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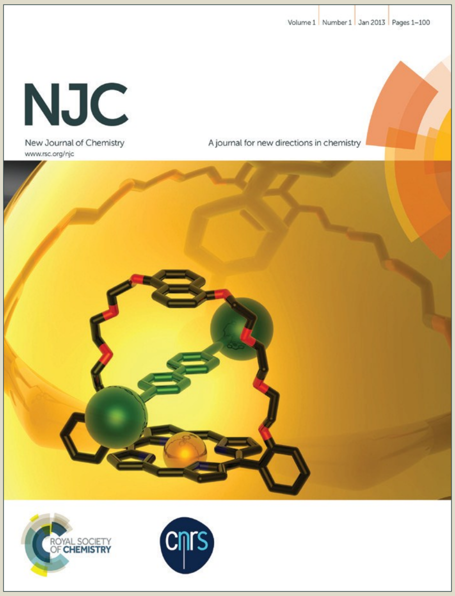

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ARTICLE TYPE

New sterically encumbered arylimido hexamolybdates for organic oxidation reactions

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Facile synthesis of mono- and di-functionalised arylimido hexamolybdates, $(^n\mathrm{Bu_4N})_2[\mathrm{Mo_6O_{18}(L1)}]$ (**1**), $(^n\mathrm{Bu_4N})_2[\mathrm{Mo_6O_{17}(L1)_2}]$ (**2**) and $(^n\mathrm{Bu_4N})_2[\mathrm{Mo_6O_{18}(L2)}]$ (**3**) (L1=4-bromo-2,6-diisopropylaniline, L2=2,2',6,6'-tetraisopropylbenzidine), has been achieved through the reaction of parent $(^n\mathrm{Bu_4N})_2[\mathrm{Mo_6O_{19}}]$ (**4**) with a series of aniline derivatives. The arylimido derivatives **1**-**3** have been characterised by both analytical and spectroscopic studies (^{1}H NMR, IR, UV-Vis and mass spectral studies), apart from structural elucidation of all the three compounds by single crystal X-ray diffraction studies. Steric hindrance at the *ortho*-positions of the arylamine seems to strengthen and effectively protect the newly formed Mo≡N bonds. The surface modification of the hexamolybdate by aryl amines results in the transformation of otherwise inactive parent compound **4** into useful catalysts **1**-**3**, which effectively catalyse the oxidation of cyclohexene to cyclohexene epoxide and benzyl alcohol to benzaldehyde and benzoic acid.

Introduction

Although polyoxomolybdates (POMs) have been known for several decades, newer anions with different size and structures continue to be discovered even in recent times.[1] The field of hybrid POMs, on the other hand, is relatively new and has tremendously grown in the last two decades.[2-5] Owing to the structural diversity and varied applications, several research groups have been carrying out investigations on different aspects in order to improve their utility as useful materials both in solid and solution state.[6-8] Polyoxomolybdates usually comprise octahedrally coordinated discrete polyanionic metal–oxide nanoclusters of Mo(VI) with adjacent polyhedra shared at corners and edges.[9-13] The Lindqvist hexamolybdate cluster, comprising $[\mathrm{Mo_6O_{19}}]^{2-}$anion, represents one of the ideal building blocks to construct new organic–inorganic hybrid assemblies.[14-19] The functionalisation can be performed by substitution of the counter cations through an electrostatically driven process[22,23] or insertion of hetero-groups in the metal-oxide sub-units of POMs under acidic conditions[20,21] or substitution of the terminal M=O groups covalently with conjugated organic species.[12,24-29]

Among the many organic hybrids of POMs, organoimido derivatives are of great interest because the organic π-electrons may extend their conjugation to the inorganic framework, thus resulting in strong d–π interactions. Such hybrids exhibit widespread applications in areas as diverse as electrochemistry, catalysis, medicine, nanomaterials, sensor design, magnetism, biochemistry and photochemistry.[8,26-46] The six terminal oxygen atoms in the hexamolybdate anion can be partially or completely replaced by organoimido ligands, depending on (a) stoichiometry of the starting materials, (b) reaction temperature, and (c) duration of the reaction.[17,36]

Interesting optical and electronic properties, desirable chemical reactivity, high stability towards oxidising conditions, and their ability to accept multiple electrons have made nano-sized POMs as promising candidates in several oxidative chemical transformations in the presence of suitable oxidants.[43] Hybrid POMs assemblies, because of their facile synthesis and combinatorial properties, have proven as multifunctional catalysts in oxidation reactions. Selective oxidation of cyclohexene to its epoxide (cyclohexene oxide) is an ever-green reaction owing to numerous applications of epoxide in synthetic organic chemistry.[48] Similarly, oxidation of benzyl alcohol to benzaldehyde is also of interest since benzaldehyde plays a key role in pharmaceutical and dye industries.[49,50]

Although large number of POM based catalysts have been reported for oxidation of substrates such as cyclohexene and benzyl alcohol, newer POMs are being explored to augment maximum selectivity in these reactions.[51-53] Further functionalisation of POMs has received attention in order to attain highest selectivity in such reactions.[54] Thus, the objective of the present work is to develop suitable organic-hybrid POMs for increasing both conversion and selectivity in oxidative chemical transformations. In order to achieve this, we have prudently introduced bulky isopropyl groups on the *ortho* position of a series of anilines (including a highly substituted benzidine derivative) and used them as starting materials for introducing arylimido ligands on one or more molybdenum centres of the hexamolybdate anion. The details are presented in this present article.

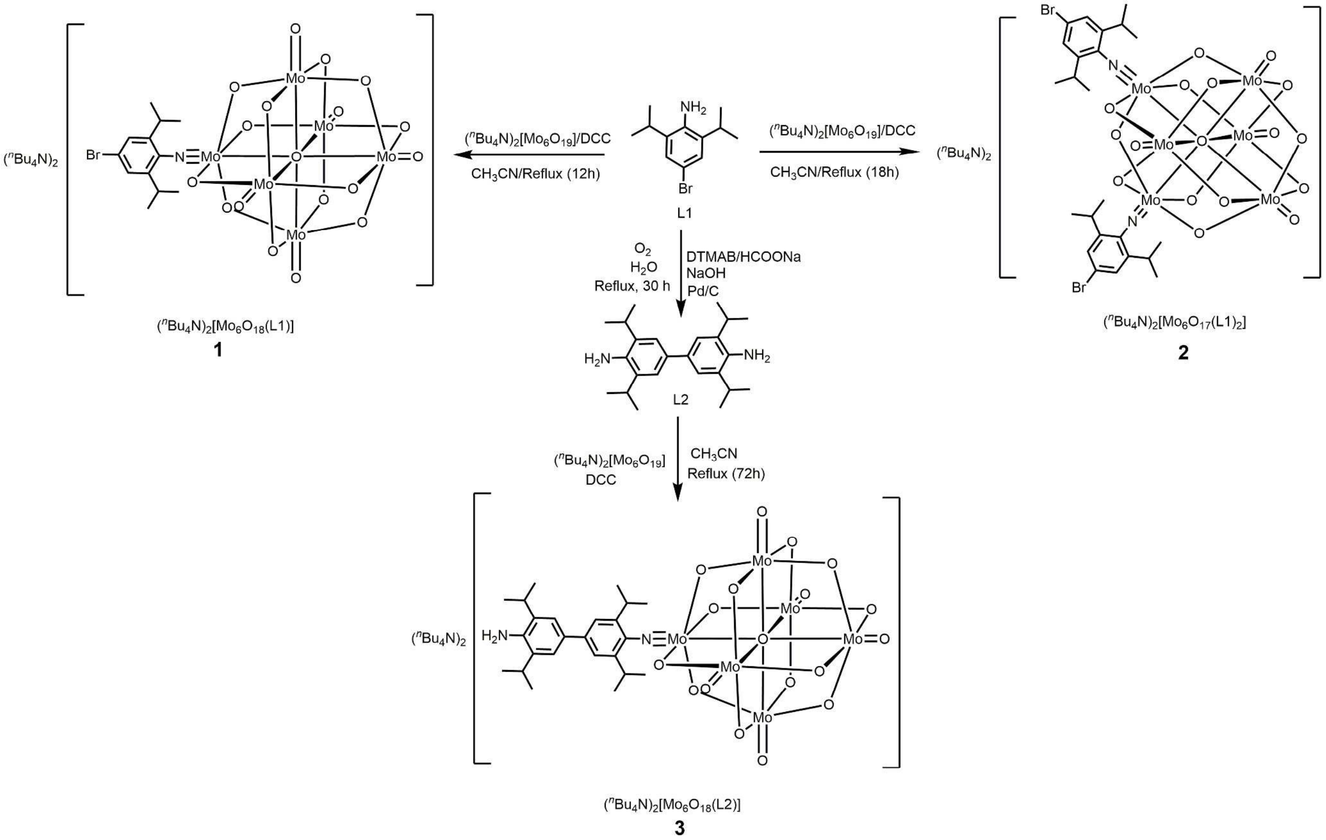
Results and Discussion

Synthesis and Characterization

When a mixture containing $(Bu_4N)_2[Mo_6O_{19}]$ (**4**), an aromatic amine and dicyclohexyl carbodiimide (DCC) is boiled under reflux in anhydrous acetonitrile under nitrogen, the corresponding organoimido derivatives $(^nBu_4N)_2[Mo_6O_{18}(L1)]$ (**1**), $(^nBu_4N)_2[Mo_6O_{17}(L1)_2]$ (**2**) and $(^nBu_4N)_2[Mo_6O_{18}(L2)]$ (**3**) (L1 = 4-bromo-2,6-diisopropylaniline, L2 = 2,2',6,6'-tetraisopropyl-benzidine) are formed. Completion of the reaction takes place in about 12-18 hours. The reaction has been found not to proceed in solvents other than acetonitrile. DCC is used as water scavenger and its quantity in the reaction mixture has to be maintained at around the same amount as water produced in the reaction mixture (a small excess amount of DCC is favoured). Use of excess DCC usually results in unexpected side reactions and reduces the yield of the desired products.[36]

The extent of substitution (either one or two of the terminal Mo=O linkages by arylimido groups Mo≡NR, leading to the formation of functionalised hybrid POMs), depends on the initial stoichiometry of the starting materials as well as the duration of the reaction under reflux conditions. For example, compound **1** is isolated as exclusive product when $(^nBu_4N)_2[Mo_6O_{19}]$ (**4**) and 4-bromo-2,6-diisopropylaniline (L1) were taken in a 1:1 stoichiometry and the reaction was carried out for only 12 h. Change of initial stoichiometry of the starting materials to 1:2 and carrying out the reaction for the same duration still produces only the mono-substituted product **1**. Extending the duration of the reaction to a total of 18 h produces the bi-substituted product **2** with no trace of **1** in the isolated reaction product. The formation of **3**, on the other hand, does not depend on the initial amount of 2,2',6,6'-tetraisopropylbenzidine (L2) added to the reaction mixture (up to 6 equivalents have been added).

Compounds **1-3** have been characterised by analytical and spectroscopic methods. The single crystals obtained from the reaction mixture were found to be pure and the elemental analysis results obtained for all the three compounds have been found to be consistent with the proposed molecular formula. The ^1H NMR spectra of compounds **1-3** are included in the ESI. All the ^1H NMR spectra exhibit clearly resolved signals, which can be unambiguously assigned. The integrated intensities of individual resonances are consistent with the proposed structure in each case. In all the three complexes, the resonances due to the ≡NR group have downfield shifted compared to the corresponding resonances in the parent ligands as a result of Mo-N bond formation. Compounds **1** and **2** exhibit a single resonance at 7.32 and 7.27 ppm, respectively, for aromatic C-H protons. The four *m,m'*-aromatic protons on coordinated L2 in **3** however exhibit two different signals at 7.39 and 7.34 ppm, owing to the non-equivalence created by binding of POM fragment on only one of the two available $–NH_2$ terminals (figure S1-S3).



Scheme 1. Synthesis of **1-3** (DCC=dicyclohexyl carbodiimide, DTMAB=dodecyltrimethylammonium bromide).

ESI-MS studies further support the molecular formula assigned to these compounds, also indicating their structural integrity in solution under mass spectral ionisation conditions. The negative ion mode ESI-MS of **1** contains a signal due to the parent ion $[Mo_6O_{18}(L1)]^{-2}$ at *m/z* 559.6452, exhibiting the expected calculated isotopic pattern for this structural unit. Similarly, compounds **2** and **3** also exhibit in their ESI-MS the parent ions at *m/z* 678.6162 ($[Mo_6O_{17}(L1)_2]^{-2}$) and 607.7228 ($[Mo_6O_{18}(L2)]^{2-}$), respectively (Figure 1).

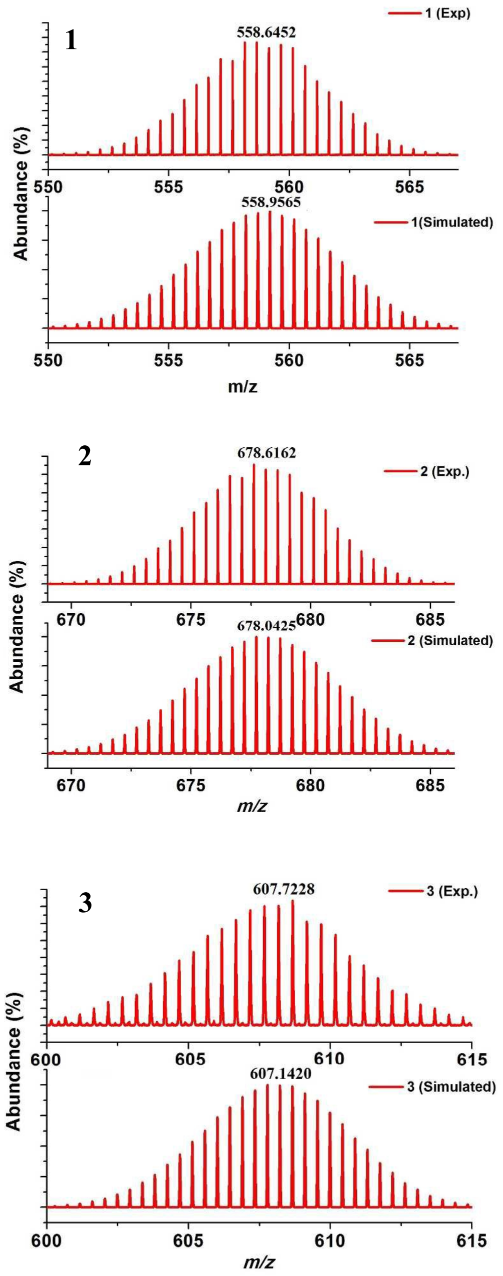


Figure 1. Experimental and calculated ESI-MS spectrum of **1** (top), **2** (middle) and **3** (bottom). Spectra recorded in CH_3CN in negative ion mode.

Two strong absorption bands in the IR spectra of **1-3** in the range 795-798 cm^{-1} and 951-954 cm^{-1} are due to ν(Mo–$O_{bridged}$–Mo) and ν(Mo–$O_{terminal}$) stretching vibrations, respectively, which are comparable to similar vibrations in the previously reported hexamolybdates.[55] The ν(Mo–N) bands appear at 971-975 cm^{-1} as a shoulder of the strong ν(Mo–$O_{terminal}$) band, indicating the formation Mo≡N bond (Figure 2).

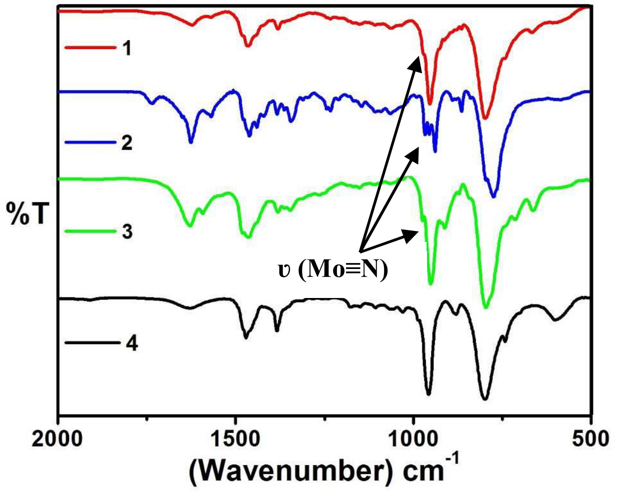


Figure 2. IR spectra of **1-4** (as KBr disc, 2000-500 cm^{-1}).

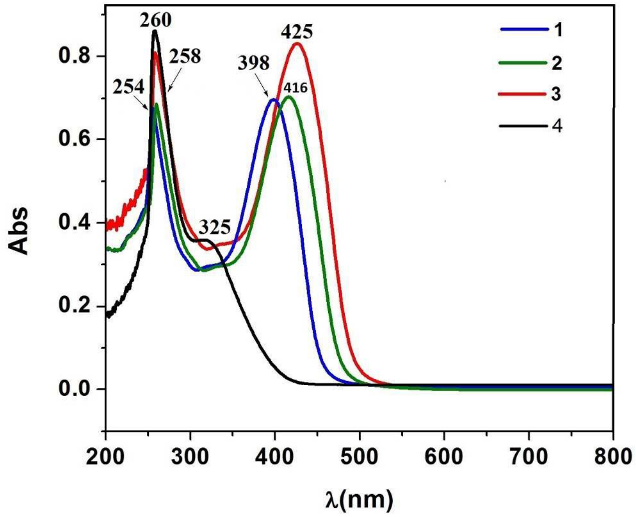


Figure 3. UV-Vis (1.0×10^{-5}M) [λ_{max}, 254(ε, 0.67 × 10^5 M^{-1} cm^{-1}), λ_{max}, 398 (ε, 0.69×10^5 M^{-1} cm^{-1}) for **1**; λ_{max}, 258(ε, 0.68 × 10^5 M^{-1} cm^{-1}), λ_{max}, 416(ε, 0.70×10^5 M^{-1} cm^{-1}) for **2**; λ_{max}, 260(ε, 0.81 × 10^5 M^{-1} cm^{-1}), λ_{max}, 425 (ε, 0.83×10^5 M^{-1} cm^{-1})for **3**; λ_{max}, 260(ε, 0.86 × 10^5 M^{-1} cm^{-1}), λ_{max}, 325 (ε, 0.35×10^5 M^{-1} cm^{-1})for **4**] spectra in DMSO.

The lowest energy electronic transition in the UV-Vis spectrum of compounds **1-3** exhibits a bathochromic shift (**1**: 398 nm, **2**: 416 nm, and **3**: 425 nm) compared to that of the parent $[Mo_6O_{19}]^{2-}$ ion (325 nm)[36,55] (Figure 3). This band is assigned to the electronic transition from the terminal oxygen *π*-type non-bonding HOMO to the molybdenum *π*-type LUMO in $[Mo_6O_{19}]^2$.[47,57] This energy gap is presumably reduced in the case of arylimido derivatives **1-3** as a result of strong *d-π* interaction between the conjugated organic ligand and the hexamolybdate framework, indicating strong electronic interaction between the metal-oxygen cluster and the organic ≡NR segment.

Thermogravimetric analysis (TGA) was performed for the new POMs in the range of 30–800 °C at the heating rate of

10 °C min^{-1} under flow of dinitrogen (see ESI, Figure S4). An initial weight loss of about 5% occurring up to 250 °C is due to the loss of adsorbed or occluded solvent molecules. In the temperature range 250-600 °C, the weight loss occurring in two stages can be assigned to the loss of organic cation and the arylamido ligands to result in the final ceramic material MoO$_3$ (40% of the initial mass) at 800 °C (Figure S4).

Molecular structure of 1 and 3

In order to ascertain the structural changes resulting from the substitution of the terminal oxo groups by arylimido functionalities, the molecular structures of **1-3** have been determined by single crystal X-ray diffraction studies. The ball and stick models of the molecular structures of mono substituted derivatives **1** and **3** are depicted in Figures 4 and 5, respectively. The terminal oxo group of the hexamolybdate cluster is replaced by sterically hindered arylimido ligands (L1 and L2). The anionic cluster is made up of six distorted octahedral molybdenum centres which themselves are arranged in the form a metal octahedron with a μ_6-O^{2-} occupying the centre of the polyhedron. In addition to the central oxygen, the molybdenum centres are further held together by twelve μ_2-oxygen centres to form the metal cage. While in the parent hexamolybdate anion each of the six Mo centres contains a terminal oxide (Mo=O) ligand, in clusters **1** and **3**, one of the six Mo centres feature a terminal imido linkage (Figures 4 and 5). Thus five of the total six Mo centres feature a distorted MoO$_6$ octahedral coordination environment (one μ_6-oxygen, one terminal oxo and four μ_2-oxygen), the sixth molybdenum reveals a distorted MoO$_5$N octahedral coordination environment (one μ_6 oxygen, four μ_2-oxygen and one terminal arylimido group).

The observed Mo-N distances (Mo(2)-N(1) 1.735(8) Å for **1** and Mo(2)-N(1) 1.748(6) Å in **3**) are suggestive of a formal Mo≡N bond in these systems. Further, these distances are also comparable to those found in other *ortho*-substituted arylimido hexamolybdates (Table 1).[55] The Mo≡N formulation is also consistent with nearly linear Mo–N–C linkages (171.3(1)° for **1** and 169.8(6)° for **3**). The bond length between imido-bearing molybdenum atom and central oxo atom (Mo(2)-O(1)=2.214 Å, **1**; Mo(2)-O(1)=2.193 Å, **3**) is slightly shorter than that of the other remaining Mo–O distances (2.350 Å, **1**; 2.363 Å, **3**) due to "trans influence" by the aryl imide moiety.

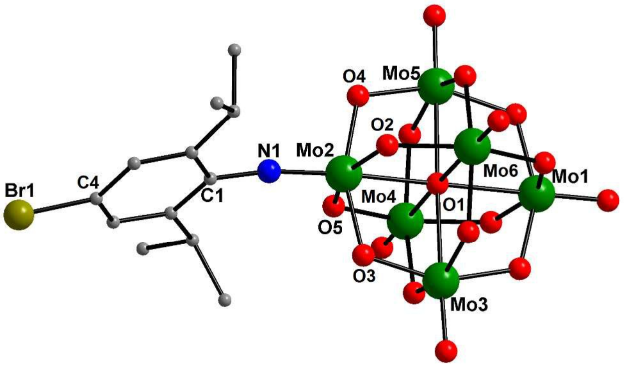


Figure 4. Molecular structure of the anion of **1.** Hydrogen atoms omitted for clarity.

In **3**, the imido-nitrogen to aryl carbon bond distance is shorter (N(1)-C(1A)=1.370(9) Å) than the other Ar-N bonds (N(2)-C(0EA)=1.410(2) Å), suggesting a complete delocalisation of the nitrogen lone pair over C-N-Mo-O segment. As a result, the central O(1) atom is shifted slightly toward the imido-bearing molybdenum atom Mo(2). The bonds between imido-bearing molybdenum atom and μ_2-oxygen atom are longer than all other Mo–O distance, because the imido-bearing molybdenum atom demonstrates weaker electropositivity than other molybdenum atoms as a consequence of coordination with better electron donating alkyl imido ligands (Figure 4 and 5).

Table 1. Structural comparison of **1-3** with a few selected alkyl and aryl imido hexamolybdates (Mo≡N-R).

S. No.	-R	Mo≡N (Å)	Mo–μ_6O (Å)^a (trans to Mo≡N)	Mo–μ_6O^b (Å) (all other)	C–N–Mo (°)	Ref.
1	Et	1.705(11)	2.261(4)	2.351(4)	178.1(10)	55
2	^{n}Pr	1.704(4)	2.229(2)	2.335(2)	177.9(5)	55
3	^{i}Pr	1.713(7)	2.229(4)	2.342(4)	175.0(7)	55
4	^{n}Bu	1.720(7)	2.229(4)	2.345(4)	178.4(8)	55
4	^{t}Bu	1.718(7)	2.230(4)	2.338(4)	178.3(8)	55
	Cy	1.750(1)	2.252(7)	2.333(7)	177.5(8)	55
5	Hex	1.709(4)	2.223(3)	2.358(3)	174.6(7)	55
6	2,6-dimethylphenyl	1.723(7)	2.230(6)	2.337(6)	178.4(7)	36
7	2,6-diisopropylphenyl	1.739(15)	2.254(10)	2.312(10)	176.3(15)	13
8	4-bromo-2,6-dimethylphenyl	1.731(4)	2.211(3)	2.345(3)	176.3(4)	56
9	4-iodo-2,6-dimethylphenyl	1.733(6)	2.222(4)	2.349 (4)	172.8(6)	36
10	4-iodo-2,6-diisopropylphenyl	1.745(2)	2.225(2)	2.375(2)	171.17 (3)	57
11	4-ethynyl-2,6-dimethylphenyl	1.729(5)	2.232(4)	2.353(4)	172.5(5)	36
12	4-bromo-2,6-diisopropylphenyl (**1**)	1.735(8)	2.214(1)	2.345(1)	171.3(1)	this work
13	4-bromo-2,6-diisopropylphenyl (**2**)	1.738(5), 1.742(5)	2.225(5), 2.227(4)	2.375(5), 2.374(4)	172.9(5), 174.4(6)	this work
14	3,3',5,5'-tetraisopropyl-[1,1'-biphenyl]-4-amine (**3**)	1.748 (6)	2.193(4)	2.363(5)	169.8(6)	this work

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Within the crystal lattice, the POM hybrid ions of **1** are organised into weakly held dimers. As shown in Figure 6, the "dimerisation" is clearly driven by π–π stacking of the aryl rings (3.97 Å).

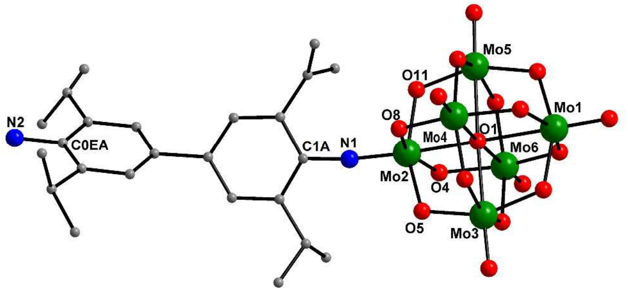


Figure 5. Molecular structure of the anion part of **3.** Hydrogen atoms omitted for clarity.

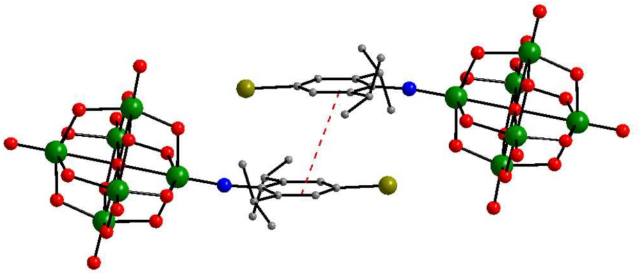


Figure 6. Dimeric structure of cluster anions of **1** formed through π-π interactions (3.97 Å).

Molecular structure of 2

Compound **2** crystallises in the triclinic space group *P* - *1*. The asymmetric part of the unit cell contains two crystallographycally independent molecules. Unlike in **1** and **3**, two terminal oxo groups of the hexamolybdate cluster have been replaced by L1 in **3**, where the arylimido moieties are *cis* to each other on the Mo_6 octahedron. The bond distances between Mo(1)-N(1) and Mo(2)-N(2) are 1.738(5) and 1.742(5) Å, respectively, once again indicating triple bond character (Table 1). The bond angles C(1)-N(1)-Mo(1) (172.9(5)^o) and C(13)-N(2)-Mo(2) (174.4(6)^o) are close to linear. The bond lengths between imido-bearing molybdenum atom and central oxo atom (Mo(1)-O(1)= 2.227(4), Mo(2)-O(1)= 2.225(4) Å) are shorter than other Mo-O bonds (Mo(4)-O(1)= 2.374(4), Mo(6)-O(1)= 2.375(4) Å) (Figure 7).

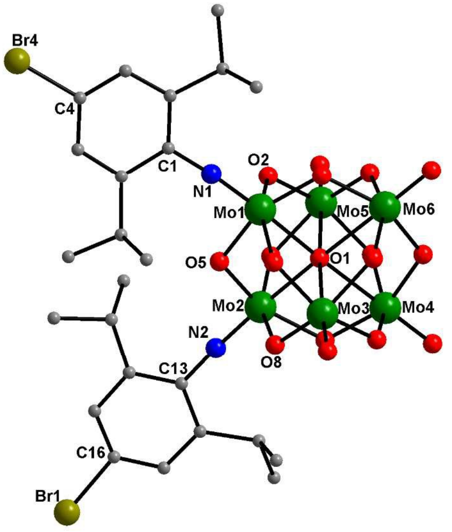
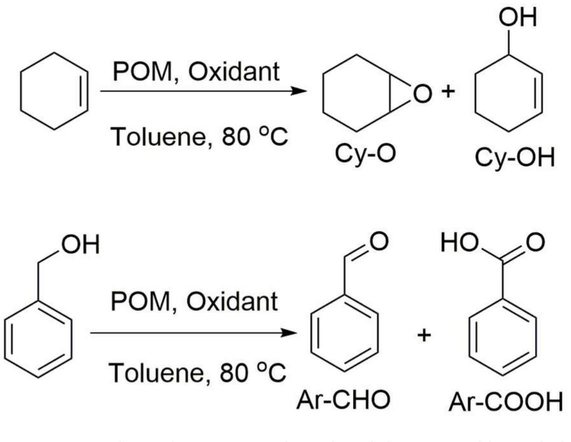


Figure 7. Molecular structure of the anion part of **2.** Hydrogen atoms omitted for clarity.

Arylimido POMs 1-3 as oxidation catalysts

Hybrid polyoxometallates have been extensively studied as oxidation catalysts, including our recent study on D4R zinc-phosphate based octa-molybdates $[Mo_8O_{26}]^{4-}$, phospha-molybdates $[PMo_{11}VO_{40}]^{4-}$, and sila-tungstates $[SiMo_{12}O_{40}]^{4-}$ for olefin expoxidation.[47] Although there are many alkyl/arylimido POMs known in the literature, their catalytic activity in organic oxidation reactions have not been explored. To test the utility of this class of compounds, cyclohexene and benzyl alcohol oxidation reactions were carried out using **1-3** as catalysts (Scheme 2).



Scheme 2. Schematic representation of cyclohexene and benzyl alcohol oxidations catalysed by POM catalysts.

Acetonitrile and toluene have often been reported as effective solvents in homogeneous cyclohexene and benzyl alcohol oxidation reactions catalysed by POMs.[58-61] Therefore, in the present study, we have performed cyclohexene oxidation using both acetonitrile and toluene as solvent with **1** as catalyst to optimise the solvent for these reactions. Toluene was found to be superior to acetonitrile since **1** showed much better catalytic activity with almost 100% selectivity for the epoxide (Table 2). On the other hand, **1** in acetonitrile, under otherwise identical conditions, exhibited lower activity and poorer selectivity (49% conversion; 2% epoxide, 51% cyclohexen-1-ol and 47% cyclohexen-1-one). Similarly the catalytic reactions were found to be ineffective at room temperature in toluene. Hence the temperature was raised to 80 ºC at which the highest conversion was observed.

The results of oxidation reactions run in toluene using cumene peroxide as the oxidant and **1**-**3** as catalysts (0.05%) at 80 ºC in toluene are summarised in Table 2. Irrespective of the catalyst employed for the oxidation of cyclohexene, its epoxide was obtained as the major product with a selectivity of ~95%. Cyclohexene-1-ol was formed as the only minor product (~5%). Unlike cyclohexene oxidation, the oxidation of benzyl alcohol under similar reaction conditions produced two major products, viz. benzaldehyde and benzoic acid with nearly equal selectivity (cf. Table 2), which is primarily due to further oxidation of benzaldehyde formed to benzoic acid.

Table 2. Product yield and selectivity % of cyclohexene and benzyl alcohol oxidations catalyzed by POM catalysts

	Cyclohexene oxidation				Benzyl alcohol oxidation			
	Conversion, (%)	Selectivity (%)		TON	Conversion, (%)	Selectivity (%)		TON
		CyO	CyOH			PhCHO	PhCOOH	
1	82	95	5	1892	39	59	41	900
2	81	94	6	1869	45	57	43	1038
3	76	95	5	1753	51	58	42	1176

Conditions: Catalyst (13 µmol); substrate (30 mmol); oxidant (6 mmol); toluene (5 ml); temperature (80 ºC) and time (48 h)

Although all three catalysts displayed similar catalytic performance for cyclohexene epoxidation, as can be seen from Table 2, catalysts **1** and **2** marginally perform better than catalyst **3**. For oxidation of benzyl alcohol, however, catalyst **3** has been found to be a better catalyst (51% conversion) than **1** (39% conversion) and **2** (45% conversion), when reactions were carried out for same amount of time (48 h). The origin of this reversed conversion efficiency between the two different substrates is not clearly understood although it is reasonable to assume that the free –NH_2 group has a definite role to play through hydrogen bonding interactions with the benzyl alcohol substrate in the early part of the catalytic cycle.

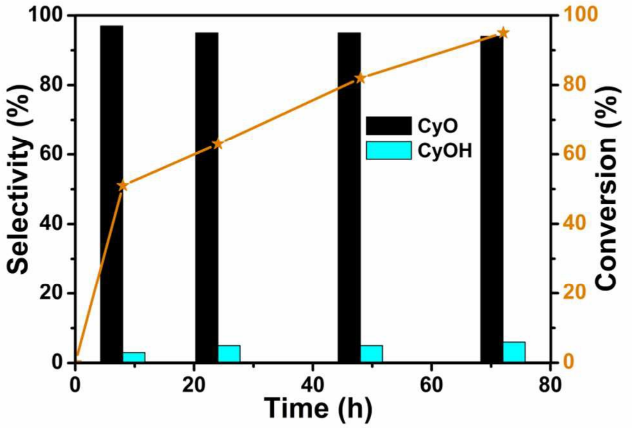


Figure 8. Effect of time on product selectivity and % conversion in cyclohexene oxidation by catalyst **1**.

It was further noted that the selectivity in case of cyclohexene oxidation is almost invariant as a function of reaction time and conversion rate as can be seen from Figure 8. In case of benzyl alcohol oxidation, the selectivity scenario is somewhat different as depicted in Figure 9. It appears that in the early stages of the oxidation reaction, the benzyl alcohol gets predominately converted into the aldehyde. After ~5 hours of the catalytic run, it appears that a second catalytic process involving the conversion of initially formed benzaldehyde to benzoic acid sets in. As a result, longer reaction runs tend to produce more of benzoic acid and hence reduce the selectivity for benzaldehyde. The turnover numbers displayed in Table 1 suggest that the POMs **1**-**3** are better catalysts for cyclohexene oxidation compared to benzyl alcohol oxidation, probably owing to the competing reactions in the latter. The integrity of the catalysts after the catalytic run have been examined by ESI mass spectral studies on **3** and it has been found that the spectrum obtained for the recovered catalyst is identical to that of the original compound **3** (see ESI, Figure S9).

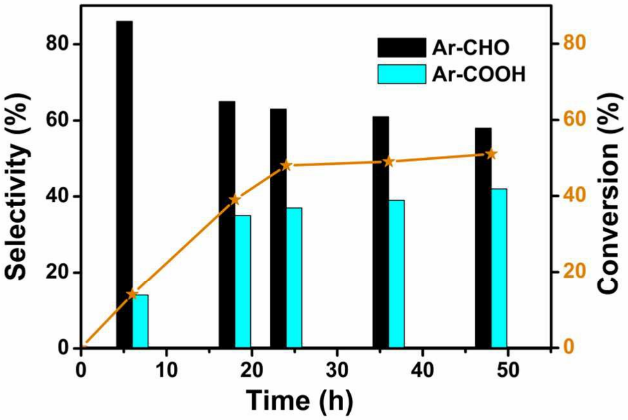


Figure 9. Effect of time on product selectivity and % conversion for benzyl alcohol oxidation by catalyst **3**.

Conclusions

It has been demonstrated that it is possible to modify the hexamolybdate anion to the corresponding arylimido derivatives by their reaction with substituted anilines. The use of 4-bromo-2,6-diisopropylaniline in one or two equivalents results in the isolation of either mono- or di-substituted arylimido hexamolybdates **1** and **2**. The free Ar-Br linkages in **1** and **2** are highly amenable for further organic reactions (viz. cross coupling C-C bond formation reactions) and hence can be useful synthons for polymeric hybrid materials incorporating polyoxomolybdates. Interestingly, the reaction of tetraisopropylbenzidine with hexamolybdates neither proceeds beyond mono-substitution nor captures the hexamolybdates at both the –NH$_2$ ends, thus leaving a highly functionalised hybrid polyoxomolybdate **3** with free –NH$_2$ group. All the three new polyoxomolybdates have been found to be efficient and selective catalysts for olefin epoxidation, while **3** was found to be more efficient for benzyl alcohol oxidation, indicating the possible role of –NH$_2$ group in the catalysis.

Experimental section

Methods, materials and instruments. Acetonitrile was purified using P_2O_5 and distilled over molecular sieves as described in the literature.[62] All the reactions were carried out under N_2 atmosphere using Schlenk line techniques. 2,6-Diisopropylaniline (Alfa Aesar), sodium molybdate (Sigma Aldrich), and dicyclohexyl carbodiimide (Merck) were procured from commercial sources and used either as received or purified where necessary. 4-Bromo-2,6-diisopropylaniline (L1) and 2,2',6,6'-tetraisopropylbenzidine (L2) were synthesized using reported procedure in the literature.[63,64] Synthesis of (^{n}Bu$_4$N)$_2$[Mo$_6$O$_{19}$] was accomplished by using a previously published report.[65]

The melting points of the new products were measured in glass capillaries and are reported uncorrected. Elemental analyses were performed on a Thermo Finnigan (FLASH EA 1112) microanalyzer. FT-IR spectra were recorded on a Perkin Elmer Spectrum One Infrared Spectrometer as KBr diluted discs. The absorption spectra were recorded on a Varian Cary Bio 100 UV-Vis spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker 400 and Varian 400 MHz NMR spectrometers. ESI-MS were recorded on a Bruker Maxis Impact or a Waters Q-TOF micro mass spectrometer. Thermogravimertic analyses were performed on Perkin Elmer Pyris Diamond TGA instrument.

Synthesis of (^{n}Bu$_4$N)$_2$[Mo$_6$O$_{18}$(L1)] (1): A mixture of 4-bromo-2,6-diisopropylaniline (L1) (0.30 g, 1.20 mmol), dicyclohexyl carbodiimide (0.25 g 1.20 mmol) and (^{n}Bu$_4$N)$_2$[Mo$_6$O$_{19}$] (1.62 g 1.20 mmol) was refluxed in 20 mL of acetonitrile under flow of nitrogen gas for 12 hours. After being cooled to room temperature, the resulting dark red solution was filtered to remove the white precipitate of N,N'-dicyclohexylurea formed. After 24 h, yellow crystals of unreacted starting material were obtained. Hence the solution was decanted and kept undisturbed for a further crystallisation. After 4 days dark red block shaped crystals of **1** formed. These crystals were found to be suitable for single crystal X-ray diffraction. M.p: >250 ^{o}C. Anal. Calcd. for $C_{44}H_{88}BrMo_6N_3O_{18}$: C, 32.97; H, 5.53; N, 2.62. Found: C, 33.04; H, 5.32; N, 2.93. FT-IR (KBr disc, cm^{-1}); 2962 (s), 2873 (s), 1463 (s), 1381 (s), 975 (s), 953 (s), 798 (s). ^{1}H NMR (400 MHz, DMSO-*d$_6$*): δ (ppm) 7.32 (s, 2 H, ArH), 3.51 (spt, 4 H, CH), 1.19 (d, 24 H, ^3J=2.16 Hz, ArCH$_3$) 3.03 (m, 16 H, NCH$_2$), 1.58 (m, 16 H, CH$_2$), 1.28 (m, 16H, CH$_2$), 0.94 (t, 24 H, CH$_3$). ESI-MS (-ve mode): *m/z* calc. for dianion $C_{12}H_{16}BrMo_6NO_{18}$ 558.9565; found 558.6462 [M]$^{-2}$.

Synthesis of (^{n}Bu$_4$N)$_2$[Mo$_6$O$_{17}$(L1)$_2$] (2): A mixture of 4-bromo-2,6-diisopropylaniline (L1) (0.61 g, 2.40 mmol), dicyclohexyl carbodiimide (0.49 g 2.40 mmol) and (^{n}Bu$_4$N)$_2$[Mo$_6$O$_{19}$] (1.62 g 1.20 mmol) was boiled under reflux in acetonitrile (20 mL) under nitrogen for 18 hours. After being cooled to room temperature, the resulting dark red solution was filtered to remove the white precipitate of N,N'-dicyclohexylurea. After 12 h, yellow crystals of unreacted starting material was formed, which were discarded and the red solution was further kept undisturbed for crystallisation. After 2 days, dark red coloured crystals of **2** were formed, which were found suitable for single crystal X-ray diffraction. M.p: >250 ^{o}C. Anal. Calcd. for $C_{56}H_{104}Br_2Mo_6N_4O_{17}$: C, 36.53; H, 5.69; N, 3.04. Found: C, 36.54; H, 5.90; N, 3.76. FT-IR (KBr disc, cm^{-1}); 2965 (s), 2873 (s), 1463 (s), 1385 (s), 971 (s), 954 (s), 795 (s). ^{1}H NMR (400 MHz, DMSO-*d$_6$*): δ (ppm) 7.27 (s, 4 H, ArH), 3.78 (spt, 4 H, CH), 2.08 (d, 48 H, ^3J=2.16 Hz, ArCH$_3$) 3.06 (m, 16 H, NCH$_2$), 1.56 (m, 16 H, CH$_2$), 1.31 (m, 16 H, CH$_2$), 0.93 (t, 24H, CH$_3$). ESI-MS (-ve mode): *m/z* calc. for dianion $C_{24}H_{32}Br_2Mo_6N_2O_{17}$ 678.0425; found 678.6162 [M]$^{-2}$.

Synthesis of (^{n}Bu$_4$N)$_2$[Mo$_6$O$_{18}$(L2)] (3): A mixture of 2,2',6,6'-tetraisopropylbenzidine (L2) (0.49 g, 1.42 mmol), dicyclohexyl carbodiimide (0.29 g 1.42 mmol) and (^{n}Bu$_4$N)$_2$[Mo$_6$O$_{19}$] (1.93 g 1.42 mmol) was heated under reflux conditions in acetonitrile (20 mL) under nitrogen flow for 72 hours. After being cooled to room temperature, the resulting dark red solution was filtered to remove the white precipitate of N,N'-dicyclohexylurea. After 24 h, yellow crystals of unreacted starting material were obtained, which was discarded by filtration. From the remaining dark red solution, dark red crystals of **3** were obtained after 4 days. M.p: >250 ^{o}C. Anal. Calcd. for $C_{56}H_{106}Mo_6N_4O_{18}$: C, 39.59; H, 6.29; N, 3.30 Found: C, 39.06; H, 5.86; N, 3.31. FT-IR (KBr disc, cm^{-1}); 3441 (b), 2961 (s), 2934 (s), 2873 (s), 1480 (s), 1469 (s), 973 (s), 951 (s), 924 (s), 796 (s). ^{1}H NMR (400 MHz, Acetone-*d$_6$*): δ (ppm) 7.39 (s, 2 H, ArH), 7.34 (s, 2 H, ArH), 4.03 (spt, 4 H, CH), 2.04 (d, 24 H, ^3J=2.16 Hz, ArCH$_3$) 3.05 (m, 16 H, NCH$_2$), 1.76 (m, 16H, CH$_2$), 1.42 (m, 16 H, CH$_2$), 0.96 (t, 24 H, CH$_3$). ESI-MS (-ve mode): *m/z* calc. for dianion $C_{24}H_{34}Mo_6N_2O_{18}$ 607.1420; found 607.7228 [M]$^{-2}$.

Catalytic oxidation studies. Prior to the catalytic oxidation of cyclohexene or benzyl alcohol, 25 ml two necked reaction flask was equipped with a magnetic stir bar. To this flask, toluene, cumene hydroperoxide, cyclohexene or benzyl alcohol and catalyst were added. The obtained catalytic mixture was stirred at 80 ºC under atmospheric pressure conditions. The progress of the catalysis was monitored by analysing aliquots of reaction mixture drawn at different time intervals. By following the similar procedure, two blank reactions (one without catalyst and another without oxidant) were also carried out for both cyclohexene and benzyl alcohol oxidation. Perkin-Elmer gas chromatograph annexed with mass spectrometer (GC-MS CLAURUS 500) was used to analyse the reaction aliquots under the flow of helium carrier gas.

X-ray crystallography of 1-3. The X-ray diffraction intensity data for **1** and **2** were collected on a Rigaku Saturn 724+ CCD diffractometer fitted with a MoKα radiation source (λ = 0.71075 Å) at 130 K and 293 K, respectively. Intensity data collection for compound **3** was done at 100 K on a Oxford SuperNova (Dual, Cu at zero, EOS) diffractometer fitted with a CuKα radiation source (λ =1.54190 Å), under continuous flow of cooled nitrogen gas. Rigaku CrystalClear software was used for data integration and indexing of reflections for compound **1** and **2**, apart from application of numerical method to correct for absorption effects. The data integration and indexing were performed using CrysAlisPro software and Gaussian method was employed to correct for absorption for **3**. All calculations were carried out using the programs in WinGX module[66] and the structures were solved by direct methods implemented in SIR-92.[67] The final refinement of the structure was carried out using full least-square methods on F^2 using SHELX-14[68] for all the compounds. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically as rigid atoms in their idealised locations. The aryl rings of arylimido group in **2** and **3** were found to be highly disordered and hence it has been refined using partial occupancies for various ring atoms. Similarly, the disorder of bromine atoms in **2** was modelled using partial occupancies. A summary of X-ray crystal data for compounds **1-3** is provided in Table 2.

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Notes and references

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† *Electronic Supplementary Information (ESI) available: [^{1}H NMR spectra, TGA and selectivity and % conversion cures]. Crystallographic data of **1-3**. CCDC 1420505-1420507. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/*

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Table 3. Summary of crystallographic data for compounds **1**-**3**.

Compounds	**1**	**2**	**3**
Formula	$C_{44}H_{88}BrMo_6N_3O_{18}$	$C_{56}H_{104}Br_2Mo_6N_4O_{17}$	$C_{56}\ H_{105.54}\ Mo_6\ N_4\ O_{18}$
F.W	1602.72	1840.89	1698.62
Cryst. syst.	triclinic	triclinic	monoclinic
Space group	*P* -1	*P* -1	$P2_1$/c
Size/mm^3	0.30 × 0.29× 0.13	0.12 × 0.12× 0.08	0.25 x 0.23 x 0.20
a/Å	11.843(8)	16.201(4)	23.8986(5)
b/Å	12.310(9)	19.611(5)	15.7862(2)
c/Å	20.833(14)	22.481(6)	20.1555(5)
α (°)	99.327(14)	98.01(5)	90.00
β (°)	99.865(12)	96.77(4)	112.883(3)
γ (°)	95.802(12)	90.14(6)	90.00
V/A° ^{3}	2927(4)	7022.4(3)	7005.6(2)
Z	2	4	4
ρ_c/Mg m^{-3}	1.819	1.740	1.611
Refl. collected	22141	52661	51470
Unique refl.	10207	24481	12339
($R_{int.}$)	0.0296	0.0225	0.0669
Final R indices [I>2sigma(I)]	0.0391	0.0529	0.0546
wR_2	0.0889	0.1533	0.1372
GOF	1.091	1.088	0.967

TOC

Surface modification of the parent hexamolybdate by aryl amines results in useful catalysts for the oxidation of cyclohexene to cyclohexene epoxide and benzyl alcohol to benzaldehyde and benzoic acid.