Electronic Supplementary Information

Homoselenacalix[4]arenes: synthetic exploration and metallosupramolecular chemistry

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1. $^1$H, $^{13}$C and $^{77}$Se NMR spectra for the novel precursors and homoselenacilix[n]arenes

10 (300 K)

10 (328 K)
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2. X-ray crystallographic general experimental data and additional figures for the structures of homoselenacalix[4]arenes 4·THF, 10, 19, 20, 21 and 22

Single crystal X-ray diffraction data for compounds 10, 19, 20 and 21 were collected on a SMART 6000 diffractometer with CCD detector using CuKα radiation (λ = 1.54178 Å, crossed Goebel mirrors) and phi and omega scans.\(^1\) Cell refinement and data reduction were performed using the program SAINT.\(^2\) Measurements for 4·THF and 22 were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). Data collection and data reduction were carried out with the Oxford Diffraction programs.\(^3\) The structures were solved by direct methods and refined by full-matrix least squares on |F\(^2\)| using the SHELXS-97 program.\(^4\) All data collections were carried out at 100(2) K to minimize solvent loss, possible structural disorder and thermal motion effects. All non-hydrogen atoms were anisotropically refined and the hydrogen atoms were placed on calculated positions with temperature factors fixed at 1.2 times U\(_{eq}\) of the parent atoms and 1.5 times U\(_{eq}\) for methyl groups. The program Mercury was used to prepare molecular graphics images.\(^5\) Some of the tert-butyl groups were disordered over two orientations, namely C26 in 10, C70 in 19 and C34 in 21 as well as the counter ions in 21 and 22 (PF\(_6^–\) located on a special position).
**Fig. S1** Overlay of the structure of homoselenacalix[4]arene 10 (shown in red) with the previously reported analogous homothiacalix[4]arene⁶ (shown in green); Se/S atoms are represented by balls.

**Fig. S2** Overlay of bicyclohomoselenacalix[4]arene 19 (shown in red) with the earlier reported analogous bicyclohomothiacalix[4]arene⁶ (shown in green), showing a different geometry around one of the heteroatom bridges.
**Fig. S3** Molecular structure of the THF solvate of homoselenacalix[4]arene 4 (thermal ellipsoids are drawn at 50% probability).

**Fig. S4** Overlay of Ag(I) complexes 21 (purple) and 22 (blue-grey), presenting approximately the same conformation of the calixarene units adopted after complexation.
**Fig. S5** Capped-sticks representation of the (non-refined) structure of bis(selenacyclophane) 20.

Fig. S6 Observed high resolution FTMS (ESI⁺) isotopic pattern for homoselenacalix[4]arene 10 ([M+Na]⁺).
Fig. S7  Observed high resolution FTMS (ESI⁺) isotopic pattern for complex 21 ([M-CF₃SO₃]⁺).
Fig. S8  Observed high resolution FTMS (ESI\textsuperscript{+}) isotopic pattern for complex 22 ([M-PF\textsubscript{6}]\textsuperscript{+}).
4. References