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Covalent polyoxomolybdate based hybrids with remarkable electron reservoir properties

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Abstract: A new polyoxomolybdate-based hybrid platform TBA$_4$[PMo$_{11}$O$_{39}${SnPhI}] is reported. The presence of a post-functionalisable iodo-aryl moiety allows the addition of a ferrocenyl moiety onto the POM. The electrochemical characterisation shows the effect of molybdenum on the electron reservoir properties of POM-based hybrids, which are further enhanced upon addition of acid.

Polyoxometalates (POMs) are a class of well-defined nanometre sized molecular oxides displaying a wide range of structures and atomic compositions.[1-3] A great variety of potential applications in catalysis, medicine, material science, molecular electronics stem from this diversity.[4-6] Mastering both the structure and the composition of these clusters is the key towards the control of their properties. Among the wide library of POMs structures, the Keggin anion $[XM_{12}O_{40}]^{n-}$ has been extensively studied, mostly in the tungstate and molybdate series (M = W and Mo respectively). Although the synthesis of these fully inorganic Keggin-type compounds is simple, they rapidly reach their limits when the addition of extra properties is sought. Moreover, their implementation into functional materials is mostly limited to methods based on electrostatic interactions,[7] causing problems in terms of leaching and sample-to-sample dispersion. To circumvent these issues, a major step towards the development of POM-based compounds has been the formation of post-functionalisable covalent organic-inorganic hybrids[8] giving access to well defined organic inorganic POM-based hybrid[9-12] or hybrid materials.[13-15] Indeed, the possibility to perform chemistry on the organic part brings virtually any functionality to close hand. In this context, we recently synthesized a family of organosilyl,[16-17] organotin[18-19] and organo germyl[15] polyoxotungstate-based platforms bearing one or two iodo aryl moieties. The synthesis of these hybrids relies on the insertion of an organo group-14 element (Si, Ge, Sn) to a monovacant POM. The iodo-aryl function provides a useful tool for post-functionalisation via organometallic cross coupling reactions.[17, 20] A large number of POM based hybrids have thus been synthesised. The

potential of these covalent hybrids for various applications such as artificial photosynthesis,[21] molecular self-healing[19] or molecular electronics[15] have been explored. In most cases, the redox properties of the POM are the core of their interest. Unfortunately, the first reduction process in the tungstate series generally occurs at low potentials, which is energetically expensive. Due to more accessible reduction processes (potentials generally shifted by +0.5 V compared to the tungstate analogues)[22] the molybdenum analogues are best suited for applications based on electronic properties.[23-25] However they are more labile and their vacant derivatives are less stable than their tungstate analogues, particularly in aqueous solutions. As a consequence, their derivatisation has been scarcely developed,[26-29] and to the best of our knowledge, no post-functionalisable hybrids of these electronically attractive polyoxomolybdates have been reported. In order to extend our methodology to the molybdate series we thus synthesised the iodoaryl functionalised hybrid TBA$_4$[PMo$_{11}$O$_{39}${Sn(p-C$_6$H$_4$I)}], named **TBA-K$^{Mo}_{Sn}$[I]**.[30]
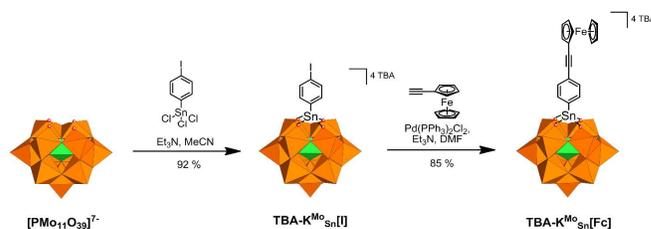
Scheme 1. Synthetic route to the POM hybrids TBA-K$^{Mo}_{Sn}$[I] and TBA-K$^{Mo}_{Sn}$[Fc].

Besides studying its electrochemical properties, we demonstrate the reliability of the post-functionalisation route by grafting a ferrocenyl moiety onto the POM. On top of the redox added value, this moiety allows us to comprehensively address the electrochemical behaviour of the POM hybrid under addition of protons. The mono-vacant derivative of the Keggin-type phosphomolybdate $[PMo_{11}O_{39}]^{7-}$ was prepared by basic degradation of $[PMo_{12}O_{40}]^{3-}$ and isolated as an

organic-solvent soluble tetrabutylammonium/proton mixed salt, following the procedure previously reported by C. L. Hill and coworkers.[26] This intermediate reacted with 1-iodo-4(trichlorotin)benzene in the presence of triethylamine to form the desired iodoaryl termimated platform $K^{Mo}_{Sn}[I]$ (Scheme 1). The presence of triethylamine is the key to avoid the formation of the complete $[PMo_{12}O_{40}]^{3-}$ anion under the acidification associated to the chloride ion release. After addition of an excess of tetrabutylammonium bromide in acetonitrile, $K^{Mo}_{Sn}[I]$ was isolated as a pure tetrabutylammonium salt by precipitation with a THF/diethyl ether mixture. Remaining mineral salts could be removed by thorough washing with water without degradation of the POM-based hybrid, attesting its resistance to hydrolysis when isolated as a tetrabutylammonium salt. Satellite peaks in the ^{31}P NMR spectrum (Fig. 1),due to the $^2J_{Sn-P}$ coupling of the central phosphorus atom with ^{117}Sn and ^{119}Sn, testifies the incorporation of the tin into the POM skeleton. The preservation of the POM structure has been confirmed by infrared spectroscopy. Integration of the ^1H NMR signals of the aryl group and comparison with that of the tetrabutylammonium counterions are indicative of a mono-functionalisation, which is further confirmed by mass spectrometry and elemental analysis.
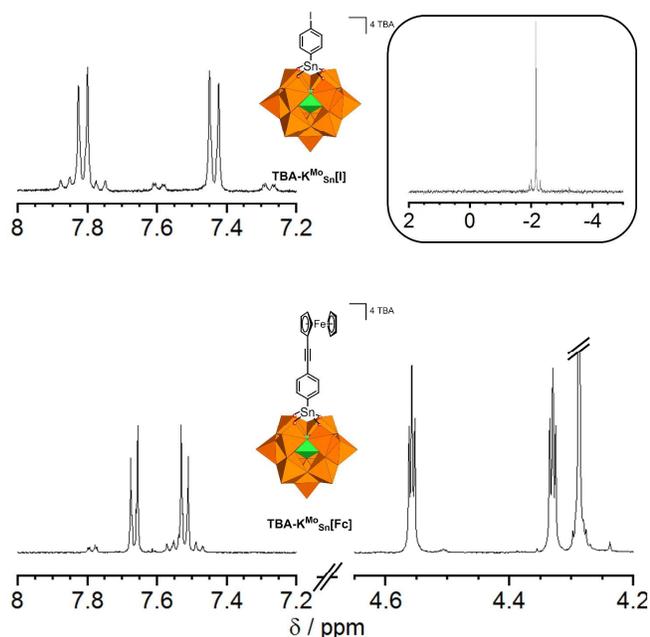
Figure 1. Enlargements of the NMR spectra of **TBA-K$^{Mo}_{Sn}$[I]** (^1H top left and ^{31}P top right, framed) and **TBA-K$^{Mo}_{Sn}$[Fc]** (^1H bottom). For full spectra, see Fig S1 and S3 in supporting information.

Cyclic voltammetry of **TBA-K$^{Mo}_{Sn}$[I]** in acetonitrile shows two quasi-reversible iso-electronic reduction waves at $E_{1/2} = -0.50$ and -0.92 V/SCE, that is 0.5 V shifted towards less negative potentials compared to those of the tungstate analogue (Fig 2).[21] The presence of protons is known to modify the redox behaviour of POMs as a consequence of a counter-cation exchange and proton assistance in the reduction processes.[22, 24, 31] Progressive addition of trifluoroacetic acid (TFA) in the solution of **TBA-K$^{Mo}_{Sn}$[I]** leads to a continuous positive shift of the reduction potentials, as well as an increase in current intensity due to multi-electronic processes (Table 1). Control over the quantity of added protons allows a precise tuning of the POM first reduction potential over the -0.5 to +0.42 V/SCE range. Whereas the redox potentials shift all along the addition of acid, the waves intensity stops increasing after the addition of *ca.* 10

equivalents of acid. Below 10 equivalents of TFA, the redox waves of the POM are ill-defined, $K^{Mo}_{Sn}[I]$ being present as a mixture of $TBA^+_{(4-x)}/H^+_x$ salts with different protonation states. After the addition of 125 equivalents of acid, three reduction waves at +0.42, +0.31 and +0.05 V/SCE are observed. ^1H, ^{31}P and IR spectroscopies confirmed the preservation of the POM structure after the addition of acid (Fig. S7 and S8).
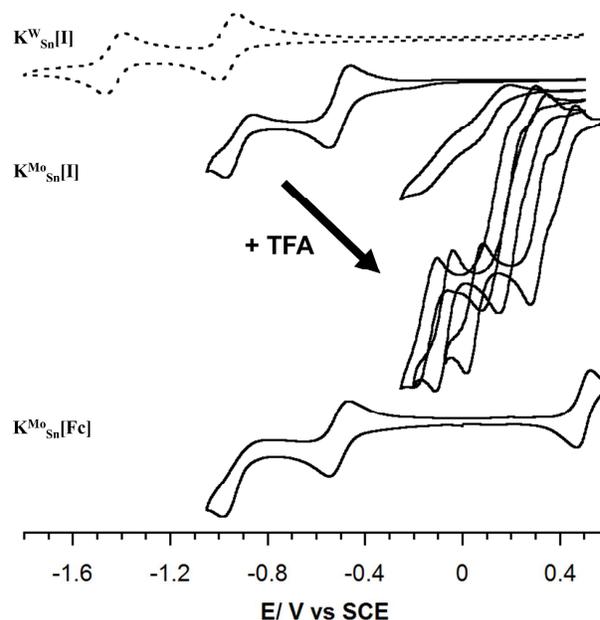
Figure 2. Cyclic voltammograms of **K$^{W}_{Sn}$[I]** (dashed), **K$^{Mo}_{Sn}$[I]** with 0, 2.5, 12.5, 25 and 125 eq of TFA (middle), and **K$^{Mo}_{Sn}$[Fc]** (bottom), 1 mM in MeCN containing 0.1 M TBAPF$_6$, scan rate 20 mV.s^{-1} (potentials are given versus SCE electrode)

In order to better understand the electrochemical behaviour of $K^{Mo}_{Sn}[I]$, the precise number of electrons exchanged along the POM reduction processes was determined by grafting a ferrocenyl moiety (Fc), as an internal redox reference, to the POM. Indeed the mono-electronic Fc oxidation wave is insensitive to the presence of protons. Moreover, its covalent attachment to the POM discards diffusion differences, ensuring an accurate interpretation of the voltammograms. The synthesis of the POM-Fc covalent hybrid was performed adapting a procedure developed in our group (Scheme 1). Sonogashira-type coupling between the iodoaryl platform **TBA-K$^{Mo}_{Sn}$[I]** and ethynyl allowed quantitative conversion of **TBA-K$^{Mo}_{Sn}$[I]** to the ferrocene-terminated derivative TBA$_4$[PMo$_{11}$O$_{39}${Sn(p-C$_6$H$_4$-C≡C-Fc)}], **TBA-K$^{Mo}_{Sn}$[Fc]**. ^1H (Fig 1), ^{31}P (Fig. S3) and IR spectroscopies are consistent with the isolation of **TBA-K$^{Mo}_{Sn}$[Fc]** as a pure compound. They are further supported by elemental analysis and mass spectrometry. The electrochemical behaviour of **K$^{Mo}_{Sn}$[Fc]** was then studied in acetonitrile. Besides the two reduction waves at $E_{1/2} = -0.50$ and -0.93 V/SCE, appearing at potentials similar to those of **TBA-K$^{Mo}_{Sn}$[I]**, cyclic voltammetry of **TBA-K$^{Mo}_{Sn}$[Fc]** in acetonitrile displays an oxidation wave at +0.50 V/SCE attributed to the ferrocenyl moiety (Fig. 2). This oxidation wave has a current-voltage profile similar to those of the two reduction waves, in agreement with monoelectronic processes centered on the POM framework. As previously described for the tungstate analogues, the redox properties of the POM and the organic fragment are fully decoupled.[17, 21, 32] Upon the progressive addition of acid, the electrochemical behaviour of **K$^{Mo}_{Sn}$[Fc]** follows the same trend as

that of the hybrid platform $\mathbf{K^{Mo}_{Sn}[I]}$ (Fig S5). After the addition of 50 equivalent of TFA, the first three reduction waves at +0.35, +0.25 and -0.09 V/SCE are twice more intense than the oxidation wave of the ferrocenyl moiety and can be thus clearly attributed to bi-electronic processes. Upon further addition of acid, as the shift of the POM reduction waves towards positive potentials increases, the first POM reduction and Fc oxidation waves start to overlap. After the addition of 250 equivalents of TFA, the first POM reduction and Fc oxidation waves are superimposed. Six electrons can then be stored in the POM at positive potentials (vs. SCE). The possibility to finely tune the reduction potentials of $\mathbf{K^{Mo}_{Sn}[Fc]}$ without modifying the oxidation potential of the ferrocenyl moiety is a way to tune the HOMO-LUMO gap of the molecule, foreshadowing applications in materials for molecular electronics.

Table 1. Redox properties of $\mathbf{K^{Mo}_{Sn}[I]}$ (1 mM in MeCN) upon addition of TFA.

TFA (eq. / POM)	$E_{1/2,1}$ (n e)	$E_{1/2,2}$ (n e)	$E_{1/2,3}$ (n e)
0	-0.50 (1)	-0.91 (1)	—
12.5	0.24 (2)	0.14 (2)	-0.14 (2)
25	0.30 (2)	0.20 (2)	-0.07 (2)
50	0.36 (2)	0.26 (2)	-0.01 (2)
125	0.42 (2)	0.31 (2)	0.05 (2)

We have described the synthesis of a new hybrid POM platform, **TBA-$\mathbf{K^{Mo}_{Sn}[I]}$**, based on a molybdenum Keggin-type backbone. The subsequent efficient grafting of the ferrocenyl moiety is a proof of the possibility to post-functionalise our platform, granting access to a versatile library of molecules with new properties. The interesting redox properties of the molybdenum-based hybrid can be further improved by the addition of acid, which produces a compound able to reversibly store six electrons at positive potentials (vs SCE). The wide range tunability of the POM reduction potentials makes the new POM hybrid appealing for applications in materials chemistry, especially in the field of molecular electronics. Its integration into materials through covalent immobilisation is currently under work.

Notes and references

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1. M. T. Pope, *Heteropoly and isopoly oxometalates*, Springer-Verlag, 1983.
2. M. T. Pope, in *Comprehensive Coordination Chemistry II*, eds. J. A. McCleverty and T. J. Meyer, Pergamon, Oxford, 2003, pp. 635.
3. M. T. Pope and A. Muller, *Angew. Chem. Int. Ed.*, 1991, **30**, 34.
4. C. L. Hill (Guest Ed.), *Thematic issue on polyoxometalates, Chem. Rev.*, 1998, **98**, 1.
5. D.-L. Long, E. Burkholder and L. Cronin, *Chem. Soc. Rev.*, 2007, **36**, 105.
6. A. Muller and L. Cronin (Guest Eds.), *Themed collection on polyoxometalate cluster science, Chem. Soc. Rev.*, 2012, **41**, 7325.
7. S. Liu and Z. Tang, *Nano Today*, 2010, **5**, 267.
8. A. Proust, B. Matt, R. Villanneau, G. Guillemot, P. Gouzerh and G. Izzet, *Chem. Soc. Rev.*, 2012, **41**, 7605.
9. C. Yvon, A. Macdonell, S. Buchwald, A. J. Surman, N. Follet, J. Alex, D.-L. Long and L. Cronin, *Chem. Sci.*, 2013, **4**, 3810.
10. I. Bar-Nahum, H. Cohen and R. Neumann, *Inorg. Chem.*, 2003, **42**, 3677.
11. S. Bareyt, S. Piligkos, B. Hasenknopf, P. Gouzerh, E. Lacôte, S. Thorimbert and M. Malacria, *J. Am. Chem. Soc.*, 2005, **127**, 6788.
12. Y. Zhu, L. Wang, J. Hao, P. Yin, J. Zhang, Q. Li, L. Zhu and Y. Wei, *Chem. Eur. J.*, 2009, **15**, 3076.
13. Y. Han, Y. Xiao, Z. Zhang, B. Liu, P. Zheng, S. He and W. Wang, *Macromolecules*, 2009, **42**, 6543.
14. M. Carraro, G. Fiorani, L. Mognon, F. Caneva, M. Gardan, C. Maccato and M. Bonchio, *Chem. Eur. J.*, 2012, **18**, 13195.
15. C. Rinfray, G. Izzet, J. Pinson, S. Gam-Derouich, J.-J. Ganem, C. Combellas, F. Kanoufi and A. Proust, *Chem. Eur. J.*, 2013, **19**, 13838.
16. B. Matt, S. Renaudineau, L. M. Chamoreau, C. Afonso, G. Izzet and A. Proust, *J. Org. Chem.*, 2011, **76**, 3107.
17. V. Duffort, R. Thouvenot, C. Afonso, G. Izzet and A. Proust, *Chem. Commun.*, 2009, 6062.
18. B. Matt, J. Moussa, L.-M. Chamoreau, C. Afonso, A. Proust, H. Amouri and G. Izzet, *Organometallics*, 2011, **31**, 35.
19. G. Izzet, M. Ménand, B. Matt, S. Renaudineau, L.-M. Chamoreau, M. Sollogoub and A. Proust, *Angew. Chem. Int. Ed.*, 2012, **51**, 487.
20. M. M. Lorion, B. Matt, S. Alves, A. Proust, G. Poli, J. Oble and G. Izzet, *Chem. Eur. J.*, 2013, **19**, 12607.
21. B. Matt, X. Xiang, A. L. Kaledin, N. Han, J. Moussa, H. Amouri, S. Alves, C. L. Hill, T. Lian, D. G. Musaev, G. Izzet and A. Proust, *Chem. Sci.*, 2013, **4**, 1737.
22. M. Sadakane and E. Steckhan, *Chem. Rev.*, 1998, **98**, 219.
23. N. Kawasaki, H. Wang, R. Nakanishi, S. Hamanaka, R. Kitaura, H. Shinohara, T. Yokoyama, H. Yoshikawa and K. Awaga, *Angew. Chem. Int. Ed.*, 2011, **50**, 3471.
24. K. Maeda, S. Himeno, T. Osakai, A. Saito and T. Hori, *J. Electroanal. Chem.*, 1994, **364**, 149.
25. R. Bakri, A. Booth, G. Harle, P. S. Middleton, C. Wills, W. Clegg, R. W. Harrington and R. J. Errington, *Chem. Commun.*, 2012, **48**, 2779.
26. L. A. Combs-Walker and C. L. Hill, *Inorg. Chem.*, 1991, **30**, 4016.
27. M. Rusu, L. Muresan, A. R. Tomsab, D. Rusuc and G. Marcua, *Synth. React. Inorg. Met.-Org. Chem.*, 2000, **30**, 499.
28. R. Neumann and M. Dahan, *Polyhedron*, 1998, **17**, 3557.
29. D. M. Fernandes, L. Cunha-Silva, R. A. S. Ferreira, S. S. Balula, L. D. Carlos, B. de Castro and C. Freire, *RSC Adv.*, 2013, **3**, 16697.
30. Acronyms used for the hybrid POMs: TBA stands for the tetrabutylammonium counter cations, K refers to the Keggin-type anion, Mo or W as superscript indicates the metal of the POM backbone, Sn as subscript relates to the primary functionalization and the term in brackets corresponds to the pending reactive function.
31. S.-X. Guo, A. W. A. Mariotti, C. Schlipf, A. M. Bond and A. G. Wedd, *Inorg. Chem.*, 2006, **45**, 8563.
32. B. Matt, C. Coudret, C. Viala, D. Jouvenot, F. Loiseau, G. Izzet and A. Proust, *Inorg. Chem.*, 2011, **50**, 7761.

Table of Content Entry

The molybdenum core confers enhanced redox properties to hybrid POM platforms further improved in the presence of acid