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

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M₆L₄12+ 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 B12F₁₂⁻ anion is confirmed by ¹H, ¹⁹F NMR and ¹³F 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.¹⁻¹¹ 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,¹² selective encapsulation¹⁷,¹⁸ and one-pot cascade reactions¹⁹ 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 under electronic or structural changes has recently gained momentum, as this may allow further control over chemical events.

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

Fig. 1  Representation of redox-states of (top) the BIAN-motif, going from left to right and (bottom) trispyridyl triazine (tpt).
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 triflate counterions are obtained by mixing of the respective building blocks [M(BIAN)-(OTf)$_2$]$_n$ (M = Pd, Pt) to form, 1,3,5-tris(pyridyl)triazine (tpt) (‘L’) in a 6:4 M:L ratio (Scheme 1). These are the first Fujita-type M$_6$L$_4$ cages that are soluble in organic media, but not in water. Pd-cage 3a forms within several hours at r.t. in CH$_2$Cl$_2$, whereas platinum cage 3b requires longer reaction times, mild heating (40 °C) and MeCN as co-solvent. Cage formation was supported by $^1$H NMR spectroscopy and X-ray crystallography (for 3a; see ESI†). DOSY NMR provided a diffusion constant of 5.37 × 10$^{-10}$ m$^2$ s$^{-1}$, corresponding to a hydrodynamic radius of 1.0 nm, which is in agreement with reported water-soluble M$_6$L$_4$ cages bearing nitrate anions. High resolution cold-spray ionization mass spectrometry (CSI MS) confirmed the elemental composition of 3a and 3b, with observable signals for [M(OTf)$_{12-x}$$-x$(OTf)]$^{3+}$ (x = 4–7) (see ESI†).

Cyclic voltammetry (CV) of 3a provided a reversible reduction and re-oxidation wave around $E_1$ = −0.4 V when scanning to a potential of −1.0 V (vs. Fc/Fc$^+$), assigned to the ligand-centered adi/aiad redox-couple. Multiple irreversible redox-events were observed at more cathodic potentials (between −1.2 and −2.2 V vs. Fc/Fc$^+$), concomitant with loss in reversibility for the first wave at −0.4 V, suggesting instability of 3a under more reducing conditions. The model compound 4a, [Pd(BIAN)(pyr)$_2$(OTf)$_2$] (see ESI† for full characterization) showed almost identical electrochemical responses, indicating (partial) decomposition upon two-electron ligand reduction. Hence, decomposition of cage 3a appears related to the intrinsically lower stability of Pd(ada$^{2-}$) vs. Pd(ai$^-$) or Pd(adi), likely due to more labile Pd–N$_P$ bonds.

We therefore switched to a platinum-based cage, as this should feature stronger metal–ligand bonds. The chemistry of BIAN with Pt is only sparsely developed, particularly when compared to that of Pd. The electrochemistry of the novel bis-pyridine adduct [Pt(BIAN)(pyr)$_2$(OTf)$_2$] 4b (see ESI† for full characterization, including XRD) indeed shows two reversible reduction events at $E_{1/2}$ = −0.5 V and $E_{1/2}$ = −1.5 V (Fig. 2). These redox-waves can be assigned to the ligand-based reduction from neutral diimino- to imino-amido-radical, i.e. [Pt(adi)(pyr)$_2$]$^{2+}$ to [Pt(aiad$^-$)(pyr)$_2$]$^2+$, and to the aiad$^-$/ada$^{2-}$ redox-couple, respectively. The complex [Pt(aiad$^-$)(pyr)$_2$]$^2+$ can also be generated using bulk electrolysis or by chemical reduction with CoCp$_2$, making it amenable for in situ EPR characterization at r.t. The observed signal is a doublet with $g = 1.99$, which is characteristic for an organic ligand-centered radical (see ESI†).

In line with the excellent stability shown by 4b across the whole relevant potential window, the new Pt-cage 3b also showed full electrochemical reversibility between 0 and −2 V. Convolution of the obtained cyclic voltammogram results in the representation depicted in Fig. 3. In agreement with the data obtained for 4b, the first reduction event (A) encountered at −0.5 V is attributed to independent reduction of all six BIAN-ligands present in the nodes of the cage, as no distribution in the redox-potential is observed for this event.

The second redox-event for 3b (B) occurs at $E_{1/2} = −1.3$ V, which is attributed to a tpt-centered reduction. In order to get more insight in these reduction events, UV/vis spectro-electro-chemistry (SEC-UV/Vis) was performed on cage 3b, the model complex 4b and the free organic linker tpt. Upon reduction of...
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). 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 M₆L₄₁₂, 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/ada* 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 ada*/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(ada*)₂](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 ada²⁻ 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 tetraethylammonium) and/or to partial encapsulation of the respective ions.

Cages 3a and 3b have an accessible interior volume of 1180 Å³, 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 B₃,F₂⁻ as potential guest, as its size and dianionic charge should be complementary to the cage. Upon addition of one equivalent of B₃,F₂⁻ 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 ¹⁹F NMR signal of B₃,F₂⁻ 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. 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-moiety into supramolecular ‘Fujita-type’ coordination cages. This has resulted in the synthesis of two novel, highly charged $M_nL_n$ cages $3a$ and $3b$ ($M = \text{Pd or Pt}$) that are soluble in organic solvents and contain redox-active ligands. Decreasing the $\text{Pd-N}_2$ bond strength upon two-electron reduction is the likely reason for electrochemical decomposition of $\text{Pd}$-cage $3a$. Pt cage $3b$ exhibits full electrochemical stability across the whole potential range of 0 to $-2.0 \text{ V}$, with all three oxidation states of the $\text{BIAn}$-ligand reversibly accessible ($\text{adi} \leftrightarrow \text{aia}^+ \leftrightarrow \text{ada}^{2+}$). Furthermore, all four $C_3$-symmetric trispyridyltriazine wall fragments undergo reversible one-electron reduction ($\text{tpt} \leftrightarrow \text{tp^*}$), 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 $4/C_0$ charged $\text{M}_6\text{L}_4$ cages. This has resulted in the synthesis of two novel, highly 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