

Cite this: *Dalton Trans.*, 2012, **41**, 11745

www.rsc.org/dalton

PAPER

New porphyrin–polyoxometalate hybrid materials: synthesis, characterization and investigation of catalytic activity in acetylation reactions†

Mehdi Araghi,^a Valiollah Mirkhani,^{*b} Majid Moghadam,^{*b} Shahram Tangestaninejad^b and Iraj Mohammadpoor-Baltork^b

Received 13th July 2012, Accepted 25th July 2012

DOI: 10.1039/c2dt31553j

New hybrid complexes based on covalent interaction between 5,10,15,20-tetrakis(4-aminophenyl)porphyrinatozinc(II) and 5,10,15,20-tetrakis(4-aminophenyl)porphyrinatotin(IV) chloride, and a Lindqvist-type polyoxometalate, $\text{Mo}_6\text{O}_{19}^{2-}$, were prepared. These new porphyrin–polyoxometalate hybrid materials were characterized by ^1H NMR, FT IR and UV-Vis spectroscopic methods and cyclic voltammetry. These spectro- and electrochemical studies provided several spectral data for synthesis of these compounds. Cyclic voltammetry showed the influence of the polyoxometalate on the redox process of the porphyrin ring. The catalytic activity of tin(IV)porphyrin–hexamolybdate hybrid material was investigated in the acetylation of alcohols and phenols with acetic anhydride. The reusability of this catalyst was also investigated.

Introduction

The interest in possible developments of mixed organic–inorganic materials with diverse properties that may lead to new applications has been continuously increasing. In a typical set-up, molecules with specific properties are selected as building blocks. Once the molecules are assembled, their properties complement each other to yield an integrated functional material. In this context, polyoxometalates (POMs) have attracted increasing attention due to their remarkable chemical, structural, and electronic versatility in order to prepare new compounds with interesting optical, magnetic or electric properties.¹ In this way, it becomes possible to utilize the high electron affinity of the POM for catalytic purposes.

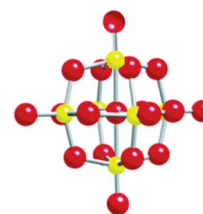
Besides, metalloporphyrins are attractive components in materials chemistry because of their photochemical excitations and rich redox chemistry. Therefore, porphyrins bearing appropriate metal ions can be used as electron donors, and they are often used as building blocks for supramolecules or artificial dyad systems.²

Compounds composed of polyoxometalates and metalloporphyrins have been rarely considered. These compounds can be envisaged as potential new bi-functional catalysts and can be expected to originate systems in which the catalytic abilities of these two species reinforce each other. On the other hand, such

associations may stabilize the metalloporphyrins against deactivation during the catalytic cycles.³ Such assemblies can be prepared by electrostatic interactions and/or coordination⁴ and used as oxidation catalysts⁵ or for electrocatalytic reductions.⁶ Although such assemblies are easy to prepare and rather robust, the relative orientation of the components and their stoichiometry are not under control. The covalent linkage of POM to porphyrin is a way to overcome this problem. Ruhlmann and co-workers reported the preparation of a metallosupramolecular system consisting of a POM sandwiched between two ruthenium(II) or zinc(II) porphyrins *via* axial ligation with a pyridinyl ligand.^{4a} Attanasio and Bachechi reported the preparation and charge transfer properties of tetraphenylporphyrinato zinc(II) complex and Keggin heteropolyanions.^{4b}

The Lindqvist anions, $\text{M}_6\text{O}_{19}^{2-}$ ($\text{M} = \text{Mo}, \text{W}$) (Fig. 1), are among the smallest members of the POM family.⁷ These anions, which exhibit high point group symmetry (O_h), are highly stable in condensed phase and even in the gas phase.⁸ In the case of the hexamolybdate ion, $\text{Mo}_6\text{O}_{19}^{2-}$, a sizable class of derivatives $\text{Mo}_6\text{O}_{18}(\text{L})^{n-}$ has been prepared in which an exogenous ligand L replaces a terminal oxo ligand within the parent structure.⁹

The protection of a hydroxy functional group is often necessary during the course of various transformations in a synthetic

Fig. 1 The structure of hexamolybdate ion $\text{Mo}_6\text{O}_{19}^{2-}$.

^aDepartment of Chemistry, Saveh Branch, Islamic Azad University, Saveh, Iran

^bDepartment of Chemistry, Catalysis Division, University of Isfahan, Isfahan 81746-73441, Iran. E-mail: moghadamm@sci.ui.ac.ir; mirkhami@sci.ui.ac.ir; Fax: +98-311-6689732; Tel: +98-311-7932712

† Electronic supplementary information (ESI) available: UV-Vis and FT IR spectra and voltammograms. See DOI: 10.1039/c2dt31553j

sequence, especially in the construction of polyfunctional molecules such as nucleosides, carbohydrates, steroids, and natural products.¹⁰ Many heterogeneous and homogeneous catalysts or reagents have been reported for acetylation of alcohols and phenols.¹¹ However, some of the reported methods for the acetylation and formylation of alcohols suffer from one or more of disadvantages, such as high temperature and drastic reaction conditions, formation of undesirable or toxic by-products, expensive reagents, hygroscopicity and thermal instability of the reagents, long reaction times, low yields of the desired products and bulk requirement of solid bed. Therefore, introduction of new methods and catalysts for the preparation of esters is still in demand.

The successful applications of metalloporphyrins as mild Lewis acid catalysts¹² prompted us to explore the potential of these complexes as catalysts for the conversion of alcohols and phenols to their corresponding esters. Recently, we reported the use of tetraphenylporphyrinatotin(IV) perchlorate,^{11r} tetraphenylporphyrinatotin(IV) trifluoromethanesulfonate,^{11u,x} tetraphenylporphyrinatotin(IV) tetrafluoroborate^{11v} and tetraphenylporphyrinatovanadium(IV) trifluoromethanesulfonate^{11w} in the acetylation of alcohols and phenols.

Recently, we reported the synthesis of manganese(III) porphyrin–polyoxometalate hybrid compound and investigated its catalytic activity in the alkene epoxidation with NaIO₄.¹³ In an attempt to expand this field, two new hybrid compounds, in which a metalloporphyrin as an electron donor is covalently attached to a Lindqvist-type polyoxometalate as acceptor molecule in a supramolecular assembly were prepared. A combined study on the preparation, characterization and catalytic application of these new polyoxometalate/metalloporphyrin associations is described here. The new compounds were prepared by reaction of Mo₆O₁₉²⁻ to metalloporphyrins carrying four 4-amino groups in the *meso* positions. The hexamolybdate–tin(IV) porphyrin, HMTP, hybrid catalyst was used as catalyst in the acylation of alcohols and phenols with acetic anhydride at room temperature.

Experimental

Reagents and synthetic procedures

All chemicals were used as received from the suppliers. Solvents were used as received or distilled and dried using the standard procedures. Tetrabutylammonium hexamolybdate, [(*n*-C₄H₉)₄N]₂[Mo₆O₁₉] was prepared according to the literature method.¹⁴ 5,10,15,20-Tetrakis(4-aminophenyl)porphyrin, 5,10,15,20-tetrakis(4-aminophenyl)porphyrinatozinc(II) (**1**) and 5,10,15,20-tetrakis(4-aminophenyl)porphyrinatotin(IV) chloride (**2**) were prepared according to known procedures.¹⁵ All the synthetic procedures were performed protected from light.

Instruments

¹H NMR spectra were recorded on a Bruker-Avance AQS 400 (MHz) NMR spectrometer using DMSO as solvent and TMS as internal standard. Elemental analyses were measured by a Perkin Elmer 2400 instrument. The amount of Mo was measured by a Leaman inductively coupled plasma (ICP) spectrometer. Atomic

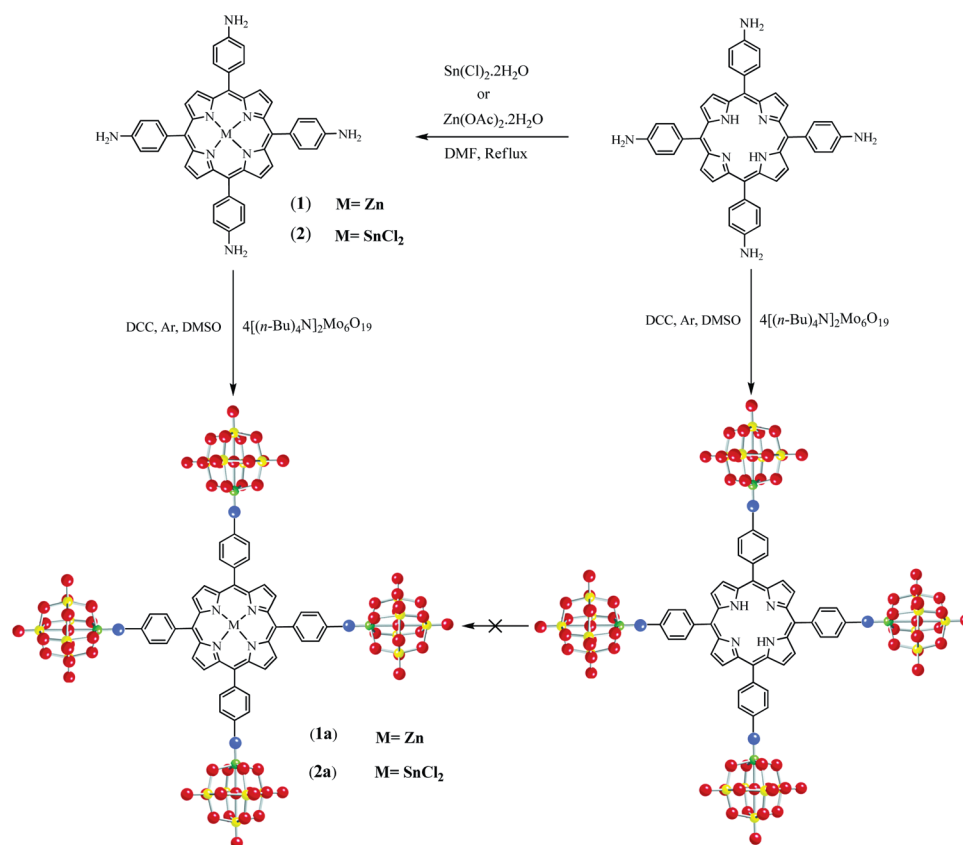
absorption analysis was carried out on a Shimadzu 120 spectrophotometer. The electronic spectra of the compounds in the UV-Vis region were recorded in DMF solution using a Shimadzu 160 UV-Vis or a Varian Cary NIR spectrophotometer. FT-IR spectra were obtained as potassium bromide pellets in the range 400–4000 cm⁻¹ with a Nicolet-Impact 400D instrument. Gas chromatography experiments (GC) were performed on a Shimadzu GC 16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m. In GC experiments, *n*-decane was used as internal standard. Redox potentials of the compounds (10⁻³ mol L⁻¹) in DMF containing 0.1 mol L⁻¹ tetrabutylammonium bromide (TBAB) as a supporting electrolyte were determined at room temperature by cyclic voltammetry with a PGSTAT30 (Eco Chemie, Utrecht, The Netherlands) electrochemical analyzer. A three-electrode cell was used, including glassy carbon electrode as working electrode, together with an Ag/AgCl (saturated KCl) and a platinum wire as reference and counter electrode, respectively. Conversions and yields were obtained by GC experiments and the products were identified after isolation and purification.

Synthesis of hybrid compound 1a

The 0.1 g (0.14 mmol) dry **1**, 0.81 g (0.59 mmol, 4.2 eq) [(*n*-C₄H₉)₄N]₂[Mo₆O₁₉] and 0.17 g (0.84 mmol, 6 eq) *N,N'*-dicyclohexylcarbodiimide (DCC) were dissolved in 10 mL anhydrous DMSO and heated to 100 °C under a dry atmosphere. The reaction was cooled to room temperature and filtered under vacuum (to remove the dicyclohexylcarbodiurea) into a flask containing 100 mL dry ether and 20 mL dry methanol. A precipitate was formed and washed several times with acetone and ether. The dried product (0.63 g, 73% yield) was stored in a desiccator. IR (cm⁻¹): 433 (m), 599 (m), 781 (s), 944 (s), 975 (sh), 1030 (m), 1180 (m), 1381 (m), 1459 (s), 1608 (s), 1664 (s), 2873 (s), 2963 (s). ¹H NMR at 400 MHz (d₆-DMSO): δ = 0.94 [t (*J* = 7.2 Hz), 96H, (CH₃CH₂CH₂CH₂N)], 1.31 [q (*J* = 7.2 Hz), 64H, (CH₃CH₂CH₂CH₂N)], 1.57 [m, 64H, (CH₃CH₂CH₂CH₂N)], 3.17 [t (*J* = 8.4 Hz), 64H, (CH₃CH₂CH₂CH₂N)], 7.67 [d (*J* = 8.4 Hz), 8H, protons 2,6-AminoPh], 8.14 [d (*J* = 8.4 Hz), 8H, protons 3,5-AminoPh], 8.93 [s, 8H, protons β-pyrrole]. UV-Vis spectra (in DMF): (λ_{max} = 377 nm). Anal. calcd for C₁₇₂H₃₁₂N₁₆O₇₂Mo₂₄Zn: C, 33.73; H, 5.13; N, 3.66; Mo, 37.60%. Found: C, 33.85; H, 5.04; N, 3.50. Mo, 37.41%.

Synthesis of hybrid compound 2a

A 0.1 g (0.12 mmol) dry **2**, 0.69 g (0.50 mmol, 4.2 eq) [(*n*-C₄H₉)₄N]₂[Mo₆O₁₉] and 0.15 g (0.72 mmol, 6 eq) *N,N'*-dicyclohexylcarbodiimide (DCC) were dissolved in 10 mL anhydrous DMSO and heated to 100 °C under a dry atmosphere. The reaction was cooled to room temperature and filtered under vacuum (to remove the dicyclohexylcarbodiurea) into a flask containing 100 mL dry ether and 20 mL dry methanol. A precipitate was formed and washed several times with acetone and ether. The dried product (0.52 g, 70% yield) was stored in a desiccator. IR (cm⁻¹): 432 (m), 599 (w), 739 (sh), 780 (s), 943 (s), 975 (sh), 1034 (w), 1181 (m), 1381 (m), 1469 (s), 1604 (s), 1624 (s), 2872 (s), 2963 (s). Anal. calcd for



Scheme 1 The preparation route for hybrid compounds.

$C_{172}H_{312}N_{16}O_{72}Mo_{24}SnCl_2$: C, 33.06; H, 5.03; N, 3.59; Mo, 36.85%. Found: C, 33.15; H, 4.92; N, 3.48. Mo, 36.67%.

General procedure for acetylation of alcohol and phenols with Ac_2O catalyzed by **2a**

To a solution of alcohol or phenol (1 mmol) and Ac_2O (2 mmol per OH group) in CH_3CN (1 mL) was added **2a** (65 mg, 0.010 mmol) and stirred at room temperature for appropriate time. The progress of the reaction was monitored by GC. After completion of the reaction, Et_2O (10 mL) was added and the catalyst was filtered. The filtrates were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to afford the crude product.

Results and discussion

Synthesis and characterization of the hybrid complexes

Usually, the association of a molecular unit to a POM is attained by electrostatic interaction.^{4a–c} However, in order to increase the stability of the hybrid material, especially in polar solvents; a covalent linkage was established between POM and porphyrin. Initially, we developed a mild and efficient synthetic route for covalent attachment of 5,10,15,20-tetrakis(4-amino-phenyl)-porphyrinatozinc(II) (**1**) and 5,10,15,20-tetrakis(4-amino-phenyl)-porphyrinatotin(IV) chloride (**2**) to a Lindqvist polyoxometalate. The covalent attachment of the hexamolybdate polyoxoanion,

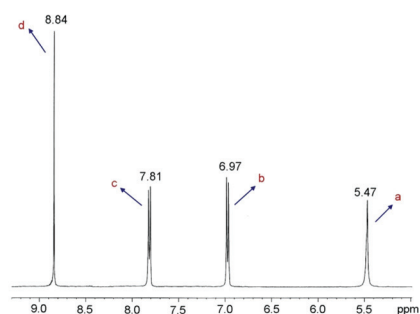
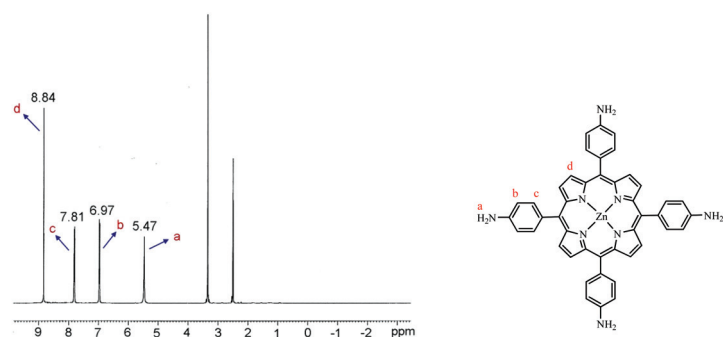
$Mo_6O_{19}^{2-}$, to porphyrins was successfully carried out using dicyclohexylcarbodiimide (DCC) as a coupling agent (Scheme 1). These reactions were carried out according to the procedure reported for the synthesis of manganese(III) counterpart and for the reaction of hexamolybdate with aromatic amines.^{13,16} Direct coupling of $Mo_6O_{19}^{2-}$ with metalloporphyrins **1** and **2** in the presence of triethylamine was unsuccessful.¹⁷ However, good results were obtained using DCC as a coupling reagent. DCC can dramatically facilitate the reaction of $Mo_6O_{19}^{2-}$ with aromatic amines.¹⁶ The hybrid compound **1a** is soluble in polar, aprotic solvents such as DMSO and DMF but hybrid compound **2a** is insoluble in aprotic solvents.

Direct metallation of free tetrakis(4-aminophenyl)porphyrin–polyoxometalate with $ZnCl_2$ and $SnCl_2$ for preparation of hybrid compounds **1a** and **2a** was not successful and did not give good yield. Therefore, the best route for preparation of these hybrid compounds is hybridization of $Zn(TNH_2PP)$ and $Sn(TNH_2PP)Cl_2$ with hexamolybdate.

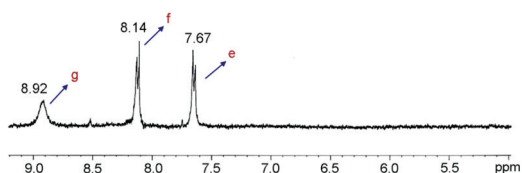
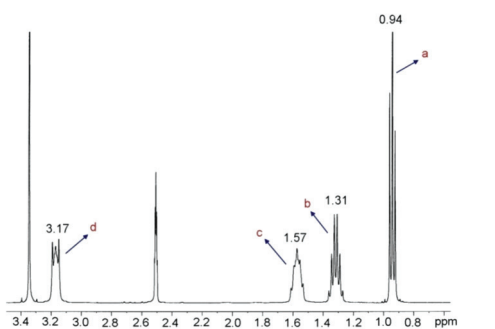
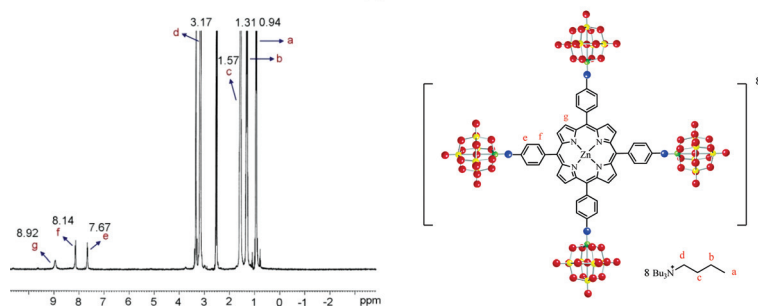
Several attempts for preparation of single crystals of these hybrid compounds failed. Therefore, these new hybrid materials were characterized by FT IR, UV-Vis and 1H NMR spectroscopic methods, and cyclic voltammetric studies. All these techniques provide more details for characterization of this new class of polyoxometalate–porphyrin hybrid materials.

Characterization of the prepared compounds

Polyoxometalates show characteristic infrared bands in the $700\text{--}1000\text{ cm}^{-1}$ region assigned to M–O and M–O–M stretching



(A)



(B)

Fig. 2 ^1H NMR spectra of (A) 5,10,15,20-tetrakis(4-aminophenyl)porphyrinatozinc(II) (**1**) and (B) hybrid compound **1a** in DMSO.

vibrations.¹⁸ These bands were observed in the IR spectra of the prepared hybrid compounds with significant changes. The bands with lower intensities at 1100–1600 cm⁻¹ and near 3000 cm⁻¹ confirmed the presence of the organic moieties in these compounds (see Fig. S1†). In the hybrid compounds, the new Mo–N stretching vibration presents at 975 cm⁻¹. Compared to the parent hexamolybdate anion, Mo–O stretching and asymmetric Mo–O_b–Mo stretching vibrations are bathochromically shifted respectively from 957 to 944 cm⁻¹ and from 799 to 781 cm⁻¹ for hybrid compound **1a** and from 957 to 943 cm⁻¹ and from 799 to 780 cm⁻¹ for hybrid compound **2a**. These observations imply that these bonds are weakened to some extent due to the stronger Mo–N bonding interaction than that of Mo–O.

The ¹H NMR spectra of compounds **1** and **1a** are shown in Fig. 2. These spectra clearly show resolved signals that can be unambiguously assigned. The signals correspond to the aromatic protons are present at 6.97–8.84 ppm for compound **1**. The –NH₂ proton signal is observed at 5.47 ppm for compound **1**. In compound **1**, the singlet at 8.84 ppm is assigned to the eight β-H protons and the two doublets (AB system) at 6.97 and 7.81 ppm (8H, *J* = 8.0 Hz) correspond to the phenyl protons. Upon hybridization of compound **1** with hexamolybdate, all these signals exhibited downfield chemical shifts compared to the compound **1**. This is due to the electron-withdrawing nature of the hexamolybdate moiety. In the hybrid compound **1a**, the aromatic proton signals are present at 7.67–8.92 ppm and the signal corresponding to the –NH₂ protons was absent in the hybrid compound **1a**. The protons *ortho* to the amine group showed the largest shift, from 6.97 to 7.67 ppm for hybrid compound **1a**.

The electronic property of the hybrid compound **1a** was also studied by UV-Vis spectrophotometry in DMF (see Fig. S2, ESI†). In the hybrid compound **1a**, the molybdenum–oxygen charge-transfer absorption peak of Mo₆O₁₉²⁻ (λ_{max} = 326 nm) was significantly shifted to the red (and λ_{max} = 377 nm). Also, the reflectance of the compound **2a** showed a bathochromic shift (λ_{max} = 369) (see Fig. S3, ESI†), which implies that the formation of the Mo–N π bonds increases the delocalization of the aromatic π electrons. It is noted previously that the strong electronic interaction between the polyoxometalate cluster and the organic moiety depends on the conjugated system.¹⁹

The electrochemical properties of the hybrid compound **1a** was also evaluated by cyclic voltammetry (CV). The CV of **1** and **1a** in DMF, containing tetrabutylammonium bromide (TBAB) (0.1 mol L⁻¹) as supporting electrolyte are shown in Fig. S4 (ESI†). All potentials are quoted relative to an Ag/AgCl (saturated KCl) electrode.²⁰ The Zn(TNH₂PP) is reduced at –1.188 and –1.631 V. The first reduction corresponds to the formation of π anion radical and the second reduction is due to the formation of porphyrin dianion. The CV of the hybrid compound showed a more complex picture. The CV of the hybrid compound **1a** showed a reduction wave at –1.78 V. This remarkable cathodic shift in the reduction potential of this compound may be associated to the more difficult reduction of the polyoxometalate due to the electron-donating properties of the porphyrin toward the polyoxometalate. This is a similar behaviour which has been reported in the attachment of 1,10-phenanthroline to hexamolybdate by Neumann and co-workers.²¹ This observation is consistent with the UV-Vis data. Also, all waves shown in the CV of the parent compound **1** showed a shift to positive

Table 1 Optimization of catalyst amount in the acetylation of 4-chlorobenzyl alcohol with Ac₂O^a

Entry	Time [min]	Catalyst amount [mg, mmol]	Yield ^b [%]
1	4	0	15
2	4	0.01 mmol ^c	20
3	4	0.01 mmol ^d	16
4	4	40 mg (0.0064 mmol)	52
5	4	50 mg (0.0080 mmol)	74
6	4	60 mg (0.0096 mmol)	95
7	4	65 mg (0.0104 mmol)	100
8	4	70 mg (0.0112 mmol)	100

^a Reaction conditions: alcohol (1 mmol), Ac₂O (2 mmol), CH₃CN (1 mL), catalyst. ^b GC yield. ^c [Sn^{IV}(TNH₂PP)Cl₂] (**2**) was used as catalyst. ^d [(*n*-Bu₄N)]₂[Mo₆O₁₉] was used as catalyst.

Table 2 Optimization of Ac₂O amount in the acetylation of 4-chlorobenzyl alcohol^a

Entry	Time [min]	Ac ₂ O [mmol]	Yield ^b [%]
1	4	0.5	36
2	4	1.0	55
3	4	1.5	82
4	4	2.0	100

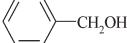
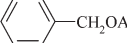
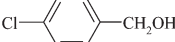
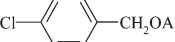
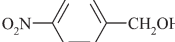
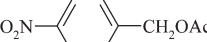
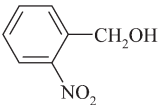
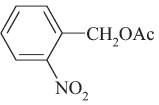
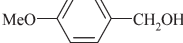
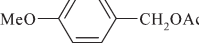
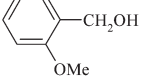
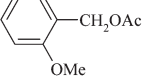
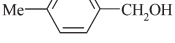
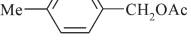
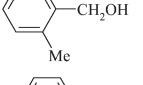
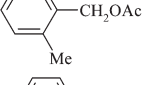
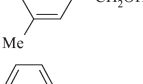
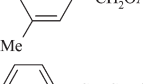
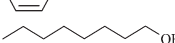
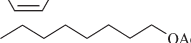




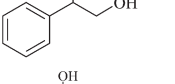
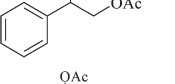
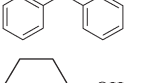
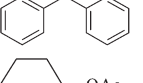
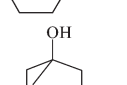
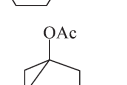




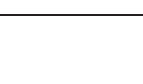
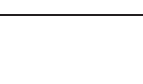
^a Reaction conditions: alcohol (1 mmol), Ac₂O, CH₃CN (1 mL), catalyst (0.01 mmol). ^b GC yield.

potentials upon attachment of polyoxometalate. This can be attributed to the relatively facile reduction of the porphyrin moiety due to the very strong electron-withdrawing effect of the polyoxometalate. All these observations confirmed that the POM cluster interacts and electronically communicates with the porphyrin moiety.

Catalytic studies

HMTF was used as catalyst in the acetylation of alcohols and phenols with acetic anhydride. First, the amount of catalyst was optimized in the acetylation of 4-chlorobenzyl alcohol with Ac₂O. The results, which are summarized in Table 1, showed that in the presence of 0.01 mmol (65 mg) of **2a**, the highest yield was obtained. In order to show the effect of hexamolybdate groups on the catalytic activity of tin(IV) porphyrin, the catalytic activity of [Sn^{IV}(TNH₂PP)Cl₂] (**2**) (0.01 mmol) was also investigated in the acetylation of 4-chlorobenzyl alcohol with Ac₂O. In this case, only 20% of the corresponding acetate was obtained (Table 1, entry 2) while in the presence of catalyst HMTF (**2a**), the reaction was completed after 4 min. The increase of catalytic activity of HMTF can be attributed to the electron-withdrawing nature of hexamolybdate which increases the electron deficiency of the tin(IV) porphyrin that is responsible for the catalytic property. These results are in consistent with the data obtained by electrochemical studies. As mentioned above, upon attachment of electron-withdrawing hexamolybdate substituents to the porphyrin ring, the electron density of the porphyrin ring decreased and therefore reduced more easily. As we reported in our previous works on the catalytic activity of tin(IV) porphyrins, the

Table 3 Acetylation of alcohols with Ac₂O catalyzed by hybrid compound **2a** at room temperature^a

Entry	Alcohol	Acetate	Time [min]	Yield ^b [%]
1			4	100
2			4	100
3			4	100
4			7	100
5			4	100
6			4	100
7			4	100
8			4	100
9			4	100
10			4	100
11			4	100
12			4	100
13			5	100
14			5	100
15			5	100
16			5	100
17			6	95
18			7	95

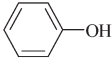
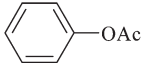
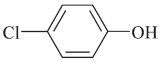
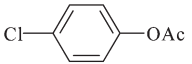
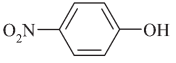
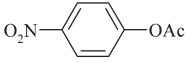
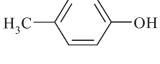
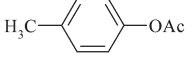

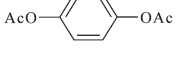
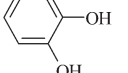
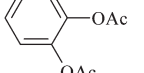
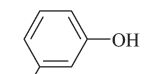
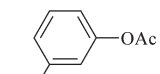
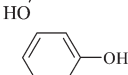
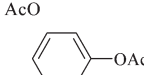
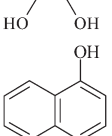
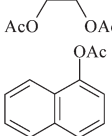
^a Reaction conditions: alcohol (1 mmol), Ac₂O (2 mmol), catalyst (1 mol%), CH₃CN (1 mL). ^b GC yield.

introduction of electron deficient ligands such as OTf⁻, BF₄⁻ and ClO₄⁻ increases the electron-deficiency of the tin center.^{11*t-v*} In the HMTP, the same role was observed by using hexamolybdate as an electron-withdrawing substituent. On the other hand, the catalytic activity of hexamolybdate (0.01 mmol) was also investigated in the acetylation of 4-chlorobenzyl alcohol with Ac₂O. The results showed that the amount of corresponding

acetate was the as same as blank experiments (Table 1, entry 3). These results clearly indicated that the tin(IV) porphyrin is the catalyst active site. Then, the amount of Ac₂O was also optimized. The results showed that in the presence of 2 mmol of Ac₂O, the reaction was completed (Table 2).

The optimized conditions which were obtained for acetylation of 4-chlorobenzyl alcohol were alcohol, Ac₂O and catalyst in a

Table 4 Acetylation of phenols with Ac₂O catalyzed by hybrid compound **2a** at room temperature^a

Entry	Phenol	Acetate	Time [min]	Yield ^b [%]
1			6	100
2			6	100
3			6	100
4			6	100
5 ^c			6	100
6 ^c			6	100
7 ^c			6	100
8 ^c			6	100
9			8	100

^a Reaction conditions: phenol (1 mmol), Ac₂O (2 mmol), catalyst (1 mol%), CH₃CN (1 mL). ^b GC yield. ^c Reaction was performed with 2 mmol of Ac₂O per OH group.

molar ratio of 100:200:1. Under these conditions, a wide variety of alcohols were subjected to acetylation with Ac₂O. The obtained results showed that different primary, secondary (including aliphatic and aromatic alcohols) and tertiary alcohols were acetylated successfully at room temperature (Table 3). As can be seen, in benzylic alcohols the nature of substituents (electron-withdrawing or electron-releasing) has no significant effect on the product yield. In the case of tertiary alcohols such as 2-methyl-1-phenyl-2-propanol (entry 18) no elimination product was observed.

Under the optimized conditions, which were described for acetylation of alcohols, the acetylation of phenols with Ac₂O was also investigated in the presence of hybrid compound **2a**. The results showed that all reactions were completed after 6 min at room temperature (Table 4). The acetylation of polyhydroxy-benzenes such as hydroquinone, pyrocatechol, resorcinol and pyrogallol was also performed. The results showed that all hydroxyl groups were acetylated and the desired poly acetates were obtained in excellent yields (Table 4, entries 5–8).

The stability of the catalyst **2a** was monitored using multiple sequential acetylation of 4-chlorobenzyl alcohol with Ac₂O. For each of the repeated reactions, the catalyst was filtered, washed exhaustively with water, methanol, acetonitrile and diethyl ether,

Table 5 Reusability of hybrid compound **2a** in the acetylation of 4-chlorobenzyl alcohol with Ac₂O^a

Run	Acetate ^b (%)	Time [min]	Sn leached ^c [%]
1	100	4	0
2	100	4	0
3	100	4	0
4	100	4	0
5	100	4	0
6	100	4	0
7	100	4	0
8	100	4	0
9	100	4	0

^a Reaction conditions: 4-chlorobenzyl alcohol (1 mmol), Ac₂O (2 mmol), catalyst (1 mol%), CH₃CN (1 mL). ^b GC yield. ^c Determined by ICP.

respectively, and dried before using with fresh 4-chlorobenzyl alcohol and Ac₂O. The catalyst was consecutively reused nine times without detectable catalyst leaching or significant loss of its activity (Table 5). The nature of the recovered catalyst was monitored using FT-IR and UV-Vis spectra of recycled catalyst (**2a**), which showed no changes in comparison with fresh catalyst (Fig. S1 G and S2 C, ESI†).

Conclusion

A new hybrid porphyrin–POM complex was prepared via covalent interaction of Zn(TNH₂PP) and Sn(TNH₂PP)Cl₂ with Mo₆O₁₉^{2–} Lindqvist type polyoxometalate. These new porphyrin–polyoxometalate hybrid materials were characterized by ¹H NMR, FT IR and UV-Vis spectroscopic methods and cyclic voltammetry. The influence of the polyoxometalate on the porphyrin ring was studied. The hexamolybdate–tin(IV) porphyrin hybrid material was used as catalyst for efficient acetylation of primary, secondary and tertiary alcohols and phenols with Ac₂O. Short reaction times, excellent yields, easy work-up and reusability and stability of the catalyst are noteworthy advantages of this method.

Acknowledgements

We are thankful to the Research Council of the University of Isfahan for financial support of this work.

Notes and references

- (a) *Polyoxometalate Chemistry: From Topology via Self-assembly to Applications*, ed. M. T. Pope and A. Müller, Kluwer Academic Publisher, Dordrecht, 2001; (b) C. L. Hill, *Chem. Rev.*, 1998, **98**, 1 (thematic issue).
- (a) K. M. Kadish, *Prog. Inorg. Chem.*, 1986, **34**, 435–605; (b) Y. Matsuda and Y. Murakami, *Coord. Chem. Rev.*, 1988, **92**, 157–192.
- I. C. M. S. Santos, S. L. H. Rebelo, M. S. S. Balula, R. R. L. Martins, M. M. M. S. Pereira, M. M. Q. Simoes, M. G. P. M. S. Neves, J. A. S. Cavaleiro and A. M. V. Cavaleiro, *J. Mol. Catal. A: Chem.*, 2005, **231**, 35–45.
- (a) C. Allain, S. Favette, L.-M. Chamoreau, J. Vaissermann, L. Ruhlmann and B. Hasenknopf, *Eur. J. Inorg. Chem.*, 2008, 3433–3441; (b) D. Attanasio and F. Bachechi, *Adv. Mater.*, 1994, **6**, 145–147; (c) A. Yokoyama, T. Kojima, K. Ohkubo and S. Fukuzumi, *Chem. Commun.*, 2007, 3997–3999; (d) R. Harada, Y. Matsuda, H. Okawa and

- T. Kojima, *Angew. Chem., Int. Ed.*, 2004, **43**, 1825–1828; (e) P. J. Hargman, D. Hargman and J. Zubietta, *Angew. Chem., Int. Ed.*, 1999, **38**, 3165–3168; (f) G. Bazzan, W. Smith, L. C. Francesconi and C. M. Drain, *Langmuir*, 2008, **24**, 3244–3249; (g) C. Yao, L.-K. Yan, W. Guan, C.-G. Liu, P. Song and Z.-M. Su, *Dalton Trans.*, 2010, **39**, 7645–7649; (h) D. Schaming, C. C. Coquelard, I. Lampre, S. Sorgues, M. Erard, X. Liu, J. Liu, L. Sun, J. Canny, R. Thouvenot and L. Ruhlmann, *Inorg. Chim. Acta*, 2010, **363**, 2185–2192; (i) A. Falber, B. P. Burton-Pye, I. Radivojevic, L. Todaro, R. Saleh, L. C. Francesconi and C. M. Drain, *Eur. J. Inorg. Chem.*, 2009, 2459–2466; (j) J. Hao, L. Ruhlmann, Y. Zhu, Q. Li and Y. Wei, *Inorg. Chem.*, 2007, **46**, 4960–4967; (k) J. Hao, Y. Xia, L. Wang, L. Ruhlmann, Y. Zhu, Q. Li and Y. Wei, *Angew. Chem., Int. Ed.*, 2008, **120**, 2666; (l) A. Tsuda, E. Hirahara, Y. S. Kim, H. Tanaka, T. Kawai and T. Haida, *Angew. Chem., Int. Ed.*, 2004, **43**, 6327–6331; (m) D. Martel and M. Gross, *J. Solid State Electrochem.*, 2007, **11**, 421–429.
- 5 (a) A. Maldotti, A. Molinari, P. Bergamini, R. Amadelli, P. Battioni and D. Mansuy, *J. Mol. Catal. A: Chem.*, 1996, **113**, 147–157; (b) A. Maldotti, A. Molinari, R. Argazzi, R. Amadelli, P. Battioni and D. Mansuy, *J. Mol. Catal. A: Chem.*, 1996, **114**, 141–150; (c) A. Molinari, A. Maldotti, R. Amadelli, A. Sgobino and V. Carassiti, *Inorg. Chim. Acta*, 1998, **272**, 197–203; (d) A. Molinari, R. Amadelli, V. Carassiti and A. Maldotti, *Eur. J. Inorg. Chem.*, 2000, 91–96.
- 6 (a) S.-Q. Liu, J.-Q. Xu, H.-R. Sun and D.-M. Li, *Inorg. Chim. Acta*, 2000, **306**, 87–93; (b) L. Gurban, A. Tézé and G. Hervé, *C. R. Acad. Sci. Paris, Sér. II*, 1998, 397–404; (c) D. Schaming, C. C. Coquelard, C. Sorgues, L. Ruhlmann and I. Lampre, *Appl. Catal.*, 2010, **373**, 160–167; (d) D. Fan and G. Li, *J. Colloid Interface Sci.*, 2010, **351**, 151–155; (e) Y. Shen, J. Liu, J. Jiang, B. Liu and S. Dong, *J. Phys. Chem. B*, 2003, **107**, 9744–9748; (f) Y. Shen, J. Liu, J. Jiang, B. Liu and S. Dong, *Electroanalysis*, 2002, **14**, 1557–1563.
- 7 (a) I. Lindqvist, *Ark. Kemi*, 1950, **5**, 247; (b) H. R. Allcock, E. C. Bissell and E. T. Shaw, *Inorg. Chem.*, 1973, **12**, 2963–2968.
- 8 (a) X. Yang, T. Waters, X.-B. Wang, R. A. J. O'Hair, A. G. Wedd, J. Li, D. A. Dixon and L.-S. Wang, *J. Phys. Chem. A*, 2004, **108**, 10089–10093; (b) T.-C. Lau, J. Wang, R. Guevremont and K. W. M. Siu, *Chem. Commun.*, 1995, 877–878; (c) M. J. Deery, O. W. Howarth and K. R. Jennings, *J. Chem. Soc., Dalton Trans.*, 1997, 4783–4788.
- 9 (a) S. Bank, S. Liu, S. N. Shaikh, X. Sun, J. Zubietta and P. D. Ellis, *Inorg. Chem.*, 1988, **27**, 3535–3543; (b) H. Kang and J. Zubietta, *J. Chem. Soc., Chem. Commun.*, 1988, 1192–1193; (c) A. Proust, R. Thouvenot and P. J. Herson, *J. Chem. Soc., Dalton Trans.*, 1999, 51–56; (d) H. Kwen, V. G. Young Jr. and E. A. Maatta, *Angew. Chem., Int. Ed.*, 1999, **38**, 1145–1146.
- 10 J. Otera, *Esterification: Methods, Reactions and Applications*, Wiley-VCH, 1st edn, 2003.
- 11 (a) P. Phukan, *Tetrahedron Lett.*, 2004, **45**, 4785–4787; (b) S. V. Pansare, M. G. Malusare and A. N. Rai, *Synth. Commun.*, 2000, **30**, 2587–2592; (c) I. Mohammadpoor-Baltork, H. Aliyan and A. R. Khosropour, *Tetrahedron*, 2001, **57**, 5851–5854; (d) S. K. De, *Tetrahedron Lett.*, 2004, **45**, 2919–2922; (e) A. K. Chakraborti and R. Gulhane, *Tetrahedron Lett.*, 2003, **44**, 6749–6753; (f) R. Dalpozzo, A. D. Nino, L. Maiuolo, A. Procopiou, M. Nardi, G. Bartoli and R. Romeo, *Tetrahedron Lett.*, 2003, **44**, 5621–5624; (g) M. L. Kantam, K. Aziz and P. R. Likhar, *Catal. Commun.*, 2006, **7**, 484–487; (h) R. Ghosh, S. Maiti and A. Chakraborty, *Tetrahedron Lett.*, 2005, **46**, 147–151; (i) A. Kamal, M. Naseer, A. Khan, K. Srinivasa Reddy, Y. V. V. Srikanth and T. Krishnaji, *Tetrahedron Lett.*, 2007, **48**, 3813–3818; (j) B. Das and P. Thirupathi, *J. Mol. Catal. A: Chem.*, 2007, **269**, 12–16; (k) T. Srikanth Reddy, M. Narasimhulu, N. Suryakiran, K. Chinni Mahesh, K. Ashalatha and Y. Venkateswarlu, *Tetrahedron Lett.*, 2006, **47**, 6825–6829; (l) J. S. Yadav, A. V. Narsaiah, A. K. Basak, P. R. Goud, D. Sreenu and K. Nagaiah, *J. Mol. Catal. A: Chem.*, 2006, **255**, 78–80; (m) R. Alletti, M. Perambuduru, S. Samantha and V. Prakash Reddy, *J. Mol. Catal. A: Chem.*, 2005, **226**, 57–59; (n) J. K. Joseph, S. L. Jain and B. Sain, *J. Mol. Catal. A: Chem.*, 2007, **267**, 108–111; (o) V. Mirkhani, S. Tangestaninejad, M. Moghadam, B. Yadollahi and L. Alipanah, *Monatsh. Chem.*, 2004, **135**, 1257–1263; (p) N. Iranpoor, H. Firouzabadi and H. Jamalalian, *Tetrahedron Lett.*, 2005, **46**, 7963–7966; (q) H. Firouzabadi, N. Iranpoor, N. Sobhani and Z. Amoozgar, *Synthesis*, 2004, 295–297; (r) H. Firouzabadi, N. Iranpoor and A. Jafari, *Lett. Org. Chem.*, 2006, **3**, 25–28; (s) M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, M. Babaghanbari, M. Zarea, L. Shariati and S. A. Taghavi, *J. Iran. Chem. Soc.*, 2009, **6**, 523–532; (t) S. Tangestaninejad, M. H. Habibi, V. Mirkhani and M. Moghadam, *Synth. Commun.*, 2002, **32**, 1337–1343; (u) M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork and R. Shaibani, *J. Mol. Catal. A: Chem.*, 2004, **219**, 73–78; (v) M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork and S. A. Taghavi, *J. Mol. Catal. A: Chem.*, 2007, **274**, 217–223; (w) S. A. Taghavi, M. Moghadam, I. Mohammadpoor-Baltork, S. Tangestaninejad, V. Mirkhani and A. R. Khosropour, *Inorg. Chim. Acta*, 2011, **377**, 159–164; (x) M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork and S. Gharaati, *C. R. Chim.*, 2011, **14**, 1080–1087; (y) M. Yadegari, M. Moghadam, S. Tangestaninejad, V. Mirkhani and I. Mohammadpoor-Baltork, *Polyhedron*, 2011, **30**, 2237–2243.
- 12 (a) T. Takanami, R. Hirabe, M. Ueno, F. Hino and K. Suda, *Chem. Lett.*, 1996, 1031–1032; (b) T. Takanami, M. Hayashi, K. Iso, H. Nakamoto and K. Suda, *Tetrahedron*, 2006, **62**, 9467–9474; (c) T. Takanami, M. Hayashi and K. Suda, *Tetrahedron Lett.*, 2005, **46**, 2893–2896; (d) K. Suda, K. Baba, S. Nakajima and T. Takanami, *Chem. Commun.*, 2002, 2570–2571; (e) K. Suda, K. Baba, S. Nakajima and T. Takanami, *Tetrahedron Lett.*, 1999, **40**, 7243–7246; (f) K. Suda, T. Kikkawa, S. Nakajima and T. Takanami, *J. Am. Chem. Soc.*, 2004, **126**, 9554–9555; (g) S. Tangestaninejad, M. H. Habibi, V. Mirkhani and M. Moghadam, *J. Chem. Res.*, 2001, **12**(S), 365–367; (h) S. Tangestaninejad, M. H. Habibi, V. Mirkhani and M. Moghadam, *Synth. Commun.*, 2002, **32**, 1337–1343; (i) M. Moghadam, S. Tangestaninejad, V. Mirkhani and R. Shaibani, *Tetrahedron*, 2004, **60**, 6105–6111; (j) S. Gharaati, M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork and F. Kosari, *Inorg. Chim. Acta*, 2010, **363**, 1995–2000; (k) M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork and S. Gharaati, *Appl. Organomet. Chem.*, 2009, **23**, 446–454; (l) M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork and S. Gharaati, *Inorg. Chim. Acta*, 2010, **363**, 1523–1528; (m) M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, M. Khajehzadeh, F. Kosari and M. Araghi, *Polyhedron*, 2010, **29**, 238–243; (n) M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork and S. A. Taghavi, *Catal. Commun.*, 2007, **8**, 2087–2095; (o) M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork and S. Gharaati, *Polyhedron*, 2010, **29**, 212–219.
- 13 M. Araghi, V. Mirkhani, M. Moghadam, S. Tangestaninejad and I. Mohammadpoor-Baltork, *Dalton Trans.*, 2012, **41**, 3087.
- 14 N. H. Hur, W. G. Klemperer and R. C. Wang, *Inorg. Synth.*, 1990, **27**, 77–78.
- 15 (a) A. Bettelheim, B. A. White, S. A. Raybuck and R. W. Murray, *Inorg. Chem.*, 1987, **26**, 1009–1017; (b) A. D. Adler, F. R. Long, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2443–2445.
- 16 Y. Wei, B. Xu, C. L. Barnes and Z. Peng, *J. Am. Chem. Soc.*, 2001, **123**, 4083–4084.
- 17 W. Clegg, R. J. Errington, K. A. Fraser, S. A. Holmes and A. Schäfer, *J. Chem. Soc., Chem. Commun.*, 1995, 455–456.
- 18 C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck and R. Thouvenot, *Inorg. Chem.*, 1983, **22**, 207–216.
- 19 (a) J. B. Strong, G. P. A. Yap, R. Ostrander, L. M. Liable-Sands, A. L. Rheingold, R. Thouvenot, P. Gouzerh and E. Maatta, *J. Am. Chem. Soc.*, 2000, **122**, 639–649; (b) B. Xu, Y. Wei, C. L. Barnes and Z. Peng, *Angew. Chem., Int. Ed.*, 2001, **40**, 2290–2292.
- 20 K. Izutsu, *Electrochemistry in Nonaqueous Solutions*, Wiley-VCH Verlag GmbH & Co. KGaA, 2002, p. 223, ch. 8.
- 21 I. Bar-Nahum, K. V. Narasimhulu, L. Weiner and R. Neumann, *Inorg. Chem.*, 2005, **44**, 4900–4902.