Rigidification of a Macrocyclic Tris-Catecholate Scaffold Leads to Electronic Localisation of its Mixed Valent Redox Product

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The catecholate groups in \([\text{Pt(L)}_3(\mu_3-\text{tctq})]\) \((\text{H}_6\text{tctq} = 2,3,6,7,10,11\text{-hexahydroxy-4b,8b,12b,12d-tetramethyltribenzotriquinacene}; \text{L} = \text{a diphosphine chelate})\) undergo sequential oxidation to their semiquinonate forms by voltammetry, with \(\Delta E_{\frac{1}{2}} = 160–170\text{ mV}\). The monoradical \([\text{Pt(dppb)}_3(\mu_3-\text{tctq})^\cdot]\) is valence-localised, with no evidence for intervalence charge transfer in its near-IR spectrum. This contrasts with previously reported \([\text{Pt(dppb)}_3(\mu_3-\text{ctc})^\cdot]\) \((\text{H}_6\text{ctc} = \text{cyclotricatechylene})\), based on the same macrocyclic tris-dioxolene scaffold, which exhibits partly delocalised (class II) mixed valency.

Dioxolenes are one of the most versatile and important non-innocent ligands for transition ions.\textsuperscript{1} The catecholate (cat)/semiquinonate (sq) redox process occurs at low potential in metal-bound dioxolenes, which can lead to stable ligand radical species and/or facile charge transfer processes between the dioxolene and coordinated metal ion. This makes catecholate ligands useful electron reservoirs for catalysis\textsuperscript{2,3} and biological redox reactions.\textsuperscript{4} Alternatively, metal-bound sq radicals can act as switchable molecular paramagnets,\textsuperscript{5} or show bulk magnetic ordering when incorporated into coordination frameworks.\textsuperscript{6} Lastly, complexes containing multiple dioxolene centres can exhibit ligand-based mixed-valency\textsuperscript{7} with intense inter-valence charge-transfer absorptions in the near-IR. This has been observed in both mononuclear \([\text{M(cat)}_3]\) complexes,\textsuperscript{8} and in complexes of more complicated organic scaffolds containing two or three linked dioxolene redox sites.\textsuperscript{9–11}

In the latter vein, we recently re-investigated the complexes \([\text{Pt(L)}_3(\mu_3-\text{ctc})]\) \((\text{H}_6\text{ctc} = \text{cyclotricatechylene}; \text{L} = 1,2\text{-bis(diphenylphosphinobenzene [dppb]}\text{ or } 1,2\text{-bis(diphenylphosphinoethane [dppe]}}); \text{Scheme 1})\), which were originally synthesised by Bohle and Stasko.\textsuperscript{12} The three catecholate groups in these complexes are oxidised sequentially, leading to \([\text{Pt(L)}_3(\mu_3-\text{ctc})^\cdot]\) \(^{\text{ESI}}\) and \([\text{Pt(L)}_3(\mu_3-\text{ctc}^{\cdot\cdot})]^\text{2+}\) radical products showing class II mixed valency by UV/vis/NIR spectroscopy,\textsuperscript{13} despite the absence of direct conjugation between their dioxolene redox centers.\textsuperscript{14} The radical products of this work were too unstable to isolate however, and could only be handled in solution below room temperature. We reasoned this might reflect a lack of steric protection about the methylene groups of the oxidised [ctc]\textsuperscript{m} macrocycle, since sq and other phenoxyl radicals are prone to atom abstraction or coupling reactions at such para substituents.\textsuperscript{15}

[Scheme 1. The compounds described in this work.]

Hence, we turned to the related tricatechol \(2,3,6,7,10,11\text{-hexahydroxy-4b,8b,12b,12d-tetramethyltribenzotriquinacene} (\text{H}_4\text{tctq}; \text{Scheme 1})\), which is a new variant of the rigid tribenzotriquinacene motif developed by Kuck\textsuperscript{16} as a bowl-shaped scaffold for supramolecular architectures\textsuperscript{17,18} and soft materials.\textsuperscript{19} Since the methylene groups linking the catechol rings in [tctq]\textsuperscript{m} are fully quaternised, we reasoned that radicals

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\textsuperscript{†}\ Electronic Supplementary Information (ESI) available: Experimental procedures for the synthesis and physical and computational characterisation of the compounds in this work; crystallographic Figures and tables; EPR spectra and simulated parameters; and computed structures, MO manifolds, orbital and spin density plots. CCDC 1885699. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/#####.
\textsuperscript{‡}\ Data supporting this study are available at http://doi.org/10.5518/#####.
derived by oxidation of \([\text{Pt(L)}_3\text{[μ3-tctq]}]\) might be more stable and easier to isolate. In the event that was not observed, but we report here that sq radicals derived from \([\text{Pt(L)}_3\text{[μ3-tctq]}]\) \((1\text{a}/1\text{b})\), Scheme 1) and \([\text{Pt(dppb)}_3\text{[μ3-tctq]}]\) \((2\text{a})\) display unexpectedly different electronic properties.

2,3,6,7,10,11-Hexamethoxy-4b,8b,12b,12d-tetramethyltribenzoquinacene is accessible in nine synthetic steps by a literature procedure \((\text{ESI}^\ddagger)\). \(\text{H}_2\text{tctq}\) was obtained by exhaustive demethylation of this precursor using \(\text{BBr}_3\). Compounds \(2\text{a}\) and \(2\text{b}\) were prepared by treatment of \(\text{H}_2\text{tctq}\) with 3 equiv of the appropriate \([\text{PtCl}_2(\text{L})]\) reagent in a \(\text{N},\text{N}\)-dimethylethacamide/methanol solvent mixture, using potassium tert-butoxide as a base. While \(2\text{a}\) is soluble in weakly interacting solvents and stable under an inert atmosphere, \(2\text{b}\) is much less soluble and apparently less stable, so more limited characterisation of that compound was achieved. Similar issues were also encountered with \(1\text{b}^\ddagger\).

Differential pulse voltammograms of \(2\text{a}\) and \(2\text{b}\) in \(\text{CH}_2\text{Cl}_2/0.1\text{M NBu}_4\text{PF}_6\) resemble those of \(1\text{a}\) and \(1\text{b}\), in showing three closely spaced low-potential oxidations \((\text{Fig. }1)\). These are assigned to sequential oxidation of the three cat rings in the \([\text{tctq}^\ddagger]\) ligand to the sq oxidation level \((\text{eq }1)\).

\[
[\text{tctq}^\ddagger]^{3+} = [\text{tctq}^*]^{5+} = [\text{tctq}^*]^{3+} = [\text{tctq}^*]^{1+}
\]

The first two processes for both compounds are chemically reversible and occur at similar potentials, but with \(E_{\text{irr}}\) ca. \(0.2\text{ V}\) higher potential, and is apparently less stable, so more limited characterisation of that compound was achieved. Similar issues were also encountered with \(1\text{b}^\ddagger\).

The UV/vis spectra of \(2\text{a}\) and \(2\text{b}\) in \(\text{CH}_2\text{Cl}_2/0.1\text{M NBu}_4\text{PF}_6\) show just one resolved maximum at \(31.7 \times 10^3\text{ cm}^{-1}\). Spectroelectrochemical generation of \([2\text{a}]^+\) from \(2\text{a}\) in this solvent at \(253\text{ K}\) proceeds isosbestically, and leads to an increase in intensity for this peak, coupled to the ingrowth of a new shoulder near ca. \(23 \times 10^3\text{ cm}^{-1}\) \((\text{Fig. }2)\). These changes strongly resemble those observed during the oxidation of mononuclear \(\text{Pt(II)}/\text{cat/diphosphine complexes}\). \(2\text{a}\) shows no intercalation charge transfer \((\text{IVCT})\) absorption above \(4000\text{ cm}^{-1}\). That implies the electronic structure of \([2\text{a}]^+\) is class I valence-localised, \(q/sq\) oxidation occurs at ca. \(0.2\text{ V}\) higher potential, and is apparently clean. The separation between the first two oxidation potentials in \(2\text{a}\) and \(2\text{b}\), \(\Delta E_{\text{irr}} = 0.16–0.17\text{ V}\), yields the comproportionation constants \(K_r = 6.8 \times 10^2\) between each oxidation level. \(\text{That is slightly smaller than for } 1\text{a}\) and \(1\text{b}\) \((\Delta E_{\text{irr}} = 0.18–0.22\text{ V}, K_r = 1–5 \times 10^3)\), which implies electronic communication between the dioxolene rings in coordinated \([\text{tctq}^\ddagger]^{3+}\) is weaker than for \([\text{ctc}^\ddagger]^{3+}\). A second series of irreversible processes at \(+0.75–1.2\text{ V}\) was observed for \(2\text{a}\), assignable to further oxidation of the dioxolene rings in \([\text{tctq}^\ddagger]^{3+}\) to the quinone level. These were less well-defined in \(2\text{b}\), which might reflect its precipitation at the electrode during the measurement.

EPR spectra of \([2\text{a}]^+\) and \([2\text{b}]^+\), generated by \(\text{in situ}\) oxidation of the neutral precursors with \(1\text{ equiv } \text{[Cp}_2\text{Fe}]\text{PF}_6\), were measured in frozen \(\text{CH}_2\text{Cl}_2\) solution at \(X\) and \(S\)-band frequencies. The spectra resemble \([1\text{a}]^+\) and other \(\text{Pt(II)/sq}\) radicals in showing weakly rhombic \(g\)-patterns, with hyperfine coupling to just one \(^{195}\text{Pt}\) nucleus \((\text{ESI}^\ddagger)\). \(2\text{a}\) shows the unpaired electrons in \([2\text{a}]^+\) and \([2\text{b}]^+\) localised on one dioxolene ring under these conditions, on the EPR timescale.

The metal-free \(\text{H}_2\text{tctq}\) cavitand has a slightly shallower bowl-shaped cavity, is \(2.513(4)\)–\(2.523(3)\) \(\AA\) atoms at the base of the bowl-shaped cavity, is 2.513(4)–

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure1}
\caption{Differential pulse voltammogram of \(2\text{a}\) and \(2\text{b}\) (\(\text{CH}_2\text{Cl}_2/0.1\text{M NBu}_4\text{PF}_6\) \(293\text{ K}\).}
\end{figure}

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\text{sq/cat} \hspace{2cm} \text{(}E_{\text{irr}}\text{/V)} & \text{q/sq} \hspace{2cm} \text{(}irr^*, E_{\text{irr}}\text{/V)} \\
\hline
\(2\text{a}\) & \(-0.34\) & \(-0.17\) & \(+0.00, 0.08\) & \(+0.75, +1.16\) \\
\(2\text{b}\) & \(-0.28\) & \(-0.12\) & \(+0.20\) & \(+0.82\) \\
\hline
\end{tabular}
\caption{Electrochemical data for the complexes in this work (\text{cat} = \text{catecholate}; \text{sq} = \text{semiquinonate}; \text{q} = \text{quinone}). Potentials are referenced against \text{Fc}^{\text{3+}}.}
\end{table}
The 2a→[2a•] oxidation at 253 K in CH₂Cl₂/0.1 M NBu₄PF₆, monitored by UV/vis/NIR spectroscopy using an optically transparent electrode. The spectra of the pure starting material and product are highlighted in black while the intermediate spectra are paler. The feature near 12 × 10³ cm⁻¹ is an artefact from a grating change in the spectrometer.

Fig. 2

Overlay of the crystallographic molecular structures of H₆tctq (white, ESI†) and H₆ctc (purple, from H₆ctc·5dmso,), showing the shallower bowl-shaped conformation of the H₆tctq macrocycle.

The calculated Mulliken spin density population (Figure 4) and UV/vis/NIR spectra of [2a•]⁺ are essentially identical to [1a•]⁺, while the spin populations for the other members of the redox series are also identical irrespective of the ligand framework (ESI†). Since the DFT calculations are independent of temperature, that therefore suggests the different mixed-valent character of [1a•]⁺ and [2a•]⁺ arises from a temperature-dependent phenomenon. As the electronic structures are identical for both species, we attribute the spin-localisation in [2a•]⁺ to the rigidity of the tctq ligand. The flexible secondary methylene groups in ctc can approach a π radial–σ-bond coplanar alignment with their bonded dioxolene groups, which would activate a through-bond interaction between the dioxolene π-systems via hyperconjugation. This orientation is less accessible with the more rigid quaternary linkages in tctq, leading to localisation of the dioxolene spins as observed in [2a•]⁺.

In conclusion, we have demonstrated that the mixed-valent character of sq radicals derived from complexed cyclotricatechylene macrocycles is sensitive to their conformational flexibility. Our current work aims to make use of this feature in host:guest systems based on this redox-active molecular framework.

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Conflicts of interest
There are no conflicts to declare.

Notes and references
1 A. 2,3,6,7,10,11-hexahydroxytribenzotriquinacene tris catechol related to Hctcq, but lacking the methyl substituents on the macrocycle methylene groups, was recently reported.26