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Reversible Guest Uptake/Release by Redox-Controlled Assembly/Disassembly of a Coordination Cage

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Abstract: *Controlling the guest expulsion process from a receptor is of critical importance in various fields. Several coordination cages have been recently designed for this purpose, based on various types of stimuli to induce the guest release. Herein, we report the first example of a redox-triggered process from a coordination cage. The latter integrates a cavity, the panels of which are based on the extended tetrathiafulvalene unit (exTTF). The unique combination of electronic and conformational features of this framework (i.e. high* π*-donating properties and drastic conformational changes upon oxidation) allows the reversible disassembly/reassembly of the redox-active cavity upon chemical oxidation/reduction, respectively. This cage is able to bind the three-dimensional* $B_{12}F_{12}^{2-}$ *anion in a 1:2 host/guest stoichiometry. The reversible redox-triggered disassembly of the cage could also be demonstrated in the case of the host–guest complex, offering a new option for guest-delivering control.*

The control of the binding/release process of a guest substance by a host molecule is of potential interest for a wide range of applications, including drug delivery, catalysis, sensing or capture of hazardous agents/pollutants. For this purpose, systems capable of tuning the host–guest binding affinity are required. On the other hand, the coordination-driven strategy has been successfully used for the building of a myriad of host molecules[1] and important efforts are currently devoted to the construction of metallacages which are able to bind/release a guest on demand.[2] A first possible approach focuses on addressable guests, the chemical modification of which (e.g. upon protonation, oxidation or irradiation)[3] leads to their release from the host. Alternatively, stimuli-responsive metallacages are gaining more and more interest. An evident interest of this approach lies in the independence on the guest structure and the fact that the latter keeps its chemical integrity along the binding/release process. In this approach, the guest release can be obtained by a change of the host cavity shape/size through a structural rearrangement of the metallacage or even by its disassembly. Outstanding results were recently described by using various stimuli, such as light[4] or addition of a chemical (e.g. protonation or component displacement),[3a,5] some of these processes being reversible. Nevertheless, to the best of our knowledge, there is still no example depicting a guest release which is redox-triggered from a coordination-driven self-assembled cage, despite this approach has been established with covalent macrocyclic hosts.[6] Additional benefits are awaited from metal-driven self-assembled receptors, since the latter involve labile metal–ligand bonds which in principle, can allow a reversible disassembly by using an appropriate stimulus. This was indeed observed by introducing a competitive chemical to the coordination cage, that is, addition of a new ligand or a metal, respectively.[4a,d,5d,e,g,i] On this basis, a cage disassembling process which would be promoted by a redox stimulus appears very appealing.

In the frame of our ongoing project related to the construction of electron-rich metal-driven self-assemblies,[7] we have been particularly interested in using ligands derived from the so-called extended tetrathiafulvalene (exTTF).[7b,e] A key feature of this unit[8] lies in the fact that, in addition to be a good π-donating molecule which can be readily oxidized to exTTF^{2+}, the oxidation process is accompanied by a drastic change of the molecular shape. The latter evolves from a highly bent butterfly-like structure in the neutral state (exTTF) to a fully aromatic unit (exTTF^{2+}) where two aromatic 1,3-dithiolium rings are grafted onto an anthracene moiety (see Figure S1 in the Supporting Information). This unique combination of electronic and structural characteristics prompts us to describe herein a coordination cage based on a new exTTF ligand, which can be reversibly disassembled through oxidation/reduction (Figure 1) and which allows to trigger the uptake/release of a guest as a function of the redox state.

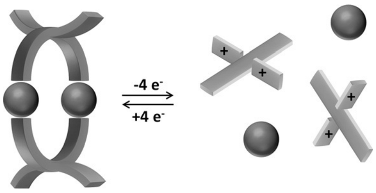

Figure 1. Diagram illustrating the redox-controlled cage disassembly/reassembly process.

The tetrapyridyl ex-TTF ligand **LTEG** was obtained in good yields in a three-step procedure (Scheme S1) from the described tetrahydroxyanthraquinone **1**.[9] Triethyleneglycol monomethyl ether (TEG) chains were introduced on the anthracene core in order to improve the solubility in various solvents (including protic solvents).

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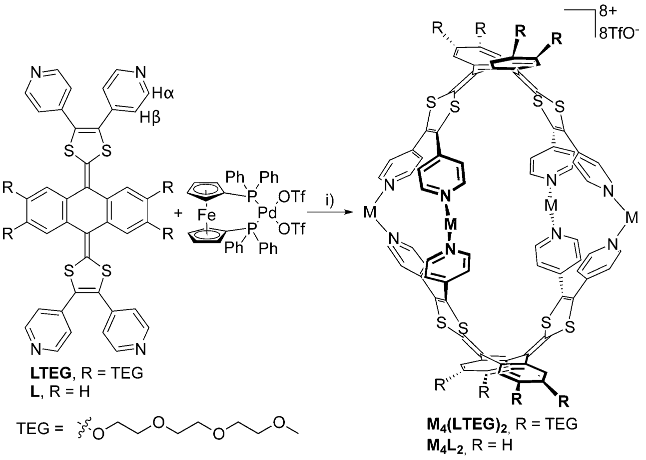
Tetrapyridyl ligand **LTEG** was engaged in a self-assembly process with *cis*-Pd(dppf)(OTf)$_2$ [dppf = bis-(diphenylphosphino) ferrocene)] in acetonitrile at room temperature (Scheme 1). The reaction converged within five minutes into a single species and could be monitored by ^{1}H, ^{31}P, ^{19}F, and diffusion-ordered (DOSY) NMR spectroscopy (Figures S8–S11). The latter experiment exhibits a single set of signals corresponding to a diffusion coefficient at about 4.8×10^{-10} m^{2}s^{-1}. Such value corresponds to a hydrodynamic radius of 13.2 Å as calculated from the Stokes–Einstein equation,[10] a size which is compatible with a M$_4$L$_2$ species. High-resolution ESI mass spectrometry unambiguously confirmed the formation of the **M$_4$(LTEG)$_2$** self-assembly with the presence of two intense isotopic patterns at m/z = 2021.2264 and 1478.6805 corresponding to the [**M$_4$(LTEG)$_2$**−3OTf]$^{3+}$ and [**M$_4$(LTEG)$_2$**−4OTf]$^{4+}$ species, respectively, and isotopic distributions in accordance with theoretical ones (Figure S12a–c). Single crystals could be grown by slow diffusion of diethyl ether in an acetonitrile solution of **M$_4$(LTEG)$_2$**. X-ray synchrotron diffraction analysis confirms the M$_4$L$_2$ geometry of the assembly, which presents a large ovoid cavity of 15.5 × 10.6 Å size (Figure 2a), very similar to the unsubstituted **M$_4$L$_2$** one devoid of TEG chains.[7e]



Scheme 1. **M$_4$(LTEG)$_2$** and **M$_4$L$_2$** self-assemblies. i) CD$_3$CN (**M$_4$(LTEG)$_2$**) or CD$_3$NO$_2$ (**M$_4$L$_2$**), RT, 5 minutes; M = [Pd(dppf)].

The electrochemical properties of ligand **LTEG** and of corresponding cage **M$_4$(LTEG)$_2$** were investigated and compared to those of **L** and **M$_4$L$_2$** respectively (Figure 3). Oxidation of **LTEG** involves one pseudo-reversible two-electron process, characteristic of exTTF derivatives at E_1^{ox} = 0.05 V versus Fc/Fc$^+$. Noticeably, a significant higher π-donating property (ΔE^{ox} = −250 mV) is observed for **LTEG** compared to ligand **L** (E_1^{ox} = 0.30 V), and is assigned to the electron-donating mesomeric effect of the four TEG substituents. The corresponding oxidation potential of cage **M$_4$(LTEG)$_2$** is positively shifted (E_1^{ox} = 0.48 V) compared to **LTEG**, as expected from metal coordination and is followed by a reversible oxidation process (E_2^{ox} = 0.86 V) attributed to the simultaneous oxidation of the four ferrocenyl co-ligand groups. Interestingly, compared to cage **M$_4$L$_2$**, both redox processes (E_1^{ox} and E_2^{ox}) are suitably separated (0.38 V) in **M$_4$(LTEG)$_2$** and allow a selective oxidation of the redox-active exTTF moiety, as a consequence of the electronic effect generated by the TEG substituents.

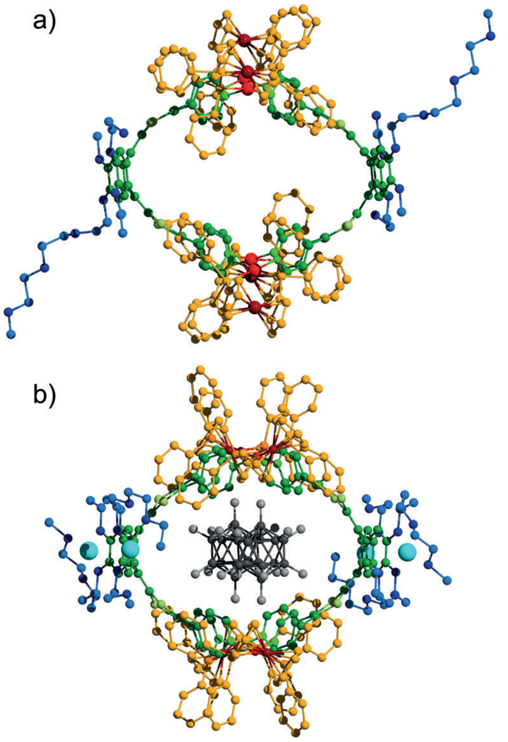


Figure 2. X-ray crystal structures of a) **M$_4$(LTEG)$_2$** and b) the (B$_{12}$F$_{12}$$^{2-}$)$_2$⊂**M$_4$(LTEG)$_2$** complex.

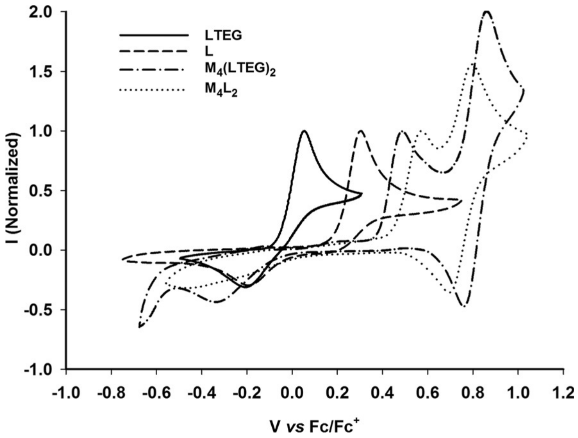


Figure 3. Normalized cyclic voltammogram of ligands **L** and **LTEG** ($C = 10^{-3}$ M), and of cages **M$_4$L$_2$** ($C = 10^{-3}$ M) and **M$_4$(LTEG)$_2$** ($C = 5\times10^{-4}$ M; CH$_3$CN, 0.1 M *n*Bu$_4$NPF$_6$, 100 mV s^{-1}, glassy carbon electrode), voltage versus Fc/Fc$^+$.

The binding ability of **M$_4$(LTEG)$_2$** was evaluated by NMR titration studies with various guests. Analogously to **M$_4$L$_2$**,[7e] the ovoid cavity made of π-extended exTTF units in **M$_4$(LTEG)$_2$**, is able to bind neutral polyaromatic guests such as perylene ($K_a = 4.6\times10^2$ L mol^{-1} in CD$_3$NO$_2$ as determined from ^{1}H DOSY NMR experiments[7e]; Figures S13–S16). Encapsulation of a spherical guest was also investigated, namely the dodecafluorododecaborate anion ($[B_{12}F_{12}]^{2-}$), the shape, size, and negative charge of which are potentially complementary to the **M$_4$(LTEG)$_2$** ovoid cavity.[4b,11] An additional interest of this guest comes from the possibility to probe the binding process in a complementary way, through ^{19}F NMR and ^{19}F DOSY NMR spectroscopy. The presence of four TEG side arms increases significantly the cage solubility, avoiding therefore solubility issues encountered with **M$_4$L$_2$**, and is expected to contribute to the binding of the K$^+$ cations. The ^{19}F NMR titration study of a CD$_3$CN solution of **M$_4$(LTEG)$_2$** by a solution of $K_2B_{12}F_{12}$ reveals two successive regimes (Figure S17). From 0 to one equivalent of $K_2B_{12}F_{12}$, the progressive appearance of one ^{19}F signal is observed at −265.4 ppm, that is, downfield shifted by approximately 3 ppm compared to the free $K_2B_{12}F_{12}$ signal (Figure 4a,b). A second signal appears at −267.2 ppm for two equivalents of added $K_2B_{12}F_{12}$, here again at a distinctive value from free $B_{12}F_{12}^{2-}$ (Figure 4c). These two regimes are attributed to distinctive binding processes in solution for the two anions, corresponding to slow and fast exchange equilibria, respectively, at the NMR time-scale. Remarkably, both $B_{12}F_{12}^{2-}$ species diffuse with the same D value (Figure 4d; $D = 4.6 \times 10^{-10}$ m^{2}s^{-1}) from ^{19}F DOSY NMR experiments. In addition, this diffusion coefficient value is very similar to the one measured from ^{1}H DOSY NMR for the **M$_4$(LTEG)$_2$** self-assembly alone ($D = 4.8 \times 10^{-10}$ m^{2}s^{-1}, Figure S11) or in the presence of two equivalents of $K_2B_{12}F_{12}$ ($D = 4.7 \times 10^{-10}$ m^{2}s^{-1}, Figure S18). Such observation illustrates the good complementarity and convergence of both ^{19}F and ^{1}H DOSY studies and suggests that up to two $B_{12}F_{12}^{2-}$ anions can be encapsulated within the self-assembly cavity.[12] This 1:2 binding process was confirmed by a Job plot analysis (Figure S19), as well as by ESI-FTICR study (Figure S20a–g) with characteristic peaks of the $(B_{12}F_{12}^{2-})_2\subset$**M$_4$(LTEG)$_2$** system (i.e. $m/z = 2123.631$ $[(B_{12}F_{12}^{2-})_2\subset$**M$_4$(LTEG)$_2$**, 2OTf$^-$ K$^+]^{3+}$, 2061.007 $[(B_{12}F_{12}^{2-})_2\subset$**M$_4$(LTEG)$_2$**, OTf$^-]^{3+}$, and 1602.233 $[(B_{12}F_{12}^{2-})_2\subset$**M$_4$(LTEG)$_2$**, 2OTf$^-$ 2K$^+]^{4+}$. Finally, the formation of the $(B_{12}F_{12}^{2-})_2\subset$**M$_4$(LTEG)$_2$** complex could be unambiguously demonstrated by an XRD experiment (Figure 2b). In the solid state, each $B_{12}F_{12}^{2-}$ anion is located between two palladium metal centers with Pd–F distances of 3.30 Å. Consequently, the cavity shape appears slightly modified to accommodate the guests, compared to free cage **M$_4$(LTEG)$_2$** (Figure 2a), with in particular interatomic Pd distances which are increased from 10.61 to 12.50 Å (Figure 2a,b). As expected, the four potassium atoms are bound by the lateral TEG chains, giving rise to a more compact organization in comparison with **M$_4$(LTEG)$_2$**.

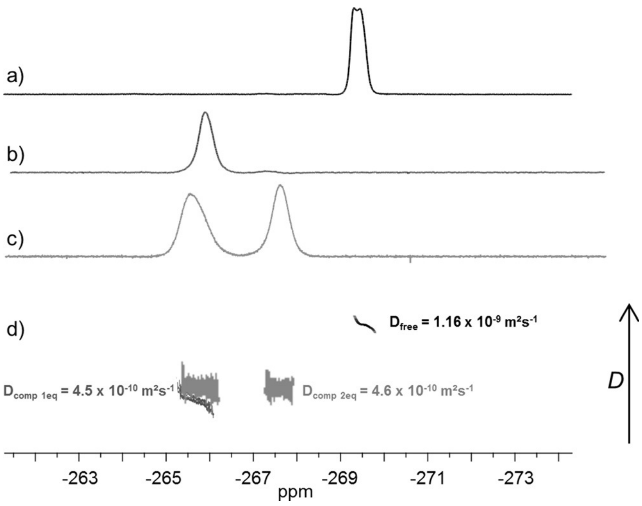


Figure 4. ^{19}F NMR spectra in CD$_3$CN of a) (2K$^+$,$B_{12}F_{12}^{2-}$); b) (2K$^+$,$B_{12}F_{12}^{2-}$) (1 equiv) in the presence of **M$_4$(LTEG)$_2$**, c) (2K$^+$,$B_{12}F_{12}^{2-}$) (2 equiv) in the presence of **M$_4$(LTEG)$_2$** and, d) the superimposed ^{19}F DOSY NMR spectrum under the conditions of (a), (b), and (c).

At this stage, considering our initial objective of controlling not only the binding but also the releasing of a guest, we were interested in exploring the conformational changes of the exTTF units within the self-assembled cage, which is known to occur upon oxidation/reduction. Selective chemical oxidation of the exTTF moiety in **M$_4$(LTEG)$_2$** was carried out with the thianthrenium radical cation [Th$^{\bullet+}$; $E' = 0.86$ V vs. Fc/Fc$^+$ (CH$_3$CN)][13] and was monitored by ^{1}H and ^{31}P NMR spectroscopy. Addition of 4 equivalents of Th$^{\bullet+}$ leads to 1) a downfield shift of the ^{31}P NMR signal (Figure S21), 2) a drastic modification in the ^{1}H NMR spectrum (Figure 5a,b) with in particular an important downfield shift of the pyridine (H$_\alpha$, H$_\beta$) and anthracenyl (H$_\delta$) signals, which now match with the ones of the oxidized, non-coordinated **LTEG^{2+}** ligand[14] (Figures 5b and S22a,b) and, 3) the appearance of three distinctive species in the corresponding ^{1}H DOSY NMR spectrum (Figure 5c), the signatures of which correspond to the oxidized ligand **LTEG^{2+}** ($D = 6.00 \times 10^{-10}$ m^{2}s^{-1}), the *cis*-

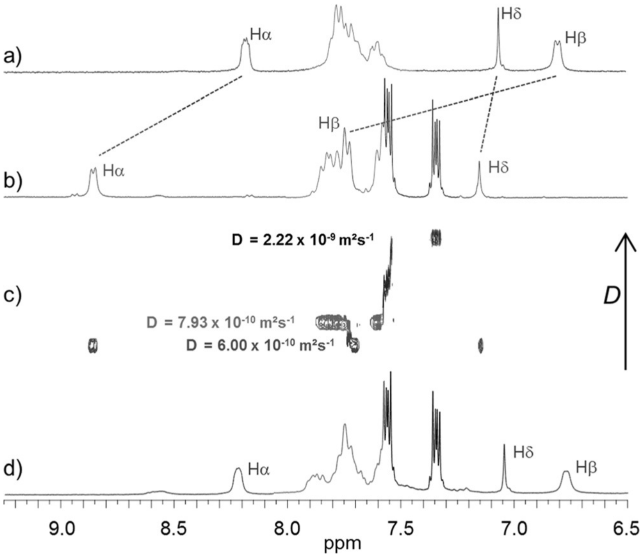


Figure 5. Evolution of the ^{1}H NMR spectra of **M$_4$(LTEG)$_2$** (CD$_3$CN, $C = 2.0 \times 10^{-3}$ M) upon stepwise oxidation/reduction: a) ^{1}H NMR spectrum of **M$_4$(LTEG)$_2$**; b) after addition of Th$^{\bullet+}$ (4 equiv; signals in black at 7.32 and 7.55 ppm correspond to the generated neutral thianthrene); c) DOSY ^{1}H NMR spectrum corresponding to (b; oxidation); d) ^{1}H NMR spectrum after subsequent addition of tetrakis(dimethylamino)ethylene (2 equiv).

Pd(dppf)(OTf)$_2$ complex ($D = 7.93 \times 10^{-10}\ m^2 s^{-1}$), and the neutral thianthrene which is generated by the redox process ($D = 2.22 \times 10^{-9}\ m^2 s^{-1}$; Figures 5 b,c and S22), respectively. These results unambiguously indicate that oxidation of the exTTF subunits to their dicationic state leads to the disassembly of the cage towards its starting constituents. Such behavior can be explained by the favorable conjunction of two factors: 1) oxidation of the exTTF subunit is accompanied by a drastic conformational change from a folded to a planar geometry on one hand, and 2) electrostatic repulsions between the oxidized **LTEG**$^{2+}$ and the positively charged palladium complex prevent the re-assembly of the system on the other hand.

An important issue concerns the reversibility of the process. Remarkably, addition of two equivalents of a reducing agent (tetrakis(dimethylamino)ethylene; $E_1' = -1.18$ V (TDAE$^{\bullet+}$) and $E_2' = -1.01$ V (TDAE^{2+}) vs. Fc/Fc$^+$)[15] to the above-mentioned mixture leads to the re-formation of the original self-assembly $\mathbf{M_4(LTEG)_2}$ as confirmed by the H_α, H_β, H_δ signals in the ^{1}H NMR spectrum (Figure 5 d), by a diffusion coefficient in the ^{1}H DOSY NMR spectrum found at a value ($D = 4.92 \times 10^{-10}\ m^2 s^{-1}$) similar to the original one (Figure S23) and by the recovery of the ^{31}P NMR signal of $\mathbf{M_4(LTEG)_2}$ (Figure S21).

Remarkably, this singular redox-controlled disassembly/reassembly process could be extended to the reversible release of the $B_{12}F_{12}^{2-}$ anion (Figure 6). Addition of 4 equivalents of Th$^{\bullet+}$ to the $(B_{12}F_{12}^{2-})_2\subset\mathbf{M_4(LTEG)_2}$ complex in CD$_3$CN, leads to the disappearance of the characteristic ^{19}F NMR signals of the encapsulated $B_{12}F_{12}^{2-}$ anions at about −265.4 and −267.2 ppm combined with the appearance of a new upfield-shifted signal assigned to the free $B_{12}F_{12}^{2-}$ anion in this solution mixture, as confirmed by the large increase of the corresponding D value ($1.56 \times 10^{-9}\ m^2 s^{-1}$) similar to the one of the free $B_{12}F_{12}^{2-}$ anion (Figure 6 b,d; Figure 4 a).[16] These observations are expected from the guest release consecutive to the cage disassembly. Noticeably, reduction of the resulting mixture with (tetrakis(dimethylamino)ethylene) leads to the spontaneous reassembly of the full host–guest system as suggested by the corresponding ^{19}F NMR spectrum (Figure 6 c) and as confirmed by the corresponding DOSY NMR spectrum which is identical to the original one (Figure 6 d).

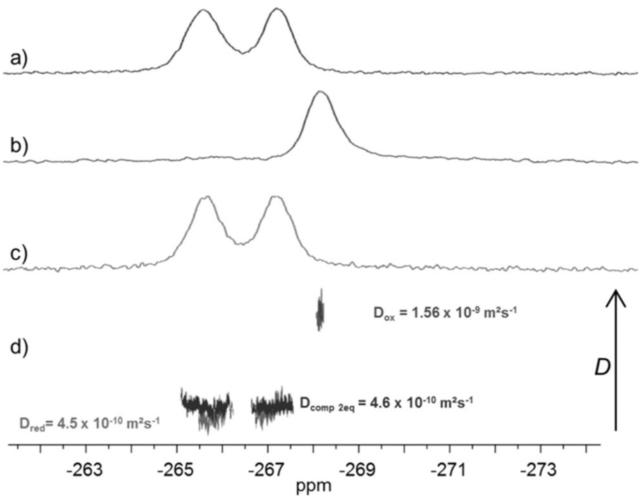


Figure 6. Evolution of the ^{19}F NMR spectra of $(B_{12}F_{12}^{2-})_2\subset\mathbf{M_4(LTEG)_2}$ (CD$_3$CN, C = 2.0×10^{-3} M) upon stepwise oxidation/reduction: a) ^{19}F NMR spectrum of $(B_{12}F_{12}^{2-})_2\subset\mathbf{M_4(LTEG)_2}$; b) after addition of Th$^{\bullet+}$ (4 equiv); c) after subsequent addition of tetrakis(dimethylamino)ethylene (2 equiv); d) corresponding DOSY ^{19}F NMR spectra of (a), (b), and (c).

In summary, we have designed a novel redox-active self-assembled coordination cage that is composed of an extended tetrathiafulvelene-based ligand and a *cis*-blocked Pd^{II} complex, characterized in solution as well as in solid state by an XRD study. This electron-rich cage is redox-active and remarkably, can be disassembled upon chemical oxidation with the thianthrenium radical cation and subsequently reassembled by reduction with tetrakis(dimethylamino)ethylene. Noteworthy, this reversible process can also be observed in the presence of a guest ($B_{12}F_{12}^{2-}$).The cage is able to bind two guest units as shown in solution and in solid state (XRD) and its disassembly occurs upon chemical oxidation, leading to the guest release. Moreover, this process is reversible upon reduction, giving rise to cage reassembly and guest binding. This proof-of-concept paves the way for the design of new redox-active cages based on alternative organic ligands and/or metal complexes and studies are underway in this direction.

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Keywords: cage compounds · self-assembly · sulfur heterocycles · supramolecular chemistry · tetrathiafulvalene

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[16] Addition of an excess (150 equiv) of KOTf in this solution shifts the ^{19}F NMR signal to −269.3 ppm, a value which corresponds to the original $K_2B_{12}F_{12}$ signal (Figure S24).

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