Reversible multi-electron storage in dual-site redox-active supramolecular cages

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Reversible multi-electron storage in dual-site redox-active supramolecular cages

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M₆L₄ supramolecular cages 3a and 3b (M = Pd, Pt), soluble in organic solvents, contain two different ligand-centered redox sites that enable the reversible storage of up to 16 electrons, as probed by CV, UV/vis spectro-electrochemistry (SEC-UV/Vis), bulk electrolysis and EPR. Encapsulation of a B_{12}F_{12}⁻ anion is confirmed by ¹H, ¹⁹F NMR and ¹⁹F DOSY NMR spectroscopy and mass spectrometry.

Supramolecular strategies are widely used in chemistry to make well-defined large architectures. Non-covalent self-assembly involving metal ions and rationally designed organic linkers provides a robust and modular method for the synthesis of a variety of porous structures. These porous structures are regularly exploited as static containers to accommodate guest molecules. In addition, they have been demonstrated to be useful for catalysis, displaying effects such as catalyst stabilization, selective reactions, and enrichment of the rate and/or selectivity of a reaction, selective activation of organometallic precursors or modification of the reaction mechanism. Selective encapsulation and one-pot cascade reactions with spatially isolated systems have also been reported.

The incorporation of stimuli-responsive components into self-assembled cages to access dynamic containers that can (reversibly) undergo electronic or structural changes has recently gained momentum, as this may allow further control over chemical events in complex mixtures. The use of light-sensitive or redox-active components that react to an external stimulus are two prevalent concepts to integrate stimulus responsivity within the design of self-assembled supramolecular architectures. The use of redox-active components for switching requires systems that undergo reversible redox event(s). Recent contributions include a small M₆L₄ cap∗ capsule with ‘single-site’ redox-active walls, allowing for an overall charge switching from 4+ to 8+, two M₄L₂ capsules with control over encapsulation properties via redox-stimuli and a large M₆L₆ assembly containing redox-active perylene bisimide (PBI) struts and Fe-bipyridine linkers, with postulated cycling between 18+ and 16− charged species.

Fujita-type M₆L₄ supramolecular cages are easy to prepare, they can bind a wide variety of guests and facilitate selective transformations of encapsulated species. These highly cationically charged containers typically feature redox-inert Pd (or Pt) diamine metal nodes linked by C₃-symmetric panels. We considered to incorporate redox-active ligands into the metal nodes to enrich the redox chemistry of envisioned cages. The bis(arylmino)-acenaphthene (BIAN) motif is well suited, as it displays three well-defined redox-states ada² and ada³ upon coordination to a transition metal (Fig. 1, top).

We herein report Fujita-type M₆L₄ metallocages, featuring redox-active BIAN-ligands, that show multiple reversible redox events. Platinum is found to provide superior redox-stability for the resulting cages compared to palladium. The redox-active C₃-symmetric trispyridyltriazine (tpt) panels of these M₆L₄ cages are a second electro-responsive site (Fig. 1, bottom). The presence of two distinctly different redox-sites provides supramolecular assemblies that can be reversibly switched over 16 charge units, as deduced.
from coulometry, MS and EPR spectroscopic data. The combined data suggest no electronic communication between the different redox-loci. We also report initial guest encapsulation studies with these new cages that are soluble in organic solvents.

Metallocages 3a and 3b with trflate counterions are obtained by mixing of the respective building blocks [M(BIAN)-

Scheme 1. Synthesis of redox-active metallocages featuring two distinctly different redox-active sites 3a and 3b. Conditions for (a) DCM, 1 hour at room temperature, (b) DCM/MeCN, 3 days at 40 °C.

Fig. 2 (A) Cyclic voltammogram of 4b scanning to −0.7 V (black line) and to −1.8 V (red line) in DCM at 100 mV s−1. (B) EPR spectrum of 4b after one-electron reduction. (C) Representation of different oxidation states of complex 4b.

Fig. 3 Semi-derivative convolution plot of BIAN-Pt cage (3b) in DCM at 100 mV s−1, demonstrating full reversibility of the supramolecular assembly. Individual reduction processes A–D are labeled above the waves.
3b or 4b, only minor changes are observed during event A (see ESI†). During event B, three broad absorptions appear between 600 and 1100 nm, which are very similar to observations made for free tpt (Fig. 4).35,36 This underlines our findings that the tpt panels indeed behave as redox-active components that are electronically independent from the BIAN-containing nodes. Hence, event B is attributed to the redox-couple tpt/tpt* present in the cage construct.

Integration of the redox-waves A and B leads to a ratio of 1 : 0.67 (Table 1). Given the coulometric data obtained for the first reduction event with 3a, involving the transfer of six electrons, and because 3b is present as a single supramolecular assembly with a stoichiometry of M₆L₄, as confirmed by DOSY NMR and HR-MS, the relative CV-integrals thus correspond to a ratio of 6 to 4 for electron-injection in adi and tpt units, respectively, meaning that each redox-active center present in 3b independently undergoes well-defined one-electron reduction (adi/aida* and tpt/tpt*). The first two redox-events in 3b relate to an overall charge change of the self-assembled cage from 12+ for parent 3b to 6+ (after event A) and subsequently to 2+ (after B) (see Fig. 5). Integration of events C + D relative to A results in a near 1 : 1 ratio (0.96 : 1). Given the similar onset redox-potential of −1.63 V compared to the CV of 4b, this combined wave likely corresponds to the second BIAN-based redox-event, i.e. the aida*/ada2− couple.

In addition, EPR spectroscopy after bulk electrochemical reduction of 3b at a potential of −0.7 V (after A) provided a signal matching that observed for reduced model complex [Pt(aida*)][pyr]₂, confirming that the signal originates from the reduced corner stones (see ESI†). Upon reducing 3b (fully) to −2.0 V (after C + D) using bulk electrolysis, this EPR signal virtually disappears. This observation is in line with the hypothesis that the last wave (C + D) converts the BIAN-cornerstones to their diamagnetic, EPR silent ad2− oxidation state. Lastly, the two subtly different events C and D (ΔE = 0.18 V) each roughly accounting for the transfer of three electrons, are proposed to arise from changes in the overall charge of the system. In portion C, the cage undergoes three BIAN-centred reductions from an overall 2+ to a 1− charge. The reduction of the three remaining BIAN-redox centres in this anionic cage requires a higher cathodic potential, ultimately leading to an overall 4− charge of the cage after event D. Thus, cage 3b exhibits reversible switching from 12+ to 4−, i.e. 16 charge-units overall, whilst remaining organic-soluble across the whole redox-regime. These data also show that all of the relevant redox-loci can be independently addressed in the respective reduction processes. The origin of the potential shift between events C and D might be related to a change from positive/neutral vs. negative overall cage charge, to a change in counter-ion (from triflate to tetrabutylammonium) and/or to partial encapsulation of the respective ions.

Cages 3a and 3b have an accessible interior volume of 1180 Å³,37 similar to the water soluble analogues, so guest encapsulation is anticipated if proper interactions with the guest molecule(s) can be established. However, typical guests that bind in water-soluble M₆L₄ cages (e.g. adamantane, ferrocene, pyrene or perylene) do not bind in cages 3a or 3b in CD₂Cl₂, as deduced from ¹H NMR spectroscopy, likely due to the absence of hydrophobic effects that drive guest encapsulation in water. We therefore switched to B₁₂F₁₂²− as potential guest, as its size and diatomic charge should be complementary to the cage. Upon addition of one equivalent of B₁₂F₁₂²− to either 3a or 3b, immediate desymmetrization and broadening of both pyridine signals is observed in the ¹H NMR spectra (see ESI†).

The guest is expected to have close contact with the electron poor tpt-walls, which causes hindered rotation of the pyridine motifs, leading to desymmetrization and broadening of the signals. The ¹³C NMR signal of B₁₂F₁₂²− shifts by 0.4 ppm compared to the free guest in CD₂Cl₂ and using ¹⁹F DOSY NMR a diffusion coefficient of 4.46 × 10⁻¹⁰ m² s⁻¹ was found, in good agreement with the diffusion coefficient of 3b (see ESI†). We are currently investigating the effects of the redox-switching of the cage on the encapsulation properties of both cages, as reduced electronic interaction or even repulsion between host and the anionic cage may be envisaged upon redox-stimulation of the various organic loci in these assemblies.

**Table 1** Electrochemical data of 3b showing the redox-potentials, peak area for each redox-event and their ratios towards the first reduction wave (A).

<table>
<thead>
<tr>
<th>Reduction wave</th>
<th>Peak position (V)</th>
<th>Peak area</th>
<th>Ratio area to A</th>
<th>Ratio × 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>−0.52 V</td>
<td>6.74 × 10⁻⁷</td>
<td>1.0</td>
<td>6.0</td>
</tr>
<tr>
<td>B</td>
<td>−1.28 V</td>
<td>4.63 × 10⁻⁷</td>
<td>0.69</td>
<td>4.1</td>
</tr>
<tr>
<td>C + D</td>
<td>−1.63 V; −1.81 V</td>
<td>6.44 × 10⁻⁷</td>
<td>0.96</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Fig. 4 SEC-UV/Vis of (top) reduction of tripyridyl triazine (tpt) to its mono-radical, anionic form (tpt*) and (bottom) response of the BIAN-Pt cage (3b) during event B.

Fig. 5 Schematic representations of the location of the different redox events (A to D) on the platinum cage.
In summary, we have successfully introduced the known redox-active BIAN-motif into supramolecular ‘Fujita-type’ coordination cages. This has resulted in the synthesis of two novel, highly charged $M_4L_4$ cages 3a and 3b ($M = \text{Pd or Pt}$) that are soluble in organic solvents and contain redox-active ligands. Decreasing the Pd–NPy bond strength upon two-electron reduction is the likely reason for electrochemical decomposition of Pd-cage 3a. Pt cage 3b exhibits full electrochemical stability across the whole potential range of $0 \text{ to } -2.0 \text{ V}$, with all three oxidation states of the BIAN-ligand reversibly accessible ($\text{adi} \leftrightarrow \text{aia}^+ \leftrightarrow \text{ada}^{2+}$). Furthermore, all four $C_3$-symmetric tripyridyltriazine wall fragments undergo reversible one-electron reduction ($\text{pt} \leftrightarrow \text{pt}^+$), as deduced from UV/Vis spectro-electrochemistry and coulometry. The cage can be electrochemically reduced in bulk solution, allowing for EPR characterization in different stages of reduction. Cage 3b can be reversibly switched from overall 12+ to 4− charge, involving storage or release of 16 electrons in total. Initial binding studies with dianionic $\text{B}_{12}\text{F}_{12}$ demonstrate the potential for these organic-soluble cages to form host–guest complexes. We anticipate that these redox stimulus-responsive self-assembled cages may be of interest for application as multi-electron storage devices in e.g. non-aqueous redox-flow batteries and for redox-switchable host-guest encapsulation and catalysis.

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Conflicts of interest
There are no conflicts to declare.

Notes and references