Transition metal decorated soft nanomaterials through modular self-assembly of an asymmetric hybrid polyoxometalate†

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An asymmetrically functionalised Wells–Dawson organic–inorganic hybrid polyoxometalate has been post-functionalised by Pt2+ coordination, and demonstrates self-assembly into surface-decorated micellar nanostructures. This multifunctional hybrid material is found to be a redox-active soft nanomaterial and demonstrates a new molecular design strategy with potential for applications in photo- or electro-catalysis.

New organic–inorganic hybrid materials, which use molecular design strategies to control their self-assembly into hierarchical structures and fine-tune their chemical properties, have attracted considerable attention in recent years for their wide-ranging potential applications. One of the most effective strategies is the use of tuneable molecular ‘building blocks’ which can confer multiple complimentary organic and inorganic functionalities. Polyoxometalates (POMs) – a class of unique, nanosized, molecular metal-oxide clusters – are particularly attractive in this regard, combining rich photo- and electro-chemical properties with stable, highly modular structures. In particular, the ability of POMs to covalently incorporate organic groups via rational, post-synthetic modification allows their physicochemical properties to be selectively tuned, and has facilitated their exploration as novel organic–inorganic amphiphiles (e.g. by incorporating long-chain hydrophobic moieties). This has led to growing interest in the use of organofunctionalised hybrid-POM species as discrete building blocks with great promise for the construction of unique soft-materials with a range of enhanced, switchable functionalities. The self-assembly of hybrid-POMs into soft nanostructures has also been shown to be dependent on a number of easily controlled factors [in addition to the design of the POM cluster itself], such as solvent, pH, cations, or coordination of metal ions, all of which open up a number of wide-ranging material design strategies.

One of the outstanding challenges in the field remains the development of multicomponent molecular building blocks into which a range of structure-directing or functional groups can be incorporated. An emerging strategy is the development of asymmetric hybrid-POMs, in which two (or more) distinct organic groups are covalently bound to the POM core. Due to considerable challenges in the synthesis and purification of such compounds however, only a select few examples have been reported to date, almost all of which are based on the minimally functional [MnMo6O24(L)2]3− Mn-Anderson cluster. Recently, our group reported the simple one-pot synthesis of the first stable, bi-functionalised asymmetric hybrid-POM based on the [P2W24O62]6− Wells–Dawson cluster. This new species, K4(C2H8N)2[P2W24O62(P(O)C21H14N3)(P(O)OC24H41)] (1) (see Scheme 1), demonstrates unique multifunctionality driven by the inclusion of both aliphatic long-chain alkane and metal-chelating terpyridine (TPY) groups, alongside the inherent photo- and redox-activity of the POM core. 1 also shows solvent-dependent self-assembly into low dispersity micellar structures, however, when we attempted to combine this with metal-functionalisation using Fe2+ ions, new dimeric clusters formed which were found to aggregate into smaller, more condensed nanostructures resembling those recently reported by Izzet and Proust, and lacking the distinct shape and hollow interior of the micellar species formed by 1.

To maximise the potential of soft materials based on asymmetric hybrid-POMs, it will be necessary to controllably combine the distinct properties of each component, such that the functionality of each sub-unit is fully exploited. Here, we demonstrate the self-assembly of an entirely new type of multifunctional Pt2+-decorated micellar nanostructure based on Pt complexes of the asymmetric POM building block 1. Pt2+. Polypyridyl complexes are known for their unique luminescent
was prepared from the asymmetric POM, \( \text{P-C18} \) appearing at 12.55 and 17.00 ppm respectively for the terpyridine-containing group (P-TPY) and the alkane-group signals for both covalently bound ligand groups, with the effect of the metal ion coordination, and the P-C18 phosphorus is slightly shielded (from 13.40 ppm) due to the interaction with the metal ion. 

CH\(_3\)CN (1 : 1 v/v) and stirred at room temperature for 72 h. This containing solution was added to a solution of AgBF\(_4\) in acetone to labilise the Pt\(^{2+}\) complex. The resultant AgCl was removed by filtration and the Pt-containing solution was added to a solution of 1 in DMF–CH\(_3\)CN (1 : 1 v/v) and stirred at room temperature for 72 h. This resulted in a yellow/orange coloured reaction mixture, which is characteristic of many \( \text{Pt(TPY)L} \) complexes. The reaction mixture was centrifuged to remove any insoluble material, before the solvent was removed in vacuo. The final product was obtained by precipitation from minimal DMF using an excess of diethyl ether. The composition and purity of Pt-1 was confirmed by \(^1\)H, \(^{31}\)P NMR and FTIR spectroscopies, ESI-MS and elemental (CHN) analysis.

The \(^{31}\)P NMR spectrum of Pt-1 obtained in DMSO-\(d_6\) shows signals for both covalently bound ligand groups, with the terpyridine-containing group (P-TPY) and the alkane-group (P-C\(_{18}\)) appearing at 12.55 and 17.00 ppm respectively (Scheme 1). Compared to 1, the phosphorus nucleus in the P-TPY group is slightly shielded (from 13.40 ppm) due to the effect of the metal ion coordination, and the P-C\(_{18}\) phosphorus is very slightly deshielded (from 16.72 ppm), indicative of some electronic communication between groups, possibly mediated by the POM core (Fig. S3, ESI†). \(^1\)H NMR peaks for the aromatic protons of P-TPY are shifted downfield relative to those of 1, suggesting successful coordination of the Pt\(^{2+}\) ion (Fig. S1 and S4, ESI†). The observation of several signals in the ESI-MS spectra of Pt-1 which closely correspond to the intact cluster additionally confirm successful preparation of the Pt-functionalised hybrid (Fig. S5 and Table S5, ESI†).

To explore the multifunctionality of Pt-1 we first studied its redox-activity. Cyclic voltammetry experiments were conducted in DMF on a 0.5 mM solution of Pt-1 with 0.1 M TBA-PF\(_6\) used as the electrolyte. In the potential range of +1.0 to −2.25 V (vs. Fe/Fe\(^+\)) five quasi-reversible redox processes are observed from −0.5 to −2.25 V as well as an irreversible oxidation at approximately +0.5 V (Fig. 1).

Processes I, II, IV and V are attributed to W\(^{VI/V}\) redox couples centred on the POM core and are found to be very slightly negatively shifted relative to those observed in 1. This suggests some (though very weak) influence on the electronic structure of the POM core by formation of the new Pt-TPY complex. Process III is assigned to TPY/TPY\(^+\) redox and has shifted positively due to stabilisation of the TPY radical anion by metal incorporation. The irreversible oxidation observed at +0.476 V can be assigned to the oxidation of Pt\(^{2+}\) to Pt\(^{3+}\), as has been observed for some similar Pt(TPY) complexes, though it should be noted that this remains unresolved in the literature. Here, we observe that the oxidation only appears once the potential is taken more negative than ca. −1.8 V vs. Fe/Fe\(^+\) on sequential scanning (Fig. S11, ESI†).

We then studied the solvent-dependent self-assembly of Pt-1 by dissolving it in a 9 : 1 (v/v) water–DMF mixture (the compound is first solubilised in DMF, to which was then added

![Scheme 1](https://example.com/scheme.jpg)

Scheme 1  Preparation of the Pt\(^{2+}\)-coordinated hybrid-POM, Pt-1, from the asymmetrically functionalised precursor, 1, showing the \(^{31}\)P NMR spectrum of Pt-1 in DMSO-\(d_6\). Colour code: blue polyhedra = \{WO\(_6\}\}, pink polyhedra = \{PO\(_4\}\}, red spheres = oxygen. Cations and solvent molecules are omitted for clarity.

![Fig. 1](https://example.com/fig1.jpg)

Fig. 1  Overlaid cyclic voltammograms of Pt-1 and precursor asymmetric POM hybrid, 1, collected from a 0.1 M solution of TBA-PF\(_6\) in DMF (see ESI† for details).
functionalised soft nanomaterials. This work demonstrates Pt-1 to form regular assemblies. The structures of the assemblies result of the high angle (approx. 160°) FeII–POM dimer derived from work as a result of the solvent-driven self-assembly of the POM–Pt-1 bic core (comprised of the interior-facing C18 chains) as a TPY-sites can only be directed outwards from the hydrophobic micelles (Fig. 2b). This is logical as the Pt-coordinating micellar structure of Pt-1 is still clearly visible. 6 The spherical assemblies formed by Pt-1 also differ significantly from the randomly shaped aggregates observed in our previous work as a result of the solvent-driven self-assembly of the POM–FeII–POM dimer derived from 1.11 The Pt-coordinating TPY-sites can only be directed outwards from the hydrophobic core (comprised of the interior-facing C18 chains) as a result of the high angle (approx. 160°) between the two distinct arylphosphonate ligands. This work demonstrates an effective strategy for the preparation of new surface-functionalised soft nanomaterials.

In summary, we have successfully postfunctionalised an asymmetrically functionalised Wells–Dawson hybrid POM by the coordination of a platinum(ii) centre using a straightforward and broadly applicable synthetic strategy. This work provides an easily accessible and versatile method for the development of new multifunctional hybrid systems with novel supramolecular architectures and tuneable functionalities for new applications as advanced materials.

EH thanks the Low Dimensional Materials and Interfaces Doctoral Training Programme at the University of Nottingham for support. JMC and GNN thank the Leverhulme Trust (RPG-2016-442) and the University of Nottingham Propulsion Futures Beacon of Excellence. The authors thank the Engineering and Physical Sciences Research Council (EPSRC) [EP/L022494/1] and the University of Nottingham for funding TEM instrumentation.

Conflicts of interest
There are no conflicts to declare.

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