CrystEngComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: P. G. P. Reddy, N. Mamidi and C. P. Pradeep, *CrystEngComm*, 2016, DOI: 10.1039/C5CE02546J.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/crystengcomm

View Article Online
DOI: 10.1039/C5CE02546J

Journal Name

COMMUNICATION

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

An organic-inorganic hybrid supramolecular framework material based on $[P_2W_{18}O_{62}]^{6-}$ cluster and Yb & Na complexes of pyridine 2,6-dicarboxylic acid: a catalyst for selective oxidation of sulfides in water with H_2O_2†

Pulikanti Guruprasad Reddy, Narsimha Mamidi and Chullikkattil P. Pradeep*

A rare earth contained polyoxometalate (RECP) hybrid, $\{(Yb(PDCH_2)_2(PDCH))\cdot Na(H_2O)_2\cdot(Na(PDCH)(H_2O)_2)\}_2[P_2W_{18}O_{62}]\cdot 14H_2O$ (1) based on $[P_2W_{18}O_{62}]^{6-}$ cluster anions and cationic Yb & Na complex units of pyridine 2,6-dicarboxylic acid ($PDCH_2$) has been synthesized under normal reaction conditions, which exhibited supramolecular 3-D framework structure in the crystal lattice. Hybrid 1 acts as a green catalyst for the selective oxidation of sulfides in water with H_2O_2 as the reagent.

Polyoxometalates (POMs) are a class of inorganic materials consisting of discrete, soluble, anionic oxide clusters of early transition metals like Mo, W, V, Nb and Ta.[1] Incorporation of rare earth (RE) ions into POM framework enhances their properties including Lewis acidity, polarity, solubility and electron transfer properties leading to their improved applications in materials science and catalysis.[2] A large number of RECPs reported over the last few decades have been reviewed recently and it was noted that a majority of these RECPs are purely inorganic in nature.[3] Therefore, the development of novel organic–inorganic hybrid RECPs has been projected as one of the potential new research directions in RECP chemistry.[3] Using appropriate multi-functional organic ligands, novel organic–inorganic hybrid RECPs or high-dimensional frameworks with new properties could be achieved.[4] However, the synthesis and characterization of new hybrid RECPs is a challenging task as the oxophilic lanthanides often react rapidly with oxygen rich POM units resulting in quick precipitation. Therefore, the development of new synthetic strategies that allow the isolation of crystalline hybrid RECPs is of fundamental importance. Also, synthetic procedures that allow disassembly and re-assembly of POM building units during synthesis are important as they lead to totally new structural assemblies.[5] In terms of materials applications, RECP hybrids containing large plenary POM units are of special interest as larger clusters exhibit better redox properties in comparison to smaller cluster archetypes.[6] Nevertheless, RECP hybrids based on large plenary clusters like $[P_2W_{18}O_{62}]^{6-}$ ({P2W18}) are rare in the literature.[7]

Meanwhile, the development of green reaction methodologies is one of the focus areas in synthetic organic chemistry. Synthetic protocols relying on environment friendly solvents and reagents are of prime importance in view of environmental safety. Particularly, reactions that use water as solvent have great advantages.[8] Selective oxidation of sulfides is an important reaction in organic chemistry because of the versatile roles of sulfoxides in pharmaceuticals, petroleum industry, polymer materials, asymmetric catalysis, natural products and oxygen transfer reagents.[9] Sulfoxidation is generally achieved by using oxidizing agents like m-chloroperbenzoic acid, $NaIO_4$, UHP, NaClO, dimethyldioxirane and oxone; many of which are known to exhibit undesirable traits like toxicity, by-product generation, longer reaction times, low yields etc.[10] Therefore, development of new methodologies for sulfoxidation using eco-friendly solvents and reagents such as water and H_2O_2 would be of considerable interest.[11]

Here in, we report a simple and flexible synthetic procedure in which coordination complex of a lanthanide metal ion (Yb) was prepared starting from a multidentate carboxylate ligand (pyridine-2,6-dicarboxylic acid, $PDCH_2$) in water, which on in situ reaction with a lacunary POM building block $[P_2W_{15}O_{56}]^{12-}$ generated a new organic-inorganic hybrid RECP $\{(Yb(PDCH_2)_2(PDCH))\cdot Na(H_2O)_2\cdot(Na(PDCH)(H_2O)_2)\}_2[P_2W_{18}O_{62}]\cdot 14H_2O$ (**1**) containing a plenary POM cluster {P2W18} (PDCH denotes singly deprotonated $PDCH_2$). Under the present reaction conditions, the lacunary POM building block $[P_2W_{15}O_{56}]^{12-}$ gets transformed into a plenary cluster {P2W18}. Hybrid **1** exhibits an interesting supramolecular framework structure in solid state assembled through H-bonding interactions between the cluster oxygens and $PDCH_2$/PDCH units of Yb & Na complexes. Catalytic property of hybrid **1** towards the oxidation of a variety of sulfides under green reaction conditions has also been tested.

---

[a] *School of Basic Sciences, Indian Institute of Technology Mandi, Mandi - 175001, Himachal Pradesh, India*

E-mail: pradeep@iitmandi.ac.in; Fax: (+91)1905 267 009

† Electronic Supplementary Information (ESI) available: [Synthetic details and characterization data are available in Electronic Supplementary Information]. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C5CE02546J

The synthetic scheme of hybrid **1** is shown in Figure 1. Hybrid **1** was characterized by various analytical and spectroscopic techniques including IR, UV-visible, EDX, thermo gravimetric analyses (TGA) and single crystal X-ray diffraction studies, see ESI† for details.

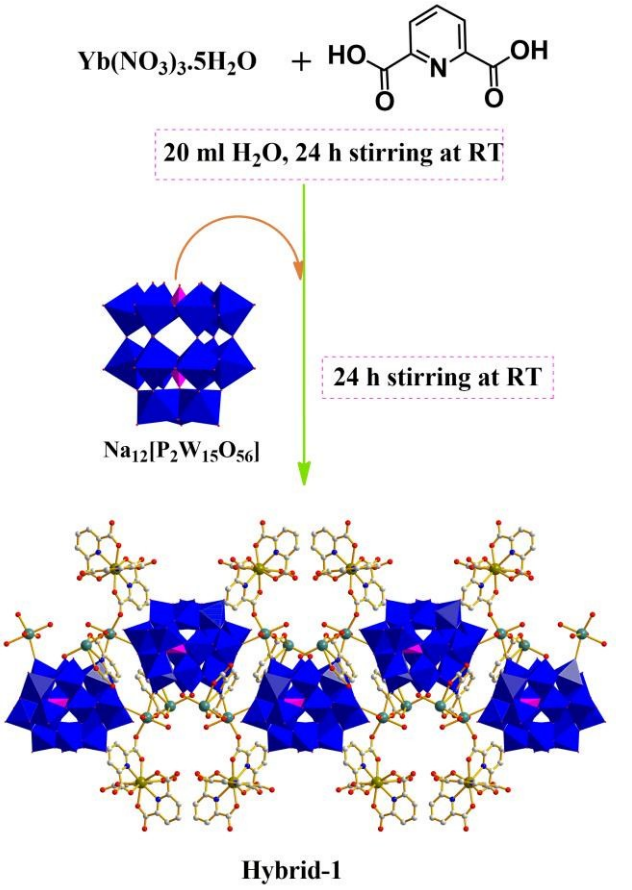


Figure 1. Synthetic route of hybrid **1**. Colour code: WO_6 - dark blue polyhedra, PO_4 – pink polyhedra, Na – cyan, Yb - pale green, C - grey, O - red and N - blue.

The single crystal X-ray analysis revealed that hybrid **1** crystallizes in monoclinic C2/*c* space group, see ESI† Table S1 for crystallographic data and Table S2 for selected bond lengths and angles. The asymmetric unit consists of a) half of the {P2W18} cluster anion, b) a cationic complex $\{(Yb(PDCH_2)_2(PDCH))\cdot Na(H_2O)_2\cdot(Na(PDCH)(H_2O)_2)\}^{3+}$ (**cat^{3+}**) and c) seven water molecules. Major contents of the asymmetric unit are shown in Figure 2(A). Out of the four $PDCH_2$ units present in **cat^{3+}**, two are singly de-protonated.

As shown in Figure 2, the structure of hybrid **1** can be thought of as consisting of two major structural sub-units: {P2W18} polyanions and **cat^{3+}** cations. The {P2W18} polyanion in hybrid **1** exhibits the classical Wells–Dawson structure, containing two α-A-$[PW_9O_{34}]^{9-}$units originating from the α-Keggin polyoxoanion by removal of a suite of three corner-sharing WO_6 octahedra. The structure of **cat^{3+}** subunit (Figure 2 (B)) consists of two differently coordinated sodium ions. The central six coordinated sodium ion (Na1) is connected to a Yb complex ion $[Yb(PDCH_2)_2(PDCH)]^{2+}$ on one side and to a sodium complex $(Na(PDCH)(H_2O)_2)$ on the other. Additionally, Na1 is

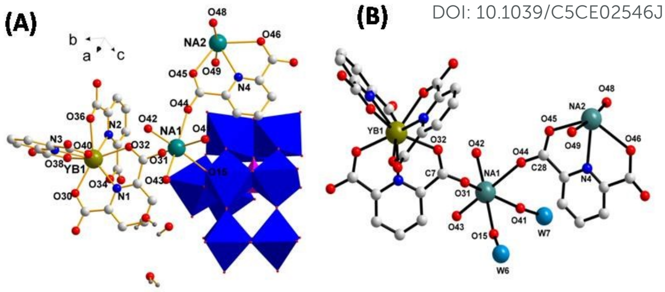


Figure 2. Asymmetric unit of hybrid **1**, (**A**); cationic complex $\{(Yb(PDCH_2)_2(PDCH))\cdot Na(H_2O)_2\cdot(Na(PDCH)(H_2O)_2)\}^{3+}$ (**cat^{3+}**) (**B**). All hydrogens have been omitted for clarity. Colour code: WO_6 - dark blue polyhedra, PO_4 – pink polyhedra, Na - cyan, Yb - pale green, C - grey, O - red and N - blue.

connected to the terminal oxygens (O15 and O41) of two {P2W18} units and hence act as a bridging unit between two adjacent {P2W18} structural sub-units. The remaining two coordination sites of Na1 are satisfied by water molecules. In the Yb complex ion $[Yb(PDCH_2)_2(PDCH)]^{2+}$, each of the three ligands (of which one is singly deprotonated) coordinate to the Yb center through two carbonyl oxygens and pyridine nitrogen in the expected tridentate coordination mode resulting in a tricapped trigonal prismatic Yb complex having D_{3h} symmetry as shown in Figure 3(B). This type of coordination geometry is common for nine-coordinated Ln(III) complexes with tris chelated tridentate ligands.[12] The coordinated carbonyl oxygen atoms from the three $PDCH_2$/PDCH ligands form the two trigonal faces of the trigonal prism defined by the atoms {O30, O34, O38} and {O32, O36, O40} while the coordinated pyridine nitrogens (N1, N2, and N3) form a plane perpendicular to the molecular C_3 axis. The trigonal faces of the trigonal prism are almost parallel, being inclined by ca. $\angle 1.2°$. The distortion from the ideal D_{3h} symmetry arises due to a rotation of the trigonal faces with respect to each other about the C_3 axis, by ca. 15°. The Yb complex ion present in hybrid **1** is structurally very similar to some of the previously reported Ln(III) complexes based on $PDCH_2$ based ligands.[12] The sodium center Na2 is penta coordinated with one PDCH ligand coordinated to Na2 in tridentate manner. The remaining coordination sites of Na2 are satisfied by two water molecules, see Figure 2(B).

In the crystal structure of hybrid **1**, each {P2W18} cluster unit is connected to four **cat^{3+}** moieties as shown in Figure 3(C). However, each of these **cat^{3+}** units is shared between two adjacent {P2W18} cluster units. Therefore, in effect, there are two **cat^{3+}** units per {P2W18} cluster anions in hybrid **1** balancing the charge. In the crystal lattice, each {P2W18} building unit is connected to two adjacent {P2W18} units on either side through bridging **cat^{3+}** units in a zig-zag 1-D chain fashion as shown in Figure 3(D). Each of these independent chains are further connected to its neighbouring chains in a 3-D manner through extensive hydrogen bonding interactions between the {P2W18} cluster oxygens and the organic $PDCH_2$/PDCH ligands of the Yb & Na complexes. The details of these H-bonding interactions are given in Table S3, ESI†. The formation of 1-D zig-zag chains from {P2W18} units through bridging **cat^{3+}** units and the inter-connection of these chains in 3-D manner through

View Article Online
DOI: 10.1039/C5CE02546J

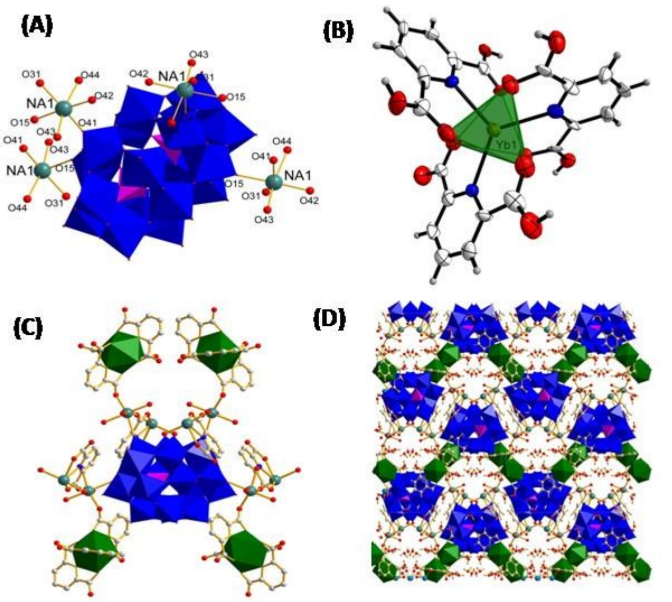
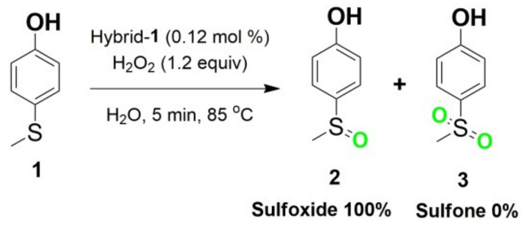


Figure 3. Coordination modes of $\{P_2W_{18}\}$ with NA1 atom, (**A**); Yb complex $[Yb(PDCH)_2(PDC)]^{2+}$, **(B**); figure showing {P2W18} unit connected to four **cat**$^{3+}$ units, the Yb complex is shown as green polyhedra, **(C);** zig-zag 1-D chain-like arrangement of $\{P_2W_{18}\}$ units in hybrid **1**, **(D)**. Colour code: WO_6 - dark blue polyhedra, PO_4 – pink polyhedra, Na - cyan, Yb – dark green, C - grey, O - red and N - blue.

various H-bonding interactions lead to the formation of a 3-D supramolecular framework structure in the crystal lattice of hybrid **1** as shown in Figure 3(D). Solvent water molecules occupy the void space in the framework structure. The total void volume of the structure is calculated to be 14.28 %.[13]

Framework structures based on Keggin or octamolybdate clusters, $PDCH_2$ based ligands and RE metal ions have been achieved earlier through hydrothermal synthetic methods.[14] However, the formation of organic-inorganic hybrid supramolecular 3-D framework structures based on plenary {P2W18} clusters and RE complexes under conventional reaction conditions is rarely reported in the literature.



Scheme 1. Optimized model catalytic reaction: sulfoxidation of 4-(methylthio)phenol using hybrid **1** as catalyst.

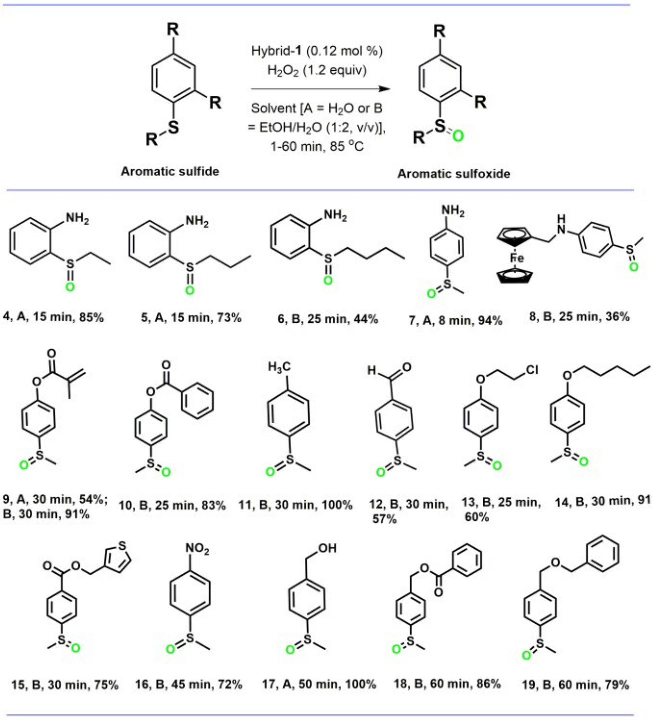
Catalytic studies

POMs and their derivatives are known to act as oxidation catalysts while a few POM hybrids have also been reported as sulfoxidation catalysts.[15] As hybrid **1** is soluble in water, we decided to explore its homogeneous catalytic activity towards the selective oxidation of various sulfides in water solvent. The catalytic experimental conditions were optimized using the oxidation of 4-(methylthio)phenol by H_2O_2 as a model reaction, see Scheme 1. Various optimization studies showed that 0.012 mol % of catalyst at 85 ^{o}C reaction temperature was enough to afford the sulfoxide products in very good yields and selectivity. In absence of the oxidizing agent H_2O_2, there was no reaction whereas the absence of catalyst led to poor yields (29%). These results showed that both H_2O_2 and catalyst are indispensable for the optimum yield of the products. The catalytic capabilities of the constituents of hybrid **1**, i.e. $Na_{12}[P_2W_{15}O_{56}]$, $PDCH_2$ and $Yb(NO_3)_3{\cdot}5H_2O$ as well as {P2W18} cluster, were also tested as controls and were found to exhibit less catalytic abilities than hybrid **1** under the given experimental conditions. These studies revealed that the hybrid **1** as a whole has better catalytic efficiency as compared to its constituents taken separately, see Table S4, ESI† for details. The catalytic oxidation of 4-(methylthio)phenol using $[P_2W_{15}O_{56}]^{12-}$ in combination with sodium salt of $PDCH_2$ was also tested in order to assess the role of lanthanide ion in the catalysis. It was noted that a combination of these starting materials gave poor yields and selectivity in comparison to hybrid **1** confirming the influential role of the lanthanide ion in the catalytic property exhibited by hybrid **1**, see Table S4, ESI†.

After optimization of the reaction conditions, we tested successfully a variety of sulfides for sulfoxidation using hybrid **1** as catalyst, see Table 1. The results show that hybrid **1** catalyses the sulfoxidation of sulfides bearing varying functional groups - from electron-withdrawing ester group to electron-donating hydroxyl group - producing the desired sulfoxides in moderate to excellent yields with good selectivity. For water insoluble substrates, ethanol-water mixed solvent system was found to be useful. The substrates bearing electron-donating functional groups were found to give better yields than those with electron-withdrawing groups, see Table 1. It was also noted that hybrid **1** is useful for the selective oxidation of sulfide functional group in substrates bearing additional functional groups such as thiophene, $-CH_2OH$, $-NH_2$ etc. Oxidation of such additional functional groups along with sulfide moiety was reported earlier in similar catalytic sulfoxidation reactions.[15] However, in the present case, we did not observe such additional oxidations, see Table 1, entry numbers 15 and 17.

A possible mechanism for the oxidation of sulfides using hybrid **1** as catalyst is given in ESI† Figure S5, which is in accordance with similar reports.[15(a)] The interaction of H_2O_2 with POM cluster generates an electrophilic intermediate which leads to an electrophilic attack on the S atom of the sulfide generating the corresponding sulfoxide, ESI† Figure S5. However, time dependant product analyses suggest the formation of sulfone with time indicating the participation of sulfoxide formed in the reaction as a substrate. The mechanism for the oxidation of sulfoxide to sulfone involves the formation of a POM-sulfoxide intermediate through the nucleophilic attack on W atom of the POM unit by the oxygen of the sulfoxide followed by a nucleophilic attack by H_2O_2 on the sulfur atom in POM-sulfoxide intermediate, see see ESI† Figure S5. The selectivity and efficiency of such reactions are susceptible to different reaction parameters.[15] We believe that the optimized reaction conditions employed in the current study promotes the selective formation of sulfoxides over sulfones as presented in Table 1 and in ESI†, Table S4. Moreover, the incorporation of POM units into porous framework structures are known to increase their catalytic performances due to the improvement in their specific surface area, stability under catalytic conditions etc.[16] Probably, this could be one of the reasons behind the improved catalytic performance of hybrid **1** as compared to the individual POM building units. The catalytic recyclability of hybrid **1** was tested using the oxidation of 4-(methylthio)phenol as a model reaction. These studies suggested that hybrid **1** could be reused for at least three times without significant reduction in catalytic activity, see ESI† Table S5, Figure S6.

Table 1. Selective oxidation of various sulfides under optimized reaction conditions



Conclusions

Herein, we have reported a simple and flexible synthetic procedure to develop a new organic-inorganic hybrid supramolecular 3-D framework RECP based on Yb & Na cationic complex units of pyridine 2,6-dicarboxylic acid and plenary Wells-Dawson type cluster anions $[P_2W_{18}O_{62}]^{6-}$. In the framework structure, $[P_2W_{18}O_{62}]^{6-}$ cluster building units are connected together in a zig-zag 1-D chain fashion by bridging cationic complex units which in turn are inter-connected through H-bonding interactions leading to the formation of a supramolecualr 3-D framework structure. Hybrid **1** was found to act as a selective oxidation catalyst for a variety of sulfides including those having additional interfering functional groups like thiophene, $-CH_2OH$, $-NH_2$ etc. under safe, mild and greener reaction conditions.

Acknowledgements

C. P. P. thanks SERB, New Delhi for funds under the fast track scheme (Grant No: SR/FT/CS-58/2011) and IIT Mandi for infrastructural facilities (AMRC, IIT Mandi) as well as financial support through Seed Grant.

Notes and references

1 (a) *Polyoxometalate Chemistry from Topology via Self-Assembly to Applications*, ed. M. T. Pope and A. Müller, Kluwer Academic Publishers, Dordrecht, Netherlands, 2001; (b) D.-L. Long, R. Tsunashima and L. Cronin, *Angew.Chem. Int. Ed.,* 2010, **49**, 1736.

2 (a) B. S. Bassil, M. H. Dickman, I. Römer, B. von der Kammer and U. Kortz, *Angew. Chem. Int. Ed.,* 2007, **46**, 6192; (b) T. Yamase, *Chem. Rev.,* 1998, **98**, 307; (c) C. Ritchie, E. G. Moore, M. Speldrich, P. Kögerler and C. Boskovic, *Angew. Chem. Int. Ed.,* 2010, **49**, 7702.

3 X. Ma, W. Yang, L. Chen and J. Zhao, *CrystEngComm,* 2015, **17**, 8175.

4 (a) D.-Y. Du, J.-S. Qin, S.-L. Li, Z.-M. Su and Y.-Q. Lan, *Chem. Soc. Rev.,* 2014, **43**, 4615; (b) M. P. Santoni, G. S. Hanan and B. Hasenknopf, *Coord. Chem. Rev.,* 2014, **281**, 64; (c) X. Feng, Y. Q. Feng, J. J. Chen, S. W. Ng, L.-Y. Wang and J. -Z. Guo, *Dalton Trans.,* 2015, **44**, 804.

5 X. –J. Feng, H. –Y. Han, Y. –H. Wang, L. –L. Li, Y. –G. Li and E. –B. Wang, *CrystEngComm*, 2013, **15**, 7267.

6 M. Góral, T. McCormac, E. Dempsey, D.-L. Long, L. Cronin and A. M. Bond, *Dalton Trans*., 2009, 6727.

7 Y. –Q. Jiao, C. Qin, H. –Y. Zang, W. –C. Chen, C. –G. Wang, T. –T. Zheng, K. –Z. Shao and Z. –M. Su, *CrystEngComm*, 2015, **17**, 2176.

8 C.-J. Li and T.-H. Chan, *Comprehensive Organic Reactions in Aqueous Media*, Wiley, New York, 2007.

9 (a) I. Fernández and N. Khiar, *Chem. Rev.,* 2003, **103**, 3651; (b) (c) J. E. Backvall, *Modern Oxidation Methods*, 2nd ed. Wiley-VCH, Weinheim, Germany, 2010.

10 (a) N. K. Jana and J. G. Verkade, *Org. Lett.,* 2003, **5**, 3787; (b) R. S. Varma, R. K. Saini and H. M. Meshram, *Tetrahedron Lett.,* 1997, **38**, 6525; (c) N. Fukuda and T. Ikemoto, *J. Org. Chem.,* 2010, **75**, 4629; (d) B. Yu, A.-H. Liu, L.-N. He, B. Li, Z.-F. Diao and Y.-N. Li, *Green Chem.,* 2012, **34**, 957.

11 R. Noyori, M. Aoki and K. Sato*, Chem. Commun.*, 2003, 1977.

12 E. G. Moore, J. Grilj, E. Vauthey and P. Ceroni, *Dalton Trans.,* 2013, **42**, 2075.

13 T. L. Spek, *Acta Cryst*., 1990, **A46**, c34.

14 (a) M. Mirzaei, H. Eshtiagh-Hosseini, N. Lotfian, A. Salimi, A. Bauzá, R. V. Deun, R. Decadt, M. Barceló-Oliver and A. Frontera, *Dalton Trans.,* 2014, **43**, 1906; (b) J. Lu, E. Shen, Y. Li, D. Xiao, E. Wang and L. Xu, *Cryst. Growth & Des.,* 2005*,* **5**, 65.

15 (a) R. Frenzel, Á. G. Sathicq, M. N. Blanco, G. P. Romanelli and L. R. Pizzio, *J. Mol. Catal. A: Chem.,* 2015, **403**, 27; (b) M. Amini, H. Naslhajian, S. M. F. Farnia and M. Hołyńska *Eur. J. Inorg. Chem.,* 2015, 3873; (c) E. Rafiee and F. Mirnezami, *J. Mol. Liq.,* 2014, **199**, 156; (d) F. Jalilian, B. Yadollahi, M. R. Farsani, S. Tangestaninejad, H. A. Rudbari and R. Habibi, *Catal. Commun.,* 2015, **66**, 107; (e) A. Rezaeifard, R. Haddad, M. Jafarpour and M. Hakimi, *ACS Sustainable Chem. Eng.,* 2014, **2**, 942.

16 X.-L. Hao, Y.-Y. Ma, H.-Y. Zang, Y.-H. Wang, Y.-G. Li and E.-B. Wang, *Chem. Eur. J.*, 2015, **21**, 3778.

View Article Online
DOI: 10.1039/C5CE02546J

Table of Content

A Yb containing polyoxometalate organic hybrid framework material has been achieved which catalyzes the selective oxidation of a variety sulfides under green reaction conditions.