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PAPER

Homoselenacalix[4]arenes: synthetic exploration and metallosupramolecular chemistry†

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Homoselenacalix[4]arenes were synthesized by a [2 + 2] reductive coupling protocol favouring the cyclotetramers. The inner and outer-rim decoration was varied and a bicyclic derivative was prepared by a similar one-pot procedure. Conformational analysis in solution and the solid state showed noticeable differences between the homoselenacalix[4]arenes and the analogous homothiacalix[4]arenes and provided insight into the metal binding potential of the Se-bridged macrocycles. The homoselenacalix[4]-arenes were found to bind Ag(I). Complexation was visualized in the solid state and different packing networks were formed depending on the counter ions applied.

Introduction

Heteracalixarenes, in which the methylene bridges of traditional calixarenes are replaced by heteroatoms (mostly S, N and O, but also Se, Si, Ge, Sn and P), have recently attracted (renewed) attention as a novel generation of macrocyclic receptors due to their high adaptability in forming complementary three dimensional cavities and their straightforward functionalization at both the upper and lower rim.[1–4] Moreover, the bridging heteroatoms introduce additional potential binding sites for specific guests in an induced-fit fashion. Comparably less studies have focused on the subclass of homoheteracalixarenes, although the CH_2XCH_2 bridges (X = O, NR, S, Se) between the aromatic units provide the opportunity to modulate the macrocycle's host–guest properties to an even further extent, as they impose increased cavity size and enhanced conformational flexibility.[5–8] Among these homoheteracalixarenes, the oxygenated analogues have been investigated most intensively and supramolecular features have been studied on a few occasions.[5] The metallosupramolecular chemistry of some homooxacalixarene derivatives in the presence of Ti and V has been studied and the resulting complexes have been explored as catalytically active substances.[5j,k] Their complexation ability towards charged (tetramethylammonium ions) and neutral (fullerenes) organic molecules has also been reported.[5] The synthesis and host–guest properties of homoaza- and homothiacalixarenes are much less developed.[6,7] The homoheteracalixarene series has recently been expanded to the selenium "isologues" of the chalcogen series, homoselenacalix[*n*]-arenes (with CH_2SeCH_2 linkages), but their supramolecular features have not been explored yet.[8]

Selenium-containing macrocycles are versatile platforms for the construction of sophisticated molecular receptors for transition metals or electron deficient moieties because of the high σ-donating ability of the Se atoms.[9] Considerable efforts have been directed to the synthesis of selenacrown ethers and mixed-donor selenoether macrocycles, as well as to the study of their ligation properties towards d- and p-block elements. In heteracyclophane chemistry, the large Se atoms lead to increased cavity size, which imposes electronic and conformational features that are quite different from O-, N- or S-containing macrocycles. In cyclic selena(*n*)alkynes, the non-bonding interactions between the chalcogen atoms have afforded a columnar structure in the solid state, with cavities allowing the inclusion of organic guest species.[10] The introduction of Se in calixarene chemistry has

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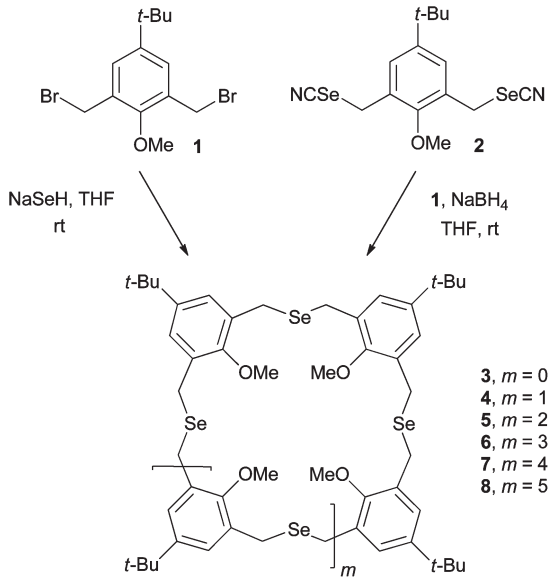
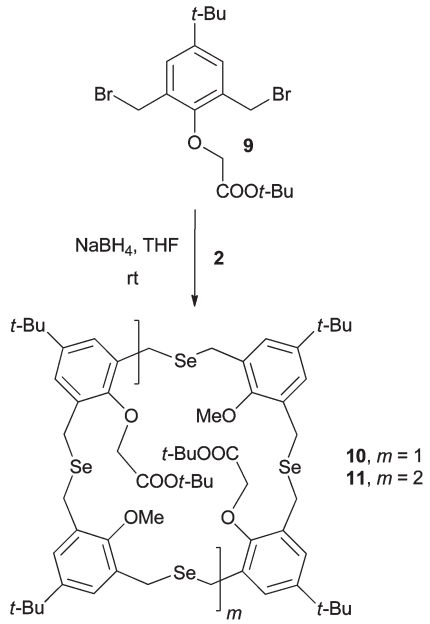
†Electronic supplementary information (ESI) available: ^{1}H, ^{13}C and ^{77}Se NMR spectra for the novel precursors and homoselenacalix[*n*]-arenes, X-ray crystallographic general experimental data and additional figures for the structures of homoselenacalix[*n*]arenes **4**·THF, **10**, **19**, **20**, **21** and **22**, and FTMS (ESI^{+}) isotopic patterns for homoselenacalix[4]-arene **10** and metal complexes **21** and **22**. CCDC 848952–848956. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob25760b



Scheme 1 Synthetic pathways towards homoselenacalix[*n*]arenes **3–8**.



Scheme 2 Synthesis of inner-rim functionalized homoselenacalix[*n*]-arenes **10** and **11**.

been limited to the periphery of the macrocycles and the construction of calix(selena)crown ethers aiming at selective metal extraction.[11] More in general, organoselenium compounds are also of significant importance because of their potential impact in biological and pharmaceutical sciences.[12]

The unique properties of Se, taken together with the considerable difference in the physical characteristics of (homo)heteracalixarenes, prompted us to continue our work on (homo)-selenacalix[*n*]arene macrocycles. In a previous communication, we have reported synthetic routes towards both symmetrical and asymmetrical homoselenacalix[*n*]arenes of varying ring size by two different approaches (Scheme 1).[8] The first method employed the nucleophilic substitution reaction of sodium hydrogen selenide (NaSeH) with 1,3-bis(bromomethyl)-5-*tert*-butyl-2-methoxybenzene (**1**) and afforded a mixture of symmetrical homoselenacalix[*n*]arenes **3–8** (n = 3–8), with some selectivity for the smallest homoselenacalix[3]arene **3**. The second approach involved a [2 + 2] reductive coupling protocol resulting in either symmetrically or asymmetrically substituted calixarenes, with pronounced selectivity for the tetrameric cyclooligomers. In this paper, we report novel synthetic routes enabling introduction of different functionalities at the intra- and extraannular positions of homoselenacalix[*n*]arene macrocycles, including methods which afford bicyclic analogues. The conformational features of the homoselenacalix[4]arene derivatives in solution and in the solid state have been analyzed. Moreover, we have also explored the metallosupramolecular complexation ability of the homoselenacalix[4]arene scaffold, focusing on Ag-mediated self-assembly in the solid state.

Results and discussion

Synthesis and characterization

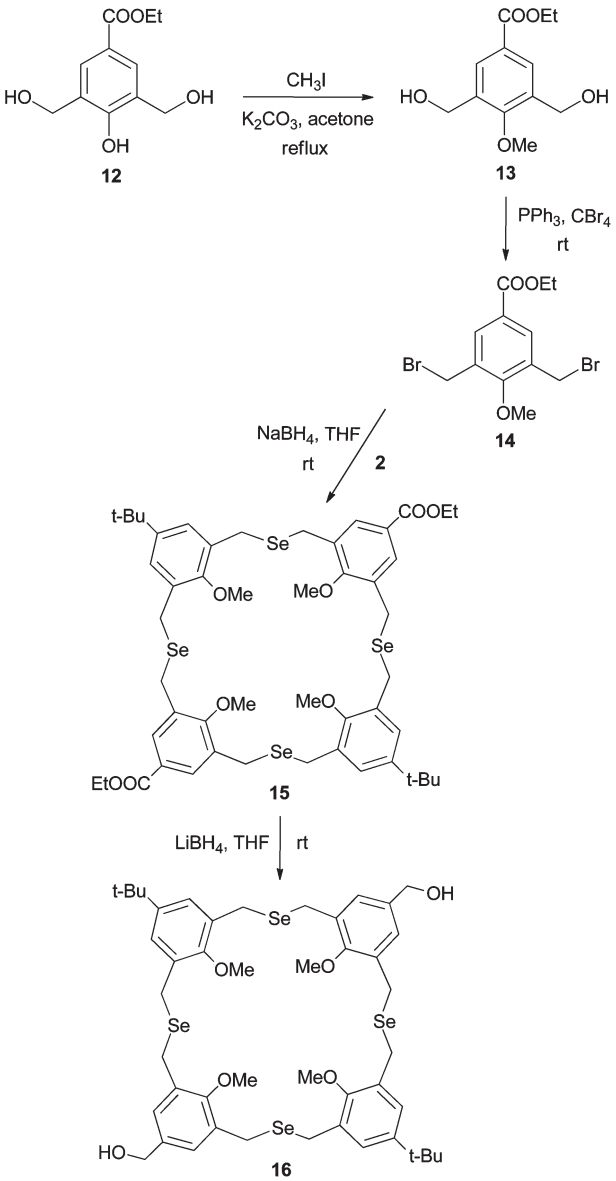
We envisioned that the introduction of specific functional moieties on the upper and lower rim of the homoselenacalix[4]arene framework could alter the conformational preference and tune the cavity size, thereby changing its ligand features. It has previously been observed for both Se and S-bridged homocalixarenes that the introduction of intraannular methoxy groups is crucial to direct the macrocyclization to the cyclic tetramers rather than the cyclic dimers (diselena[3.3]-metacyclophanes).[7g,8] An initial attempt to deprotect the methoxy groups of parent homoselenacalix[4]arene **4** with BBr_3 was not successful, as it was difficult to selectively deprotect the methoxy groups without affecting the macrocycle. Therefore, the desired intraannular substituents should be introduced prior to macrocyclization. First of all, an asymmetrical homoselenacalix[4]arene macrocycle **10** was synthesized, carrying alternate methoxy and *tert*-butyl ester groups at the intraannular positions (Scheme 2). Initially, the optimized conditions reported for the synthesis of **4** were applied.[8] However, the [2 + 2] reductive coupling reaction between *tert*-butyl 2-[2,6-bis(bromomethyl)-4-*tert*-butylphenoxy]acetate (**9**) and bisselenocyanate **2** using an excess of $NaBH_4$ under high dilution conditions (2.6 mM of each of the building blocks) afforded the desired macrocycle **10** in negligible amounts only. Analysis of the crude reaction mixture by ESI-MS (electrospray ionization-mass spectrometry) revealed, besides the formation of the [2 + 2] coupling product and some higher homologues, the presence of products with a single diselenide linkage within the macrocyclic skeleton (in spite of the reductive conditions employed). As these macrocycles all have comparable polarity, they could not be separated and purified effectively by standard column chromatography (on silica). Deaeration of the reaction mixture over a longer time and/or slight changes in the reaction parameters (*e.g.* adding an excess of $NaBH_4$ or proceeding to reflux conditions) did not enable us to exclude the introduction of a diselenide linkage. A possible hypothesis as to why the diselenide formation is only observed in this case (and not during the synthesis of **4**)[8] might be that there is a higher tendency to relieve ring strain when the more bulky *tert*-butyl

acetate moieties are employed as inner substituents. On the other hand, such a tendency was not observed for the synthesis of the di- and tetrasubstituted homothiacalix[4]arene analogues (*via* reaction of **9** with a bismercapto precursor) either.[7g,13] Optimization of the procedure, affording a maximum amount of cyclotetramer **10**, was achieved by repeating the reaction at an enhanced concentration (10.4 mM) of the building blocks. Thus, dropwise addition of $NaBH_4$ to a mixture of **9** and **2** in a 1 : 1 ratio at a concentration of 10 mM in THF afforded homoselenacalix[4]arene **10** in 38% yield, while homoselenacalix[6]arene **11** was additionally obtained in 22% yield (Scheme 2). Polymer/oligomer formation significantly increased at an even higher concentration (26 mM) of the building blocks.

The ^{1}H NMR spectrum of A_2B_2-type homoselenacalix[4]arene **10** in $CDCl_3$ at room temperature (rt) displayed broadened, partly separated signals for several protons (*e.g.* the methoxy and methylene groups), in contrast to the sharp singlet signals observed for A_4-type homoselenacalix[4]arene **4**.[8] From this observation, it seems that the inner-rim *tert*-butyl acetate moieties impart restricted mobility to the calixarene framework. The broad multiplets were converted to singlet signals at 328 K due to the enhanced conformational flexibility of the macrocycle at this temperature (see the ESI†). For the corresponding thia analogue, geminal coupling of the methylene protons was still observed at 328 K and sharp signals were only seen upon heating at or above 350 K.[7g] This observation can be correlated to the larger size of the Se atom (and hence longer C–Se bonds, *vide infra*), which in turn results in higher conformational flexibility. The shielding effect experienced by the protons of the two inner methoxy groups (at δ 3.19/3.14 ppm at 300 K) points to a small (if any) contribution of cone-type conformations in solution. On the other hand, a sharp singlet signal was observed for the methylene groups of the enlarged [3 + 3] coupling product **11**, indicating its fast conformational interconversion at ambient temperature.

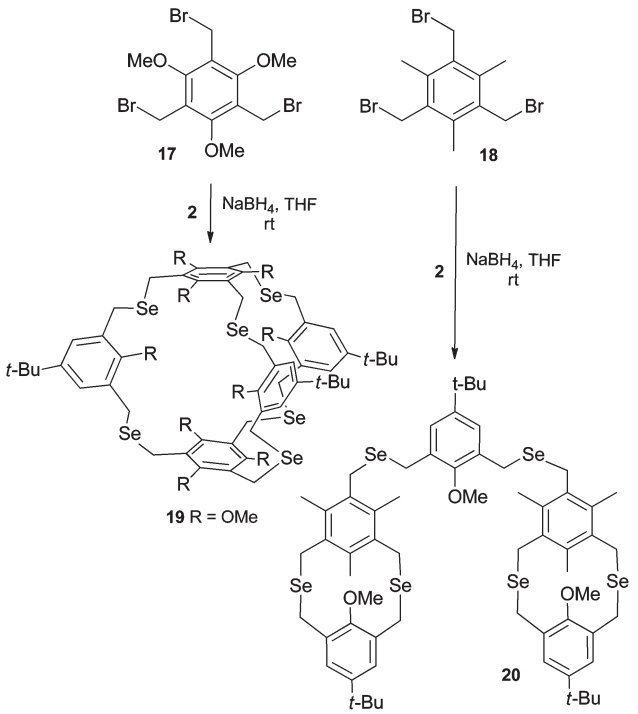
Outer-rim functionalized homoselenacalix[4]arenes were obtained by a similar pre-macrocyclization functionalization strategy. This involved the use of building blocks already bearing the desired functional groups, which then underwent macrocyclization by a reductive coupling protocol (Scheme 3). Dibromo precursor **14** was obtained by methylation of ethyl 4-hydroxy-3,5-bis(hydroxymethyl)benzoate (**12**), followed by bromination under Appel reaction conditions. Homoselenacalix[4]arene **15**, bearing alternate ethyl ester and *tert*-butyl groups at the extraannular positions, was obtained in an isolated yield of 42% *via* the optimized procedure used for the synthesis of **4**.[8] Higher cyclic oligomers were also observed, but these could not efficiently be purified chromatographically. The bis(hydroxymethyl)-substituted cyclotetramer **16** was obtained in 87% yield by reduction of the diester with $LiBH_4$ in THF at rt. This compound may be easily modified further on for the preparation of more sophisticated homoselenacalixarene receptors. The ^{1}H NMR spectra of **15** and **16** showed similar trends as observed in the case of parent homoselenacalix[4]arene **4**.[8] The shielded signals for the methoxy protons (at δ 3.47/3.36 ppm for **15** and 3.59/3.31 ppm for **16** at rt) indicated once more the preference for non-cone conformations in solution.

Bicyclic "cage" (homo)heteracalixarene structures, in which all macrocyclic ring systems have a calixarene structure, may



Scheme 3 Synthesis of outer-rim functionalized homoselenacalix[4]arenes **15** and **16**.

have particular advantages in host–guest chemistry due to their restricted flexibility.[3c,g,5b,6f] We have recently reported on the synthesis of a bicyclic analogue of a homothiacalix[4]arene using a one-pot reaction.[7g] We have chosen the same monomer, 1,3,5-tris(bromomethyl)-2,4,6-trimethoxybenzene (**17**), to prepare a similar bicyclohomoselenacalixarene. The methoxy groups were introduced as it was shown that they play a crucial role for the selective formation of the cyclic tetramer.[8] Thus, a three-fold ring-closing substitution reaction (under reductive conditions) between bisselenocyanate **2** and electrophilic component **17**, in a 3 : 2 molar ratio, furnished bicyclohomoselenacalixarene **19** in 23% yield (Scheme 4). A significant reduction in the yield was observed upon repeating the reaction at a higher concentration of the monomers. An attempt to prepare a similar cage compound in a stepwise manner starting from homoselenacalix[4]arene **16** was unsuccessful due to the failure to obtain the



Scheme 4 Synthetic pathway towards bicyclic selenacyclophanes **19** and **20**.

dibrominated analogue in pure form from diverse bromination trials (Br_2/HBr, PPh_3/CBr_4, PPh_3/NBS). The cage-type molecule **19** exhibits a symmetrical structure in solution, as evidenced from its simple ^{1}H NMR spectrum. The methoxy protons of the nucleophilic component (at δ 3.29 ppm) were shifted up-field considerably in comparison to the methoxy protons of the electrophilic component (at δ 3.74 ppm), suggesting that they are pointing more directly into the formed cavity. This observation is comparable to the case of the structurally analogous bicyclohomothiacalixarene, which suggests that the conformations of these molecules in solution are similar.[7g]

Treatment of bisnucleophile **2** with an alternative capping component, 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (**18**), under the same coupling conditions and at the same ratio, provided a compound with a molecular mass (ESI-MS) matching the analogous cage product (in 27% yield). However, the ^{1}H NMR spectrum was considerably more complicated. Doublets were observed for the geminal protons of the bridging methylene groups. Moreover, one of the methyl groups of the electrophilic moieties showed an unusual upfield shift (at δ 1.29 ppm) as compared to the other methyl groups (at δ 2.42 ppm). These observations pointed towards the formation of a product with restricted rotation, as in the [1 + 1] selenacyclophane products.[8,14] Single crystal X-ray diffraction analysis allowed us to identify the formation of bis(selenacyclophane) molecule **20** (see Fig. S5†), as presented in Scheme 4, which explains the extensive splitting and shielding noticed for the bridging methylene and methyl groups, respectively. This observation once more confirms the profound effect of the intraannular substituents on the macrocyclization outcome, *i.e.* the absence of an interior methoxy group on either of the monomers favours the [1 + 1] coupling product.[7g,8] Bis(selenacyclophane) **20** also shows a strongly deviating ^{77}Se NMR signal (at δ 259 ppm *vs.* 312–325 ppm for the homoselenacalix[4]arenes), which might be used as a signature of [1 + 1] product formation.

Thus, by carefully choosing the monomers a bridged homoselenacalix[4]arene analogue **19** with a compact π-cavity was synthesized in a one-pot approach, composed of three phenyl rings as "walls" and two extra phenyl rings as "top" and "bottom caps". The enriched π-donor environment produced by the six three-dimensionally preorganized aryl groups of the bicyclic ligand may provide a nice steric fit for specific cations such as alkali metals and ammonium ions.

Solid-state structural elucidation

To confirm the structure and analyze the conformation of the synthesized macrocycles in the solid state, single crystals of compounds **10** and **19** were grown from saturated solutions in chloroform. Compound **10** crystallized in the monoclinic *P*2/*n* space group as a chloroform solvate (Fig. 1). There are one half of the homoselena[4]calixarene (the other half is generated by an inversion centre) and one molecule of $CHCl_3$ present in the asymmetric unit. The calixarene adopts a 1,2-alternate conformation, as observed earlier for its sulfur isologue.[7g] Nevertheless, the overall geometry of both molecules differs significantly. Choosing the mean plane defined by the Se atoms as a reference plane, the dihedral angles with the aromatic rings span between 56.7° (for the rings with the ester substituents on the lower rim) and 58.1° (for the rings with the methoxy groups on the lower rim), whereas the corresponding values for the related homothiacalix[4]arene were 73.1° and 25.7°, respectively.[7g] The geometries around the dimethylene–Se/S bridges are also dissimilar. In **10**, Se atoms are alternatingly pointing outside and inside of the macrocycle, whereas in the previous compound all S atoms were pointing towards the inside (see Fig. S1†). The two C–C–Se–C torsion angles defined by each bridge are associated with *anti*

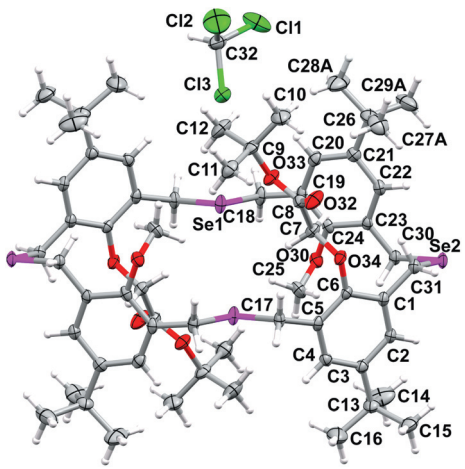


Fig. 1 Molecular structure of the chloroform solvate of homoselenacalix[4]arene **10** with an atom labelling scheme (thermal ellipsoids are drawn at 50% probability). Unlabeled atoms are related to labelled atoms by the symmetry operation 1 − *x*, 1 − *y*, −*z*. Disorder on the *tert*-butyl group C26 is omitted for clarity.

angles with values of 175.7(2)° and −167.8(2)° around Se1 and *gauche* angles of 62.4(2)° and 50.3(2)° around Se2. As the C–Se–C bridges are very flexible, the presence of weak C32–H32···O32 hydrogen bonds between the cyclophane ring and the solvent molecule (with a C···O bond length of 3.171(5) Å and a C–H–O angle of 162°) could be the cause of the adopted geometry. The C–Se bond lengths are in the range 1.949(3)–1.969(3) Å and the angles vary from 94.5(1)–97.4(1)°. These values are comparable with previous reports.[8] Additionally, there is a network of weak C–H···π interactions which further stabilize the adopted conformation. Further intramolecular interactions, such as C7–H7B···Cg1 (where Cg1 is the centroid of C19–C24) and C25–H25A···Cg2 (where Cg2 is the centroid of C1–C6), with C···Cg distances of 3.616(4) and 3.707(5) Å, involve ester and methoxy groups, respectively, whereas intermolecular ones such as C17–H17B···Cg2 and C30–H30A···Cg1 (with C···Cg distances of 3.598(3) and 3.339(3) Å, respectively) involve dimethyleneselena bridges.

Bicyclohomoselenacalix[4]arene **19** crystallized as a chloroform solvate in the triclinic *P*1 space group with one calixarene molecule and two $CHCl_3$ molecules in the asymmetric unit (Fig. 2). The bicyclic molecule consists of five aryl moieties. Three of these building blocks, originating from precursor **2** (with methoxy and *tert*-butyl groups in the *p*-position of each other), are alternating with two building blocks derived from precursor **17** (with three methoxy groups in positions 1, 3 and 5), with each cycle containing four aromatic units. As mentioned above, the molecule showed a similar conformation in solution as reported earlier for the analogous bicyclohomothiacalix[4]-arene.[7g] In the solid state, the conformation of the molecules also remained more or less the same (see Fig. S2†). The most striking differences concern the geometry of one of the dimethylene–Se/S bridges and the orientation of one of the methoxy groups on the arene bearing three methoxy substituents. Both of them can be the result of the location of solvent molecules (C79) in the crystal lattice. Weak C79–H79···Se16^{i} interactions, with a C–Se distance of 3.556(5) Å (symmetry operation: (i) x, $-1+y$, $1+z$), probably cause the change in angular geometry of the Se bridge as well as the 'self-inclusion' of the O11–C12 methoxy group, which in this case is pointing towards the macrocyclic ring. This indicates once again the flexibility of the C–Se–C bridges of the macrocycle, whose geometry can be easily influenced.

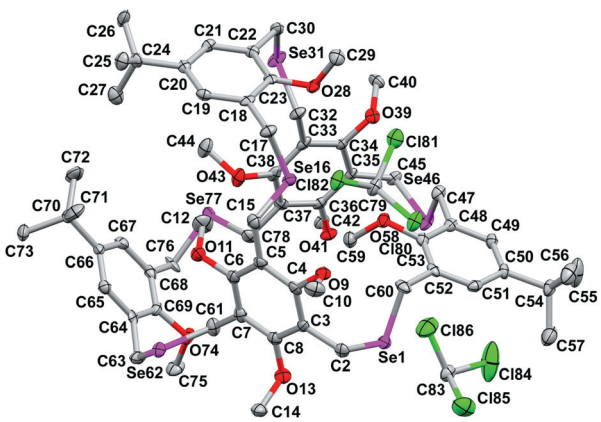


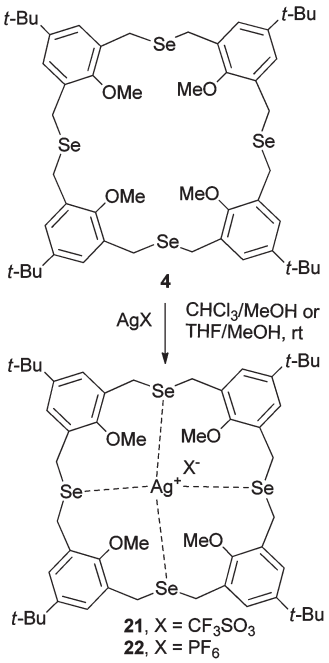
Fig. 2 Molecular structure of the chloroform solvate of bicyclohomoselenacalixarene **19** with an atom labelling scheme (thermal ellipsoids at 50% probability). Hydrogen atoms as well as the disordered *tert*-butyl group on C70 are omitted for clarity. The C–C–Se–C angles around the Se atoms are as follows: Se1 174.0(4)° and −76.5(4)°, Se16 −175.5(4)° and 117.0(5)°, Se31 176.4(4)° and 55.2(4)°, Se46 −160.8(4)° and 73.6(4)°, Se62 −177.6(4)° and 63.1(4)°, Se77 177.9(4)° and −66.6(5)°.

Metallosupramolecular chemistry

Metallosupramolecular architectures based on Se-bridged macrocycles have been investigated by a number of groups around the world.[9] The discovery of selenacoronands by Pinto and co-workers in 1989 has initiated research on the formation of metal complexes having unexpected electronic structures and redox properties different from those of the corresponding oxa and thia counterparts.[9a] Metal complexation for a wide range of middle and late transition metals has been studied over the last decade.[9g,t] Metallocomplexes composed of macrocyclic selenoether ligands and p-block ions of group 15 (As, Sb and Bi) were recently studied by Reid and co-workers.[9d–f] These ions often showed strong binding and were stabilized by a combination of primary interactions with the halogen counter ions and secondary interactions with Se. On the other hand, unsaturated selena-crown ethers, which are conformationally more restricted and possess different electronegativity for the Se atoms as compared to the corresponding saturated systems, exhibited different complexation behaviour and showed excellent inclusion features for Ag(I) ions.[9m] Mixed donor macrocycles having harder donor atoms such as N or O and softer Se atoms within the same molecular cavity are reported to behave as heterodinuclear macrocyclic ligands able to coordinate both hard and soft guest ions or molecules. Panda and co-workers synthesized Se/N macrocycles of varying ring size and their coordination complexes with Ni(II), Pd(II), Pt(II) and Hg(II) have been reported.[9k,l,n] The encapsulation of transition metals like Cu(I), Ag(I), Pd(II) and Pt(II) in mixed Se/O macrocycles has also been reported recently.[9b,c,i]

From the above examples, it is clear that homoselenacalixarenes possess the intrinsic potential to complex metal cations. The binding potential of the novel macrocycles was initially evaluated using homoselenacalix[4]arene **4** and Ag(I) salts.[15,16] Mixing of **4** in THF or $CHCl_3$ with one equivalent of $AgCF_3SO_3$ or $AgPF_6$ in MeOH at rt resulted in the formation of monomeric complexes [Ag-**4**]CF_3SO_3 (**21**) and [Ag-**4**]PF_6 (**22**) as off-white solids in high yields (Scheme 5). ESI-MS analysis showed an intense peak at *m*/*z* 1184, which corresponds to the monomer of the [Ag-**4**]$^+$ ionic species in agreement with the existence of a 1 : 1 complex in solution. The ^{1}H NMR spectra of complexes **21** and **22** showed broadened signals with only negligible chemical shift differences compared to precursor **4**.

We successfully determined the crystal structures of the Ag(I) cationic calixarene complexes mentioned above, *i.e.* with triflate (**21**) and hexafluorophosphate (**22**) counter ions. Compound **21** crystallized in the monoclinic $P2_1/c$ space group with two calixarene Ag(I) complexes of approximately the same conformation and two disordered triflate counter ions in the asymmetric unit. On the other hand, **22** crystallized (from THF) in the tetragonal *P*4*n*2 space group with one quarter of the calixarene's Ag(I)



Scheme 5 Synthesis of Ag(I) complexes **21** and **22**.

cationic complex, with the silver ion located on a special position with fourfold rotational symmetry (Wyckoff position 2a), and half of the PF_6^- counter ion, with P15 and F17 located on special positions (Wyckoff positions 2c and 4h, respectively), in the asymmetric unit (Fig. 3). The cationic complexes in **21** and **22** do not differ much (see Fig. S4†). The calixarene moieties in **21** and **22** keep the 1,3-alternate conformation as in the parent homoselenacalix[4]arene **4**,[8] but because the Se atoms are approaching the metal centers, a slight tilting of the aromatic rings is observed, as well as a change in the orientation of the methoxy groups which in this case are pointing outwards of the macrocycle to create the space needed for encapsulation of the Ag^+ ion (Fig. 4).

The Ag(I) atoms in both complexes are coordinated by Se atoms pointing towards the ring interior, to form a distorted tetrahedral geometry around the metal centre, with Se–Ag–Se angles

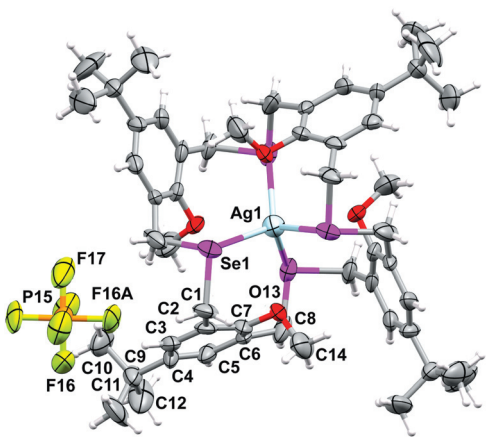


Fig. 3 Molecular structure of **22** with an atom labelling scheme of the asymmetric unit (thermal ellipsoids at 50% probability).

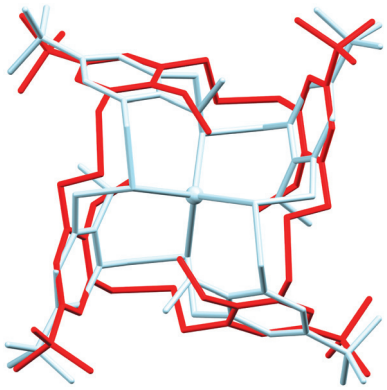


Fig. 4 Overlay of homoselenacalix[4]arene **4**·THF (red) with its Ag(I) complex **22** (grey); the silver ion is represented as a ball. The C–C–Se–C torsion angles have alternating *gauche*/*anti* geometry. For crystallographic information on **4**·THF, see the ESI.†

of 124.51(2)° and 82.35(4)° for **21** and angles varying from 125.98(4)° (Ag1) and 126.29(4)° (Ag2) to 82.61(3)° (Ag1) and 81.70(3)° (Ag2) for **22**. One pair of Ag–Se distances in **22** seems to be quite long, *i.e.* 3.244(2) Å (Ag1)/3.203(2) Å (Ag2), but taking into account the similarity between complexes **21** and **22** (Fig. S4†), we can conclude that coordination nevertheless takes place. The remaining Ag–Se distances with values of 2.950(1) Å for **21** and in the range of 2.773(1)–2.869(1) Å for **22** are in good agreement with previous reports.[9h,m]

The difference between the crystal structures of **21** and **22** was more noticeable at the supramolecular level. In both structures the Ag(I) calixarene complexes are forming layers which are separated by the counter ions they interact with. As the shape and the size of the counter ions differ, this results in different arrangements (Fig. 5). The smaller and spherically shaped PF_6^- ion in **22** facilitates the formation of a more complementary packing, whereas in **21** the presence of the bigger elongated $CF_3SO_3^-$ ion led to the occurrence of solvent accessible voids (PLATON estimates the accessible space at 10.1% of the total cell volume),[17] which could have originally been occupied by MeOH molecules (the solvent used during synthesis and crystallization). As the crystals got dry, the solvent molecules left and the space remained as a molecular shift was partially precluded by the counter ions. This could explain the bad quality of the crystal and the resulting poor data set.

Conclusions

In the presented study, we have reported efficient and flexible methods for the synthesis and functionalization (at the upper and lower rim) of homoselenacalix[4]arenes through a [2 + 2] reductive coupling protocol. ^{1}H NMR studies revealed a great similarity in the up-field shift of the intraannular methoxy protons of all homoselenacalix[4]arenes, pointing towards the preference for non-cone conformations in solution. Furthermore, we have extended our studies to the successful single-step synthesis of a three-dimensionally preorganized bicyclohomoselenacalixarene. The methoxy groups in the building blocks were proven to be essential to obtain high selectivity for the formation of the (bicyclo)homoselenacalix[4]arenes. In addition, the ability of the

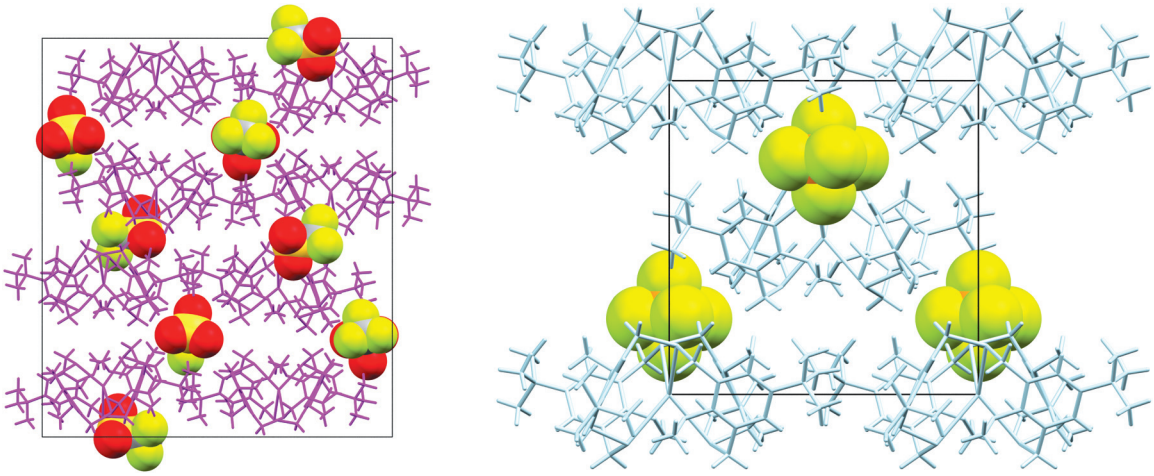


Fig. 5 Representation of the packing down the *a* axis (**21** on the left and **22** on the right). Counter ions are shown in space-filling representation. Disorder is not shown for clarity.

parent homoselenacalix[4]arene ligand to form a metallosupramolecular architecture through coordination of a Ag(I) ion by the bridging Se atoms is demonstrated. This work clearly illustrates the structural diversity that can be achieved for Se-bridged calixarenes by carefully optimized reaction conditions and shows the potential benefits of the introduction of soft Se atoms towards host–guest chemistry. Further supramolecular features of this class of expanded homoheteracalixarenes are currently actively being pursued within our group.

Experimental section

General experimental methods

NMR spectra were acquired on commercial instruments (Bruker Avance 300 MHz, Bruker AMX 400 MHz or Bruker Avance II$^+$ 600 MHz) and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (^{1}H) or the internal (NMR) solvent signals (^{13}C).[18] *J* values are given in Hz. The ^{77}Se NMR spectra were recorded using Ph_2Se_2 in $CDCl_3$ as an external reference (δ 463 ppm).[19] Mass spectra were run using an HP5989A apparatus (CI and EI, 70 eV ionisation energy) with an Apollo 300 data system or a Thermo Finnigan LCQ Advantage apparatus (ESI). Exact mass measurements were acquired on a Bruker Daltonics Apex2 FT-ICR instrument (performed in the ESI mode at a resolution of 60 000). Melting points (not corrected) were determined using a Reichert Thermovar apparatus. For column chromatography 70–230 mesh silica 60 (E. M. Merck) was used as the stationary phase. Chemicals received from commercial sources were used without further purification. Reaction solvents (THF, ethanol, methanol) were used as received from commercial sources. Additions in (high-dilution) macrocyclization reactions were performed at a constant rate with the aid of an infusion pump.

Safety precautions

The most convenient procedure to prepare NaSeH involves reduction of Se with $NaBH_4$. It allows rapid and easy preparation of NaSeH without the necessity of generating dangerously toxic H_2Se. NaSeH is an unstable compound and decomposes in moist air with the formation of polyselenides and precipitation of Se. It should be used directly as prepared (in a fume hood) in solution or suspension without isolation.[20]

Experimental and characterization data

5-*tert*-Butyl-2-methoxy-1,3-bis(selenocyanatomethyl)benzene (2). Experimental and characterization data can be retrieved from one of our previous manuscripts.[8] Material identity and purity were confirmed by mp, MS, ^{1}H and ^{13}C NMR.

7,15,23,31-Tetra-*tert*-butyl-33,34,35,36-tetramethoxy-2,3,10,11,18,19,26,27-octahomo-3,11,19,27-tetraselenacalix[4]arene (4). Experimental and characterization data can be retrieved from one of our previous manuscripts.[8] Material identity and purity were confirmed by mp, MS, ^{1}H and ^{13}C NMR.

***tert*-Butyl 2-[2,6-bis(bromomethyl)-4-*tert*-butylphenoxy]acetate (9).** Experimental and characterization data can be retrieved from one of our previous manuscripts.[7g] Material identity and purity were confirmed by mp, MS, ^{1}H and ^{13}C NMR.

Synthesis of homoselenacalix[*n*]arenes 10 and 11. A solution of $NaBH_4$ (0.039 g, 1.01 mmol, 2.2 equiv.) in ethanol (12 mL) was added over 2 h to a stirred mixture of **2** (0.207 g, 0.51 mmol) and **9** (0.184 g, 0.51 mmol) in degassed THF (50 mL) at rt. The mixture was subsequently stirred for 10 h and then concentrated to 10 mL. CH_2Cl_2 (50 mL) was added and the organic solution was washed with distilled water (3 × 50 mL), dried over $MgSO_4$, filtered, and then evaporated to dryness to afford the crude product mixture. Purification by column chromatography (silica, eluent CH_2Cl_2–heptane–diethyl ether 45 : 45 : 1) afforded **10** (0.123 g, 38%) and **11** (0.073g, 22%) as off-white solids. **10**: mp 70–72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.22 (s, 4H; ArH), 7.04 (s_{br}, 4H; ArH), 4.58–4.40 (m, 4H; OCH_2), 4.15–4.05 (d_{br}, 4H; CH_2), 3.95–3.60 (m, 12H; CH_2), 3.22–3.07 (d_{br}, 6H; OCH_3), 1.48 (s, 18H; *t*-Bu), 1.28 (s, 18H; *t*-Bu) and 1.25 (s, 18H; *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C

168.5 (CO), 153.9, 153.8, 152.7, 147.0, 132.9, 132.8, 131.1, 127.2 (CH), 126.7 (CH; br), 82.1 (O-*t*-Bu), 71.3 (OCH_2), 60.96 (OCH_3), 60.86 (OCH_3), 34.44, 34.38, 31.55 (CH_3), 31.52 (CH_3), 28.3 (CH_3), 23.2 (CH_2), 22.2 (CH_2) and 22.1 (CH_2); ^{77}Se NMR (76.3 MHz, $CDCl_3$) δ_{Se} 312; IR (ATR) ν_{max}/cm^{-1} 2959, 2950, 2926, 1750, 1729, 1479, 1460, 1363, 1214, 1153, 1095, 1053, 1007, 879, 836 and 580; MS (ESI^+) *m*/*z* 1301.8 $[M + Na]^+$; FTMS (ESI^+) calcd for $C_{62}H_{88}O_8Se_4Na$ $[M + Na]^+$: 1301.3046; found: *m*/*z* 1301.3093.[21]

11: mp 72–74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.16 (s, 6H; ArH), 7.12 (s, 6H; ArH), 4.55 (s, 6H; OCH_2), 3.93 (s, 12H; CH_2), 3.87 (s, 12H; CH_2), 3.79 (s, 9H; OCH_3), 1.51 (s, 27H; O-*t*-Bu), 1.27 (s, 27H; *t*-Bu) and 1.26 (s, 27H; *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 168.6 (CO), 153.9, 152.9, 147.4, 147.0, 132.3, 132.0, 126.9 (CH), 82.0 (O-*t*-Bu), 71.4 (OCH_2), 61.7 (OCH_3), 34.3, 31.56 (CH_3), 31.51 (CH_3), 28.4 (CH_3), 23.2 (CH_2) and 23.0 (CH_2); ^{77}Se NMR (76.3 MHz, $CDCl_3$) δ_{Se} 313; IR (ATR) ν_{max}/cm^{-1} 2967, 2949, 2926, 1749, 1733, 1478, 1419, 1364, 1214, 1154, 1103, 1053, 1004, 881, 844 and 582; MS (ESI^+) *m*/*z* 1938.3 $[M + Na]^+$.

Ethyl 4-hydroxy-3,5-bis(hydroxymethyl)benzoate (12). This compound has been prepared according to the procedure reported by Shabat *et al*.[22] Material identity and purity were confirmed by MS, ^{1}H and ^{13}C NMR.

Ethyl 3,5-bis(hydroxymethyl)-4-methoxybenzoate (13). To a mixture of ethyl 4-hydroxy-3,5-bis(hydroxymethyl)benzoate (**12**) (4.00 g, 17.7 mmol) and K_2CO_3 (12.26 g, 88.8 mmol, 5 equiv.) in acetone (100 mL), MeI (5.04 g, 35.4 mmol, 2 equiv.) was added. The mixture was stirred at reflux temperature for 12 h and then concentrated under reduced pressure. CH_2Cl_2 (100 mL) was added and the organic solution was washed with distilled water (3 × 50 mL), dried over $MgSO_4$, filtered, and then evaporated to dryness to afford the crude product mixture. Purification by column chromatography (silica, eluent ethyl acetate–CH_2Cl_2 80 : 20) afforded **13** (3.3 g, 77%) as an off-white solid. mp 69–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.00 (s, 2H; ArH), 4.73 (s, 4H; CH_2), 4.35 (q, *J* = 7.1, 2H; CH_2), 3.86 (s, 3H; OCH_3), 2.59 (s_{br}, 2H; OH) and 1.38 (t, *J* = 7.1, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 166.3 (CO), 159.9 (CO), 134.3, 130.4 (CH), 126.7, 62.4 (OCH_3), 61.2 (CH_2), 60.5 (CH_2) and 14.4 (CH_3); IR (ATR) ν_{max}/cm^{-1} 3363, 2959, 1696, 1308, 1204, 1102, 1081, 1009, 914, 770, 671 and 550; MS (ESI^+) *m*/*z* 240 $[M + H]^+$; FTMS (ESI^+) calcd for $C_{12}H_{16}O_5Na$ $[M + Na]^+$: 263.0895; found: *m*/*z* 263.0895.

Ethyl 3,5-bis(bromomethyl)-4-methoxybenzoate (14). A solution of **13** (2.00 g, 8.33 mmol) and CBr_4 (4.08 g, 25 mmol, 3 equiv.) in CH_2Cl_2 (40 mL) was prepared in a 100 mL flask and cooled down to 0 °C. A solution of PPh_3 (3.27 g, 25 mmol, 3 equiv.) in CH_2Cl_2 (10 mL) was added and the temperature was gradually increased to rt. After stirring the resulting mixture for another 12 h, the reaction mixture was added to water (40 mL). CH_2Cl_2 (70 mL) was added and the organic solution was washed with distilled water (3 × 50 mL), dried over $MgSO_4$, filtered, and then evaporated to dryness to afford the crude product mixture. Purification by column chromatography (silica, eluent CH_2Cl_2–heptane 70 : 30) afforded **14** (2.37 g, 80%) as an off-white solid. mp 119–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.06 (s, 2H; ArH), 4.56 (s, 4H; CH_2), 4.38 (q, *J* = 7.1, 2H; CH_2), 4.07 (s, 3H; OCH_3) and 1.40 (t, *J* = 7.1, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 165.3 (CO), 160.4 (CO), 133.6 (CH), 132.4, 127.4, 62.6 (OCH_3), 61.4 (OCH_2), 26.9 (CH_2) and 14.5 (CH_3); IR (ATR) ν_{max}/cm^{-1} 3054, 2990, 2961, 2831, 1711, 1603, 1474, 1368, 1314, 1224, 1200, 1028, 989, 955, 767, 597 and 579; MS (ESI^+) *m*/*z* 367 $[M+H]^+$; FTMS (ESI^+) calcd for $C_{12}H_{14}Br_2O_3$ $[M^+]$: 365.9289; found: *m*/*z* 365.9271.

7,23-Bis(ethoxycarbonyl)-15,31-di-*tert*-butyl-33,34,35,36-tetramethoxy-2,3,10,11,18,19,26,27-octahomo-3,11,19,27-tetraselenacalix[4]arene (15). A solution of $NaBH_4$ (0.031 g, 0.81 mmol, 3 equiv.) in ethanol (12 mL) was added over 3 h to a stirred mixture of **2** (0.109 g, 0.27 mmol) and **14** (0.100 g, 0.27 mmol) in degassed THF (200 mL) at rt. The mixture was subsequently stirred for 1 h and then concentrated to 10 mL. CH_2Cl_2 (50 mL) was added and the organic solution was washed with distilled water (3 × 50 mL), dried over $MgSO_4$, filtered, and then evaporated to dryness to afford the crude product mixture. Purification by column chromatography (silica, eluent CH_2Cl_2–heptane–diethyl ether 46 : 30 : 24) afforded **15** (0.063 g, 42%) as an off-white solid. mp 136–138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.85 (s, 4H; ArH), 7.11 (s, 4H; ArH), 4.34 (q, *J* = 7.1, 4H; CH_2), 3.79 (s, 8H; CH_2), 3.77 (s, 8H; CH_2), 3.47 (s, 6H; OCH_3), 3.36 (s, 6H; OCH_3), 1.38 (t, *J* = 7.1, 6H; CH_3) and 1.27 (s, 18H; *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 165.9 (CO), 160.0 (CO), 153.7, 146.9, 133.0, 131.7, 131.2 (CH), 126.9 (CH), 126.1, 61.12 (OCH_3), 61.05 (OCH_2), 34.3, 31.5 (CH_3), 22.6 (CH_2), 21.6 (CH_2) and 14.5 (CH_3); ^{77}Se NMR (76.3 MHz, $CDCl_3$) δ_{Se} 324; IR (ATR) ν_{max}/cm^{-1} 2954, 2867, 1480, 1361, 1245, 1217, 1185, 1093, 1033, 1000, 897, 879 and 580; MS (ESI^+) *m*/*z* = 1131.3 $[M + Na]^+$.

7,23-Bis(hydroxymethyl)-15,31-di-*tert*-butyl-33,34,35,36-tetramethoxy-2,3,10,11,18,19,26,27-octahomo-3,11,19,27-tetraselenacalix[4]arene (16). A solution of $LiBH_4$ (1.6 mL, 2 M in THF) in dry THF (10 mL) was added dropwise to a stirred mixture of **15** (0.109 g, 0.16 mmol) in dry THF (20 mL) at 0 °C. The temperature was gradually increased to rt. After stirring the resulting mixture for 2 days, the reaction mixture was added to water (40 mL). Ethyl acetate (30 mL) was added and the organic solution was washed with distilled water (3 × 30 mL), dried over $MgSO_4$, filtered, and then evaporated to dryness to afford the crude product mixture. Purification by column chromatography (silica, eluent CH_2Cl_2–ethyl acetate 90 : 10) afforded **16** (0.140 g, 87%) as an off-white solid. mp 140–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.18 (s, 4H; ArH), 7.05 (s, 4H; ArH), 4.51 (s, 4H; CH_2), 3.76 (s, 8H; CH_2), 3.75 (s, 8H; CH_2), 3.59 (s, 6H; OCH_3), 3.31 (s, 6H; OCH_3), 3.00 (s_{br}, 2H; OH) and 1.28 (s, 18H; *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 155.5 (CO), 153.4, 147.4, 137.0, 133.1, 131.5, 128.6, 127.0 (CH), 64.8 (CH_2OH), 61.6 (OCH_3), 61.2 (OCH_3), 34.4, 31.5 (CH_3), 22.0 (CH_2) and 21.8 (CH_2); ^{77}Se NMR (76.3 MHz, $CDCl_3$) δ_{Se} 325; IR (ATR) ν_{max}/cm^{-1} 3385, 2855, 1478, 1432, 1360, 1295, 1234, 1185, 1109, 1046, 998, 880, 856 and 592; MS (ESI^+) *m*/*z* 1046.9 $[M + Na]^+$.

1,3,5-Tris(bromomethyl)-2,4,6-trimethoxybenzene (17). This compound has been prepared according to the procedure

reported by Castellano *et al.*[23] Material identity and purity were confirmed by MS, ^{1}H and ^{13}C NMR.

1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (18). This compound has been prepared according to the procedure reported by Van der Made and Van der Made.[24] Material identity and purity were confirmed by MS, ^{1}H and ^{13}C NMR.

Synthesis of bicyclohomoselenacalix[4]arene 19. A solution of $NaBH_4$ (0.038 g, 1.01 mmol) in ethanol (12 mL) was added over 2 h to a stirred mixture of **2** (0.135 g, 0.34 mmol) and **17** (0.100 g, 0.22 mmol) in degassed THF (150 mL) at rt. The mixture was subsequently stirred for 3 h and then concentrated to 10 mL. CH_2Cl_2 (50 mL) was added and the organic solution was washed with distilled water (3 × 50 mL), dried over $MgSO_4$, filtered, and then evaporated to dryness to afford the crude product mixture. Purification by column chromatography (silica, eluent CH_2Cl_2–heptane–diethyl ether 67 : 26 : 7) afforded **19** (0.039 g, 23%) as an off-white solid. mp 216–218 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.17 (s, 6H; ArH), 3.83 (s, 12H; CH_2), 3.78 (s, 12H; CH_2), 3.74 (s, 18H; OCH_3), 3.29 (s, 9H; OCH_3) and 1.27 (s, 27H; *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 157.2, 153.9, 146.9, 131.6, 126.8 (CH), 123.2, 62.3 (OCH_3), 61.1 (OCH_3), 34.4, 31.5 (CH_3), 22.8 (CH_2) and 16.6 (CH_2); ^{77}Se NMR (76.3 MHz, $CDCl_3$) δ_{Se} 322; IR (ATR) ν_{max}/cm^{-1} 2955, 2877, 1570, 1487, 1463, 1428, 1258, 1193, 1167, 1087, 999, 895, 845 and 599; MS (ESI$^+$) *m*/*z* 1483.1 $[M + Na]^+$.

Synthesis of bis(selenacyclophane) 20. A solution of $NaBH_4$ (0.038 g, 1.01 mmol) in ethanol (12 mL) was added over 2 h to a stirred mixture of **2** (0.150 g, 0.38 mmol) and **18** (0.100 g, 0.25 mmol) in degassed THF (150 mL) at rt. The mixture was subsequently stirred for 3 h and then concentrated to 10 mL. CH_2Cl_2 (50 mL) was added and the organic solution was washed with distilled water (3 × 50 mL), dried over $MgSO_4$, filtered, and then evaporated to dryness to afford the crude product mixture. Purification by column chromatography (silica, eluent CH_2Cl_2) afforded **20** (0.048 g, 27%) as an off-white solid. mp 221–223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.33 (s, 6H; ArH), 4.01 (s, 4H; CH_2), 3.99 (s, 4H; CH_2), 3.89 (s, 3H; OCH_3), 3.78 (dd, *J* = 26.8/14.4, 8H; CH_2), 3.65 (d, *J* = 18.2, 4H; CH_2), 3.19 (d, *J* = 17.0, 4H; CH_2), 3.11 (s, 6H; OCH_3), 2.43 (s, 12H; CH_3), 1.36 (s, 9H; CH_3) and 1.29 (s, 27H; *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 155.8, 154.0, 147.0, 146.5, 138.9, 136.7, 132.6, 132.3, 130.7, 128.9, 127.5 (CH), 126.8 (CH), 62.0 (OCH_3), 61.6 (OCH_3), 34.54, 34.48, 31.6 (CH_3), 31.5 (CH_3), 29.6, 25.4 (CH_2), 22.9 (CH_2), 21.6 (CH_2), 18.3 (CH_2), 16.1 (CH_3) and 15.0 (CH_3); ^{77}Se NMR (76.3 MHz, $CDCl_3$) δ_{Se} 258; IR (ATR) ν_{max}/cm^{-1} 2819, 2726, 2672, 1692, 1479, 1460, 1246, 1184, 1169, 1010, 934, 876, 831, 619 and 576; MS (ESI$^+$) *m*/*z* 1386.8 $[M + Na]^+$.

Synthesis of Ag(I) complexes 21 and 22. A solution of $Ag^+CF_3SO_3^-$ (0.007 g, 0.028 mmol) or $Ag^+PF_6^-$ (0.007 g, 0.028 mmol) in methanol (3 mL) was added to a solution of homoselenacalix[4]arene **4** (0.030 g, 0.028 mmol) in THF (10 mL) at rt and the mixture was stirred for 10 h. The resulting solution was evaporated to dryness and washed with diethyl ether to afford the monomeric complexes **21** (0.034 g; 91%) and **22**, respectively (0.031 g; 86%), as off-white solids. **21**: mp 222–224 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.17 (s, 8H; ArH), 3.78 (s_{br}, 16H; CH_2), 3.15 (s_{br}, 12H; OCH_3) and 1.27 (s, 36H; *t*-Bu); IR (ATR) ν_{max}/cm^{-1} 2950, 2938, 2232, 1488, 1290, 1226, 1153, 1101, 1022, 988, 937, 849, 629 and 574; MS (ESI$^+$) *m*/*z* 1184.6 $[M - CF_3SO_3]^+$; FTMS (ESI$^+$) calcd for $C_{52}H_{72}AgO_4Se_4$ $[M - CF_3SO_3]^+$: 1185.1150; found: *m*/*z* 1185.1184. **22**: mp 194–196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.20 (s, 8H; ArH), 3.83 (s_{br}, 16H; CH_2), 3.17 (s_{br}, 12H; OCH_3) and 1.28 (s, 36H; *t*-Bu); IR (ATR) ν_{max}/cm^{-1} 2956, 2935, 2225, 2204, 1993, 1484, 1289, 1248, 1132, 998, 1022, 842, 825, 656 and 570; MS (ESI$^+$) *m*/*z* 1184.3 $[M - PF_6]^+$; FTMS (ESI$^+$) calcd for $C_{52}H_{72}AgO_4Se_4$ $[M - PF_6]^+$: 1185.1150; found: *m*/*z* 1185.1207.

Crystal structure determination

X-ray crystallographic general experimental data are outlined in the ESI.† In the case of bis(selenacyclophane) **20**, the data were limited and their quality was very poor. However, as all our efforts to collect a better data set failed, we decided to mention the structure in the text as we could prove formation of the presented molecule (see Fig. S5†). It crystallized as a dichloromethane solvate in the triclinic *P*1 space group with unit cell parameters *a* = 9.774(5), *b* = 17.634(10), *c* = 18.839(10) Å, *α* = 77.619(10), *β* = 80.539(11), *γ* = 79.259(11)° and *V* = 3090(3) Å^3. For structure **21**, the crystal quality was rather poor, which could be caused by release of the solvent molecules.

Crystal data for 4. $C_{52}H_{72}O_4Se_4{\cdot}2(C_4H_8O)$, *M* = 1221.14, colourless block, 0.32 × 0.18 × 0.09 mm^3, tetragonal, space group $I4_1/a$ (No. 88), *a* = *b* = 28.310(4), *c* = 14.618(3) Å, *V* = 11 716(3) Å^3, *Z* = 8, D_c = 1.385 g cm^{-3}, F_{000} = 5056, KM4CCD, MoKα radiation, *λ* = 0.71073 Å, *T* = 100(2) K, $2\theta_{max}$ = 52.8°, 94 873 reflections collected, 5998 unique (R_{int} = 0.0597). Final GooF = 1.079, R_1 = 0.0364, wR_2 = 0.0844, *R* indices based on 4733 reflections with $I > 2\sigma(I)$ (refinement on F^2). Lp and absorption corrections applied, μ = 2.552 mm^{-1}.

Crystal data for 10. $C_{62}H_{88}O_8Se_4{\cdot}2(CHCl_3)$, *M* = 1515.90, colourless rod, 0.4 × 0.2 × 0.15 mm^3, monoclinic, space group $P2_1/n$ (No. 14), *a* = 10.8677(13), *b* = 12.6155(10), *c* = 26.392(5) Å, *β* = 95.784(8)°, *V* = 3600.0(9) Å^3, *Z* = 2, D_c = 1.398 g cm^{-3}, F_{000} = 1552, SMART 6000, CuKα radiation, *λ* = 1.54178 Å, *T* = 100(2) K, $2\theta_{max}$ = 143.4°, 30 601 reflections collected, 6885 unique (R_{int} = 0.0777). Final GooF = 1.055, R_1 = 0.0456, wR_2 = 0.1082, *R* indices based on 5837 reflections with $I > 2\sigma(I)$ (refinement on F^2). Lp and absorption corrections applied, μ = 4.871 mm^{-1}.

Crystal data for 19. $C_{63}H_{84}O_9Se_6{\cdot}2(CHCl_3)$, *M* = 1697.80, colourless plate, 0.4 × 0.2 × 0.1 mm^3, triclinic, space group *P*1 (No. 2), *a* = 14.9433(4), *b* = 16.7585(4), *c* = 17.4804(4) Å, *α* = 109.7050(10), *β* = 98.3310(10), *γ* = 112.9910(10)°, *V* = 3595.47(16) Å^3, *Z* = 2, D_c = 1.568 g cm^{-3}, F_{000} = 1708, SMART 6000, CuKα radiation, *λ* = 1.54178 Å, *T* = 100(2) K, $2\theta_{max}$ = 141.6°, 70 888 reflections collected, 13 363 unique (R_{int} = 0.0980). Final GooF = 1.033, R_1 = 0.0497, wR_2 = 0.1095, *R* indices based on 10 164 reflections with $I > 2\sigma(I)$ (refinement on F^2). Lp and absorption corrections applied, μ = 6.067 mm^{-1}.

Crystal data for 21. $C_{52}H_{72}AgO_4Se_4CF_3SO_3$, M = 1333.89, colourless rod, 0.4 × 0.2 × 0.1 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 13.801(7), b = 27.671(12), c = 31.568(16) Å, β = 93.689(14)°, V = 12 030(10) Å^3, Z = 8, D_c = 1.473 g cm^{-3}, F_{000} = 5376, SMART 6000, CuKα radiation, λ = 1.54178 Å, T = 100(2) K, $2\theta_{max}$ = 133.2°, 21 230 reflections collected, 21 230 unique (R_{int} = 0.0000). Final GooF = 1.071, R_1 = 0.0837, wR_2 = 0.1718, R indices based on 18 418 reflections with $I > 2\sigma(I)$ (refinement on F^2). Lp and absorption corrections applied, μ = 6.225 mm^{-1}.

Crystal data for 22. $C_{52}H_{72}AgO_4Se_4PF_6$, M = 1329.78, colourless prism, 0.38 × 0.25 × 0.11 mm^3, tetragonal, space group $P4n2$ (No. 118), $a = b$ = 13.994(2), c = 14.223(3) Å, V = 2785.4(8) Å^3, Z = 2, D_c = 1.586 g cm^{-3}, F_{000} = 1336, KM4CCD, MoKα radiation, λ = 0.71073 Å, T = 100(2) K, $2\theta_{max}$ = 52.7°, 11 491 reflections collected, 2855 unique (R_{int} = 0.0721). Final GooF = 0.988, R_1 = 0.0512, wR_2 = 0.0887, R indices based on 1461 reflections with $I > 2\sigma(I)$ (refinement on F^2). Lp and absorption corrections applied, μ = 3.065 mm^{-1}.

CCDC 848952–848956 contain the supplementary crystallographic data for this paper (compounds **19**, **4**·THF, **21**, **22** and **10**, respectively).

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Notes and references

1 Heteracalixarene reviews: (*a*) B. König and M. H. Fonseca, *Eur. J. Inorg. Chem.*, 2000, 2303; (*b*) P. Lhoták, *Eur. J. Org. Chem.*, 2004, 1675; (*c*) N. Morohashi, F. Narumi, N. Iki, T. Hattori and S. Miyano, *Chem. Rev.*, 2006, **106**, 5291; (*d*) T. Kajiwara, N. Iki and M. Yamashita, *Coord. Chem. Rev.*, 2007, **251**, 1734; (*e*) H. Tsue, K. Ishibashi and R. Tamura, Heterocyclic supramolecules I, in *Topics in Heterocyclic Chemistry*, ed. K. Matsumoto, Springer, Heidelberg, 2008, vol. 17, p. 73; (*f*) W. Maes and W. Dehaen, *Chem. Soc. Rev.*, 2008, **37**, 2393; (*g*) M.-X. Wang, *Chem. Commun.*, 2008, 4541; (*h*) C.-S. Zuo, O. Wiest and Y.-D. Wu, *J. Phys. Org. Chem.*, 2011, **24**, 1157; (*i*) M.-X. Wang, *Acc. Chem. Res.*, 2012, **45**, 182.

2 Azacalixarenes: (*a*) Y. Miyazaki, T. Kanbara and T. Yamamoto, *Tetrahedron Lett.*, 2002, **43**, 7945; (*b*) M.-X. Wang, X.-H. Zhang and Q.-Y. Zheng, *Angew. Chem., Int. Ed.*, 2004, **43**, 838; (*c*) H.-Y. Gong, Q.-Y. Zheng, X.-H. Zhang, D.-X. Wang and M.-X. Wang, *Org. Lett.*, 2006, **8**, 4895; (*d*) H. Tsue, K. Ishibashi, S. Tokita, K. Matsui, H. Takahashi and R. Tamura, *Chem. Lett.*, 2007, **36**, 1374; (*e*) H. Tsue, K. Ishibashi, S. Tokita, H. Takahashi, K. Matsui and R. Tamura, *Chem.–Eur. J.*, 2008, **14**, 6125; (*f*) B. Yao, D.-X. Wang, Z.-T. Huang and M.-X. Wang, *Chem. Commun.*, 2009, 2899; (*g*) E.-X. Zhang, D.-X. Wang, Z.-T. Huang and M.-X. Wang, *J. Org. Chem.*, 2009, **74**, 8595; (*h*) M. Xue and C.-F. Chen, *Chem. Commun.*, 2011, 2318; (*i*) M. Touil, M. Elhabiri, M. Lachkar and O. Siri, *Eur. J. Org. Chem.*, 2011, 1914; (*j*) A. I. Vicente, J. M. Caio, J. Sardinha, C. Moiteiro, R. Delgado and V. Félix, *Tetrahedron*, 2012, **68**, 670; (*k*) H. Tsue, H. Takahashi, K. Ishibashi, R. Inoue, S. Shimizu, D. Takahashi and R. Tamura, *CrystEngComm*, 2012, **14**, 1021.

3 Oxacalixarenes: (*a*) M.-X. Wang and H.-B. Yang, *J. Am. Chem. Soc.*, 2004, **126**, 15412; (*b*) J. L. Katz, M. B. Feldman and R. R. Conry, *Org. Lett.*, 2005, **7**, 91; (*c*) J. L. Katz, K. J. Selby and R. R. Conry, *Org. Lett.*, 2005, **7**, 3505; (*d*) W. Maes, W. Van Rossom, K. Van Hecke, L. Van Meervelt and W. Dehaen, *Org. Lett.*, 2006, **8**, 4161; (*e*) D.-X. Wang, Q.-Y. Zheng, Q.-Q. Wang and M.-X. Wang, *Angew. Chem., Int. Ed.*, 2008, **47**, 7485; (*f*) W. Van Rossom, W. Maes, L. Kishore, M. Ovaere, L. Van Meervelt and W. Dehaen, *Org. Lett.*, 2008, **10**, 585; (*g*) S. Ferrini, S. Fusi, G. Giorgi and F. Ponticelli, *Eur. J. Org. Chem.*, 2008, 5407; (*h*) M.-L. Ma, X.-Y. Li and K. Wen, *J. Am. Chem. Soc.*, 2009, **131**, 8338; (*i*) W. Van Rossom, M. Ovaere, L. Van Meervelt, W. Dehaen and W. Maes, *Org. Lett.*, 2009, **11**, 1681; (*j*) D.-X. Wang, Q.-Q. Wang, Y. Han, Y. Wang, Z.-T. Huang and M.-X. Wang, *Chem.–Eur. J.*, 2010, **16**, 13053; (*k*) S.-Z. Hu and C.-F. Chen, *Chem. Commun.*, 2010, 4199; (*l*) X.-Y. Li, L.-Q. Liu, M.-L. Ma, X.-L. Zhao and K. Wen, *Dalton Trans.*, 2010, **39**, 8646; (*m*) M. E. Alberto, G. Mazzone, N. Russo and E. Sicilia, *Chem. Commun.*, 2010, 5894; (*n*) W. Van Rossom, L. Kishore, K. Robeyns, L. Van Meervelt, W. Dehaen and W. Maes, *Eur. J. Org. Chem.*, 2010, 4122; (*o*) W. Van Rossom, O. Kundrát, T. H. Ngo, P. Lhoták, W. Dehaen and W. Maes, *Tetrahedron Lett.*, 2010, **51**, 2423; (*p*) W. Van Rossom, K. Robeyns, M. Ovaere, L. Van Meervelt, W. Dehaen and W. Maes, *Org. Lett.*, 2011, **13**, 126; (*q*) Y. Chen, D.-X. Wang, Z.-T. Huang and M.-X. Wang, *Chem. Commun.*, 2011, 8112; (*r*) C. Gargiulli, G. Gattuso, A. Notti, S. Pappalardo, M. F. Parisi and F. Puntoriero, *Tetrahedron Lett.*, 2012, **53**, 616; (*s*) W. Van Rossom, J. Caers, K. Robeyns, L. Van Meervelt, W. Maes and W. Dehaen, *J. Org. Chem.*, 2012, **77**, 2791; (*t*) L.-W. Kong, M.-L. Ma, L.-C. Wu, X.-L. Zhao, F. Guo, B. Jiang and K. Wen, *Dalton Trans.*, 2012, **41**, 5625.

4 Selenacalixarenes: J. Thomas, W. Van Rossom, K. Van Hecke, L. Van Meervelt, M. Smet, W. Maes and W. Dehaen, *Chem. Commun.*, 2012, 43.

5 Homooxacalixarenes: (*a*) B. Masci, M. Finelli and M. Varrone, *Chem.–Eur. J.*, 1998, **4**, 2018; (*b*) K. Araki and H. Hayashida, *Tetrahedron Lett.*, 2000, **41**, 1807; (*c*) B. Masci, S. Saccheo, M. Fonsi, M. Varrone, M. Finelli, M. Nierlich and P. Thuéry, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2001, **57**, 978; (*d*) N. Komatsu and T. Chishiro, *J. Chem. Soc., Perkin Trans.*, 2001, 1532; (*e*) E. A. Shokova and V. V. Kovalev, *Russ. J. Org. Chem.*, 2004, **40**, 607; (*f*) E. A. Shokova and V. V. Kovalev, *Russ. J. Org. Chem.*, 2004, **40**, 1547; (*g*) B. Masci, S. L. Mortera, D. Persiani and P. Thuéry, *J. Org. Chem.*, 2006, **71**, 504; (*h*) J. K. Choi, A. Lee, S. Kim, S. Ham, K. No and J. S. Kim, *Org. Lett.*, 2006, **8**, 1601; (*i*) S. Kohmoto, Y. Someya, H. Masu, K. Yamaguchi and K. Kishikawa, *J. Org. Chem.*, 2006, **71**, 4509; (*j*) J. M. Notestein, L. R. Andrini, V. I. Kalchenko, F. G. Requejo, A. Katz and E. Iglesia, *J. Am. Chem. Soc.*, 2007, **129**, 1122; (*k*) C. Redshaw, M. A. Rowan, L. Warford, D. M. Homden, A. Arbaoui, M. R. J. Elsegood, S. H. Dale, T. Yamato, C. P. Casas, S. Matsui and S. Matsuura, *Chem.–Eur. J.*, 2007, **13**, 1090; (*l*) P. M. Marcos, J. R. Ascenso, M. A. P. Segurado, R. J. Bernardino and P. J. Cragg, *Tetrahedron*, 2009, **65**, 496; (*m*) X.-L. Ni, S. Wang, X. Zeng, Z. Tao and T. Yamato, *Org. Lett.*, 2011, **13**, 552; (*n*) K. Cottet, P. M. Marcos and P. J. Cragg, *Beilstein J. Org. Chem.*, 2012, **8**, 201.

6 Homoazacalixarenes: (*a*) H. Takemura, *J. Inclusion Phenom. Macrocyclic Chem.*, 2002, **42**, 169; (*b*) K. Ito, M. Noike, A. Kida and Y. Ohba, *J. Org. Chem.*, 2002, **67**, 7519; (*c*) C. Kaewtong, S. Fuangswasdi, N. Muangsin, N. Chaichit, J. Vicens and B. Pulpoka, *Org. Lett.*, 2006, **8**, 1561; (*d*) S. Khan, J. D. Singh, R. K. Mahajan and P. Sood, *Tetrahedron Lett.*, 2007, **48**, 3605; (*e*) C. Kaewtong, G. Jiang, Y. Park, T. Fulghum, A. Baba, B. Pulpoka and R. Advincula, *Chem. Mater.*, 2008, **20**, 4915; (*f*) M. Arunachalam, I. Ravikumar and P. Ghosh, *J. Org. Chem.*, 2008, **73**, 9144; (*g*) H. Takemura, Y. Yonebayashi, T. Nakagaki and T. Shinmyozu, *Eur. J. Org. Chem.*, 2011, 1968.

7 Homothiacalixarenes: (*a*) R. H. Mitchell and V. Boekelheide, *J. Am. Chem. Soc.*, 1974, **96**, 1547; (*b*) M. Tashiro and T. Yamato, *J. Org. Chem.*, 1981, **46**, 1543; (*c*) T. Takido, M. Toriyama, K. Ogura, H. Kamijo, S. Motohashi and M. Seno, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2003, **178**, 1295; (*d*) K. Kohno, M. Takeshita and T. Yamato, *J. Chem. Res.*, 2006, 251; (*e*) M. Ashram, *J. Inclusion Phenom. Macrocyclic Chem.*, 2006, **54**, 253; (*f*) H. A. Tran and P. E. Georghiou, *New J. Chem.*, 2007, **31**, 926; (*g*) J. Thomas, K. Van Hecke, K. Robeyns, W. Van Rossom, M. P. Sonawane, L. Van Meervelt, M. Smet, W. Maes and W. Dehaen, *Chem.–Eur. J.*, 2011, **17**, 10339.

8 Homoselenacalixarenes: J. Thomas, W. Maes, K. Robeyns, M. Ovaere, L. Van Meervelt, M. Smet and W. Dehaen, *Org. Lett.*, 2009, **11**, 3040.

9 (*a*) R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J. H. Gu, B. D. Johnston and B. M. Pinto, *J. Am. Chem. Soc.*, 1989, **111**, 6582; (*b*) A. Mazouz, P. Meunier, M. M. Kubicki, B. Hanquet, R. Amardeil, C. Bornet and A. Zahidi, *J. Chem. Soc., Dalton Trans.*, 1997, 1043; (*c*) C. Bornet, R. Amardeil, P. Meunier and J. C. Daran, *J. Chem. Soc., Dalton Trans.*, 1999, 1039; (*d*) A. J. Barton, A. R. J. Genge, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 2000, 2163; (*e*) A. J. Barton, N. J. Hill, W. Levason and G. Reid, *J. Am. Chem. Soc.*, 2001, **123**, 11801;

(*f*) N. J. Hill, W. Levason and G. Reid, *Inorg. Chem.*, 2002, **41**, 2070; (*g*) W. Levason, S. D. Orchard and G. Reid, *Coord. Chem. Rev.*, 2002, **225**, 159; (*h*) T. Shimizu, M. Kawaguchi, T. Tsuchiya, K. Hirabayashi and N. Kamigata, *J. Org. Chem.*, 2003, **5**, 1443; (*i*) M. J. Hesford, W. Levason, M. L. Matthews and G. Reid, *Dalton Trans.*, 2003, 2852; (*j*) R. Pietschnig, S. Schfer and K. Merz, *Org. Lett.*, 2003, **5**, 1867; (*k*) S. Panda, H. B. Singh and R. J. Butcher, *Chem. Commun.*, 2004, 322; (*l*) S. Panda, H. B. Singh and R. J. Butcher, *Inorg. Chem.*, 2004, **43**, 8532; (*m*) T. Shimizu, M. Kawaguchi, T. Tsuchiya, K. Hirabayashi and N. Kamigata, *J. Org. Chem.*, 2005, **70**, 5036; (*n*) S. Panda, S. S. Zade, H. B. Singh and R. J. Butcher, *Eur. J. Inorg. Chem.*, 2006, 172; (*o*) U. Patel, H. B. Singh and R. J. Butcher, *Eur. J. Inorg. Chem.*, 2006, 5089; (*p*) W. Levason, J. M. Manning, M. Nirwan, R. Ratnani, G. Reid, H. L. Smith and M. Webster, *Dalton Trans.*, 2008, 3486; (*q*) S. Gonzalez-Calera, D. J. Eisler, J. V. Morey, M. McPartlin, S. Singh and D. S. Wright, *Angew. Chem., Int. Ed.*, 2008, **47**, 1111; (*r*) G. Hua, Y. Li, A. M. Z. Slawin and J. D. Woollins, *Angew. Chem., Int. Ed.*, 2008, **47**, 2857; (*s*) W. Levason, J. M. Manning, G. Reid, M. Tuggey and M. Webster, *Dalton Trans.*, 2009, 4569; (*t*) A. Panda, *Coord. Chem. Rev.*, 2009, **253**, 1056; (*u*) G. Hua, J. M. Griffin, S. E. Ashbrook, A. M. Z. Slawin and J. D. Woollins, *Angew. Chem., Int. Ed.*, 2011, **50**, 4123.

10 (*a*) D. B. Werz, R. Gleiter and F. Rominger, *J. Am. Chem. Soc.*, 2002, **124**, 10638; (*b*) D. B. Werz, F. R. Fischer, S. C. Kornmayer, F. Rominger and R. Gleiter, *J. Org. Chem.*, 2008, **73**, 8021; (*c*) A. Lari, R. Gleiter and F. Rominger, *Eur. J. Org. Chem.*, 2009, 2267.

11 (*a*) K. Goto, T. Saiki and R. Okazaki, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1998, **136**, 475; (*b*) X. Hu, Y. Chen, Z. Tian and J. Xue, *J. Chem. Res. (S)*, 1999, 332; (*c*) X. Zeng, X. Han, L. Chen, Q. Li, F. Xu, X. He and Z.-Z. Zhang, *Tetrahedron Lett.*, 2002, **43**, 131; (*d*) H. Li, W. Xiong, Y. Yan, J. Liu, H. Xu and X. Yang, *Mater. Lett.*, 2006, **60**, 703; (*e*) D.-B. Qin, X.-S. Zeng, F.-B. Xu, Q.-S. Li and Z.-Z. Zhang, *Chin. J. Chem.*, 2006, **24**, 674.

12 (*a*) C. W. Nogueira, G. Zeni and J. B. T. Rocha, *Chem. Rev.*, 2004, **104**, 6255; (*b*) K. P. Bhabak and G. Mugesh, *Acc. Chem. Res.*, 2010, **43**, 1408.

13 Reports on the faster selenol/diselenide exchange compared to thiol/disulfide exchange: (*a*) J. C. Pleasants, W. Guo and D. L. Rabenstein, *J. Am. Chem. Soc.*, 1989, **111**, 6553; (*b*) D. Steinmann, T. Nauser and W. H. Koppenol, *J. Org. Chem.*, 2010, **75**, 6696.

14 (*a*) R. H. Mitchell, *Tetrahedron Lett.*, 1975, **16**, 1363; (*b*) R. H. Mitchell, *Can. J. Chem.*, 1980, **58**, 1398.

15 Wang *et al.* recently reported metallosupramolecular architectures based on Ag complexation by azacalix[*n*]arenes: (*a*) C.-Y. Gao, L. Zhao and M.-X. Wang, *J. Am. Chem. Soc.*, 2011, **133**, 8448; (*b*) C.-Y. Gao, L. Zhao and M.-X. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 824.

16 It is noteworthy that, during our ongoing studies, we have crystallized compound **4** from THF and performed an X-ray study (see Fig. S3†), which revealed formation of the THF solvate with the same distorted 1,3-alternate conformation of the homoselenacalix[4]arene framework as was noticed for the chloroform solvate[8] (the overall conformation of both molecules stays more or less the same). The solvent molecules occupy *ca.* the same space in the crystal lattice voids, surrounded by *tert*-butyl groups of neighbouring calixarenes. It seems that the solvent molecules do not really influence the overall conformation of the calixarene, even though there are weak C–H···O interactions present between either C–H moieties from the aromatic rings and the O atom from THF or between C–H moieties from the $CHCl_3$ molecules and the O atom of one of the calixarene's methoxy substituents. This could be because of their similar location.

17 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2001.

18 H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512.

19 H. Duddeck, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1995, **27**, 1.

20 J. Mochowski and L. Syper, Sodium Hydrogen Selenide, in *Encyclopedia of Reagents for Organic Synthesis*, John Wiley & Sons, 2001.

21 Both the calculated and experimental masses refer to the 100% intensity peak of the isotopic distribution.

22 K. Haba, M. Popkov, M. Shamis, R. A. Lerner, C. F. Barbas III and D. Shabat, *Angew. Chem., Int. Ed.*, 2005, **44**, 716.

23 E. H. Li, A. Homan, A. J. Lampkins, I. Ghiviriga and R. K. Castellano, *Org. Lett.*, 2005, **7**, 443.

24 A. W. Van der Made and R. H. Van der Made, *J. Org. Chem.*, 1993, **58**, 1262.

