

## Post-functionalization of a Photoactive Hybrid Polyoxotungstate

Jamie M. Cameron,<sup>a, b</sup> Satomi Fujimoto,<sup>a</sup> Rong-Jia Wei,<sup>a</sup> Graham N. Newton<sup>\*b, c</sup> and Hiroki Oshio<sup>\*a</sup>

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A new post-functionalization strategy for hybrid polyoxometalate (POM) clusters is presented, whereby the electronic properties and visible-light driven oxidative reactivity of the POM core can be altered by controlled addition of transition metal ions. The structure of three new metal-functionalised derivatives of a phosphonate hybrid-POM are discussed, alongside a comparison of their electrochemical, photo-chemical and photo-oxidative properties.

### Introduction

Polyoxometalates (POMs) have attracted increasing interest in recent years as a result of their appealing physical and chemical properties,<sup>1</sup> including their reversible multi-electron redox behaviour, photochemical reactivity<sup>2</sup> and extraordinary wealth of potential structures and compositions.<sup>3</sup> In particular, the ability of POMs to form meta-stable 'lacunary' derivatives (where one or more metal sites is selectively hydrolysed to form a reactive vacancy) provides an almost limitless toolbox for the design, synthesis and post-synthetic modification or tuning of new functional materials.<sup>4</sup> Indeed, a significant factor in the rapid growth of POM chemistry over the past few decades has been the keen interest in so-called transition metal substituted POMs (TMSPs) which have been explored for a range of magnetic, catalytic and electronic applications.<sup>5</sup> Similarly, the ability to tether organic moieties to the lacunary sites of POM clusters<sup>6</sup> has offered a means to combine fascinating complimentary functionalities into a single molecular ensemble,<sup>7</sup> opening interesting new avenues in biotechnology, supramolecular self-assembly and materials design.<sup>8</sup>

Recently, we have shown how the coordination of organophosphonate moieties within such vacancies can be used to photo-activate a Dawson-type polyoxotungstate cluster,  $K_6[P_2W_{17}O_{61}(P(O)C_6H_4CO_2H)_2]$  (**1**) (see Figure 1) under visible light irradiation.<sup>9</sup> This approach is particularly interesting as it allows for direct enhancement of the POMs' inherent photo-activity, which involves generation of a highly reactive charge-separated state (incorporating an oxo-centred radical) upon

excitation of the  $O \rightarrow W$  LMCT band.<sup>2, 10</sup> We have also recently demonstrated how this hybridization strategy can be used to directly tune the electronic structure of the POM, allowing a means to controllably alter its electrochemical and photochemical properties.<sup>11</sup> This method potentially opens up a range of new possibilities for interesting catalytic functionalities, however, the scope of such work is limited by the difficulty in combining the attractive features of organic-inorganic hybrid POMs with the ability to selectively add function directly to the POM core *via* coordination of secondary metal ions, or even polynuclear metal complexes.<sup>4, 12</sup> In effect, this has led to something of an 'either-or' problem in the molecular design of new multi-functional POM complexes, where it has proven difficult to combine or reconcile inorganic and organic functionalisation strategies.

Herein, we demonstrate a new post-functionalization approach for organophosphonate hybridized polyoxometalate clusters in which additional transition metal ions may be appended to the hybridized POM core by a facile one-pot reaction strategy. This allows for the modification of both the electronic properties of the POM and its ability to act as a photo-oxidation catalyst in the decomposition of a common textile-industry pollutant.

### Results and Discussion

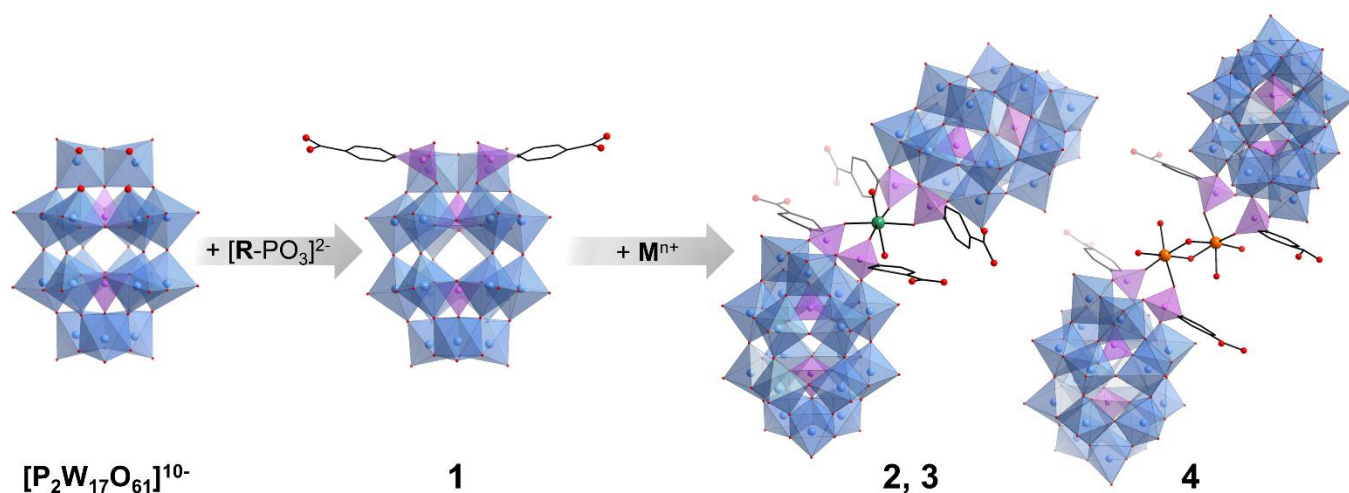
The benzoic acid hybridized organophosphonate-POM, **1**, can be synthesized in good yield as previously reported.<sup>9</sup> It is interesting to note that this compound was initially envisaged, in-part, to serve as a stable, redox-active building block in the synthesis of new multifunctional molecules, oligomers or coordination polymers, where the appended carboxylate moieties would serve as the primary means of structural expansion. With this in mind, the one-pot reaction of **1** with a series of 1<sup>st</sup> row transition metals ( $Mn^{2+}$ ,  $Co^{2+}$  and  $Zn^{2+}$ ) under a variety of conditions was expected to yield at least one, if not more, of the aforementioned complexes. Instead, we identified

<sup>a</sup> Graduate School of Pure and Applied Sciences, University of Tsukuba, Tennodai 1-1-1, Tsukuba, 305-8571, Japan. E-mail: oshio@chem.tsukuba.ac.jp

<sup>b</sup> GSK Carbon Neutral Laboratories for Sustainable Chemistry, University of Nottingham, NG7 2GA, UK.

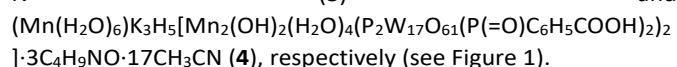
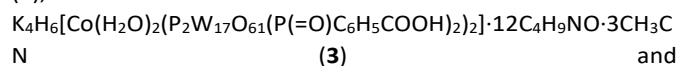
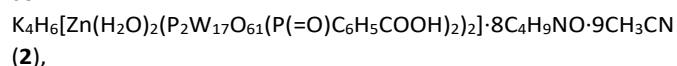
<sup>c</sup> School of Chemistry, University of Nottingham, University Park Nottingham, NG7 2RD, UK. E-mail: graham.newton@nottingham.ac.uk

Electronic Supplementary Information (ESI) available: Full experimental procedures, syntheses, crystallographic data and supporting spectroscopic and electrochemical characterisation are provided. CCDC Numbers: 1831504-1831506. For ESI and crystallographic data in electronic format see DOI: 10.1039/x0xx00000x.



**Figure 1.** Schematic of the sequential hybridisation and post-functionalisation strategy employed herein, showing combined polyhedral/ball-and-stick representations of the crystal structures of compounds **1-4**. Colour code: blue polyhedra =  $\{WO_6\}$ , purple polyhedra =  $\{PO_4\}$  or  $\{PO_3C\}$ , green sphere = Zn or Co, orange spheres = Mn, red spheres = O. Cations, protons and solvent molecules have been removed for clarity.

a series of dimeric cluster species in which the *bis*-phosphonate position, rather than the carboxylate moieties themselves, acted as a coordinating centre for the transition metal cations. Each new species could be synthesized under effectively identical one-pot conditions (see SI) and could be characterized as:



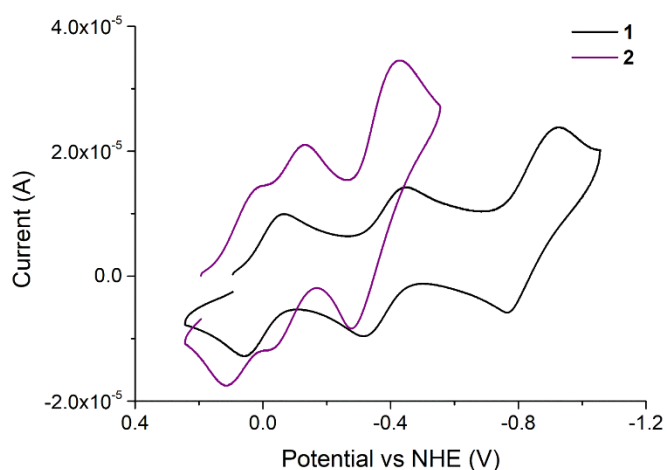
respectively (see Figure 1). Structural analysis of **2** clearly demonstrates how the neighbouring terminal P=O sites ( $d_{P=O(avg)} = 1.50 \text{ \AA}$ )<sup>13</sup> on the *bis*-phosphonate moiety are able to act as a bidentate coordinating site towards a single  $Zn^{2+}$  ion, forming a 1:1 dimeric complex between the two hybrid-POM units. In this case, the  $Zn^{2+}$  cation bridges the two POM sub-units at almost right angles through a  $\mu_2$ -oxo bridge to each of the four individual phosphonate groups, whilst two axial aqua ligands (average bond length =  $2.14 \text{ \AA}$ ) complete the octahedral coordination sphere. Interestingly, there is a clear hydrogen bonding interaction between the benzoic acid moieties, whereby the clusters are organized into well-ordered 1D chain-like arrays with a mean distance of *ca.*  $2.5 \text{ \AA}$  between the carboxylate moieties on each cluster unit. This suggests that the carboxylate groups on each POM remain protonated, providing one possible rationale for why no metal coordination takes place at these positions.

This result is especially noteworthy as we believe it is one of the very few examples of controllable post-functionalization of a hybrid-POM species with a heterometal group. In fact, the structure of **2** can be almost directly compared in a structural sense with the previously reported metal-bridged TMSP dimer species:  $\{Zr(P_2W_{17})_2\}$ .<sup>14</sup> Whilst we do note that this somewhat unexpected coordination mode has been observed previously in similar Keggin-type clusters,<sup>15</sup> it has only been reported in cases where the POM core retains at least one vacant lacunary

site with which to help coordinate additional transition metal species.

Whilst compound **3** is effectively isostructural to **2**, compound **4** is instead linked into a dimeric species by a  $\{Mn_2(OH)_2\}^{2+}$  unit in which two  $\mu_2$ -hydroxo ions ( $d_{Mn-O(H)} = 2.12 - 2.34 \text{ \AA}$ ) bridge the  $Mn^{2+}$  centres between each POM subunit (Figure 1). As in the case of compounds **2** and **3**, aqua ligands complete the coordination sphere of the cations, resulting in coordination environments with  $d_{Mn(avg)} = 2.18$  and  $2.21 \text{ \AA}$  for Mn1 and Mn2 respectively, consistent with their assignment as  $Mn^{2+}$  ions and correlating with bond valence sum calculations.<sup>16</sup> As before, this structure can also be related to a previously reported  $\{Zr_2(P_2W_{17})_2\}$  TMSP dimer.<sup>14</sup> In all cases, complimentary electrospray ionisation mass spectrometric (ESI-MS) analysis has been used to verify the identity of each cluster in tandem with additional spectroscopic analyses (including FT-IR and elemental analysis – see SI for additional details).

The cyclic voltammetry of compounds **2-4** was also studied as a comparison to that of compound **1**. In all cases, small positive shifts of around  $60 - 70 \text{ mV}$  were observed between the half-wave potential of the first redox couple of the post-functionalised compounds versus the parent hybrid complex, indicating substantial modification of the LUMO energy of all



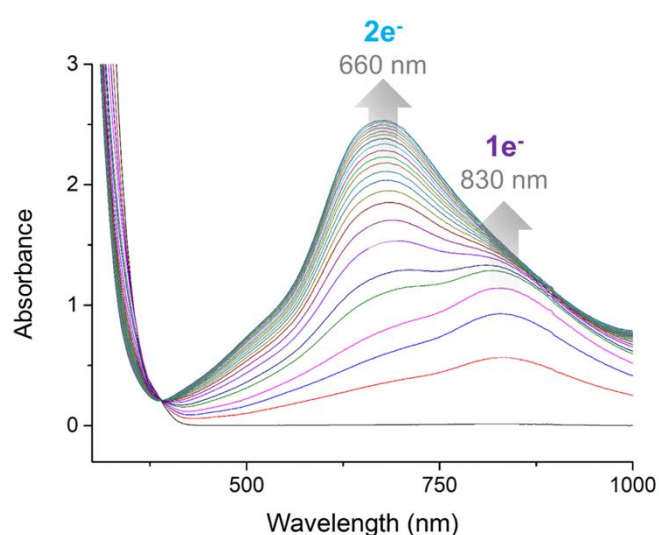
**Figure 2.** Overlaid cyclic voltammograms of 0.1 mM solutions of compounds **1** and **2** (as representative of compounds **3** and **4**) measured in DMF at a scan rate of 0.1 V s<sup>-1</sup>, highlighting the clear positive shift in redox potentials between the metal-functionalised and native hybrid cluster ( $E_{1/2}$  values for compounds **1-4** are tabulated below in Table 1). All scans are made from the open circuit potential in the negative direction.

**Table 1.** Half-wave redox potentials observed for compounds **1-4** obtained by cyclic voltammetry (potentials referenced vs NHE).

	$E_{1/2}$ (1 <sup>st</sup> ) / V	$E_{1/2}$ (2 <sup>nd</sup> ) / V	$E_{1/2}$ (3 <sup>rd</sup> ) / V
<b>1</b>	0.0	-0.38	-0.84
<b>2</b>	0.07	-0.08	-0.35
<b>3</b>	0.06	-0.08	-0.34
<b>4</b>	0.06	-0.14	-0.43

three metal-functionalised species. More significant positive shifts were observed on the subsequent redox processes, whereby the general trend is that of considerably more positive second and third redox half potentials (in the order of 200-300 and 400-500 mV respectively) in **2-4** relative to **1** (see Figure 2, Table 1 and SI). This clearly indicates that metal coordination at the *bis*-phosphonate site has a significant and direct effect on the redox properties of the POM. It is also important to note that in more commonly studied hybrid systems where metal cations have been coordinated to appended ligand groups (e.g. terpyridine), the electronic communication between the metal and the POM is generally so poor that the redox properties of the metal-oxide cluster are essentially unchanged.<sup>17</sup> Here, the adoption of phosphonate ligands allows the electronic structure of the POM to be directly addressed by the addition of metals at the adventitiously formed bi-dentate *bis*-phosphonate coordination site.

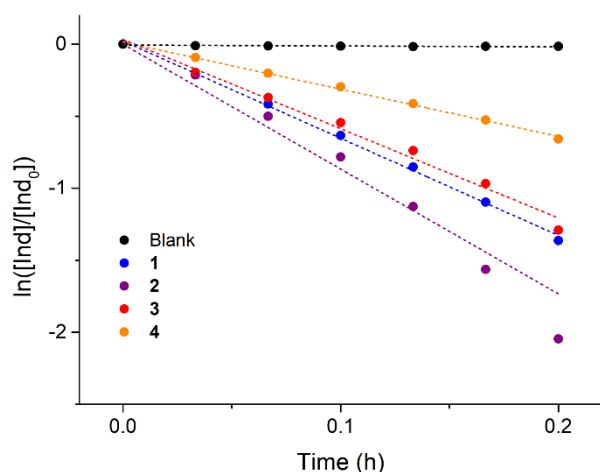
Given that we have recently shown how modification of the redox potential of the POM core through hybridization with organophosphate moieties alone can also be used to both alter and selectively tune photo-activity,<sup>9,11</sup> we were interested to explore the related properties of compounds **2-4**. Each compound was thus dissolved in degassed *n*-dimethylformamide (DMF) and irradiated with a Xe-lamp equipped with either a 390 nm or 420 nm cut-off filter. Above 390 nm, a clear 2-step, 2e<sup>-</sup> reduction can be observed in all cases (*via* photochemical oxidation of the solvent and a concurrent proton coupled reduction on the POM) whereby an initial,



**Figure 3.** Time resolved UV-vis spectra showing the photoreduction of **2** over 1 h in degassed DMF under irradiation at  $\lambda > 390$  nm. Notably, the metal-functionalised clusters are readily reduced by up to two electrons under visible light in the absence of oxygen. Data is shown at 2 minute intervals.

relatively fast 1e<sup>-</sup> reduction occurs within *ca.* 10 minutes with a maximum at 830 nm before a shoulder at *ca.* 660 nm quickly subsumes the initial peak, appearing to saturate at around 60 minutes irradiation time (see Figure 3). At higher wavelength irradiation, each cluster appears to saturate at the singly reduced state ( $\lambda_{\text{max}} = 830$  nm) after 50 minutes of irradiation. Note that these optical assignments are in good agreement with supporting spectroelectrochemical analyses (see SI for details). Considering the broad similarities between the electrochemical and photochemical properties of both **1** and compounds **2-4**, we were interested to see how metallation of the hybrid POM would affect its photo-oxidative reactivity. Indigo dye has been employed recently by us and others as a convenient model pollutant for similar assays of photo-oxidation catalysis.<sup>9, 18</sup> Compounds **2-4**, alongside compound **1** (as a known comparison), were dissolved in aerated DMF<sup>19</sup> alongside 5 equivalents of Indigo dye and irradiated under the same conditions as above using a Xe-lamp with a 420 nm cut-off filter. UV-vis spectroscopy was subsequently used to track the decomposition of Indigo over the course of each reaction and the results are presented in Figure 4. In each case, the reaction followed pseudo-first order kinetics, allowing comparable rate constants to be extracted from each measurement (Table 2).

Unlike in the photo-reduction measurements described above, a dramatic difference in the rate of substrate photo-oxidation was observed, where the photo-catalytic efficacy of each compound could be ranked as follows: **2** (Zn) > **1** > **3** (Co) > **4** (Mn). This trend was somewhat surprising since it contravenes our previous observations on how the photo-oxidative ability of each compound should be related almost exclusively to its electronic structure (specifically, the energies associated with the electrochemically-relevant LUMO level).<sup>11</sup> Given the broad similarity between both the observed redox behaviours of compounds **2-4** and their optical absorption profiles at the irradiation wavelengths employed above (see SI), an alternative



**Figure 4.** Plot of Indigo dye (Ind) decomposition vs. time for compounds **1-4** against a blank control (monitored by UV-vis spectroscopy at 613 nm). Reaction conditions: irradiation; Xe lamp ( $\lambda > 390$  nm), solvent = DMF,  $[\text{Ind}]_0 = 20 \mu\text{M}$ ,  $[\mathbf{1}] = 8 \mu\text{M}$ ,  $[\mathbf{2-4}] = 4 \mu\text{M}$ .

**Table 2.** Pseudo-first order rate constants for the photocatalytic decomposition of Indigo dye.

	$k_{\text{obs}} (\lambda > 390 \text{ nm}) (\text{s}^{-1})$	$k_{\text{obs}} (\lambda > 420 \text{ nm}) (\text{s}^{-1})$
<b>1</b>	$1.9 \times 10^{-3}$	$1.4 \times 10^{-4}$
<b>2</b>	$3.0 \times 10^{-3}$	$1.9 \times 10^{-4}$
<b>3</b>	$1.7 \times 10^{-3}$	$1.1 \times 10^{-4}$
<b>4</b>	$0.9 \times 10^{-3}$	$2.6 \times 10^{-5}$

explanation is required. Whilst the photo-chemical reactivity of POMs is often considered to be a complex radical driven process,<sup>10</sup> and is therefore non-trivial to fully characterize, one plausible explanation may be found by considering the relative ability of each metal ion to competitively quench the radical driven oxidation of the substrate. This would be in broad agreement with previous studies showing that transition metal ions – and particularly those with non-zero spin states (*i.e.*  $\text{Co}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$ ) – can act as effective radical quenchers.<sup>20</sup> It may also explain why of all the complexes, only **2** shows an increase in photo-oxidative performance over **1** (which is to be expected given its more positive first reduction potential, relative to **1**) as the closed shell, redox-silent  $\text{Zn}^{2+}$  ion is known to be a very poor quencher for triplet radical species.<sup>20a</sup> Correspondingly, the large suppression of reaction rate observed for compound **4** may be due in part to the ability of  $\text{Mn}^{2+}$  cations to quench oxidizing radical intermediates, however, the fact that **4** is also comparatively metal-rich (formulated as having 1.5  $\text{Mn}^{2+}$  centres per POM unit, as compared to the other metal-functionalised compounds which possess 0.5 metal ions per POM unit) may also be significant.

## Conclusions

In summary, we have reported a new post-functionalisation strategy which allows for the combination of organic-inorganic hybrid polyoxometalate chemistry with more traditional

transition-metal substitution approaches. The unexpected preference of secondary metal cations for coordination with the terminal oxygen groups on the bis-phosphonate moiety can be argued to represent an extension of the lacunary functionality of the parent  $\{\text{P}_2\text{W}_{17}\}$  anion, allowing the POM reactivity and electronic properties to be addressed directly whilst retaining the associated hybrid functionality of the appended ligand groups. For instance, the substantial positive shifts observed in the redox properties of the composite complexes **2-4** facilitate the  $2e^-$  reduction of the POM under irradiation with high-energy visible light ( $\lambda > 390$  nm), a key requirement in next-generation materials for solar fuel production and other multi-electron catalytic processes. This potentially paves the way for the application of such species in new dyadic or triadic assemblies in which the tuneable electrochemical and photochemical properties of the POM can be combined with the near-limitless molecular design approaches available to hybrid-POM chemistry and the modular reactivity of transition-metal substituted POM species.

## Conflicts of interest

The authors have no conflicts to declare.

## Acknowledgements

This work was supported by JSPS KAKENHI Grant Number JP16H06523 (Coordination Asymmetry). This work was also supported by the JSPS Postdoctoral Fellowship for Foreign Researchers (J.M.C., R.-J.W.). G.N.N thanks the University of Nottingham and the University of Nottingham Advanced Molecular Materials Research Priority Area for support.

## Notes and references

- M. T. Pope, A. Müller, *Angew. Chem. Int. Ed.*, 1991, **30**, 34.
- a) C. Streb, *Dalton Trans.*, 2012, **41**, 1651; b) J. M. Cameron, D. J. Wales and G. N. Newton, *Dalton Trans.*, 2018, DOI: 10.1039/C8DT00400E.
- a) H. N. Miras, J. Yan, D. L. Long, L. Cronin, *Chem. Soc. Rev.*, 2012, **41**, 7403; b) J. M. Sumliner, H. Lv, J. Fielden, Y. V. Geletii, C. L. Hill, *Eur. J. Inorg. Chem.*, 2014, **2014**, 635; c) L. Vila-Nadal and L. Cronin, *Nat. Rev. Mater.*, 2017, **2**, 15.
- a) O. Oms, A. Dolbecq, P. Mialane, *Chem. Soc. Rev.*, 2012, **41**, 7497; b) B. S. Bassil, U. Kortz, *Dalton Trans.*, 2011, **40**, 9649.
- a) S.-S. Wang, G.-Y. Yang, *Chem. Rev.*, 2015, **115**, 4893; b) C. Busche, L. Vila-Nadal, J. Yan, H. N. Miras, D.-L. Long, V. P. Georgiev, A. Asenov, R. H. Pedersen, N. Gadegaard, M. M. Mirza, D. J. Paul, J. M. Poblet, L. Cronin, *Nature*, 2014, **515**, 545; c) C. Ritchie, V. Baslon, E. G. Moore, C. Reber, C. Boskovic, *Inorg. Chem.*, 2011, **51**, 1142; d) Q. Yin, J. M. Tan, C. Besson, Y. V. Geletii, D. G. Musaev, A. E. Kuznetsov, Z. Luo, K. I. Hardcastle, C. L. Hill, *Science*, 2010, **328**, 342; e) X.-B. Han, Z.-M. Zhang, T. Zhang, Y.-G. Li, W. Lin, W. You, Z.-M. Su, E.-B. Wang, *J. Am. Chem. Soc.*, 2014, **136**, 5359.
- a) A. Dolbecq, E. Dumas, C. R. Mayer, P. Mialane, *Chem. Rev.*, 2010, **110**, 6009; b) Y.-F. Song, R. Tsunashima, *Chem. Soc. Rev.*, 2012, **41**, 7384.
- a) A. Proust, B. Matt, R. Villanneau, G. Guillemot, P. Gouzerh, G. Izzet, *Chem. Soc. Rev.*, 2012, **41**, 7605; b) J. J. Walsh, A. M. Bond, R. J. Forster, T. E. Keyes, *Coord. Chem. Rev.*, 2016, **306**, Part 1, 217.

- 8 a) P. Yin, T. Li, R. S. Forgan, C. Lydon, X. Zuo, Z. N. Zheng, B. Lee, D. Long, L. Cronin and T. Liu, *J. Am. Chem. Soc.*, 2013, **135**, 13425-13432; b) A. Blazevic and A. Rompel, *Coord. Chem. Rev.*, 2016, **307**, 42-64; c) P. Gao, Y. Wu and L. Wu, *Soft Matter*, 2016, **12**, 8464-8479; d) K. Kastner, A. J. Kibler, E. Karjalainen, J. A. Fernandes, V. Sans and G. N. Newton, *J. Mater. Chem. A*, 2017, **5**, 11577-11581.
- 9 J. M. Cameron, S. Fujimoto, K. Kastner, R.-J. Wei, D. Robinson, V. Sans, G. N. Newton and H. H. Oshio, *Chem. Eur. J.*, 2017, **23**, 47-50.
- 10 a) E. Papaconstantinou, *Chem. Soc. Rev.*, 1989, **18**, 1; b) T. Yamase, *Catal. Surv. Asia*, 2003, **7**, 203.
- 11 S. Fujimoto, J. M. Cameron, R.-J. Wei, K. Kastner, D. Robinson, V. Sans, G. N. Newton and H. Oshio, *Inorg. Chem.*, 2017, **56**, 12169-12177.
- 12 a) S.-T. Zheng and G.-Y. Yang, *Chem. Soc. Rev.*, 2012, **41**, 7623-7623; b) A. Sartorel, M. Bonchio, S. Campagna and F. Scandola, *Chem. Soc. Rev.*, 2013, **42**, 2262-2280; c) C. Boskovic, *Acc. Chem. Res.*, 2017, **50**, 2205-2214.
- 13 B. Gamoke, D. Neff and J. Simons, *J. Phys. Chem. A*, 2009, **113**, 5677-5684.
- 14 K. Stroobants, V. Goovaerts, G. Absillis, G. Bruylants, E. Moelants, P. Proost, T. N. Parac-Vogt, *Chem. Eur. J.*, 2014, **20**, 9567.
- 15 a) R. Villanneau, D. Racimor, E. Messner-Henning, H. Rousselière, S. Picart, R. Thouvenot, A. Proust, *Inorg. Chem.*, 2011, **50**, 1164; b) R. Villanneau, A. B. Djamâa, L.-M. Chamoreau, G. Gontard, A. Proust, *Eur. J. Inorg. Chem.*, 2013, **2013**, 1815.
- 16 Bond valence sums: Mn1 = 2.16; Mn2 = 1.97. Note that this data should be considered as tentative due to the poor quality of the crystals of **4** and the correspondingly poor diffraction data obtained.
- 17 a) B. Matt, J. Fize, J. Moussa, H. Amouri, A. Pereira, V. Artero, G. Izzet, A. Proust, *Energy Environ. Sci.*, 2013, **6**, 1504; b) A. Parrot, G. Izzet, L.-M. Chamoreau, A. Proust, O. Oms, A. Dolbecq, K. Hakouk, H. El Bekkachi, P. Deniard, R. Dessapt, P. Mialane, *Inorg. Chem.*, 2013, **52**, 11156.
- 18 a) J. Tucher, K. Peuntinger, J. T. Margraf, T. Clark, D. M. Guldi, C. Streb, *Chem. Eur. J.*, 2015, **21**, 8716; b) A. Seliverstov, C. Streb, *Chem. Commun.*, 2014, **50**, 1827.
- 19 Note that unlike the photo-reduction experiments described above, aerated solvent is necessary to facilitate the catalytic degradation of the substrate. This suggests that mass transfer of diffused O<sub>2</sub> may be an important consideration for the design of future POM-driven reactions. See for instance: M. Lechner, R. Güttel and C. Streb, *Dalton Trans.*, 2016, **45**, 16716-16726.
- 20 H. Linschitz, L. Pekkarinen, *J. Am. Chem. Soc.*, 1960, **82**, 2411.; b) J. A. Kemlo, T. M. Shepherd, *Chem. Phys. Lett.*, 1977, **47**, 158.