Ar-CH₂Ar), 6.95 (8H, s, Ar-H), 7.70 (8H, m, Ar-H), 7.82 (8H, m, Ar-H). ¹³C-NMR (125 MHz, CDCl₃, 25 °C): δ(ppm) = 29.4, 31.5, 33.7, 35.2, 38.8, 68.6, 123.1, 132.1, 132.9, 133.8, 143.7, 154.4, 168.1. Anal. Calcd. for Cs₂H₂NO₃O₂: C, 75.62%; H, 6.63%; N, 4.01%; Found: C, 75.86%; H, 6.56%; N, 4.01%.

Compound 9

The synthesis was adapted from an already published procedure.¹⁹

A mixture of 9 (2.00 g, 1.36 mmol) and hydrazine (13.3 mL, 272 mmol) in 70 mL of THF/EtOH (1/1) mixture was stirred and...
refluxed for 24h. After cooling to room temperature, 150 mL of distilled H₂O was added and the reaction mixture was filtered. The white solid thus obtained was washed three times with EtO (3x30 mL). The white solid was dried for 4h under vacuum at 100 °C, affording the pure compound 12 in 1.3-A conformation (1.25 g, 97%). mp = 274 °C. 1H-NMR (500 MHz, CDCl₃, 25 °C): δ(ppm) = 1.23 (8H, m, -CH₂-CH₂-CH₂-), 1.28 (36H, s, -C(CH₃)₃), 2.44 (8H, t, NH₂-CH₂-), 3.90 (8H, t, Ar-O-CH₃), 7.33 (8H, s, Ar-H). 13C-NMR (125 MHz, CDCl₃, 25 °C): δ(ppm) = 31.3, 33.3, 34.3, 39.4, 67.1, 127.8, 128.1, 145.5, 157.1. Anal. Calc. for C₃₆H₄₅N₃O₃: C, 76.78%; H, 8.07%; N, 5.89%; Found: C, 76.64%; H, 8.16%; N, 5.90%.

**Compound 5**

2-Pyridinercarboxaldehyde 14 (440 µL, 4.55 mmol) and 11 (0.5 g, 0.56 mmol) were dissolved in 40 mL of a EIOH/DMF (1/1) mixture and stirred at room temperature during 2 days. Then, 100 mL of CHCl₃ was added and the white precipitate thus formed was filtered and washed three times with ether (3x30 mL). The filtrate was placed in a 1 L refrigerator, which caused further precipitation. The solid was filtered and combined with the first batch, affording the desired compound 5 in 1.3-A conformation as a white solid (0.47 g, 63%). mp = 124 °C. 1H-NMR (300 MHz, CDCl₃, 25 °C): δ(ppm) = 1.23 (36H, s, -C(CH₃)₃), 1.47 (8H, m, J = 7.5 Hz, -CH₂-CH₂-CH₂-), 3.46 (8H, t, J = 6.0 Hz, -N=CH₂-), 3.51 (8H, t, J = 8.5 Hz, -O=CH₂-), 3.81 (8H, s, Ar-Ch₂Ar), 6.97 (8H, s, Ar-H), 7.26 (4H, m, J = 6.0 Hz, Pyr-H), 7.69 (4H, t, J = 7.5 Hz, Pyr-H), 7.98 (4H, d, J = 7.5 Hz, Pyr-H), 8.23 (4H, s, -CH₂N-), 5.60 (4H, d, J = 4.5 Hz, Pyr-H). 13C-NMR (100 MHz, CDCl₃, 25 °C): δ(ppm) = 30.3, 31.6, 33.9, 58.4, 68.3, 120.8, 124.5, 125.7, 133.6, 143.8, 149.2, 154.6, 154.8, 161.3. MS (ESI), m/z: [M⁺] calculated 313.66, measured 313.67. Anal.Calc. for C₃₅H₃₅N₃O₃: C, 77.89%; H, 7.84%; N, 9.08%; Found: C, 77.76%; H, 8.00%; N, 9.86%. UV-vis (CHCl₃/MeOH (1/1)): λmax (nm)/ε (mol⁻¹L⁻¹cm⁻¹) = 238(52064). IR (cm⁻¹): νOH 1651.

**Compound 6**

2-Pyridinercarboxaldehyde 14 (560 µL, 5.84 mmol) and compound 12 (0.7 g, 0.73 mmol) were dissolved in 40 mL of a EIOH/DMF (1/1) mixture, and stirred at room temperature during 2 days. 100 mL of CHCl₃ was added and the white precipitate thus formed was filtered and washed several times with petroleum ether (100 mL). The filtrate was placed during one week in a refrigerator to complete the precipitation. The solid was filtered and combined with the first batch, affording the desired compound 6 in 1.3-A conformation as a white solid (0.75 g, 78%). mp = 182 °C. 1H-NMR (300 MHz, CDCl₃, 25 °C): δ(ppm) = 1.20 (36H, s, -C(CH₃)₃), 1.44 (8H, m, J = 7.5 Hz, -CH₂-CH₂-CH₂-), 3.45 (8H, t, J = 6.5 Hz, -N=CH₂-), 4.00 (8H, t, J = 7.5 Hz, -O=CH₂-), 7.26 (4H, m, J = 5.5 Hz, Pyr-H), 7.33 (8H, s, Ar-H), 7.69 (4H, t, J = 7.5 Hz, Pyr-H), 8.00 (4H, d, J = 7.7 Hz, Pyr-H), 8.24 (4H, s, -CH₂N-), 5.89 (4H, d, J = 5.0 Hz, Pyr-H). 13C-NMR (125 MHz, CDCl₃, 25 °C): δ(ppm) = 29.9, 31.3, 31.4, 34.3, 58.3, 66.8, 120.8, 124.5, 127.6, 128, 136.4, 145.6, 149.2, 154.8, 156.8, 161.5. MS (ESI), m/z: [M⁺] calculated 313.69, measured 313.62. Anal. Calc. for C₃₅H₃₅N₃O₃: C, 72.95%; H, 7.36%; N, 8.53%; Found: C, 71.98%; H, 7.46%; N, 8.22%. UV-vis (CHCl₃/MeOH (1/1)): λmax (nm)/ε (mol⁻¹L⁻¹cm⁻¹) = 261(49560). IR (cm⁻¹): νOH 1651.

**Crystallisation conditions**

**Compound 6**: A CHCl₃ (0.5 mL) solution of compound 6 (5 mg, 3.82 mol) was placed in a closed beaker containing acetone. Slow vapour diffusion of acetone into the solution of the ligand 6 produced, after several days, colourless crystals suitable for X-ray diffraction (Formula: 2(C₃₅H₃₅N₃O₃)₂CHA). 

**Compound 7**: A solution in CHCl₃ (0.5 mL) of compound 7 (5 mg, 4.03 mol) was placed in a closed beaker containing hexane. Slow vapour diffusion of hexane into the solution of 7 produced colourless, after several days, crystals suitable for X-ray diffraction (Formula: C₁₉H₁₉O₄N₄).

**6-(AgSbF₆)₂**: In a crystallisation tube (20 x 4 mm), a solution of compound 6 (3.00 mg, 2.29 mol) in CHCl₃ (1 mL) was layered with a CHCl₃/iso-ProOH (1/1) mixture (0.1 mL). A solution of AgSbF₆ (2.02 mg, 6.80 mol) in MeOH (1 mL) was carefully added. At room temperature, slow diffusion in the dark produced, after several days, colourless crystals suitable for X-ray diffraction (3.9 mg, 63 % yield). Anal. Calc. for C₁₉H₁₉O₄S₂Ag₂SbF₆(CHCl₃): C, 43.78%; H, 2.25%; N, 5.30%. Found: C, 43.42%; H, 2.20%; N, 5.26%.

**6-(AgAsF₆)₂**: In a crystallisation tube (20 x 4 mm), a solution of 6 (3.00 mg; 2.29 mol) in CHCl₃ (1 mL) was layered with a CHCl₃/iso-ProOH (1/1) mixture (0.1 mL). A solution of AgAsF₆ (2.02 mg; 6.80 mol) in MeOH (1 mL) was carefully added. At room temperature, slow diffusion in the dark produced, after several days, colourless crystals suitable for X-ray diffraction (2.60 mg, 60 % yield). Anal. Calc. for...
6-(AgBF₄): In a crystallization tube (20 x 4 mm), a solution of the ligand (3.00 mg; 2.29 mol) dissolved in 0.5 mL of CHCl₃ (1 mL) was layered with a CHCl₃ isopropanol (1/1) mixture (0.1 mL). A solution of AgBF₄ (1.30 mg; 6.67 mol) in MeOH (1 mL) was carefully added. At room temperature, slow diffusion in the dark produced, after several days, colourless crystals suitable for X-ray diffraction (2.00 mg, 51 % yield). Anal. Calcd. for C₂H₇NO₄S₂·2(AgBF₄): C, 49.86%; H, 5.28%; N, 6.08%. Found: C, 55.30%; H, 5.44%; N, 8.41%.

8-(AgPF₆): In a flask, 3.0 mg of the ligand 8 (2.19 mol) dissolved in 0.5 mL of CH₂Cl₂ was mixed with 1.20 mg of AgPF₆ (6.57 mol) dissolved in 0.5 mL of MeOH. Slow vapour diffusion of Et₂O produced, after several days, colourless crystals suitable for X-ray diffraction studies (2.70 mg, 66 % yield). Anal. Calcd. For C₂H₇NO₄S₂·H₂O·2(AgPF₆): C, 47.38%; H, 5.68%; N, 5.62%.

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Formation of tetranuclear silver complexes in the solid state with short Ag-Ag distance displaying argentophilic interactions.

Supramolecular chemistry, Calixarene

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