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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^{2−} 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.^{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 enhancement of the rate and/or selectivity of a reaction,^{13,14} selective activation of organometallic precursors¹⁵ or modification of the reaction mechanism.¹⁶ Selective encapsulation^{17,18} 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 in complex mixtures.^{20–22} 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 M₂L₄⁴⁺ capsule with ‘single-site’ redox-active walls,²³ allowing for an overall charge switching from 4+ to 8+, two M₄L₂ capsules with control over encapsulation properties *via* redox-stimuli^{24,25} and a large M₄L₆⁸⁺ assembly containing redox-active perylene bisimide (PBI) struts and Fe-bipyridine linkers, with postulated cycling between 18+ and 16− charged species.²⁶

Fujita-type M₆L₄¹²⁺ supramolecular cages are easy to prepare, they can bind a wide variety of guests and facilitate selective transformations of encapsulated species.²⁷ 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.²⁸ The bis(arylimino)-acenaphthene (BIAN) motif is well suited, as it displays three well-defined redox-states **adi**, **aia**^{•+} and **adi**²⁺ upon coordination to a transition metal (Fig. 1, top).²⁹

We herein report Fujita-type M₆L₄ metallocages, featuring redox-active BIAN-ligands, that show multiple reversible reductive 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

Fig. 1 Representation of redox-states of (top) the BIAN-motif, going from left to right and (bottom) trispyridyl triazine (**tpt**).

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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.

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] (M = Pd, Pt)^{29,30} (**1a** and **1b**) ('M') and 1,3-5-tris(pyridyl)-triazine (**tpt**) ('L') in a 6 : 4 M : L ratio (Scheme 1). These are the first Fujita-type M₆L₄ cages that are soluble in organic media, but not in water. Pd-cage **3a** forms within several hours at r.t. in CH₂Cl₂, whereas platinum cage **3b** requires longer reaction times, mild heating (40 °C) and MeCN as co-solvent. Cage formation was supported by ¹H NMR spectroscopy and X-ray crystallography (for **3a**; see ESI†). DOSY NMR provided a diffusion constant *D* of 5.37 × 10^{−10} m² s^{−1}, corresponding to a hydrodynamic radius of 1.0 nm,³¹ which is in agreement with reported water-soluble M₆L₄-cages bearing nitrate anions.³² 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(OTf)]^{x+} (x = 4–7) (see ESI†).

Cyclic voltammetry (CV) of **3a** provided a reversible reduction and re-oxidation wave around *E*_{1/2} = −0.4 V when scanning to a potential of −1.0 V (vs. Fc/Fc⁺), assigned to the ligand-centered **adi/aia**^{•−} redox-couple.²⁹ Coulometry provided support for reduction of all six BIAN moieties in the first reduction event at −0.4 V in **3a**, with 5.5 electrons transferred per cage (see ESI†). 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(**aia**^{•−}) or Pd(**adi**), likely due to more labile Pd–N_{py} bonds.

We therefore switched to a platinum-based cage, as this should feature stronger metal–ligand bonds.³³ The chemistry of BIAN with Pt is only sparsely developed, particularly when compared to that of Pd.³⁴ 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

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**.

neutral diimino- to imino-amido-radical, *i.e.* [Pt(**adi**)(pyr)₂]²⁺ to [Pt(**aia**^{•−})(pyr)₂]⁺, and to the **aia**^{•−}/**ada**^{2−} redox-couple, respectively. The complex [Pt(**aia**^{•−})(pyr)₂]⁺ can also be generated using bulk electrolysis or by chemical reduction with CoCp₂, 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-electrochemistry (SEC-UV/Vis) was performed on cage **3b**, the model complex **4b** and the free organic linker **tpt**. Upon reduction of

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.

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

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**/**aia**^{•-} 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

Fig. 5 Schematic representations of the location of the different redox events (A to D) on the platinum cage.

corresponds to the second BIAN-based redox-event, *i.e.* the **aia**^{•-}/**ada**²⁻ 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(**aia**^{•-})(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 **ada**²⁻ oxidation state. Lastly, the two subtly different events C and D ($\Delta E = 0.18$ 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 dianionic 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 ¹⁹F 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)

Reduction wave	Peak position (V)	Peak area	Ratio area to A	Ratio × 6
A	−0.52 V	6.74 × 10 ^{−7}	1.0	6.0
B	−1.28 V	4.63 × 10 ^{−7}	0.69	4.1
C + D	−1.63 V; −1.81 V	6.44 × 10 ^{−7}	0.96	5.8

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_6L_4 cages **3a** and **3b** ($M = Pd$ or Pt) that are soluble in organic solvents and contain redox-active ligands. Decreasing the Pd- N_{Py} 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 to -2.0 V, with all three oxidation states of the BIAN-ligand reversibly accessible ($adi \leftrightarrow aia^{\bullet-} \leftrightarrow ada^{2-}$). Furthermore, all four C_3 -symmetric trispyridyltriazine wall fragments undergo reversible one-electron reduction ($tpt \leftrightarrow tpt^{\bullet-}$), 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 $B_{12}F_{12}^{2-}$ 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.

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