Physical and electrochemical modulation of polyoxometalate ionic liquids via organic functionalization

Alexander J. Kibler,a Carmen Martín,a Jamie M. Cameron,a Agata Rogalska,a Jairton Dupont,a,b Darren A. Walsh,a Graham N. Newtona\*

[a] A. J. Kibler, Dr. C. Martin, Dr. J. M. Cameron, A. Rogalska, Dr. D. A. Walsh, and Dr. G. N. Newton  
GSK Carbon Neutral Laboratories for Sustainable Chemistry,  
Jubilee Campus, University of Nottingham,  
Nottingham, NG7 2GA, UK  
E-mail: graham.newton@nottingham.ac.uk

[b] Prof. J. Dupont  
Institute of Chemistry, UFRGS,

Av. Bento Gonçalves, 9500,

Porto Alegre 91501-970, Rio Grande do Sul, Brazil

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**Abstract:** The synthesis and characterization of two new organic-inorganic hybrid polyoxometalate ionic liquids (POM-ILs) is described. The POM-ILs were formed by pairing bulky trihexyl(tetradecyl)phosphonium cations, [THTP]+, with organosiloxane and organophosphonate-functionalized Keggin-type POMs [PW11O39(SiPh)2O]3− and [PW11O39(P(O)Ph)2]3−. The functionalized POM-ILs were found to be more thermally stable than their molecular precursors and comparison of their electrochemical properties showed that the tunable electronic structures of the POM anions determined the redox chemistry of the hybrid materials.

Introduction

Polyoxometalates (POMs) are discrete anionic metal oxide clusters with a variety of attractive properties, such as photosensitivity, redox activity, and high thermal and chemical stability.[1-4] These properties make POMs of potential interest in a range of applications including catalysis,[5-9] electrical-energy storage,[10-13] and sensing,[14-16] to name but a few. An increasingly important sub-class of POMs are organic inorganic-hybrid POMs,[17, 18] in which a near-limitless selection of organic groups can be incorporated through either weak electrostatic interactions (Class I)[19] or *via* direct covalent functionalization of the POM structure itself (Class II).[20, 21] Hybridisation can impart a diverse range of functionalities to POMs, and has resulted in the use of hybrid POMs in photocatalysis,[22, 23] supramolecular assembly,[24-26] and biotechnology/therapeutics.[27-29] Each approach brings its own rewards and challenges. Class I hybrids are more easily synthesized and permit wide-ranging and facile modification of the physical properties but are less durable and particularly susceptible to changes in the solution conditions (ionic strength, pH, etc.). Conversely, Class II materials are generally chemically stable and their properties can be finely tuned through covalent functionalisation of the parent POM (including direct modification of the POM’s electronic properties through interaction with appended organic groups),[30, 23] however the synthesis these materials is significantly more demanding than that of Class I materials.

The physical properties of Class I materials are largely governed by the nature of the counter-cation associated with the anionic metal-oxide cluster.[31-33] A recent development is the functionalisation of POMs to form hybrid POM-ionic liquid phases (POM-ILs). Ionic liquids (ILs) are materials that are composed entirely of ions and which are liquid below 100 °C. Interest in ILs has exploded over the past few decades in large part due to their non-volatility, high ionic conductivity and excellent thermal and electrochemical stability. In addition, the physicochemical properties depend on the cation/anion combinations.[34] An almost unlimited number of cation/anion pairs can be used to synthesise ILs, meaning that the properties can be tuned for specific tasks.[35-37] ILs can dissolve a wide variety of substrates and it is notable that a number POM/IL solutions have been explored recently for catalytic applications, in particular.[38, 39]

Conversely, POM-ILs are an entirely novel class of hybrid inorganic/organic materials which can be synthesized by pairing POM anions with bulky, asymmetric cations featuring quaternized phosphorus or nitrogen centers.[40-42] In this way, the inherent multi-redox, photoactive and catalytic properties of POMs can be combined with the unique liquid-phase characteristics of conventional ILs, leading to the formation of new species with the potential to act as dual role catalyst/solvent systems, redox-active electrolyte species, or new liquid nanocomposite materials.[43-47] For instance, an excellent recent example by Yang et al. has demonstrated the use of a POM-IL as an effective esterification catalyst with novel self-separating properties, enabling its easy recycling and re-use.[48] In addition, recent examples by Cavaliero et al. and Streb et al. have also shown how transition metal substituted POM (TMSP) clusters can be used to form interesting POM-ILs in which the thermal characteristics of the IL could be altered by the introduction of different metal ions, whilst the electronic properties and/or reactivity of the TMSPs were retained in the POM-IL phase.[47,49,50] The incorporation of covalently-hybridized POMs in new POM-IL phases is currently, to the best of our knowledge, unexplored. Such an approach could potentially allow the physical, chemical, and electronic properties of the POM-IL to be finely tuned *via* the near-limitless molecular design possibilities offered by Class II hybrid POMs.



**Scheme 1.** Synthetic scheme for the synthesis of compound **2**. Blue spheres/polyhedra, W; magenta, P; red, O; grey, C; white, H. Cations are included only as text for clarity.

Herein, we describe the synthesis and characterisation of two new organic-inorganic hybrid POM-ILs. The POM-ILs were formed by pairing bulky trihexyltetradecylphosphonium cations ([THTP]+) with the organofunctionalized Keggin-type polyoxometalates [PW11O39(SiPh)2O]3− and [PW11O39(P(O)Ph)2]3−. We have also synthesised a previously-reported POM-IL incorporating the plenary Keggin polyoxometalate, [PW12O40]3- and compare its properties to those of our novel materials.

All POM-ILs were synthesised *via* simple cation-metathesis reactions, but particularly careful consideration was given to the preparation of the hybrid-POM-ILs to maximise the purity of the resulting material. Thus, for the plenary Keggin-based POM-IL (THTP)3[PW12O40] (**{PW12}**) the synthesis followed cation-exchange methods adapted from previously reported methods.[43] However, in the case of the hybrid analogues, it was necessary to first isolate the hybridised cluster as either a tetra-N-butylammonium, [TBA]+) or potassium salt, to ensure that minimal free ligand or other side products would be incorporated into the resulting IL. The siloxane hybrid POM-IL (THTP)3[PW11O39(SiPh)2O] (**1**) (where Ph = -C6H5) was first synthesised using a modified literature procedure,[51] in which two equivalents of trichlorophenylsilane were grafted directly onto the lacunary [PW11O39]7- cluster to yield (TBA)3[PW11O39(SiPh)2O] (TBA-**1**). Cation exchange was performed under biphasic conditions (3:2 v/v water:cyclohexane) at 80 °C with an excess of trihexyltetradecylphosphonium chloride to yield **1**. The phosphonate hybrid-POM-IL (THTP)3[PW11O39(P(O)Ph)2] (**2**) was synthesised using a similar method, but beginning from the K+ salt (K-**1**) to minimise decomposition of the hydrolytically-unstable, phosphonate-functionalised lacunary Keggin species.[52]  The POM-IL, **2**, was prepared under anhydrous conditions in dry acetonitrile at 35 ºC, to minimise degradation of the phosphonate-hybrid. In each case, the composition and purity of the resulting hybrid-POMs and their corresponding POM-ILs were assessed using standard spectroscopic techniques (full details of which can be found in the supporting information).

One of the key aspects of this study was to probe the thermal properties of this new class of POM-IL and determine their relative stability. In particular, it was postulated that the IL environment may help to stabilize the hybrid-systems with respect to the degradation of the POM-bound organic unit when compared to their classical solid starting materials. Measurements were conducted under argon at a heating rate of 10 °C min-1 on the [THTP]+ salts **1**, **2** and **{PW12}** and their pre-cation exchange analogues TBA-**1**, K-**2** and TBA-**{PW12}.** The TGA results are summarized in Figures 2 and S21. In all cases, the [THTP]+ salts were found to exhibit enhanced thermal stability relative to the [TBA]+ and K+ salts. Of particular note, however, were the decomposition profiles of the hybrid POM-ILs **1** and **2**. For instance, TBA-**1** exhibited a single weight loss event (23.6 % Tonset = 280 °C), corresponding to the loss of three [TBA]+ moieties and the appended phenyl groups (*calc.* 24.3 %), whereas the POM-IL, **1**, exhibited a single sharp weight loss (32.3 %, Tonset = 420 °C) corresponding to the loss of three [THTP]+ cations (*calc.* 33.3 %).

Interestingly, the potassium salt K-**2** showed a broad multistep decomposition process with an onset of around 100 °C, resulting



**Figure 2.** TGA weight loss profiles of compounds **1** (a) and **2** (b), and their precursor salts TBA-**1** and K-**2**, measured under argon at a heating rate of 10 °C min-1. In each case, the key weight loss steps are annotated and correspond to (a) the loss of 3 [TBA]+ + 2 {C6H5} (*calc.* 24.28 %) or 3 [THTP]+ (*calc.* 33.33 %), respectively, and: (b) the loss of 2 {C6H5} (*calc.* 5.07 %) or 3 [THTP]+ (*calc.* 33.14 %), respectively.

in a total weight loss of 4.7 % at 750 °C which corresponds to the slow loss and volatilisation of both phenyl moieties on the hybrid POM (*calc.* 5.1 %). In marked contrast, the IL **2** showed one sharp weight loss of 31.5 % with an onset at 420 °C (almost identical to the siloxane-functionalised hybrid POM-IL, **1**) corresponding to the loss of three [THTP]+ units and decomposition of the IL (*calc.* 33.1 %). In the case of both **1** and **2**, TGA analysis highlights the significantly improved thermal stability of the POM-ILs, both in relation to their precursors and to neat [THTP]Cl which has been shown to thermally decompose at around 350 °C under similar conditions.[53] This indicates that synergistic effects between both the phosphonium cation and POM components may improve the stability of the overall POM-IL, possibly as a result of so-called ‘shrink-wrapping’ cation-anion interactions.[54] In addition, the hybrid POM-IL species **1** is shown to be thermally stable in air up to at least 350 °C (see SI).

To investigate the temperature-dependent, phase-change behavior of the hybrid materials, differential scanning calorimetry (DSC) measurements of **1**, **2** and **{PW12}** were carried out (see SI). We hypothesised that the introduction of organic groups onto the lacunary polyoxometalate, which both lower the symmetry of the POM and alter its electrostatic surface potential (i.e. overall charge), would impact on its interaction with the bulky cation groupos and affect the physical properties of the bulk IL material. As expected, **{PW12}** underwent an irreversible amorphous transition at around 65 °C (previously reported as a melting process),[43] followed by a second reversible melting step at around 130 °C, while **1** and **2** yielded generally featureless DSC profiles across the full temperature range measured (‑100°C to 300°C) (see SI), indicating that the hybrid systems were considerably more amorphous in structure (in contrast to the more symmetric and obviously crystalline **{PW12}**-based material). These observations are mirrored in corresponding PXRD analyses of the materials, which show that the hybrid POM-IL 1 (as an example) lacks crystallinity at room temperature whilst the **{PW12}**-based material shows moderate crystallinity until heated beyond 130 °C, at which point it too becomes increasingly amorphous, even when cooled to room temperature (see SI).

Cyclic voltammetry was conducted on samples of **1**, **2** and **{PW12}** in acetonitrile, with [TBA][PF6] as the supporting electrolyte (Figure 3). The cyclic voltammogram (CV) of each species showed four clear redox couples in the potential range +0.2 V to −3.0 V. The ratio of the anodic to cathodic peak currents, *i*p,a/*i*p,c, was about 1 in each case, as expected for freely-diffusing species undergoing a mass-transport controlled faradaic reaction. The peak-to-peak separation for each couple was in the region of 70 to 100 mV, which is slightly higher than that expected for a fully electrochemically-reversible redox couple (59/*n*, where *n* is the number of electrons transferred during the redox reaction), indicating that sluggish electron transfer influenced the voltammetric responses. Comparison of the three CVs shows that the peak currents increased in the order **1** < **2** < **{PW12}**. This difference is due to the increased steric bulk of **1** and **2**, relative to that of **{PW12}**,which decreases the rate of mass transport of the hybrids to the electrode surface.

The CV of each species is similar to that obtained previously during cyclic voltammetry of the parent POMs (see SI), demonstrating that the redox behavior of the materials was dominated by the POM redox center, as expected. Figure 3a shows that **2** exhibited an additional redox couple centred at about −1.25 V. This can be attributed to the presence of the lacunary POM [PW11O39]7-, the hydrolysed decomposition product of the organophosphorus hybrid (Figure S18). The organophosphorus hybrid system exhibited the most positive first redox process, centred at −0.18 V vs Fc/Fc+. This is, to the best of our knowledge, amongst the most positive redox potentials ever observed in organic media for a polyoxotungstate cluster. The clear shift of the redox potential of the hybrid demonstrates the impact of hybridisation on the LUMO energy of the redox center. That the LUMO energy can be readily tuned using facile synthetic approaches offers significant scope for the use of these strategies in the development of redox species for bespoke catalytic applications.

Conclusions

Two novel organic-inorganic hybrid polyoxometalate ionic liquids (POM-ILs) were synthesized and found to exhibit contrasting physical properties to their plenary analogues, due to the nature

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| |  |  |  |  |  | | --- | --- | --- | --- | --- | | **Table 1.** Observed mid-point redox potentials (*E*) and peak-to-peak separations (*E*) for Compounds **1**, **2** and **{W12}**.[a] | | | | | |  | *E*1/V (*E*1) | *E2*/V (*E*2) | *E3*/V (*E*3) | *E4*/V (*E*4) | | **{PW12}** | –0.67 (0.08) | –1.16 (0.07) | –1.90 (0.07) | –2.42 (0.07) | | **1** | –0.77 (0.10) | –1.29 (0.08) | –1.93 (0.08) | –2.35 (0.09) | | **2** | –0.19 (0.07) | –0.73 (0.09) | –1.40 (0.08) | –1.92 (0.09) | | [a] All potential reported vs Fc/Fc+. *E* = (*Ep,c* *+ Ep,a*)/2, where *Ep,c* = peak cathodic potential and *Ep,a* = peak anodic potential. | | | | | |



**Figure 3.** The anionic structures and cyclic voltammograms of a) **2**, b) **1**, c) **{PW12}**, collected for 0.25 mM solutions in MeCN with 0.1 M TBA(PF6) electrolyte, using a glassy carbon working electrode, a Pt wire counter electrode and Ag wire as reference electrode. All potentials are reported relative to that of the ferrocene/ferrocinium redox couple.

of the modified POMs. The two hybrid materials exhibited similar thermal stabilities and phase behaviors, due to the size, charge and surface potential energy of the polyoxometalate components, however their electrochemistry differed due to the electronic nature of the tether employed. Interestingly, the organophosphonate hybrid POM-IL exhibited dramatically improved thermal stability, relative to the potassium salt of the same anion. These dramatic improvements in stability clearly warrant further study as they may facilitate both the stabilization of new hybrid-POM complexes and the study of these hybrid-POM-IL materials in high-temperature applications. The independent tuneability of the physical and electronic nature of these POM-ILs make them especially attractive as bespoke catalyst/solvent systems and as electrolyte materials in energy storage and conversion applications. Our further work will explore their potential applications as tunable redox liquids.

Acknowledgements

The authors gratefully acknowledge support from the University of Nottingham. AJK thanks the EPSRC Centre for Doctoral Training in Sustainable Chemistry (EP/L015633/1) for his studentship.

**Keywords:** polyoxometalates • ionic liquids • redox properties • hybrid materials • thermal properties

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| COMMUNICATION | | | | |
| Two hybrid POM-ILs were formed by pairing bulky phosphonium cations with organosiloxane and organophosphonate-functionalized Keggin-type polyoxometalates. The hybrid POM-ILs were found to exhibit rich electrochemistry determined by the nature of the POM modification, and to be more thermally stable than their molecular precursors. |  |  |  | Redox Liquids  Alexander J. Kibler, Carmen Martín, Jamie M. Cameron, Agata Rogalska, Darren A. Walsh, Jairton Dupont, Graham N. Newton\*  Page No. – Page No.  Physical and electrochemical modulation of polyoxometalate ionic liquids via organic functionalization |
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