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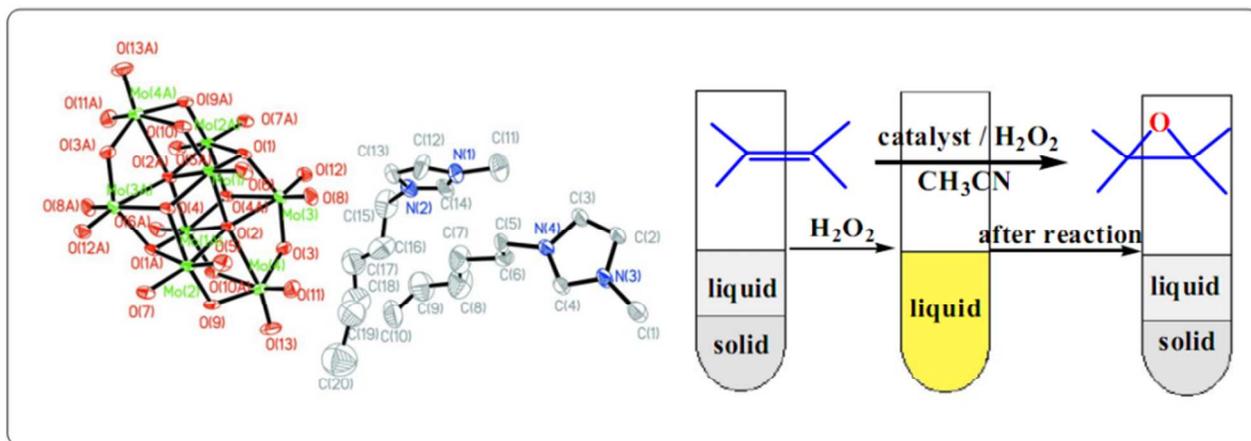
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PAPER

# Olefin epoxidation with hydrogen peroxide using octamolybdate based self-separating catalysts

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Mo<sub>8</sub>O<sub>26</sub><sup>4-</sup> based organic polyoxomolybdate salts of general formula [Hmim]<sub>4</sub>Mo<sub>8</sub>O<sub>26</sub> (Hmim = 1-hexyl-3-methylimidazolium), [Dhmim]<sub>4</sub>Mo<sub>8</sub>O<sub>26</sub> (Dhmim = 1,2-dimethyl-3-hexylimidazolium) and [Hpy]<sub>4</sub>Mo<sub>8</sub>O<sub>26</sub>·H<sub>2</sub>O (Hpy = 1-hexylpyridinium) have been prepared and characterized. These compounds were applied as catalysts for olefin epoxidation using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as oxidant in CH<sub>3</sub>CN. The polyoxomolybdate salts exhibit excellent catalytic performance and are also self-separating, a great advantage for catalyst recycling. The catalysts can be reused at least 10 runs without significant loss of activity.

## Introduction

Epoxides are very important key raw materials for a wide variety of chemicals such as glycols, glycol ethers, alkanolamine, and polymers.<sup>1</sup> So far, various compounds including inorganic metal oxides and organometallic compounds have been applied as catalysts for olefin epoxidations using oxygen, ozone, hydrogen peroxide or organic peroxides as oxidants.<sup>2</sup> In particular, hydrogen peroxide based catalytic epoxidation has received much attention since hydrogen peroxide is a cheap, mild and environmentally benign reagent that produces only water as by-product.<sup>3</sup> Today, H<sub>2</sub>O<sub>2</sub> has already been successfully used in industry for propylene epoxidation using TS-1 zeolite as heterogeneous catalyst.<sup>4</sup> While in the case of homogeneous catalysis, although some molecular organometallic compounds such as CH<sub>3</sub>ReO<sub>3</sub> (MTO),<sup>5</sup> MoO<sub>2</sub>X<sub>2</sub>L<sub>2</sub>,<sup>6</sup> Cp\*MoO<sub>2</sub>Cl<sup>7</sup> etc. have proven to be excellent catalysts for epoxidations on a laboratory scale, they are not applied in larger scale industrial processes since these types of organometallic catalysts are rather expensive to produce and their reusability in an industrial scale process is so far not convincingly established.<sup>8</sup>

Polyoxometalates (POMs), owing to their good catalytic features such as high activity and selectivity, controllable redox and acidic properties at atomic or molecular levels, have also been studied as oxidation catalysts in the past decades.<sup>9</sup> Among various POMs, the classic Ishii-Venturello system has attracted much interest in oxidation reactions and has been extensively investigated.<sup>10</sup> In the Ishii-Venturello system, the Venturello anion ([PO<sub>4</sub>[WO(O<sub>2</sub>)<sub>2</sub>]<sub>4</sub>]<sup>3-</sup>) is combined with a quaternary ammonium cation under formation of an inorganic-organic hybrid salt, which can be used as phase transfer catalyst using H<sub>2</sub>O<sub>2</sub> as primary oxidant for epoxidation of various olefins under rather mild conditions.<sup>11</sup> It has additionally been found that some Keggin- or Lindqvist-types of hybrid POMs such as [C<sub>n</sub>mim]PW<sub>12</sub>O<sub>40</sub>, [C<sub>n</sub>mim]W<sub>6</sub>O<sub>19</sub> can be also used as catalysts for oxidations and esterification.<sup>12</sup>

Despite these catalysts showing high activity towards epoxidations, it is not convenient to separate such a catalyst in a homogeneous system. Xi et al. have developed an interesting

“reaction-controlled phase-transfer catalysis” system using [π-C<sub>5</sub>H<sub>5</sub>NC<sub>16</sub>H<sub>33</sub>]<sub>3</sub>[PO<sub>4</sub>(WO<sub>3</sub>)<sub>4</sub>] as a phase transfer catalyst for propylene epoxidation, and the system was also proven to be active for other olefins.<sup>13</sup> In Xi’s system, the catalyst precursor is insoluble, but the active species formed is soluble in the reaction medium, therefore the system manifests a solid - liquid - solid phase transfer of the catalyst during the reaction. Thus the catalyst is “self-separating” after the completion of the reaction and recycled simply by filtration.<sup>13</sup> Subsequently, it was found that PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> or PO<sub>4</sub>[WO(O<sub>2</sub>)<sub>2</sub>]<sub>4</sub><sup>3-</sup> anion based compounds also show self-separation phenomena in catalysis.<sup>14</sup> These kinds of catalysts combine the advantages of both homogeneous and heterogeneous catalysts, thus they are very promising catalysts for industrial applications.<sup>15</sup>

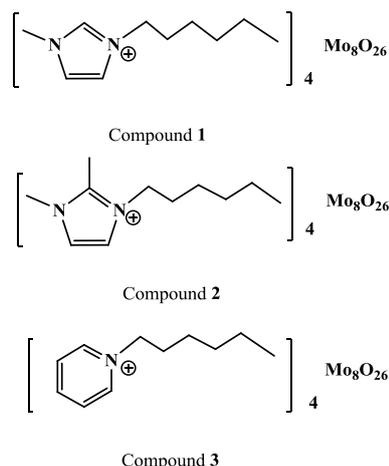
Recently, we have found that alkylimidazolium / alkylpyridinium octamolybdates exhibit high activity towards olefin epoxidations when using 30 % H<sub>2</sub>O<sub>2</sub> as oxidant. Moreover, these compounds display self-separation properties in catalysis, and the catalysts could be used at least 10 times without significant loss of activity, indicating good catalyst stability. Mo<sub>8</sub>O<sub>26</sub><sup>4-</sup> based salt is a type of cheap and easily prepared POM materials.<sup>16</sup> However, not much work has been done with respect to their catalytic performance so far,<sup>17</sup> and almost no studies have targeted their self-separating property. Despite Deng et. al.<sup>17a</sup> have mentioned that [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>4</sub>[α-Mo<sub>8</sub>O<sub>26</sub>] could be self-precipitating in the sulfide oxidation catalytic system, ethyl acetate had to be added to precipitate the catalyst. In this work, a highly efficient, “green” method, allowing for good catalyst recycling for olefin epoxidations using 30 % aqueous hydrogen peroxide as oxidant and alkylimidazolium or alkylpyridinium octamolybdates as catalysts is presented.

## Results and Discussion

### Synthesis and Characterization

Three Mo<sub>8</sub>O<sub>26</sub><sup>4-</sup> based organic polyoxomolybdate salts of formula [Hmim]<sub>4</sub>Mo<sub>8</sub>O<sub>26</sub> (Hmim = 1-hexyl-3-methylimidazolium), [Dhmim]<sub>4</sub>Mo<sub>8</sub>O<sub>26</sub> (Dhmim = 1,2-dimethyl-3-hexylimidazolium) or [Hpy]<sub>4</sub>Mo<sub>8</sub>O<sub>26</sub>·H<sub>2</sub>O (Hpy = 1-hexylpyridinium) have been

synthesized. The structures are shown in Scheme 1.



**Scheme 1** Structures of compounds 1-3

All three compounds were characterized by FT - IR, <sup>1</sup>H - NMR, ESI - MS (positive mode) and elemental analysis (see experimental section). The melting point and decomposition temperature were determined with a micro melting point apparatus and by thermogravimetric analysis (TGA). All the three compounds are not conventional ionic liquids since they are solids below 100 °C. The melting point for **1** is about 158 °C, whereas compounds **2** and **3** decompose directly at higher temperatures but no melting process is observed below the decomposition temperature. TGA data indicate that all examined compounds show negligible volatility and high thermal stability with a decomposition onset temperature around 300 °C (see Table 1).

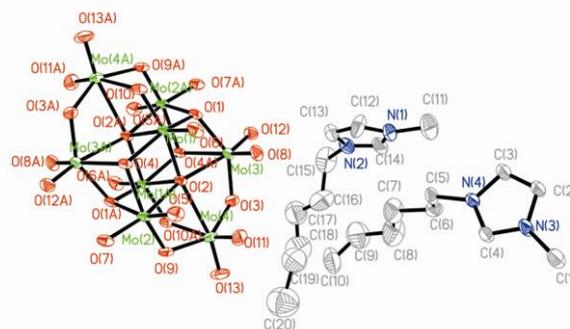
**Table 1** Physical property and characterization of compounds 1-3

Catalyst	Decomp. tem. (°C)	IR (cm <sup>-1</sup> )				
[Hmim] <sub>4</sub> Mo <sub>8</sub> O <sub>26</sub>	300	946	910	841	710	665
[Dhmim] <sub>4</sub> Mo <sub>8</sub> O <sub>26</sub>	290	956	911	837	714	650
[Hpy] <sub>4</sub> Mo <sub>8</sub> O <sub>26</sub> ·H <sub>2</sub> O	310	947	911	836	717	632

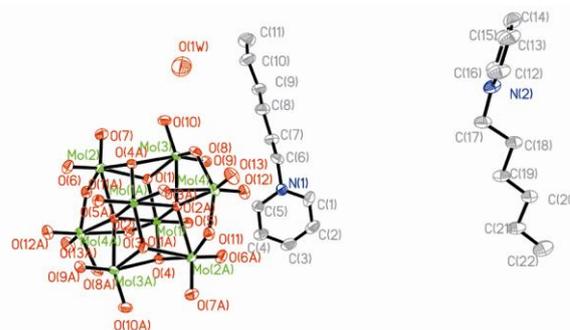
FT-IR spectra were used to clarify the structure of the Mo<sub>8</sub>O<sub>26</sub><sup>4-</sup> anions. All three compounds show similar IR spectra on Mo-O bond stretching. The IR spectra exhibit several characteristic Mo-O stretching bands in the region of 700 - 1000 cm<sup>-1</sup> (see the data in Table 1). The values are in good accordance with those published in the literature.<sup>16,17</sup> The single-crystal X-ray structures were obtained for compounds **1** and **3**, which further confirm the results of the spectroscopic analysis (Figure 1 and 2).

A summary of experimental data on the crystal determination can be found in the experimental section. Selected bond distances of the Mo<sub>8</sub>O<sub>26</sub><sup>4-</sup> anions of **1** and **3** are given in Table 2. Both compounds show an array of eight edge-shared MoO<sub>6</sub> octahedra, which includes different types of Mo - O bonds: terminal Mo - O<sub>t</sub>, bridging Mo - O<sub>μ2</sub>, Mo - O<sub>μ3</sub> and Mo - O<sub>μ5</sub>, indicating a typical β - octamolybdate.<sup>17b,18</sup> According to the X-ray structure of compound **1**, the averaged bond distance for terminal Mo=O is 1.697 Å. The bridging Mo-O-Mo (with two coordinated oxygen) bonds have an averaged distance of 1.911 Å, the triple coordinated oxygen atoms exhibit a Mo-O distance 1.942 Å, the five-coordinated oxygens exhibit an averaged Mo-O bond distance of 2.336 Å. Beside these well-established dominating bond distances there are some “intermediate” bond lengths as

2.002, 2.008, 2.332, 2.329 and 2.455 Å originating from non-regular three and five coordinated oxygen atoms. Anomalous bond distances were obtained for Mo(1)-O(10)-Mo(4) bridge with as big variations as 1.748 and 2.280 Å. Possibly the intermolecular interaction with Hmim cations leads to more pronounced variations in Mo-O bond distances than observed in “normal” [Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> complexes. In aqueous solution, only three different Mo-O bond distances are found, namely 1.70, 1.90 and 2.30 Å for “isolated” [Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> anions.<sup>19</sup> These values are in good agreement with some of the averaged distances (1.697, 1.911 and 2.336 Å) obtained for compound **1**. These values can be characteristic to the most “regular” basic octahedral units. It is interesting to note that the Mo-O bond stretching vibrations are in an (almost) linear relationship with the Mo-O bond distances. It is known that there are several empirical relations between stretching frequencies (or the derived force constants) and the bond distances. A Badger's type of relation exhibits a linear correlation between (ν/1000)<sup>2</sup> and 1/r<sup>3</sup>, where ν is the stretching frequency (cm<sup>-1</sup>) and r is the bond distance (Å). Accordingly, the series of IR bands for compound **1** at 946, 910, 840, 710 and 665 cm<sup>-1</sup> (Table 1) can be correlated to 1.697, 1.911, 1.942, 2.049 and 2.336 Å Mo-O bond distances, respectively. Very similar conclusion can be drawn for compound **3**, since both the IR spectra and the X-ray structures are very similar to that of compound **1**. Similarly, the Mo-O stretching Raman frequencies of solid Na<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> at 990 (IR), 939, 925, 881, 821 and 768 cm<sup>-1</sup> can be correlated to the Mo-O bond distances, 1.700, 1.772, 1.832, 1.937, 2.058 and 2.436 Å, respectively.<sup>21</sup> It is further noteworthy that the linear correlation is valid for both the octahedral and tetrahedral units of the anion structure.



**Figure 1** ORTEP view of compound **1** showing vibrational ellipsoids at the 50 % probability level. H atoms are omitted for clarity.



**Figure 2** ORTEP view of compound **3** showing vibrational ellipsoids at the 50 % probability level. H atoms are omitted for clarity.

**Table 2** Selected bond distances (Å) for Compound **1** and **3**<sup>a</sup>

	Mo-O <sub>t</sub>		Mo-O <sub>μ2</sub>	
<b>1</b>	Mo(1)-O(6)	1.693(5)	Mo(1)-O(10)	1.748(5)
	Mo(2)-O(5)	1.690(5)	Mo(2)-O(9)	1.892(5)
	Mo(2)-O(7)	1.698(5)	Mo(3)-O(3)	1.892(5)
	Mo(3)-O(12)	1.701(5)	Mo(4)-O(3)	1.926(5)
	Mo(3)-O(8)	1.704(5)	Mo(4)-O(9)	1.934(5)
	Mo(4)-O(11)	1.696(6)	Mo(4)-O(10)#1	2.280(5)
	Mo(4)-O(13)	1.699(6)		
<b>3</b>	Mo(1)-O(5)	1.694(3)	Mo(1)-O(3)	1.748(3)
	Mo(2)-O(6)	1.698(3)	Mo(2)-O(11)#1	1.899(3)
	Mo(2)-O(7)	1.701(3)	Mo(3)-O(8)	1.882(3)
	Mo(3)-O(9)	1.701(3)	Mo(4)-O(11)	1.927(3)
	Mo(3)-O(10)	1.702(3)	Mo(4)-O(8)	1.934(3)
	Mo(4)-O(13)	1.694(3)	Mo(4)-O(3)#1	2.308(3)
	Mo(4)-O(12)	1.698(3)		
	Mo-O <sub>μ3</sub>		Mo-O <sub>μ5</sub>	
<b>1</b>	Mo(1)-O(4)	1.941(4)	Mo(1)-O(2)	2.136(4)
	Mo(1)-O(1)	1.942(5)	Mo(1)-O(2)#1	2.356(4)
	Mo(2)-O(4)	2.002(4)	Mo(2)-O(2)	2.334(4)
	Mo(2)-O(1)#1	2.332(4)	Mo(3)-O(2)	2.318(4)
	Mo(3)-O(1)	2.008(5)	Mo(4)-O(2)	2.455(4)
	Mo(3)-O(4)#1	2.329(4)		
<b>3</b>	Mo(1)-O(4)	1.962(3)	Mo(1)-O(2)#1	2.135(2)
	Mo(1)-O(1)	1.951(3)	Mo(1)-O(2)	2.352(2)
	Mo(2)-O(4)#1	2.002(3)	Mo(2)-O(2)	2.376(2)
	Mo(2)-O(1)	2.310(3)	Mo(3)-O(2)#1	2.353(2)
	Mo(3)-O(1)	2.001(3)	Mo(4)-O(2)#1	2.388(2)
	Mo(3)-O(4)#1	2.299(3)		

<sup>a</sup>Symmetry codes: #1 -x,-y,-z+2 (**1**), #1 -x,-y+2,-z+2 (**3**)

### Epoxidation of olefins

Compounds **1-3** were examined as catalysts for the epoxidation of different olefins (including cyclooctene, cyclohexene, styrene, 1-hexene and 1-dodecene) using 30 % hydrogen peroxide as oxidant. Details concerning the catalytic reaction are given in the Experimental Section. Blank reactions show no cyclooctene conversion with excess amounts of H<sub>2</sub>O<sub>2</sub> in the absence of catalyst at 60 °C.

The reaction was first carried out by using compound **1** as catalyst and cyclooctene as standard substrate in different solvents, at various temperatures and different amount of oxidant or catalyst. Data for cyclooctene conversion and epoxide yield can be found in Table 3 and 4. Data in Entry 1, 2, 3, 4 and 8 of Table 3 reflect solvent effects on catalytic performance: EtOH and CH<sub>3</sub>CN mediated reactions resulted in the best conversions and epoxide yields, whereas EtOAc, benzene and toluene only gave a medium or low conversion and yield. It was observed that compound **1** was insoluble in all solvents examined at 60 °C. However, after adding 1.2 equiv. of H<sub>2</sub>O<sub>2</sub> (30 %) solution, the white catalyst powder changed its color to yellow (indicating the formation of a reaction product with hydrogen peroxide, most likely the actual catalyst/active species) and dissolved very fast, forming a homogeneous solution when using EtOH and CH<sub>3</sub>CN as solvents. In the case of EtOAc, benzene or toluene as solvents, the catalyst could not be dissolved in the organic / water biphasic system which is formed. This results in only a low conversion and epoxide yield. In CH<sub>3</sub>CN a self-precipitation of the catalyst after the completion of reaction took place, similar to the phenomenon observed by Xi et al.<sup>13</sup> with respect to [π-C<sub>5</sub>H<sub>5</sub>NC<sub>16</sub>H<sub>33</sub>]<sub>3</sub>[PO<sub>4</sub>(WO<sub>3</sub>)<sub>4</sub>] in catalyzed propylene epoxidation. Such catalysts combine the advantages of both homogeneous and heterogeneous reactions. Since the catalyst undergoes a solid-

liquid-solid phase transfer during the reaction, it can be easily recycled by filtration.

**Table 3** Epoxidation of *cis*-cyclooctene using compound **1** as catalyst

Entry <sup>a</sup>	Solvent	n(H <sub>2</sub> O <sub>2</sub> ):n(olefin)	Conv. (%) <sup>b</sup>	Yield (%) <sup>c</sup>	Temp. (°C)
1	EtOH	1.2	94	92	60
2	EtOAc	1.2	45	44	60
3	benzene	1.2	11	10 <sup>d</sup>	60
4	toluene	1.2	56	49	60
5	CH <sub>3</sub> CN	1.2	51	49	25
6	CH <sub>3</sub> CN	1.2	60	57	40
7	CH <sub>3</sub> CN	1.2	60	57	50
8	CH <sub>3</sub> CN	1.2	90	87	60
9	CH <sub>3</sub> CN	1.2	90	87	70
10	CH <sub>3</sub> CN	1.0	81	76	60
11	CH <sub>3</sub> CN	1.5	98	93	60
12	CH <sub>3</sub> CN	2.0	99	97	60

<sup>a</sup>Reaction conditions: *cis*-cyclooctene (2 mmol), [Hmim]<sub>4</sub>Mo<sub>8</sub>O<sub>26</sub> (1.5 mol %), solvent (1 mL), t = 1 h; <sup>b</sup>Conversion to cyclooctene oxide was calculated by GC analysis; <sup>c</sup>Isolated yield after column chromatography;

<sup>d</sup>Yield was calculated based on GC analysis.

Based on the advantage of self-separation for the catalyst, CH<sub>3</sub>CN was applied as solvent for further studies. In a further set of experiments, the temperature effect on catalytic performance has been studied. The reaction at 70 °C exhibits the highest cyclooctene conversion and the best isolated epoxide yield (Table 3, entry 9). The corresponding data are slightly lower at 60 °C. Since H<sub>2</sub>O<sub>2</sub> molecule may decompose faster at higher temperatures, it is nevertheless favorable to carry out the reaction at 60 °C. Entry 8, 10 - 12 in Table 3 indicate the effect of oxidant amount on catalytic performance. 1.0 to 2.0 equiv. of H<sub>2</sub>O<sub>2</sub> to substrate was applied in catalysis. It was observed that a molar equivalent amount of H<sub>2</sub>O<sub>2</sub> was not enough to complete the oxidation reaction. While adding ≥ 1.5 equiv. of H<sub>2</sub>O<sub>2</sub>, more than 98 % of conversion can be achieved. Thus at least 1.5 equiv. of H<sub>2</sub>O<sub>2</sub> are necessary to complete the catalytic reaction.

Table 4 shows the effect of the applied catalyst amount on the catalytic performance. In general, the higher the amount of catalyst applied, the higher are conversion and yield. When increasing the catalyst amount up to 2 mol %, the reaction reaches almost 100 % of cyclooctene conversion, no diol byproduct was observed in the reactions.

**Table 4** Epoxidation of *cis*-cyclooctene with different amounts of compound **1** as catalyst.

Entry <sup>a</sup>	Catalyst amount (mol %)	Conv. (%) <sup>b</sup>	Yield (%) <sup>c</sup>
1	0.25	46	31
2	0.5	72	70
3	1	88	83
4	1.5	98	93
5	2	100	98
6	2.5	100	97
7	3	100	98

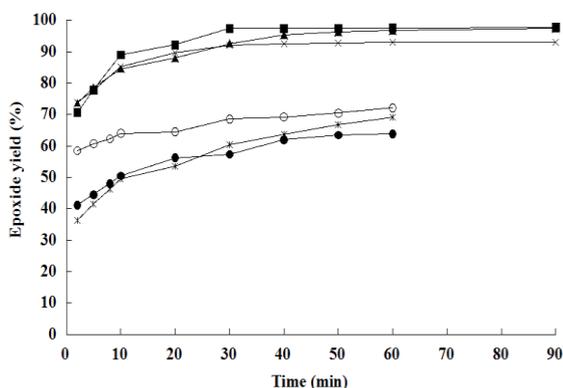
<sup>a</sup>Reaction conditions: *cis*-cyclooctene (2 mmol), acetonitrile (1 mL), n(H<sub>2</sub>O<sub>2</sub>):n(olefin) = 1.5, t = 1 h at 60 °C.

<sup>b</sup>Conversion to cyclooctene oxide was calculated by GC analysis.

<sup>c</sup>Isolated yield after column chromatography.

Based on the examination of the catalytic performance for compound **1**, all the three compounds were further examined in details on their catalytic behaviour for cyclooctene epoxidation, with both 1.5 and 0.5 mol % amount of catalyst applied. All compounds examined show quite high catalytic activity and selectivity towards cyclooctene epoxide, no diol being observed

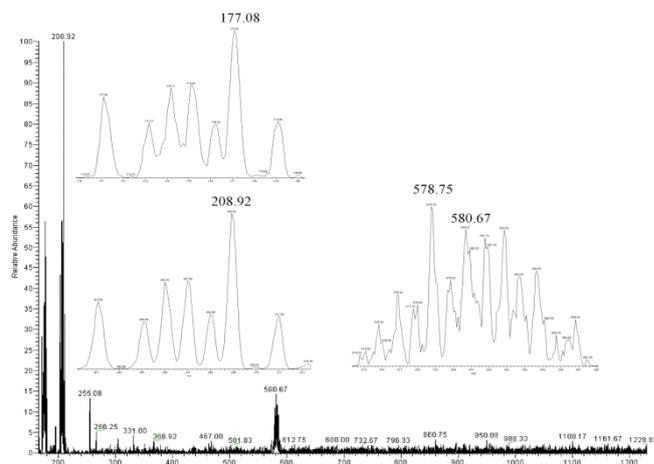
according to the GC analysis. When adding 1.5 mol % of catalyst **1** - **3** to the system, > 70 % cyclooctene epoxide was obtained within 2 minutes and ca. 96 % after 30 minutes. Both compounds **1** and **2** as catalysts lead to almost 100 % epoxide yield within 1.5 h. Compound **3** reaches an epoxide yield of 93 % after 1.5 hours. The turnover frequencies (TOFs) for compounds **1** - **3** are 622, 621 and 628 h<sup>-1</sup>, respectively (calculated after 5 min reaction time). Due to similar activity with 1.5 mol % of catalyst, it is difficult to compare the catalyst performance in more detail. Therefore, the system was further examined with a decreased catalyst amount (0.5 mol %). It can be seen from Figure 3 that compound **1** shows higher activity than compound **2** and **3** in the initial reaction phase, whereas **1** and **2** result in a similar epoxide yields after 1.5 hours. The TOFs with 0.5 mol % of catalyst amount are in general higher than that with 1.5 mol % of catalyst, with the values of 1488 (**1**), 984 (**2**) and 1080 (**3**) h<sup>-1</sup> (calculated after 5 min of the reaction), respectively. Despite compound **3** displays a higher TOF than that of compound **2**, the final epoxide yield is lower. Moreover, the epoxide yields do not increase after 40 minutes for both amounts of catalyst applied for compound **3**. Similar to compound **1**, compound **2** and **3** also exhibited a self-separation phenomenon in CH<sub>3</sub>CN. It was observed that all the catalyst solid dissolved immediately after adding H<sub>2</sub>O<sub>2</sub> to the system at 60 °C, however the precipitation occurred already within 10 minutes for each reaction with both 1.5 mol % and 0.5 mol % amount of catalyst applied, indicating a fast reaction rate and that most H<sub>2</sub>O<sub>2</sub> molecules had been consumed within 10 minutes of starting the reaction. As can also be observed from Figure 3, all the reactions already give quite high epoxide yields after 2 minutes of reaction, and the yields keep increasing rapidly before 10 minutes, and slow down thereafter. Due to the low concentration of H<sub>2</sub>O<sub>2</sub> after 10 minutes, the reaction activity decreases significantly and the catalyst precipitation occurs.



**Figure 3** Time-dependent yield of cyclooctene epoxide in the presence of compounds **1-3** as catalysts at 60 °C with 1.5 mol % (■ **1**, ×**3**, ▲**2**), 0.5 mol % (○**1**, \***2**, ●**3**) of catalyst amount.

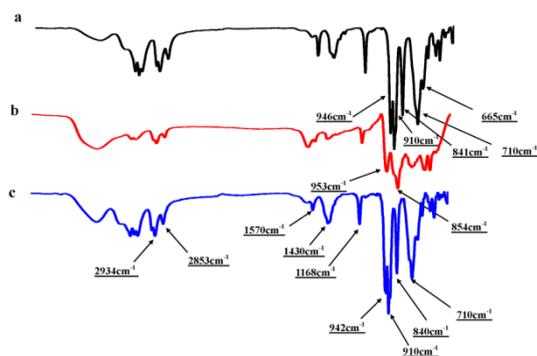
It is well established that ( $\{\text{PO}_4[\text{MO}(\text{O}_2)_2]_4\}^{3-}$ ) (M = Mo, W) is the active species when using  $\text{PM}_{12}\text{O}_{40}^{4-}$  based POM as catalyst and H<sub>2</sub>O<sub>2</sub> as oxidant for epoxidation.<sup>10</sup> However, not much work has been done on the examination and isolation of catalytic active species for  $[\text{Mo}_8\text{O}_{26}]^{4-}$  anion based catalysts. Galindo<sup>22</sup> *et al.* had successfully isolated a tetraperoxo-octamolybdate derivative with the formula of  $[\text{Hdmpz}]_4[\text{Mo}_8\text{O}_{22}(\text{O}_2)_4(\text{dmpz})_2] \cdot 2\text{H}_2\text{O}$  as an intermediate during the preparation of the oxodiperoxo species  $[\text{MoO}(\text{O}_2)_2(\text{dmpz})_2]$ . Another reported peroxy-octamolybdate is  $[\text{NH}_4]_4[\text{Mo}_8\text{O}_{24}(\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ .<sup>23</sup> To the best of our knowledge, these are the only two peroxy-octamolybdates reported in literature. Since the isolation of these intermediates is

governed by serendipity, an efficient synthetic route to this compound has still not been established and complex mixtures were obtained in all cases. The reaction between compound **1** and H<sub>2</sub>O<sub>2</sub> was studied in order to examine the catalytic species in our work. FT-IR and negative ESI-MS measurements were performed to detect the possible active species towards epoxidation. When adding 30 % H<sub>2</sub>O<sub>2</sub> to a suspension of compound **1** in acetonitrile at 60 °C, the solid dissolves completely and finally results in a yellow solution, indicating the formation of an active species. Nevertheless, the ionic peak representing the peroxy-octamolybdate could not be detected in the ESI-MS spectra. Instead, a peak indicating the dissociated oxodiperoxo species  $\text{MoO}(\text{O}_2)_2$  ( $m/z = 177.08$ ) was observed, which may be the possible active species in catalysis (Figure 4).



**Figure 4** ESI-MS (negative mode) measurement of the isolated active species

Figure 5 shows the IR spectra of compound **1** (5a), after the reaction with excess H<sub>2</sub>O<sub>2</sub> (5b), and the recycled compound **1** (5c). It can be observed that the catalyst precursor has Mo=O vibrations at 946 cm<sup>-1</sup>, and the bridging Mo-O-Mo vibrations in the range of 665 - 910 cm<sup>-1</sup>. However, after the reaction with excess H<sub>2</sub>O<sub>2</sub>, the bridging Mo-O-Mo vibration peaks disappear. Instead, a peroxy-bond absorption peak  $\nu$  (O-O) at 854 cm<sup>-1</sup> (stretching vibration) can be observed (Figure 5b).<sup>13a</sup> The disappearance of bridging Mo-O-Mo vibrations further confirms the dissociation of the cluster structure, which is in accordance with the ESI-MS data. Interestingly, the cluster structure of  $\text{Mo}_8\text{O}_{26}^{4-}$  is recovered after H<sub>2</sub>O<sub>2</sub> is completely consumed. As can be seen from the spectra of recycled compound **1** (Figure 5c), no vibrational changes are observed for the recycled compound, indicating good stability of the catalyst.



**Figure 5** Infrared spectra of pure compound **1**(a), after the reaction with  $\text{H}_2\text{O}_2$  (b), recycled compound **1** (c).

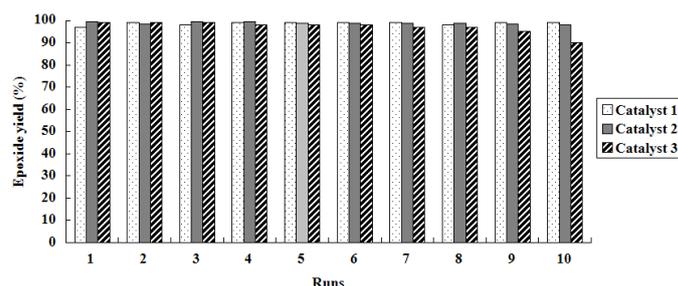
5 Besides cyclooctene, the catalytic system was also applied to other olefins. Excellent activity for different olefins can also be achieved, even for terminal olefins such as 1-hexene and 1-dodecene. However, a significant amount of diol can be detected in the case of the epoxidation of cyclohexene, while the oxidation of styrene resulted in the formation of benzyl aldehyde as main product.

**Table 5** Epoxidation of different olefins.

Entry <sup>a</sup>	Olefins	Conv. (%) <sup>b</sup>	Yield (%) <sup>c</sup>
1	cyclohexene	96	44 <sup>d</sup>
2	styrene	100	91 <sup>e</sup>
3	1-hexene	99	96
4	1-dodecene	91	87

<sup>a</sup>Reaction conditions: *cis*-cyclooctene (2 mmol),  $[\text{Hmim}]_4\text{Mo}_8\text{O}_{26}$  (1.5 mol %), acetonitrile (1 mL),  $n(\text{H}_2\text{O}_2):n(\text{olefin}) = 1.5$ ,  $t = 4$  h at  $60^\circ\text{C}$ ; <sup>b</sup>Conversion to cyclooctene oxide was calculated by GC analysis; <sup>c</sup>Isolated yield after column chromatography; <sup>d</sup>The 1,2-cyclohexanediol was detected as major byproduct; <sup>e</sup>The main product was benzyl aldehyde. The selectivity to styrene oxide was less than 2 %.

15 **Recycling and reuse of compounds 1-3 as epoxidation catalyst**  
Owing to the self-precipitation feature of the catalysts, compounds **1-3** were recycled directly by filtration after the reaction. Comparing to the recycling process for  $[(n\text{-C}_4\text{H}_9)_4\text{N}][\alpha\text{-Mo}_8\text{O}_{26}]^{17a}$  reported by Deng *et al.*, no additional organic solvent is necessary to precipitate the solid in our system. The recovered solid was just washed with water, and then used directly as catalyst for the next run. The recycling yields for all the catalysts were higher than 95 %. The losses are largely ascribed to the workup and may be quantitative after some optimization. Fresh *cis*-cyclooctene and  $\text{H}_2\text{O}_2$  were then added for a new reaction cycle. Figure 6 shows the reuse of compounds **1-3** as catalyst for *cis*-cyclooctene epoxidation at  $60^\circ\text{C}$  with 1.5 mol % of catalysts for 1 hour. Compounds **1** and **2** can be reused for at least ten cycles without significant decrease of yield, proving that this system has persistent activity during the recycling experiments.



**Figure 6** Reuse of compounds **1-3** for epoxidation of *cis*-cyclooctene at  $60^\circ\text{C}$ .

35

## Experimental

### General Methods

All chemicals were purchased from the Sinopharm Chemical Reagent Co. Ltd of China or Acros and used without further purification.  $^1\text{H}$  NMR spectra were recorded on a 500-MHz Bruker Avance DPX-500 spectrometer. IR spectra were recorded on a PerkinElmer Frontier FT-IR spectrometer. Catalytic runs were monitored by GC methods on an Agilent 6890 instrument using a capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ). Microanalyses of the obtained products were performed with a Flash EA 1112 series elemental analyzer. Melting points were determined by an X-6 micro melting point apparatus (Beijing Tech Instrument Co. Ltd). Thermogravimetric (TGA) and differential scanning (DSC) analysis were conducted utilizing a Netzsch-STA 409 PC system, and typically about 10mg of each sample were heated from  $25^\circ\text{C}$  to  $1000^\circ\text{C}$  at  $10\text{Kmin}^{-1}$ . ESI-MS spectra were recorded by an LCQ Fleet ESI mass spectrometer. The imidazolium or pyridinium bromine salts were prepared according to the literature.<sup>24</sup>

### Synthesis and characterization

Compounds **1-3** were prepared according to the published procedures<sup>17b</sup>.

60 A solution of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (4.8 g, 20 mmol) was dissolved in 30 mL of water, then the solution was acidified with HCl (37 %, ca. 10 mL) to a pH value of 4.5. The resulting mixture was refluxed for 1 h. After cooling down the solution to room temperature, imidazolium or pyridinium bromine salts (ca. 10 mmol) were added and a white solid was precipitated immediately in the solution. After 30 min, the water solution was evaporated to about 5 mL at  $100^\circ\text{C}$ . Then the precipitate was filtered and thoroughly washed successively with water, ethanol for three times. Recrystallization of the solid from acetonitrile afforded white crystals.

#### Characteristic data:

65 Compound **1**,  $[\text{C}_{10}\text{H}_{19}\text{N}_2]_4\text{Mo}_8\text{O}_{26}$  (1852.00): Yield, 81% (white crystal); Elemental analysis calcd.: C, 25.93, H, 4.13, N, 6.05; found: C, 25.82, H, 3.98, N, 6.01; IR (KBr,  $\text{cm}^{-1}$ ): see Table 1;  $^1\text{H}$ -NMR (500 MHz,  $d^6$ -DMSO, r.t., ppm):  $\delta = 9.13$  (s, 1H,  $mz\text{-H}^2$ ), 7.77 (s, 1H,  $mz\text{-H}^4$ ), 7.70 (s, 1H,  $mz\text{-H}^5$ ), 4.18 (t, 2H,  $\text{CH}_2$ ), 3.88 (s, 3H,  $\text{NCH}_3$ ), 1.80 (m, 2H,  $\text{CH}_2$ ), 1.28 (m, 6H,  $3 \times \text{CH}_2$ ), 0.87 (m, 3H,  $\text{CH}_3$ ); ESI-MS (methanol,  $m/z$ , %): cation, 167.1 ( $\text{C}_{10}\text{H}_{19}\text{N}_2^+$ , 100%).

80 Compound **2**,  $[\text{C}_{11}\text{H}_{21}\text{N}_2]_4\text{Mo}_8\text{O}_{26}$  (1908.88): Yield, 76% (white crystal); Elemental analysis calcd.: C, 27.69, H, 4.44, N, 5.87; found: C, 27.52, H, 4.38, N, 5.88; IR (KBr,  $\text{cm}^{-1}$ ): see Table 1;  $^1\text{H}$ -NMR (500 MHz,  $d^6$ -DMSO, r.t., ppm):  $\delta = 7.64$  (s, 1H,  $mz\text{-H}^4$ ), 7.61 (s, 1H,  $mz\text{-H}^5$ ), 4.10 (t, 2H,  $\text{CH}_2$ ), 3.75 (s, 3H,  $\text{NCH}_3$ ), 1.70 (m, 2H,  $\text{CH}_2$ ), 1.27 (s, 6H,  $3 \times \text{CH}_2$ ), 0.87 (t, 3H,  $\text{CH}_3$ ); ESI-

MS (methanol, m/z, %): cation, 181.1 (C<sub>11</sub>H<sub>21</sub>N<sub>2</sub><sup>+</sup>, 100%). Compound **3**, [C<sub>11</sub>H<sub>18</sub>N<sub>4</sub>]<sub>4</sub>Mo<sub>8</sub>O<sub>26</sub>·H<sub>2</sub>O (1858.59): Yield, 82% (white crystal); Elemental analysis calcd.: C, 28.43, H, 4.01, N, 3.01; found: C, 28.45, H, 3.98, N, 3.04; IR (KBr, cm<sup>-1</sup>): see Table 1; <sup>1</sup>H-NMR (500 MHz, d<sup>6</sup>-DMSO, r.t., ppm): δ = 9.13 (d, 2H, py-H<sup>2,6</sup>), 8.62 (t, 1H, py-H<sup>4</sup>), 8.17 (t, 2H, py-H<sup>3,5</sup>), 4.61 (t, 2H, CH<sub>2</sub>), 1.91 (m, 2H, CH<sub>2</sub>), 1.28 (m, 6H, 3×CH<sub>2</sub>), 0.85 (t, 3H, CH<sub>3</sub>); ESI-MS (methanol, m/z, %): cation, 164.1 (C<sub>11</sub>H<sub>18</sub>N<sup>+</sup>, 100%).

### 10 General procedure for the epoxidation of olefins

In a typical reaction, compound **1** (55.6mg, 30μmol) was applied as catalyst and added to 1 mL of CH<sub>3</sub>CN in the reaction vessel in air. Olefin (2 mmol) was added and followed by the addition of H<sub>2</sub>O<sub>2</sub> at 60 °C to start the reaction. The course of the reactions was monitored by quantitative GC analysis. Samples were taken at regular time intervals, diluted with acetonitrile, and treated with a catalytic amount of MgSO<sub>4</sub> and MnO<sub>2</sub> to remove water and to destroy the unreacted peroxide. The resulting slurry was filtered and the filtrate injected onto a GC column. The conversion of olefins and the formation of epoxides were calculated from calibration curves (r<sup>2</sup> > 0.999) recorded prior to the reaction. For the recycling experiment: the white solid was filtered after cooling down the reaction residue to room temperature. The solid was washed with water for 3 times and then dried under vacuum to obtain pure recycled catalyst. Fresh substrate and H<sub>2</sub>O<sub>2</sub> were then added for a new reaction cycle.

### Single-Crystal X-ray Structure Determinations

Details of the X-ray experiment, crystal parameters, data collections and refinements are summarized in Table 6. Single crystals were mounted on a Bruker XRDR3M / ESYSTCM diffractometer operating at 50 kV and 30 mA equipped with a MoK<sub>α</sub> radiation source (λ=0.71073 Å). Data collection were performed at 273(2) K and 188 (2) K with a ω/φ diffraction measurement method and reduction was performed using the SMART and SAINT software with frames of 0.3° oscillation in the θ range 1.5<θ<26.2°. The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F<sup>2</sup> using the SHELXTL package.<sup>25</sup>

**Table 6** Crystal data and structure refinement for Compounds **1** and **3**

	<b>1</b>	<b>3</b>
Empirical formula	C <sub>40</sub> H <sub>76</sub> N <sub>8</sub> Mo <sub>8</sub> O <sub>26</sub>	C <sub>44</sub> H <sub>74</sub> Mo <sub>8</sub> N <sub>4</sub> O <sub>27</sub>
Formula weight	1852.00	1858.59
Temperature (K)	273(2)	188(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic P2(1)/n	Monoclinic P2(1)/n
Unit cell dimensions	a = 16.3997(11) Å b = 10.8045(7) Å c = 17.5797(12) Å α = 90° β = 96.3800(10)° γ = 90°	a = 15.6345 (9) Å b = 12.1211 (7) Å c = 16.5893 (10) Å α = 90° β = 94.6030(10)° γ = 90°
Volume (Å <sup>3</sup> )	3095.7(4)	3133.7(3)
Z, Calculated density (mg/m <sup>3</sup> )	2, 1.905	2, 1.970
Absorption coefficient	1.645 mm <sup>-1</sup>	1.628 mm <sup>-1</sup>
F(000)	1680	1836
Crystal size (mm)	0.2 × 0.18 × 0.16	0.23 × 0.17 × 0.10
θ range for data collection (°)	1.80 to 26.04	1.72 to 26.01
Limiting indices	-20 ≤ h ≤ 20 -12 ≤ k ≤ 13 -20 ≤ l ≤ 21	-19 ≤ h ≤ 17 -14 ≤ k ≤ 14 -18 ≤ l ≤ 20
Reflections collected /	19112 / 6079	19651 / 6162

unique Completeness to θ = 26.01°	[R(int) = 0.0411] 99.5 %	[R(int) = 0.0390] 99.8 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	6079 / 30 / 370	6162 / 0 / 381
Goodness-of-fit on F <sup>2</sup>	1.041	1.025
Final R indices [I>2σ(I)]	R <sub>1</sub> = 0.0539 wR <sub>2</sub> = 0.1392	R <sub>1</sub> = 0.0345 wR <sub>2</sub> = 0.0720
R indices (all data)	R <sub>1</sub> = 0.0753 wR <sub>2</sub> = 0.1552	R <sub>1</sub> = 0.0460 wR <sub>2</sub> = 0.0773
Largest diff. peak and hole (e.Å <sup>-3</sup> )	1.653 and -1.253	0.658 and -0.458

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-997672 (**1**), and CCDC-997673 (**3**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk.)

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### Conclusions

Three [Mo<sub>8</sub>O<sub>26</sub><sup>4-</sup>] based polyoxomolybdate salts of general formula [Hmim]<sub>4</sub>Mo<sub>8</sub>O<sub>26</sub> (Hmim = 1-hexyl-3-methylimidazolium), [Dhmim]<sub>4</sub>Mo<sub>8</sub>O<sub>26</sub> (Dhmim = 1,2-dimethyl-3-hexyllimidazolium) and [Hpy]<sub>4</sub>Mo<sub>8</sub>O<sub>26</sub>·H<sub>2</sub>O (Hpy = 1-hexylpyridinium) have been prepared and used to catalyze the epoxidation of different olefins including cyclooctene, cyclohexene, styrene and 1-octene. They can be used as efficient catalysts when using 30% of H<sub>2</sub>O<sub>2</sub> as oxidant and acetonitrile as solvent. In general, octamolybdate based catalysts exhibit high catalytic performance towards the epoxidation of cis cyclooctene. More importantly, since these insoluble compounds form soluble active species after adding oxidant and are able to self-precipitate after the completion of the reaction, the compounds can be used as self - separating catalysts. Recycling experiments indicate that the catalysts can be recycled and reused at least 10 times without significant loss of activity, indicating good stability of the catalysts. Negative ESI-MS data indicate that the dissociated oxidiperoxo compounds might be the catalytic active species for the epoxidation reactions.

### Notes and references

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