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Postfunctionalization of Polyoxometalates: An Efficient Strategy to Construct Organic-inorganic Zwitterionic

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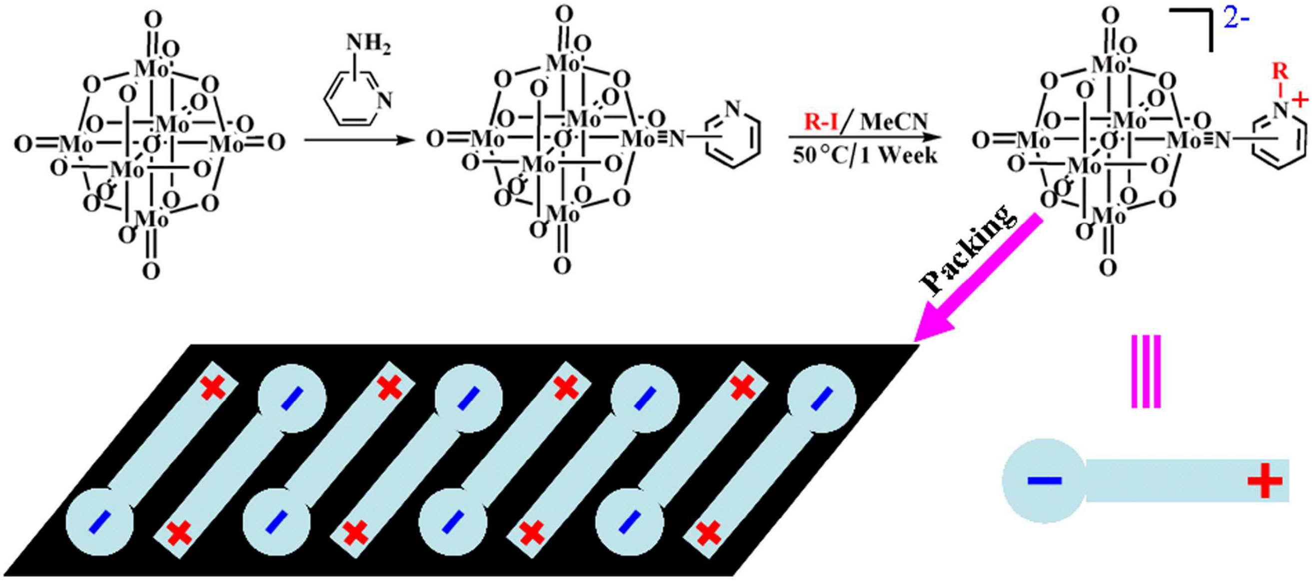

A class of monoorganoimido-substituted hexamolybdates containing a pyridine group have been firstly synthesized. Furthermore, a reaction protocol of alkylation based on the resulting pyridine-functionalized hexamolybdates has been developed, with which a type of zwitterionic clusters have been successfully obtained.

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A class of monoorganoimido-substituted hexamolybdates containing a pyridine group have been firstly synthesized. Furthermore, a reaction protocol of alkylation based on the resulting pyridine-functionalized hexamolybdates has been developed, with which a type of zwitterionic clusters have been successfully obtained.

Zwitterions represent a unique class of compounds, in which a negatively charged moiety and a positively charged moiety are connected covalently. The ionic feature of zwitterionic compounds arising from the charged components promotes its solubility, a common example is the amino acid widely existing as zwitterion in biologic systems. On the other hand, contrast to ionic compounds the covalent connection between the positive and negative charge centre gives rise to a permanent dipole moment in these zwitterionic compounds, resulting in directional intermolecular interactions which are widely used in supramolecular assemblies[1-3] and catalysts.[4,5] To design zwitterionic compounds, positively charged aminomium, phosphonium and metal complexes are usually used as the cationic fragment while negatively charged carboxylate, sulfate, sulfonate, phosphate, borate, niobate and carbanion are often chosen for the anionic fragment.[1,4,6] In this sense, polyoxometalates (POMs)[7] which are a rich class of anionic metal-oxide cluster should be good building blocks to construct organic-inorganic zwitterionic clusters via the functionalization of POMs.

The functionalization of POMs via covalent bonds has given much focus in the past decades,[8] because of the potential applications of the resulting products in catalysis,[8a,9] and material science.[8a,10] Especially, the imidoylization, which has been proved to be an efficient and important approach towards the covalent organic functionalization of POMs, has received continuous interest[8a,8c,11] due to the anionic inorganic cluster and the organic moieties linked by metal-nitrogen multiple bonds, resulting in synergistic effect between the inorganic cluster and organic fragments.[12] Till now, in addition to the development of four methods for the functionalization of POMs with organoimido ligands[13-16], a large number of organoimido derivatives of POMs containing remote halo, ethenyl, ethynyl, nitro, amino, hydroxyl and terpyridine have been reported.[11] However, to the best of our knowledge, pyridine-functionalized POMs via metal-nitrogen multiple bonds have rarely been investigated. More importantly, these pyridine-functionalized hexamolybdates are good precursors to construct zwitterions via an alkylation at the heterocyclic nitrogen atom, in order to afford needed properties.

At the beginning, we tried to obtain the zwitterionic cluster by the direct imidoylization of hexamolybdate with hetero N-alkylated pyridinium functionalized with an amino group over the heterocycle. However, this effort failed because the alkylation of heterocyclic nitrogen not only decreased the solubility of the resulting pyridinium salts in acetonitrile but also decreased the reactivity of amino group in the heterocyclic ring. Therefore, an alternative synthetic strategy, namely, the postfunctionalization of the resulting pyridine-functionalized hexamolybdate is taken into account. Actually, much effort has been devoted to the postfunctionalization of hybrid POMs,[8a,8c] and till now, several approaches which include click reaction,[17] Sonogashira coupling reaction,[18] Heck coupling reaction,[19] Diels-Alder reaction,[20] esterification,[21] imidization,[22] amidation[23] as well as oxidation of an alcohol group and reduction of an aldehyde group[20] on functionalized POMs have been developed. Keeping in view all the available methods, in this current work we firstly synthesized a class of pyridine-functionalized hexamolybdates and then explored their alkylation at the heterocyclic nitrogen site, giving rise to a type of zwitterionic clusters, shown in Scheme 1.

A reaction of the hexamolybdate ion with 3-methyl-2-aminopyridine, 3-aminopyridine or 4-aminopyridine in the ratio of

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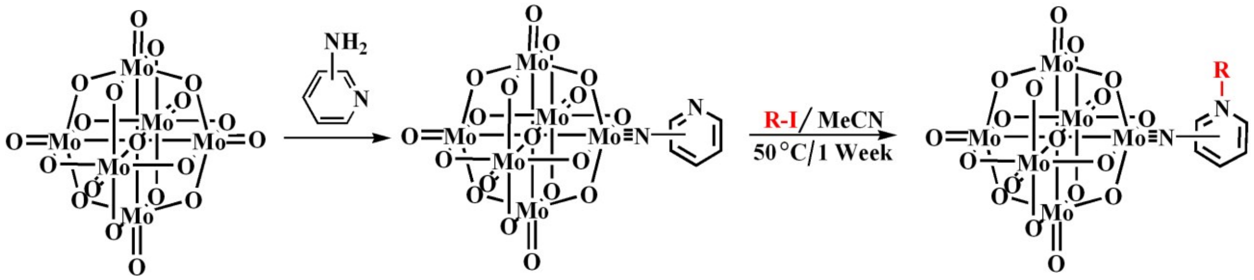
1:1 using the well-established DCC protocol can give rise to the corresponding monosubstituted organoimido derivatives. ORTEP viewing of the cluster anions within these compounds are shown in Fig. 1. It can be seen that one terminal oxo atom (O_t) of the hexamolybdate cluster has been replaced by one organoimido ligand. The Mo–N bonds are found to be 1.721 (1.726), 1.702 and 1.728 Å in compounds **Mo$_6$-Me-2Py**, **Mo$_6$-3Py** and **Mo$_6$-4Py**, respectively, and the nearly linear Mo–N–C angles are respectively refined as 177.9° (176.5°), 170.9° and 157.8°, indicating triple bond has formed between the Mo and bounded N atoms.



Scheme 1 Alkylation of pyridine-functionalized hexamolybdate with iodoalkanes.

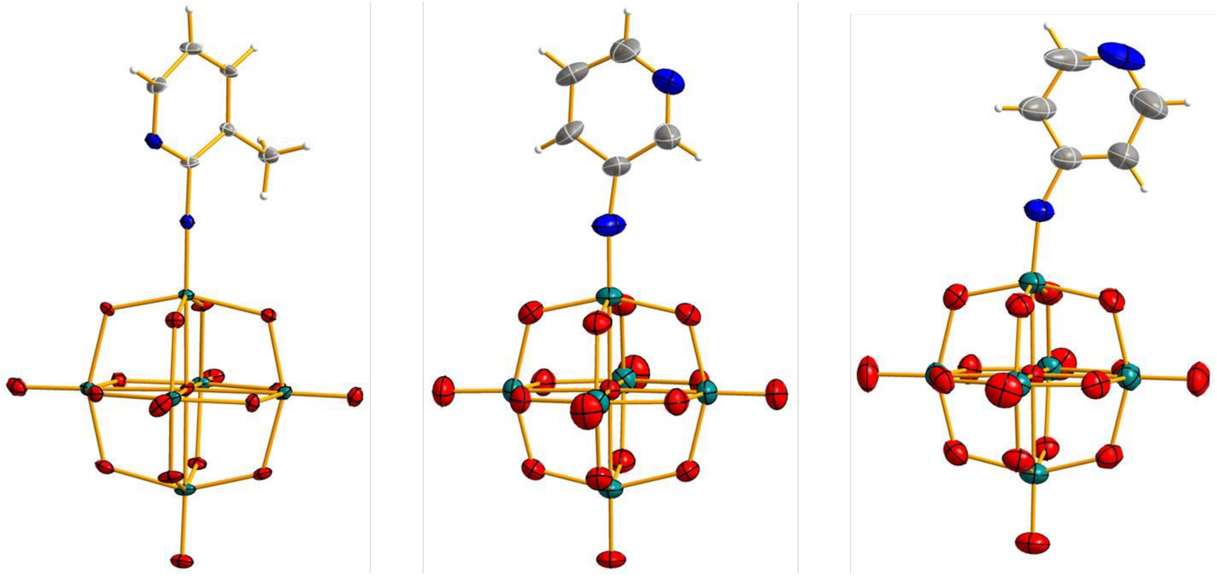


Fig. 1 ORTEP viewing of the cluster anions within compounds Mo6-Me-2Py (left), Mo6-3Py (middle) and Mo6-4Py (right) (25% probability ellipsoids) Mo teal, O red, N blue, C gray, H white.

To investigate the nucleophilicity of the heterocyclic nitrogen, the natural charge at the heterocyclic nitrogen atom in compounds **Mo$_6$-Me-2Py**, **Mo$_6$-3Py** and **Mo$_6$-4Py** has been calculated using DFT-B3LYP method[24,25] (for details see ESI). As can be seen from Table 1, compared to that in free aminopyridine ligands, the natural negative charge at the heterocyclic nitrogen atom decreased to -0.4652 in compound **Mo$_6$-Me-2Py** while increased to -0.4734 and -0.4997 in compounds **Mo$_6$-3Py** and **Mo$_6$-4Py**, respectively, indicating the order of the nucleophilicity of the heterocyclic nitrogen atom is **Mo$_6$-4Py** > **Mo$_6$-3Py** > **Mo$_6$-Me-2Py**. However, it should be pointed out that the stability indicated by the yields (shown in ESI) is in the order of **Mo$_6$-Me-2Py** ~ **Mo$_6$-3Py** > **Mo$_6$-4Py**. In addition, there is a much more hindrance effect on the alkylation at heterocyclic nitrogen for compounds **Mo$_6$-Me-2Py**. Therefore, **Mo$_6$-3Py** was chosen as the substrate for the further study of alkylation.

Table 1. The natural charge at the heterocyclic nitrogen site in aminopyridines and corresponding organoimido hexamolybdates calculated at the level of B3LYP/BS1 (LANL2DZ basis set for molybdenum and the 6-31G(d) basis set for other atoms)

	3Me-2-R-Py	3-R-Py	4-R-Py
R = NH_2	-0.5104	-0.4375	-0.4868
R = $Mo_6O_{18}N$	-0.4652	-0.4734	-0.4997

The reaction of **Mo$_6$-3Py** and iodoalkanes in acetonitrile with stirring under a wide range of temperature can give rise to the desired products, in which the heterocyclic nitrogen atom is alkylated. However, attempts to further recrystallize for the corresponding X-ray quality single crystals failed. By opitimizing the conditions of reaction, it was found that orange block crystals can be successfully obtained when the reaction takes place slowly at 50° without stirring.

To characterize these alkylated products based on pyridine-functionalized organoimido hexamolybdates, several measurements including IR, UV-Vis, ^{1}H NMR and ESI-MS have been conducted. The IR spectra of compounds **Mo$_6$-3Py-Me** and **Mo$_6$-3Py-Et** are similar to that of **Mo$_6$-3Py** because of the unchangeable nature of anion cluster, presented in Fig. S1. However, the strong peak around 952 cm^{-1} which was assigned to the stretching vibrations of the Mo-O$_t$ bonds exhibits hypsochromic shift to 958 and 957 cm^{-1} in compounds **Mo$_6$-3Py-Me** and **Mo6-3Py-Et**, respectively. Meanwhile, the shoulder peak which is corresponding to the nature of the monosubstituted organoimido derivatives of hexamolybdate has *ca* 6 cm^{-1} hypsochromic shift in compounds **Mo$_6$-3Py-Me** and **Mo$_6$-3Py-Et**, compared to that in **Mo$_6$-3Py**. In addition, the intensity of the peaks which are corresponding to the stretching vibrations of the C-H bonds in Bu$_4$N$^+$ cation obviously decreased because of the decrease of negative charge of the resulting anionic clusters from -2 to -1. Moreover, from the UV-Vis absorption spectra (shown in Fig. S2), it can be seen that the lowest energy electronic transition absorption bands which locate at 343 and 346 nm for compounds **Mo$_6$-3Py-Me** and **Mo$_6$-3Py-Et**, respectively, have slightly bathochromic shift compared to that in **Mo$_6$-3Py**, implying the formation of alkylated products. Additionally, for ^{1}H NMR spectra of compounds **Mo$_6$-3Py-Me** and **Mo$_6$-3Py-Et**, displayed in Fig. S3 and S4, all of resolved signals can be unambiguously assigned. Importantly, the ratios of the integrations of signals corresponding to pyridinium groups (N-methyl pyridine in compound **Mo$_6$-3Py-Me**, while N-ethyl pyridine in compound **Mo$_6$-3Py-Et**) as well as the cation of Bu$_4$N$^+$ in compounds **Mo$_6$-3Py-Me** and **Mo$_6$-3Py-Et** are 3:1, indicating the counter Bu$_4$N$^+$ cation has decreased due to the reduce of negative charge of the cluster anion while the N alkylization, which is in agreement with the above mentioned result of IR. Furthermore, the ESI-MS of compounds **Mo$_6$-3Py-Me** and **Mo$_6$-3Py-Et** (Fig. S5 and S6) exhibit clearly resolved peaks which are corresponding to the alkylated products [Mo$_6$O$_{18}$NPy-R]$^-$ (for **Mo$_6$-3Py-Me**, 971.9 is assigned to [Mo$_6$O$_{18}$NC$_5$H$_4$NCH$_3$]$^-$, and for **Mo$_6$-3Py-Et**, 984.6 is assigned to [Mo$_6$O$_{18}$NC$_5$H$_4$NC$_2$H$_5$]$^-$).

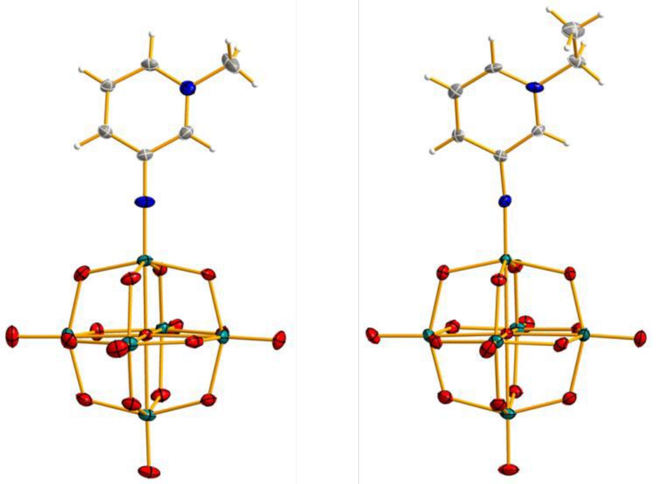


Fig. 2 ORTEP viewing of the cluster anions within compounds **Mo$_6$-3Py-Me** (left, 25% probability ellipsoids) and **Mo$_6$-3Py-Et** (right, 50% probability ellipsoids) Mo teal, O red, N blue, C grey, H white.

To further confirm the structures of **Mo$_6$-3Py-Me** and **Mo$_6$-3Py-Et**, single-crystal X-ray diffraction investigations have been performed. Compounds **Mo$_6$-3Py-Me** and **Mo$_6$-3Py-Et** both crystallize in triclinic system, $P\overline{1}$ space group, with an asymmetric unit containing two crystallographically independent anionic clusters, one counter 1-methyl-3-aminopyridine or 1-ethyl-3-aminopyridine cation for **Mo$_6$-3Py-Me** and **Mo$_6$-3Py-Et**, respectively, and one counter Bu$_4$N$^+$ cation as well as one solvent molecule of acetonitrile. The ORTEP drawings of anionic clusters within compounds **Mo$_6$-3Py-Me** and **Mo$_6$-3Py-Et** are presented in Fig. 2. As can be seen from Fig. 2, compounds **Mo$_6$-3Py-Me** and **Mo$_6$-3Py-Et** remain the typical structural features as those of mono-organoimido-functionalized hexamolybdates: one of the terminal oxo atoms (O$_t$) of the hexamolybdate cluster has been replaced by one organoimido ligand. Obviously, the heterocyclic nitrogen atom was bounded to an alkyl group (methyl for compound **Mo$_6$-3Py-Me**, and ethyl for compound **Mo$_6$-3Py-Et**). Correspondingly, the typical triple bond of Mo-N has been elongated ca 0.03 and 0.04 Å in compound **Mo$_6$-3Py-Me** and **Mo$_6$-3Py-Et**, respectively.

In addition, there exist interesting supramolecular structures assembled from the anionic clusters via the dipole-dipole interaction and intermolecular hydrogen bonding interactions in the solid state of **Mo$_6$-3Py-Me** and **Mo$_6$-3Py-Et**. As shown in Fig. 3, the neighbouring clusters at the same orientation in compound **Mo$_6$-3Py** assembled into a supramolecular 1D chain via the hydrogen bonding interactions (C3-H3…O9) between C3-H3 of pyridine group and the *trans* terminal oxygen (O9). While in compounds **Mo$_6$-3Py-Me** and **Mo$_6$-3Py-Et**, the permanent dipole moment arising from the covalent linking of negatively charged cluster and positively charged heterocyclic nitrogen atom arrays as parallel and alternately inverse, and the shortest distance between the positive charged nitrogen and the bridge oxygen atom is found to be 3.752 and 3.824 Å, respectively, indicating there exist the dipole-dipole interaction. In addition, the hydrogen bonding interactions (presented in Table S1 and S2) also play somewhat role for the formation of 1D supramolecular double chain. Regarding to determining the strength of the dipole-dipole interaction and applying to the supramolecular assembly, some further experiments are required and have been already started.

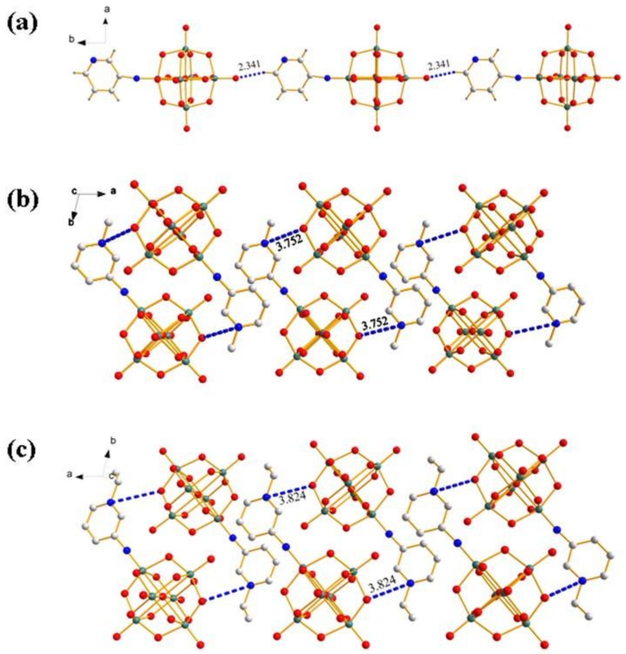


Fig. 3 Packing digram within **Mo$_6$-3Py (a), Mo$_6$-3Py-Me (b)** and **Mo$_6$-3Py-Et (c)** (Omit all hydrogen atoms for showing clearly, Mo teal, O red, N blue, C white)

In summary, a series of pyridine-functionalized mono arylimido substituted hexamolybdates have been synthesized. Moreover, the reactivity of their alkylation at the heterocyclic nitrogen atom has been explored, and a type of alkylated products which are POM-based organic-inorganic hybrid zwitterions have also been successfully obtained. Based on the results obtained here, an efficient strategy to construct zwitterionic clusters *via* the postfunctionalization of organically derivatized POMs has been developed. The supramolecular assembly and the property of nonlinear optics about these zwitterionic compounds are in progress in our laboratory.

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Notes and references

Crystal data for **Mo_6-Me-2Py**: F = $C_{80}H_{162}Mo_{12}N_{10}O_{36}$, Mr = 2991.48, triclinic, space group $P\bar{1}$, a = 15.7964(15) Å, b = 19.5355(14) Å, c = 20.3243(16) Å, α =112.383(7)°, β =98.552(7)°, γ = 96.467(7)°, V = 5635.8(8) $Å^3$, Z = 2, ρ_c = 1.763 mg/mm^3, T = 100 K, R_{int} = 0.0526, R_1 = 0.0753, wR_2 = 0.1677.

Crystal data for **Mo_6-3Py**: F = $C_{37}H_{76}Mo_6N_4O_{18}$, Mr = 1440.66, monoclinic, space group *C2/c*, a = 19.306(4) Å, b = 15.312(3) Å, c = 20.714(4) Å, α = γ = 90°, β = 117.82(3)°, V = 5415.6(19) $Å^3$, Z = 4, ρ_c = 1.767 mg/mm^3, T = 296 K, R_{int} = 0.0598, R_1 = 0.0601, wR_2 = 0.1538.

Crystal data for **Mo_6-4Py**: F = $C_{37}H_{76}Mo_6N_4O_{18}$, M r = 1440.66, orthorhombic, space group *P*bca, a = 16.934(3) Å, b = 20.054(4) Å, c = 32.431(7) Å, α = β = γ = 90°, V = 11014(4) $Å^3$, Z = 8, ρ_c = 1.738 mg/mm^3, T = 296 K, R_{int} = 0.0918, R_1 = 0.0607, wR_2 = 0.1502.

Crystal data for **Mo_6-3Py-Me**: F = $C_{36}H_{62}Mo_{12}N_8O_{36}$, Mr = 2334.22, triclinic, space group $P\bar{1}$, a = 10.943(2) Å, b = 17.471(12) Å, c = 17.804(4) Å, α = 94.53(3)°, β = 91.26(3)°, γ = 104.75(3)°, V = 3278.3(11) $Å^3$, Z = 2, ρ_c = 2.365 mg/mm^3, T = 153 K, R_{int} = 0.0426, R_1 = 0.0615, wR_2 = 0.1603.

Crystal data for **Mo_6-3Py-Et**: F = $C_{39}H_{68}Mo_{12}N_8O_{36}$, Mr= 2376.29, triclinic, space group $P\bar{1}$, a = 10.885(2) Å, b = 17.838(4) Å, c = 18.104(4) Å, α = 94.83(3), β = 91.43(3)°, γ = 105.85(3)°, V = 3365.5(12) $Å^3$, Z = 2, ρ_c = 2.345 mg/mm^3, T = 153 K, R_{int} = 0.0316, R_1 = 0.0450, wR_2 = 0.0832.

1 T. H. Rehm and C. Schmuck, *Chem. Soc. Rev.*, 2010, **39**, 3597

2 (a) G. Gröger, W. Meyer-Zaika, C. Böttcher, F. Gröhn, C. Ruthard and C. Schmuck, *J. Am. Chem. Soc.*, 2011, **133**, 8961; (b) F. Rodler, J. Linders, T. Fenske, T. Rehm, C. Mayer and C. Schmuck, *Angew. Chem. Int. Ed.*, 2010, **49**, 8747.

3 (a) C. Schmuck, T. Rehm, K. Klein and F. Gröhn, *Angew. Chem. Int. Ed* 2007, *46*, 1693; (b) F. Rodler, W. Sicking and C. Schmuck, *Chem. Commun.*, 2011, **47**, 7953; (c) C. Schmuck, T. Rehm, F. Gröhn, K. Klein and F. Reinhold *J. Am. Chem. Soc.* 2006, **128**, 1430; (d) T. Rehm and C. Schmuck, *Chem. Commun.*, 2008, 801; (e) G. Gröger, V. Stepanenko, F. Würthner and C. Schmuck, *Chem. Commun.*, 2009, 698.

4 M. Stradiotto, K. D. Hesp and R. J. Lundgren, *Angew. Chem. Int. Ed.*, 2010, **49**, 494.

5 (a) V. Nair, R. S. Menon, A. R. Sreekanth, N. Abhilash and A. T. Biju, *Acc. Chem. Res.*, 2006, **39**, 520; (b) W. Meng, H.-T. Zhao, J. Nie, Y. Zheng, A. Fu and J.-A. Ma, *Chem. Sci.*, 2012, **3**, 3053.

6 (a) S. E. Creutz, I. Krummenacher, C. R. Clough and C. C. Cummins, *Chem. Sci.*, 2011, **2**, 2166; (b) R. C. Neu, E. Otten, A. Lough and D. W. Stephan, *Chem. Sci.*, 2011, **2**, 170; (c) M. Sajid, A. Klose, B. Birkmann, L. Liang, B. Schirmer, T. Wiegand, H. Eckert, A. J. Lough, R. Fröhlich, C. G. Daniliuc, S. Grimme, D. W. Stephan, G. Kehr and G. Erker, *Chem. Sci.*, 2013, **4**, 213.

7 (a) M. T. Pope, *Comprehensive Coordination Chemistry II*, A. G. Wedd Ed., Elsevier, Oxford 2004, **4**, 635; (b) C. L. Hill, *Comprehensive Coordination Chemistry II*, A. G. Wedd Ed., Elsevier, Oxford, 2004, **4**, 679; (c) M. T. Pope and A. Müller, Eds., *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*, Kluwer, Dordrecht 2001; (d) T.Yamase and M. T. Pope, Eds, *Polyoxometalate Chemistry for Nano-Composite Design*, Kluwer Academic, New York, 2002; (e) A.Müller, P. Kogerler and A. W. M. Dress, *Coord. Chem. Rev.*, 2001, **222**, 193; (f) D. L. Long, E. Burkholder and L.Cronin, *Chem. Soc. Rev.*, 2007, **36**, 105; (g) A. Muller and P. Gouzerh, *Chem. Soc. Rev.*, 2012, **41**, 7431.

8 (a) A. Proust, B. Matt, R. Villanneau, G. Guillemot, P. Gouzerha and G. Izzet, *Chem. Soc. Rev.*, 2012, **41**, 7605; (b) A. Dolbecq, E. Dumas, C. R. Mayer and P. Mialane, *Chem. Rev.* 2010, **110**, 6009 (c) A. Proust, R. Thouvenot and P. Gouzerh, *Chem. Commun.* 2008, 1837; (d) P. Gouzerh and A. Proust, *Chem. Rev.* 1998, **98**, 77.

9 P. C. Yin, J. Wang, Z. C. Xiao, P. F. Wu, Y. G. Wei and T. B. Liu, *Chem. –Eur. J.*, 2012, **18**, 9174.

10 W. Qi and L. X. Wu, *Polym. Int.*, 2009, **58**, 1217.

11 J. Zhang, F. P Xiao, J. Hao and Y. G. Wei, *Dalton Trans.*, 2012, **41**, 3599.

12 D. E. Katsoulis, *Chem. Rev.* 1998, **98**, 359.

13 (a) Y. Du, A. L. Rheingold and E. A. Maatta, *J. Am. Chem. Soc.*, 1992, **114**, 346; (b) A. Proust, R. Thouvenot, M. Chaussade, F. Robert and P. Gouzerh, *Inorg. Chim. Acta,* 1994, **224**, 81; (c) T. R. Mohs, Y. Du, B. Plashko and E. A. Maatta, *Chem. Commun.,* 1997, 1707.

14 (a) W. Clegg, R. J. Errington, K. A. Fraser, C. Lax and D. G. Richards, In *Polyoxometalates: from Platonic Solids to Anti-Retroviral Activity*; M. T. Pope, A. Muller, Eds.; Dordrecht/Boston/London, 1994; Vol. Kluwer Academic Publishers, p 113; (b) J. B. Strong, G. P. A. Yap, R. Ostrander, L. M. Liable-Sands, A. L. Rheingold, R. Thouvenot, P. Gouzerh and E. A. Maatta, *J. Am. Chem. Soc.*, 2000, **122**, 639.

15 W. Clegg, R. J. Errington, K. A. Fraser, S. A. Holmes and A. Schäfer, *J. Chem. Soc., Chem. Commun*. 1995, 455.

16 Y. G. Wei, B. B. Xu, C. L. Barnes and Z. H. Peng, *J. Am. Chem. Soc.* 2001, **123**, 4083.

17 F. Odobel, M. Séverac, Y. Pellegrin, E. Blart, C. Fosse, C. Cannizzo, C. R. Mayer, K. J. Elliott and A. Harriman, *Chem. -Eur. J.*, 2009, **15**, 3130.

18 (a) B. Xu, Y. G. Wei, C. L. Barnes and Z. H. Peng, *Angew. Chem., Int. Ed.,* 2001, **40**, 2290; (b) M. Lu, W. M. Nolte, T. He, D. A. Cortley and J. M. Tour, *Chem. Mater.* 2009, **27**, 442; (c) V. Duffort, R. Thouvenot, C. Afonso, G. Izzet and A. Proust, *Chem.Commun.* 2009, 6062.

19 Y. L. Zhu, L. S. Wang, J. Hao, J. Yin, P. C. Yin, J. Zhang, Q. Li, L. Zhu and Y. G. Wei, Y. *Chem.-Eur. J.*, 2009, **15**, 3076.

20 J. F. W. Keana, M. D. Ogan, Y. Lü, M. Beer and J. Varkey, *J. Am. Chem. Soc.*, 1986, **108**, 7957.

21 L. Zhu, Y. L. Zhu, X. Meng, J. Hao, Q. Li, Y. G. Wei and Y. B. Lin, *Chem.-Eur. J.*, 2008, **14**, 10923.

22 (a) P. R. Marcoux, B. Hasenknopf, J. Vaissermann and P. Gouzerh, *Eur. J. Inorg. Chem.*, 2003, 2406; (b) Y.-F. Song, D.-L. Long and L. Cronin, *CrystEngComm*, 2010, **12**, 109.

23 Y.-F. Song, N. McMillan, D.-L. Long, J. Thiel, Y. Ding, H. Chen, N. Gadegaard, L. Cronin, *Chem.-Eur. J.* 2008, **14**, 2349.

24 A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648.

25 C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785.