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Polymer and non-polymer-grafted dioxidomolybdenum(VI) complexes having ONO donor ligand and their catalytic activities for the oxidative bromination of organic substrates
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#### 41 ABSTRACT

The ligand H<sub>2</sub>sal-iah (I), derived from salicylaldehyde and indole-3-acetic hydrazide, reacts with 42  $[Mo^{VI}O_2(acac)_2]$  in methanol to give dioxidomolybdenum(VI) complex  $[Mo^{VI}O_2(sal-$ 43 iah)(MeOH)] (1). Drop wise addition of 30% aqueous H<sub>2</sub>O<sub>2</sub> to the methanolic solution of 1 44 vields complex  $[Mo^{VI}O(O_2)(sal-iah)(MeOH)]$  (2). Complex 1 has been grafted via covalent 45 bonding through imino nitrogen of the indole to chloromethylated polystyrene cross-linked with 46 5% divinylbenzene {now abbreviated as PS- $[Mo^{VI}O_2(sal-iah)(MeOH)]$  (3)}. All these complexes 47 are characterized by various spectroscopic techniques (IR, electronic, <sup>1</sup>H and <sup>13</sup>C NMR) and 48 thermal as well as field-emission scanning electron micrographs (FE-SEM) studies. The crystal 49 50 structure of **1** has been determined, confirming the ONO binding mode of **I**. The polymer-grafted 51 complex 3 catalyzes the oxidative bromination, by H<sub>2</sub>O<sub>2</sub>, of styrene and *trans*-stilbene. Under the optimized reaction conditions, the oxidative bromination of styrene gave 98 % conversion in 2 h 52 time where 2-bromo-1-phenylethane-1-ol and 1,2-dibromo-1-phenylethane are the main products 53 and 1-phenylethane-1,2-diol is the product obtained by the attack of nucleophile water on the  $\alpha$ -54 carbon of 2-bromo-1-phenylethane-1-ol. Oxidative bromination of trans-stilbene gave 96% 55 conversion with 2,3-diphenyloxirane (trans-stilbene oxide), 1,2-dibromo-1,2-diphenylethane 56 and 2-bromo-1,2-diphenylethanol as the products. Suitable reaction mechanisms for both 57 reactions have been suggested. Neat complex [Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)] (1) is equally active but 58 59 the recyclability and heterogeneity tests of polymer-grafted complex makes it better over neat analog. 60

#### 61

### 62 1. Introduction

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64 Catalytic applications of molybdenum complexes in oxidation and oxygen-transfer 65 reactions including oxidation of sulfides [1-22] have extensively been studied. Immobilizations 66 of these homogeneous catalysts on solid support find limited mention in the literature though 67 such catalysts have potential prospect for technological applications [23, 24] because solid 68 supported catalysts meet the industrial demand of recyclability and thermal stability along with 69 high turnover rates and environment-friendly synthetic routes to fine chemicals [25-29].

Recently our attention was drawn on the oxidative bromination of organic substrates by
 vanadium complexes, a reaction normally promoted by vanadium haloperoxidase enzymes [30-

32]. These homogeneous as well as heterogeneous vanadium complexes satisfactorily catalyze
the oxidative bromination of styrene, trans-stilbene and salicylaldehyde [33-40]. Such functional
similarities have also been demonstrated by some homogeneous molybdenum complexes [4143].

We have recently immobilized dioxidovanadium(V) complex of indole-derived ONO 76 donor ligand H<sub>2</sub>sal-iah (I, Scheme 1) onto chloromethylated polystyrene cross-linked with 77 divinyl benzene (PS-CH<sub>2</sub>Cl) for the development of more environmentally benign heterogeneous 78 catalyst and have explored their use as possible functional model for haloperoxidase enzymes. 79 Insertion of spacer (extra CH<sub>2</sub> group) between polymer support and catalyst improved the 80 performance of the catalyst by allowing the better interaction of catalytic centre with substrates 81 and oxidant during catalytic reaction [44]. We now report the immobilization of 82 83 dioxidomolybdenum(VI) complex of H<sub>2</sub>sal-iah (I, Scheme 1) onto chloromethylated polystyrene. Its characterization and catalytic potential towards the oxidative bromination of styrene and 84 trans-stilbene are reported here. The corresponding non polymer-grafted molybdenum complex 85 has also been prepared for comparing its catalytic performance. 86





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### 92 **2. Experimental**

93 2.1. Materials

Chloromethylated polystyrene [18.9 % Cl (5.35 mmol Cl per gram of resin)] cross-linked with 5 % divinylbenzene was obtained from Thermax Limited, Pune, India. Analytical reagent grade ammonium molybdate, molybdenum trioxide (S. D. Fine, India), salicylaldehyde (Sisco Research, India), *trans*-stilbene (Lancaster, England), indole-3-acetic hydrazide, styrene (Aldrich, USA) and 30 % aqueous H<sub>2</sub>O<sub>2</sub>, (Rankem, India) were used as obtained. H<sub>2</sub>sal-iah (**I**)

<sup>90</sup> Scheme 1. Structure of ligand H<sub>2</sub>sal-iah (I)

[44] and [Mo<sup>VI</sup>O<sub>2</sub>(acac)<sub>2</sub>] [45] were prepared according to methods reported in the literature.
Other chemicals and solvents of analytical reagent grades were used without purifications.

101

### 102 *2.2. Physical methods and analysis*

Molybdenum content in polymer-grafted complex was obtained by Inductively Coupled 103 104 Plasma spectrometry (ICP; Labtam 8440 plasma lab). C, H and N analyses of the neat complex 105 were obtained with an Elementar model Vario-EL-III. Thermogravimetric analysis was carried out using Perkin Elmer (Pyris Diamond) having weight sensitivity of 0.2 µg under oxygen 106 atmosphere. IR spectra were recorded (16 scans) as KBr pellets on a Nicolet NEXUS Aligent 107 1100 FT-IR spectrometer having a resolution of 4 cm<sup>-1</sup>. Electronic spectra of the polymer-108 grafted complexes were recorded with a medium scan speed in Nujol on a Shimadzu 1601 UV-109 Vis spectrophotometer having 0.1 nm wavelength accuracy by layering a mull of the sample on 110 the inside of one of the cuvettes while keeping the other one layered with Nujol as reference. 111 Spectra of ligand and neat complexes were recorded in methanol. <sup>1</sup>H and <sup>13</sup>C NMR spectra were 112 obtained using Bruker Avance III 500 MHz spectrometer. The energy dispersive X-ray analysis 113 (EDX) of anchored complex was obtained on a FEI Quanta 200 FEG. The samples were coated 114 with a thin film of gold to prevent surface charging, to protect the surface material from thermal 115 damage by the electron beam and to make the sample conductive. A Shimadzu 2010 plus gas-116 chromatograph fitted with an Rtx-1 capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m) and a FID 117 detector was used to analyze the reaction products and their quantifications were made on the 118 basis of the relative peak area of the respective product. The identity of the products was 119 confirmed using a GC-MS Perkin-Elmer, model Clarus 500 and comparing the fragments of each 120 product with the library available. 121

122

#### 123 *2.3. Synthesis*

### 124 2.3.1. [Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)] (1)

125 A stirred solution of  $[Mo^{VI}O_2(acac)_2]$  (0.329 g, 1 mmol) dissolved in methanol (15 mL) 126 was added to a solution of H<sub>2</sub>sal-iah (0.293 g, 1 mmol) in methanol (25 mL) and the resulting 127 reaction mixture was stirred for ca. 6 h at room temperature. After reducing the solvent volume

to ca. 10 mL and standing the solution in air for 24 h, the orange crystalline compound precipitated which was filtered off, washed with methanol and dried *in vacuo*. Yield 0.42 g (93%) *Anal*. Cal. for  $C_{18}H_{17}N_3O_5Mo$  (451.29): C, 47.91; H, 3.80; N, 9.31; Mo. Found: C, 47.8; H, 4.0; N, 8.9%.

- 132
- 133  $2.3.2. [Mo^{VI}O(O_2)(sal-iah)(MeOH)]$  (2)

Aqueous 30% H<sub>2</sub>O<sub>2</sub> (ca. 2 mL) was added dropwise to complex **1** (0.451 g, 1 mmol) dissolved in methanol (50 mL) with constant stirring at ambient temperature. After ca. 4 h, the solvent was slowly reduced to 10 mL by passing air through the solution and kept at room temperature for slow precipitation of complex. The precipitated solid was filtered, washed with cold methanol (2 × 4 mL) and dried in air. Yield 0.23 g (50%) *Anal*. Cal. for C<sub>18</sub>H<sub>17</sub>N<sub>3</sub>O<sub>6</sub>Mo (467.29): C, 46.27; H, 3.67; N, 8.99. Found: C, 46.1; H, 3.7; N, 8.8%.

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# 141 2.3.3. PS-[Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)] (3)

142 Chloromethylated polystyrene (1.0 g) was allowed to swell in DMF (8 mL) for 2 h. A 143 solution of  $[Mo^{VI}O_2(\text{sal-iah})(\text{MeOH})]$  (1.0 g, 2.2 mmol) in DMF (8 mL) was added to the above 144 suspension followed by triethylamine (1.33 g) in ethylacetate (7 mL), and the obtained reaction 145 mixture was heated at 80 °C for 24 h with continuous but slow stirring. After cooling to room 146 temperature, the polymer-grafted complex was separated by filtration, washed with hot DMF, 147 followed by hot methanol and dried in an oven in air at 110 °C.

148

### 149 2.4. X-Ray crystal structure determination

Three-dimensional X-ray data for 1 were collected on a Bruker SMART Apex CCD 150 diffractometer at room temperature, using a graphite monochromator and Mo- $K_{\alpha}$  radiation ( $\lambda$  = 151 0.71073 Å) by the  $\phi$ - $\omega$  scan method. Reflections were measured from a hemisphere of data 152 collected from frames each of them covering  $0.3^{\circ}$  in  $\omega$ . Of the 33032 reflections measured, all 153 154 were corrected for Lorentz and polarization effects and for absorption by multi-scan methods based on symmetry-equivalent and repeated reflections, 4475 independent reflections exceeded 155 the significance level  $(|F|/\sigma|F|) > 4.0$ . Complex scattering factors were taken from the 156 program package SHELXTL [46]. The structures were solved by direct methods and refined by 157

full matrix least-squares on  $F^2$ . Hydrogen atoms were left to refine freely, except to C(4) and C(18) which were included in calculation positions and refined in the riding mode. Refinements were done with allowance for thermal anisotropy of all non-hydrogen atoms. Further details of the crystal structure determination are given in Table 1. A final difference Fourier map showed no residual density outside: 0.432 and -0.464 e.Å<sup>-3</sup>. A weighting scheme w =  $1/[\sigma^2(F_o^2) +$ (0.046900 P)<sup>2</sup> + 0.172800 P] was used in the latter stages of refinement.

164

### 165 **Table 1**

166 Crystal data and structure refinement for [Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)](1).

Formula	C <sub>18</sub> H <sub>17</sub> MoN <sub>3</sub> O <sub>5</sub>
Formula weight	451.29
Т, К	293(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	15.3299(4)
b/Å	15.1955(4)
c/Å	7.8411(2)
$\beta/^{\circ}$	103.8140(10)
V/Å <sup>3</sup>	1773.72(8)
Z	4
F <sub>000</sub>	912
$D_{\text{calc}}/\text{g cm}^{-3}$	1.690
$\mu/\mathrm{mm}^{-1}$	0.776
<i>θ</i> / (°)	1.37 to 31.89
R <sub>int</sub>	0.0418
Crystal size/ mm <sup>3</sup>	$0.21\times0.18\times0.16$
Goodness-of-fit on F <sup>2</sup>	1.093

#### ¥. 2

	$R_1[I>2\sigma(I)]^a$	0.0311
	$wR_2$ (all data) <sup>b</sup>	0.0971
	Largest differences peak and hole (eÅ <sup>-3</sup> )	0.432 and -0.464
167	${}^{a}R_{1} = \Sigma   F_{o}  -  F_{c}   / \Sigma  F_{o}  . {}^{b}wR_{2} = \{\Sigma[w(  F_{o} )]   K_{o}    K_{o}  \}$	$ ^{2} -  F_{c} ^{2} ^{2} ^{2} /\Sigma[w(F_{o}^{4})] ^{1/2}$
168		
169	2.5. Catalytic activity	
170	The catalytic oxidation bromination of s	tyrene and <i>trans</i> -stilbene was carried out in a 100
171	ml flask at ca. 40 °C. Polymer-grafted catalyst w	vas kept in MeOH for 1 h before use.
172		
173	2.5.1. Oxidative bromination of styrene	
174	Catalyst (0.015 g), styrene (1.04 g, 10	mmol), KBr (2.38 g, 20 mmol), aqueous 30 %
175	$H_2O_2$ (2.27 g, 20 mmol) and 70 % aqueous HCl	$O_4$ (2.86 g, 20 mmol, added in four equal portions
176	at $t = 0$ , 30, 60 and 90 min.) were stirred at 40	°C in a biphasic dichloromethane-water (40 mL
177	50%, v/v) mixture) system for 2 h. At every	15 minutes small aliquot of the reaction mixture
178	present in organic layer was withdrawn and ana	lyzed quantitatively by gas chromatography.
179	2.5.2. Oxidative bromination of trans-stilbene	
180	Catalyst (0.015, g) trans-stilbene (0.90 g	5 mmol), KBr (2.38 g, 20 mmol), aqueous 30 %
181	$H_2O_2$ (2.27 g, 20 mmol) and 70 % aqueous HCl	O <sub>4</sub> (2.86 g, 20 mmol, added in four equal portions
182	at $t = 0$ , 30, 60 and 90 min.) were stirred at 40	°C in a biphasic chloroform-water (40 mL 50%,
183	v/v) mixture) system for 2 h. After 2h the re	action mixture was washed with water and the
184	organic layer was separated. Various reaction	products were analyzed by gas chromatography
185	using this organic layer. The separation and ide	entification of the reaction products were done as
186	reported earlier [44].	
187		
188	3. Results and discussion	

189 3.1. Synthesis and characterization

Reaction between equimolar amounts of ligand  $H_2$ sal-iah (I) and  $[Mo^{VI}O_2(acac)_2]$  in 190 refluxing MeOH gave [Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)] (1) [Eq. (1)]. Its reaction with 30 % *aq*.  $H_2O_2$  in 7 191

methanol gave complex [Mo<sup>VI</sup>O(O<sub>2</sub>)(sal-iah)(MeOH)] (2) [Eq. (2)]. Both the complexes are
fairly soluble in methanol, DMF and DMSO. Scheme 2 presents the structures proposed for these
complexes, which are based on the elemental analyses, spectroscopic characterization (IR,
electronic, <sup>1</sup>H and <sup>13</sup>C NMR), thermogravimetric patterns and single crystal X-ray analysis of 1.
The ligand coordinates through its dianionic (ONO) functionalities.

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$$[Mo^{VI}O_2(acac)_2] + H_2sal-iah + MeOH \rightarrow [Mo^{VI}O_2(sal-iah)(MeOH)] + 2Hacac \quad (1)$$
  
199 
$$[Mo^{VI}O_2(sal-iah)(MeOH)] + H_2O_2 \rightarrow [Mo^{VI}O(O_2)(sal-iah)(MeOH)] + H_2O \quad (2)$$
  
200

The reaction of chloromethylated polystyrene (cross linked with 5% divinylbenzene) with dioxidomolybdenum(VI) complex **1** in DMF at 80 °C in the presence of triethylamine leads to the formation of polymer-anchored complex PS-[Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)] (**3**). During this process, the labile proton of NH group of the indole reacts with CH<sub>2</sub>Cl group of polymer. The whole synthetic procedures are presented in Scheme 2. The ICP-MS analysis of molybdenum in the polymer-grafted complexes suggests molybdenum loading of 0.45 mmol g<sup>-1</sup> of polymer in **3**.

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208

209 Scheme 2. Proposed structures of complexes 1, 2 and 3, and synthetic route to prepare 3; PS (or

ball) represents the backbone of the chloromethylated polystyrene.

### 211 *3.2. Structure description*

The ORTEP diagram for the compound  $[Mo^{VI}O_2(\text{sal-iah})(\text{MeOH})]$  (1) is shown in Fig. 1. 212 Fig. S1 (see supporting information) presents the intermolecular hydrogen bonds and  $\pi$ - $\pi$ 213 interactions. Selected bond distances and angles are given in Table 2. The structure of the 214 complex is mononuclear and adopts a six-coordinated distorted octahedral geometry. In this 215 complex phenolic oxygen, alcohol oxygen and azomethine nitrogen atoms of the ligand, which 216 acts as tridentate, and two oxo groups coordinate to molybdenum centre. One methanol molecule 217 completes the coordination sphere. The O=Mo=O angle is 106.05(9)° and Mo=O distances are 218 1.6851(18) and 1.7024(15) Å. The Mo-O-C angle and Mo-O distance for Mo-OHCH<sub>3</sub> in 1 are 219 125.13(16)° and 2.3794(17) Å, respectively, similar to other examples in literature [47]. 220

The asymmetric unit of complex 1 contains only single molecule of  $[Mo^{VI}O_2(sal$ iah)(MeOH)]. The indole groups of the two complexes interact by  $\pi$ - $\pi$  interactions (see Fig. S1). The distances between centroids is:  $d_{c1-c2} = 3.750$  Å {c1 [N(3O), C(10O), C(11O), C(12O), C(17O)], c2 [C(12A)-C(13A)-C(14A)-C(15A)-C(16A)-C(17A)]}. Intermolecular hydrogen bonds are present in the crystal packing (see Table 3).



227

- **Fig. 1.** ORTEP plot of complex [Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)] (1). All the non-hydrogen atoms are
- presented by their 30% probability ellipsoids.
- 230
- 231
- 232

### 233 **Table 2**

235		
	Bond lengths	1
-		X
	Mo(1)-O(1)	1.9157(16)
	Mo(1)-O(2)	1.6851(18)
	Mo(1)-O(3)	1.7024(15)
	Mo(1)-O(4)	2.3794(17)
	Mo(1)-O(5)	2.0133(14)
	Mo(1)-N(1)	2.2364(18)
-	Bond angles	1
-		
	O(2)-Mo(1)-O(3)	106.05(9)
	O(2)-Mo(1)-O(1)	100.68(10)
	O(3)-Mo(1)-O(1)	103.42(8)
	O(2)-Mo(1)-O(5)	95.32(9)
	O(3)-Mo(1)-O(5)	96.32(7)
	O(1)-Mo(1)-O(5)	149.90(7)
	O(2)-Mo(1)-N(1)	96.36(8)
	O(3)-Mo(1)-N(1)	155.51(7)
	O(1)-Mo(1)-N(1)	81.51(6)
	O(5)-Mo(1)-N(1)	71.45(6)
	O(2)-Mo(1)-O(4)	171.04(8)
	O(3)-Mo(1)-O(4)	81.90(7)
	O(1)-Mo(1)-O(4)	81.07(8)
	O(5)-Mo(1)-O(4)	79.46(7)
	N(1)-Mo(1)-O(4)	75.13(6)

Bond lengths [Å] and bond angles [°] for  $[Mo^{VI}O_2(sal-iah)(MeOH)](1)$ .

### 236 **Table 3**

Hydrogen bonds for complex  $[Mo^{VI}O_2(sal-iah)(MeOH)]$  (1).

238 D-H...A d(D-H) d(H...A) d(D...A) <(DHA) N(3)-H(3N)...O(3)#1 0.75(3)3.098(3) 2.42(3)151(3) O(4)-H(4O)...N(2)#2 170(3) 0.71(2)2.05(3)2.751(2)

Symmetry transformations used to generate equivalent atoms: #1 - x + 1, -y, -z + 1#2 x,-y+1/2,z-1/2

241

3.3. Field Emission-scanning Electron Micrograph (FE-SEM) and Energy Dispersive X-Ray
Analysis (EDX) studies

The images of field emission-scanning electron micrographs (Fe-SEM) of single beads of 244 pure chloromethylated polystyrene and polymer-grafted complex PS-[Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH] 245 (3) are presented in Fig. 2. The pure chloromethylated polystyrene bead has smooth and flat 246 surface while anchored complex shows slight roughening of the top layer suggesting the 247 incorporation of metal complex into polymer matrices. However, the poor loading of the metal 248 complex does not allow extracting any accurate information on the morphological changes in 249 terms of exact orientation of ligand coordinated to the metal ion. The estimation of ca. 9.2 weight 250 percentage of molybdenum content for PS-[Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH] (3) by energy dispersive X-251 ray analysis (EDX), however, confirms the grafting of metal complex onto polystyrene beads. 252 This observation further suggests that part of the covalently bonded complexes is present on the 253 surface while remaining is at various sites. 254



- Fig. 2. Scanning electron micrographs (SEM) of chlomethylated polystyrene (left) and PS [Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)] (3) (right).
- 259 *3.4. Thermogravimetric study*

Thermogravimetric analysis profile of [Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)] (1) under an oxygen 260 atmosphere shows that it is stable up to ca. 120 °C and then loses 7 % (Anal. Cal. 7.1%) weight 261 between 120 to 180 °C equivalent to one coordinated methanol. On further increasing the 262 temperature, the solvent free complex decomposes in two major fragments with exothermic 263 weight loss which completes at ca. 540 °C. The obtained residue at this temperature is 31% 264 which is close to the theoretical value of 31.9%. The polymer-grafted complex PS-[Mo<sup>VI</sup>O<sub>2</sub>(sal-265 iah)(MeOH)] (3) starts losing weight at ca. 80 °C and this step' completes at ca. 170 °C with a 266 267 total loss of ca. 9% suggesting the presence of coordinated as well as trapped solvent. Thereafter, it decomposes in several fragments with exothermic weight loss at higher temperature. 268 Quantitative measurement of weight loss and distinction between decomposition pattern of 269 complex and polymer matrix at various stages were not possible due to overlapping nature of the 270 decompositions. However, the final residues of 6.7 % (equivalent to 0.47 mmol  $g^{-1}$  of Mo in 3) 271 at ca. 520 °C suggest the formation of MoO<sub>3</sub> and metal complex is grafted into polymer support. 272

273

256

274 *3.5. IR spectral studies* 

IR spectral data of the ligand and its neat and anchored complexes are presented in Table 4. The neat complex **1** exhibits two sharp bands at 911 and 940 cm<sup>-1</sup> due to  $v_{sym}$ (O=Mo=O) and  $v_{asym}$ (O=Mo=O) modes, respectively [48]. The corresponding polymer-bound molybdenum

complex displays these bands at 903 cm<sup>-1</sup> and 957 cm<sup>-1</sup>. Complex  $[Mo^{VI}O(O_2)(sal-iah)(MeOH)]$ (2) exhibits a sharp band at 965 cm<sup>-1</sup> which is assigned due to v(Mo=O) stretch. In addition, it exhibits three IR active vibrational modes associated with the peroxido moiety  $[Mo(O_2)]^{2+}$  at 910, 635 and 556 cm<sup>-1</sup> which are assigned due to the O–O intra stretching, asymmetric Mo(O<sub>2</sub>) stretching and symmetric Mo(O<sub>2</sub>) stretching, respectively [49]. These bands confirmed the  $\eta^2$ coordination of the peroxo group to the molybdenum.

Ligand H<sub>2</sub>sal-iah (I) exhibits four distinct bands at 3400, 3186, 1670 and 1618  $cm^{-1}$  due 284 to v(OH), v(NH), v(C=O) and v(C=N) modes, respectively. The presence of sharp bands due to 285 v(NH) and v(C=O) is indicative of its ketonic nature in the solid state. The absence of these 286 bands in the spectra of all complexes is consistent with the enolisation of the amide functionality 287 and subsequent coordination of enolic oxygen to the metal ion after proton replacement. A new 288 band appearing at ca. 1270  $\text{cm}^{-1}$  is assigned to the v(C–O)(enolic) stretching of the coordinated 289 hydrazone fragment. The band due to azomethine group moves towards lower wave number by 290 11 cm<sup>-1</sup> (in 1), 5 cm<sup>-1</sup> (in 2) and 9 cm<sup>-1</sup> (in 3) indicating the coordination of azomethine nitrogen 291 to the molybdenum. The band corresponding to the free –OH group present in H<sub>2</sub>sal-iah is also 292 present in complexes 1 and 2 possibly suggesting the presence of coordinated methanol. The 293 presence of multiple bands of medium intensity observed in the region 2800–2900 cm<sup>-1</sup> in all 294 complexes suggests the existence of -CH<sub>2</sub> group. 295

The chloromethylated polystyrene displays strong peaks at 1264 and 673 cm<sup>-1</sup> [50]. The absence of these peaks in PS-[Mo<sup>VI</sup>O<sub>2</sub>((sal-iah)(MeOH)] (**3**) suggests the covalent bonding of chloromethylated polystyrene with [Mo<sup>VI</sup>O<sub>2</sub>((sal-iah)(MeOH)] (cf. Scheme 2) through nitrogen of the indole ring. This is further supported by the absence of v(NH) band that appears at 3250 cm<sup>-1</sup> in **1**.

301

### 302 *3.6. UV-visible spectral study*

Fig. 3 (A and B) reproduces spectra of ligand, neat and polymer-grafted complexes and Table 5 includes UV-visible spectral data. Ligand H<sub>2</sub>sal-iah (**I**) exhibits three spectral bands at 220, 279 and 321 nm in the UV region corresponding to  $\sigma \rightarrow \sigma^*$ ,  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively. The additional band at 289 nm having intensity similar to  $\pi \rightarrow \pi^*$  transition is possibly due to its splitting. All these bands also appear in the spectra of complexes **1** and **2** with

slight variations. In addition, they also exhibit a low intense band at 380 (in 1) and ca. 400 nm (in 2) originating due to the transfer of charge from phenolate oxygen atom to an empty d-orbital of the molybdenum atom (LMCT). Spectrum of 3 recorded in Nujol<sup>®</sup> has very similar but broad electronic spectral patterns [Fig. 3(B)]. The expected LMCT transition in 3 could only be observed around 386 nm as a weak shoulder in Nujol possibly due to poor loading of complex in polymer matrix while bands in the UV region are similar to that observed in 1 and 2.

314

### 315 **Table 4**

316 IR spectral data  $(cm^{-1})$  of compounds

Compound	υ(OH)	υ(NH)	υ(C=O)	v(C=N	v(Mo=O)
H <sub>2</sub> sal-iah (I)	3400	3186	1670	1618	
$[Mo^{VI}O_2((sal-iah)(MeOH)](1)$	3400	3250		1607	911(s), 940(s)
$[Mo^{VI}O(O_2)(sal-iah)(MeOH)] (2)^{a}$	3400	3250	-	1613	965
PS-[Mo <sup>VI</sup> O <sub>2</sub> (sal-iah)(MeOH] (3)	3400	-	-	1609	903(s), 957(s)



<sup>318</sup> 



- **Fig. 3.** (A): Electronic spectra of (a)  $H_2$ sal-iah (I), (b) [Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)] (1) and (c)
- 321 [Mo<sup>VI</sup>O(O<sub>2</sub>)(sal-iah)(MeOH)] (2) recorded in methanol. (B): Electronic spectrum of PS-
- 322  $[Mo^{VI}O_2(sal-iah)(MeOH)]$  (3) recorded after despersing it in nujol<sup>®</sup>.
- 323

### 324 **Table 5**

325 Electronic spectral data of ligand and complexes.

Compound	Solvent	$\lambda_{\text{max}} / \text{nm} (\epsilon / \text{M}^{-1} \text{cm}^{-1})$
$H_2$ sal-iah (I)	MeOH	$220(5.98 \times 10^4), 279(3.42 \times 10^4), 289(3.04 \times 10^4),$
		321(1.48×10 <sup>4</sup> )
[Mo <sup>VI</sup> O <sub>2</sub> (sal-iah)(MeOH)] (1)	МеОН	220(4.56×10 <sup>4</sup> ), 279(2.30×10 <sup>4</sup> ), 289(2.06×10 <sup>4</sup> ),
		320(0.96×10 <sup>4</sup> ), 380(2.06×10 <sup>3</sup> )
$[Mo^{VI}O(O_2)(sal-iah)(MeOH)] (2)$	MeOH	218(3.91×10 <sup>4</sup> ), 279(2.33×10 <sup>4</sup> ), 289(2.16×10 <sup>4</sup> ),
		322(1.37×10 <sup>4</sup> ), 400(2.55×10 <sup>3</sup> )
$PS-[Mo^{VI}O_2(sal-iah)(MeOH)] (3)$	Nujol	219, 278, 315, 386

326 327

### 328 3.7. <sup>1</sup>H and <sup>13</sup>C NMR studies

The <sup>1</sup>H NMR spectra of H<sub>2</sub>sal-iah (I) and [Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)] (1) are shown in Fig. 329 4 and their typical chemical shifts are presented in Table 6. The <sup>1</sup>H NMR spectrum of ligand 330 exhibits single singlet for phenolic -OH proton while two sets of singlet with about 1:2 ratio 331 each for azomethine (-CH=N-), methylene (-CH<sub>2</sub>-), NH (of -C(O)-NH- group) and NH (of 332 indole) protons, indicating its existence in two isomeric forms. The absence of signal due to NH 333 of -C(O)-NH- group in the complexes supports the enolisation of the ketonic group and 334 consequent replacement of H by the metal ion. Similarly, absence of phenolic proton signal in 335 complexes indicates the coordination of the phenolic oxygen after proton replacement. The two 336 azomethine signals appearing at 8.38 and 8.41 ppm merge into one and resonate at down field 337 due to the coordination of the azomethine nitrogen. Protons associated with aromatic, methyl and 338 339 NH (of indole group) groups appear at nearly same positions in ligand as well as in complexes. Thus, <sup>1</sup>H NMR data supplement the inference obtained by IR spectral study. 340



349 (unresolved).

The <sup>13</sup>C NMR spectra of H<sub>2</sub>sal-iah (I) and  $[Mo^{VI}O_2(sal-iah)](1)$  have been recorded which 351 also supplement <sup>1</sup>H NMR spectral information for the elucidation of the structure of the 352 complex. Table 7 provides <sup>13</sup>C NMR spectral data and Fig. S2 reproduces their spectra. 353 Assignments of the peaks are based on the intensity patterns of the chemical shift and on the 354 coordination-induced shifts ( $\Delta\delta$ ) of the signals for carbon atoms in the vicinity of the 355 coordinating atoms [51]. Similar to the <sup>1</sup>H NMR spectrum, H<sub>2</sub>sal-iah (I) exhibits two sets of 356 357 signal for most carbons while complex resonates single set of signal for each carbon except to those carbons where centre of symmetry exist. For carbons where centre of symmetry exist e.g. 358 aromatic carbons, they exhibit less number of signals. A large coordination-induced shift for C1 359 (carbon bearing phenolic oxygen), C7 (carbon bearing azomethine nitrogen) and C8 (carbon 360 bearing enolic oxygen) atoms demonstrate the coordination of these functionalities to the 361 molybdenum. A considerable up field shift of methylene (C9) carbon has also been noticed in 362 complex. A new signal at 49 ppm suggests the coordination of methanol to the molybdenum. 363

364

### 365 **Table 7**

<sup>13</sup>C NMR spectral data of ligand and complexes

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- 368
- 369 370

$O \rightarrow V / OMe$
15 - 16 - 9 - C - 1 - 2 - 0 - 1 - 2 - 0 - 1 - 2 - 0 - 1 - 2 - 0 - 1 - 2 - 0 - 0 - 1 - 2 - 0 - 0 - 0 - 0 - 0 - 0 - 0 - 0 - 0
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Compound	$C_1$	C <sub>2</sub> -C <sub>5</sub>	$C_6$	C <sub>7</sub>	$C_8$	C <sub>9</sub>	$C_{10}, C_{11}, C_{12}$	C <sub>13</sub> - C <sub>17</sub>	C <sub>18</sub>
I	156.8,	116.6, 116.8, 131.3,	118.8,	141.4,	167.5,	29.7,	108.3, 108.4,	111.80, 111.89, 119.07,	-
	157.8	131.6, 119.9, 120.5,	118.9	147.4	172.7	31.8	124.3, 124.4,	119.09, 119.1, 119.7, 121.4,	
		127.8, 129.9					136.5, 136.6	121.5, 127.3, 127.6	
1	159.7	118.9,135.1,121.5,	118.9	155.7	174.5	28.3	108.5, 124.5,	111.8, 120.5, 121.8, 119.2,	49.0
		134.5					136.6	127.6	

371

### 372 *3.8. Catalytic activity studies*

### 373 *3.8.1. Oxidative bromination of styrene*

Vanadium (neat as well as polymer supported) and neat molybdenum complexes have been used as catalyst to study oxidative bromination of styrene [33,34,37-40,43]. We have

considered polymer supported complex PS-[Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)] (**3**) to carry out the oxidative bromination of styrene using 30 % aqueous  $H_2O_2$  as an oxidant and three products namely 1,2-dibromo-1-phenylethane, 2-bromo-1-phenylethane-1-ol and 1-phenylethane-1,2-diol were obtained along with small amount of un-identified product; Scheme 3. The main products were identified and confirmed by <sup>1</sup>H NMR spectroscopy as well as by GC–MS after their separation, and are the same as reported earlier [33,34,37-40,43].







394

With the objective to conclude suitable reaction conditions for the maximum conversion of styrene different parameters, namely, the amounts of catalyst, oxidant (mol of  $H_2O_2$  per mol of styrene), HClO<sub>4</sub> and KBr were tested. Acid was found to be essential to carry out the catalytic bromination.

In order to optimize the catalyst amount, three different amounts of catalyst i.e. 0.010, 399 0.015 and 0.020 g were taken for the fixed amount of styrene (1.04 g, 10 mmol), H<sub>2</sub>O<sub>2</sub> (2.27 g, 400 20 mmol), KBr (2.38 g, 20 mmol) and HClO<sub>4</sub> (1.43 g, 10 mmol, added in four equal portions at t 401 = 0, 15, 30 and 45 min of the reaction time) in  $CH_2Cl_2-H_2O$  (40 mL, v/v) solvent system and the 402 reaction was carried out at 40 °C for 2 h. As shown in Fig. 5(a), a maximum of 67 % conversion 403 was achieved with 0.010 g of catalyst. Upon increasing catalyst amount to 0.015 g the 404 conversion of styrene improved to 75 % but no appreciable improvement was noted with 0.020 g 405 of catalyst. Therefore, 0.015 g of catalyst was considered optimum for the maximum conversion 406 of styrene. 407

The amount of  $HClO_4$  was optimized by taking substrate to  $HClO_4$  ratios of 1:1, 1:2 and 408 1:3 under above reaction conditions; Fig. 5 (b). The addition of HClO<sub>4</sub> to the catalytic reaction 409 mixture in four equal portion at t = 0, 15, 30 and 45 min for each set of reaction was the 410 minimum condition to avoid decomposition of the catalyst. At a substrate to HClO<sub>4</sub> ratio of 1:1, 411 only 75% conversion was obtained in 2 h of reaction time but this conversion reached 96% at 412 molar ratio of 1:2. On increasing this ratio further to 1:3 reduced the conversion time but the 413 overall conversion of styrene remained nearly constant. Therefore, styrene to HClO<sub>4</sub> molar ratio 414 of 1:2 was taken for further optimization of other parameters. Other acid like H<sub>2</sub>SO<sub>4</sub> could also 415 be used successfully with nearly same result. 416

To understand the effect of oxidant, three different styrene : aqueous 30 %  $H_2O_2$  molar ratios viz. 1:1, 1:2, and 1:3 were considered for a fixed amount of styrene (1.04 g, 10 mmol) and catalyst (0.015 g). As illustrated in Fig. 5 (c), increasing the styrene to oxidant ratio from 1:1 to 1:2 increases the conversion from 67 to 96%. However, further increasing this ratio to 1:3 shows no predominant conversion. Thus substrate to  $H_2O_2$  ratio of 1:2 was considered the best one for the maximum oxidative bromination of styrene.

Similarly, for styrene (1.04 g, 10 mmol), catalyst (0.010 g),  $CH_2Cl_2-H_2O_2$  (40 mL, v/v), H<sub>2</sub>O<sub>2</sub> (2.27 g, 20 mmol) and aqueous HClO<sub>4</sub> (2.86 g, 20 mmol, added as mentioned above), three different amounts of KBr i.e.10, 20 and 30 mmol were taken and the reaction was carried out at 40 °C. The obtained conversion was only 44 % with 10 mmol KBr but increasing the amount to 20 mmol improved this conversion to 96% which further improved to 99% at 30 mmol KBr as shown in Fig. 5 (d). Therefore, 20 mmol KBr was considered the best one for the maximum conversion of styrene.

Table 8 provides conversion of styrene under different reaction conditions and selectivity of different reaction products under particular condition after 2 h of reaction time. From the data presented in Table 8, it is clear that the best suited reaction conditions for the maximum oxidative bromination of 10 mmol of styrene are (entry no. 4): PS-[Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH] (0.015 g), HClO<sub>4</sub> (2.86 g, 20 mmol ), aqueous 30% H<sub>2</sub>O<sub>2</sub> (2.27 g, 20 mmol) and KBr (2.38 g, 20 mmol) (for GC traces see Fig. S3).

436



**Fig. 5.** (a) Effect of amount of catalyst on the oxidative bromination of styrene. (b) Effect of amount of  $HClO_4$  on the oxidative bromination of styrene. (c) Effect of amount of  $H_2O_2$  ( $H_2O_2/$ styrene molar ratio) on the oxidative bromination of styrene. (d) Effect of amount of KBr on the oxidative bromination of styrene. For reaction conditions refer to Table 8.



#### 442

**Fig. 6.** Consumption of styrene and variation in the selectivity of different reaction products as a



445

### 446 **Table 8**

447 Results of oxidative bromination of styrene (1.04 g, 10 mmol) using catalyst PS-[Mo<sup>VI</sup>O<sub>2</sub>(sal-

448 iah)(MeOH)] (3) after 2 h of reaction time.

Entry	KBr	$H_2O_2$	HClO <sub>4</sub>	Catalyst	CH <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O	% Conv.,		% selec	tivity	
No.	(g, mmol,	(g, mmol,	(g, mmol,	(g)	(V/V, mL)	TOF $(h^{-1})$	% Mono-	% Di-	% Di-ol	%
	eq.) <sup>a</sup>	eq.)	eq.)				bromo	bromo		others
1	2.38, 20, 2	2.27, 20, 2	1.43, 10, 1	0.010	20 /20	67, 1506	35.4	1.9	59.9	2.7
2	2.38, 20, 2	2.27, 20, 2	1.43, 10, 1	0.015	20/20	75, 1124	37.2	2.7	59.1	1.1
3	2.38, 20, 2	2.27, 20, 2	1.43, 10, 1	0.020	20/20	76, 854	39.2	1.4	56.8	2.6
4	2.38, 20, 2	2.27, 20, 2	2.86, 20, 2	0.015	20/20	96, 1439	45.0	2.0	51.2	1.7
5	2.38, 20, 2	2.27, 20, 2	4.29, 30, 3	0.015	20/20	99, 1484	13.5	2.8	81.4	2.3
6	2.38, 20, 2	1.13, 10, 1	2.86, 20, 2	0.015	20/20	67, 1004	38.3	2.9	57.6	1.2
7	2.38, 20, 2	3.39, 30, 3	2.86, 20, 2	0.015	20/20	99, 1484	29.2	2.2	66.2	2.5
8	1.19, 10, 1	2.27, 20, 2	2.86, 20, 2	0.015	20/20	44, 659	55.0	2.3	41.9	0.8
9	3.57, 30, 3	2.27, 20, 2	2.86, 20, 2	0.015	20/20	99, 1484	24.7	1.9	71	2.4

449 <sup>a</sup> eq. = equivalent amount

450

For 96% conversion of styrene after 2 h of reaction time under these conditions, the selectivity of the reaction products follows the order: 1-phenylethane-1,2-diol (51.2%) > 2-bromo-1phenylethane-1-ol (45.0%) > 1,2-dibromo-1-phenylethane (2.0%). The consumption of styrene

and the selectivity of different products under the optimized reaction conditions have also been 454 analyzed as a function of time and are presented in Fig. 6. The selectivity of the formation of 1-455 phenylethane-1,2-diol and 2-Bromo-1-phenylethane-1-ol starts with ca. 46 and 48%, 456 respectively. With time these conversions slowly change and end up at 51.2 and 45.0%, 457 respectively. The selectivity of the formation of 1,2-dibromo-1-phenylethane and other un-458 identified products always remains below 2% during these periods. Catalytic potential of 3 459 compares well with the activities shown by other molybdenum and vanadium complexes 460 [33,34,37-40,43]. 461

462

The catalytic activity of the recovered catalyst from two fresh runs, after washing with 463 acetonitrile and drying, was also carried out and result shows about 95% conversion, indicating 464 465 the recyclability of the catalyst. Under the above reaction conditions the catalytic activity of neat complex  $[Mo^{VI}O_2(sal-iah)(MeOH)]$  (1) gave 92% conversion where selectivity of the reaction 466 products is similar to the one obtained by supported complex. Thus, catalytic potential of 467 supported as well as neat complexes both are good but the recyclability of the supported catalyst 468 469 makes it better over the non-supported one. In the absence of catalyst, the reaction mixture gave ca. 45% conversion of styrene under above optimized reaction conditions. 470

#### 471 *3.8.2. Oxidative bromination of trans-stilbene*

A biphasic chloroform-water system was found to be suitable to carry out oxidative 472 bromination of *trans*-stilbene. Oxidative bromination of trans-stilbene gave mainly three 473 products: i) 2,3-diphenyloxirane (trans-stilbene oxide), ii) 2-bromo-1,2-diphenylethanol and iii) 474 1,2-dibromo-1,2-diphenylethane; Scheme 4. About 2 h was required to acquire equilibrium with 475 476 maximum conversion. The reaction conditions for the maximum oxidative bromination of *trans*stilbene were also optimized considering all these parameters stated above such as amounts of 477 catalyst, aqueous 30% H<sub>2</sub>O<sub>2</sub>, KBr and 70% HClO<sub>4</sub>. Details of the reaction conditions, the 478 corresponding oxidative brominated and other products, and % selectivity of different products 479 480 under various conditions are summarized in Table 9. It is clear from the table that the optimized reaction conditions (entry no. 5) for this reaction are: *trans*-stilbene (0.90 g, 5 mmol)), KBr (2.36 481 g, 20 mmol) aqueous 30 % H<sub>2</sub>O<sub>2</sub> (2.27 g, 20 mmol) catalyst precursor (0.015 g), aqueous 70% 482 HClO<sub>4</sub> (2.86 g, 20 mmol) and CHCl<sub>3</sub>/H<sub>2</sub>O (40 mL, 50% v/v). Under these conditions, a 483

maximum of 96 % conversion of *trans*-stilbene was obtained where selectivity of the reaction 484 products follows the order: 2-bromo-1,2-diphenylethanol (49.0%) > 1,2-dibromo-1,2-485 diphenylethane (47.5%) > 2,3-diphenyloxirane (*trans*-stilbene oxide) (1.9%) (for GC traces see 486 Fig. S4). 487

The catalytic activity obtained here compares well with the literature. NH<sub>4</sub>VO<sub>3</sub> catalyzed 488 oxidative bromination of trans-stilbene with moderate conversion in aqueous medium in the 489 presence of H<sub>2</sub>O<sub>2</sub>, KBr and HBr has been reported by Hirao et al. [52]. A maximum of 91% 490 conversion of *trans*-stilbene with the selectivity order of 2,3-diphenyloxirane (*trans*-stilbene 491 oxide) (66%) > 1.2-dibromo-1.2-diphenylethane (24%) > 2-bromo-1.2-diphenylethanol (8%)492 was obtained by PS-im[ $V^{V}O_{2}(pan)$ ] (Hpan = 1-(2-pyridylazo)-2-naphthol) [40]. 493

The catalytic activity of the recovered catalyst shows almost similar (93 %) conversion 494 and neat complex [Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)] gave 90% conversion with essentially similar 495 selectivity of reaction products. Control experiment without catalyst under above reaction 496 497 conditions gave only 51 % conversion of trans-stilbene while only 2 % conversion of was obtained in the absence of KBr. In the absence of oxidant and KBr, no formation of trans-498 499 stilbene oxide confirms that dioxido group of catalyst does not transfer its oxygen to the substrate directly. Thus, neat as well as supported catalyst both enhances the reaction while the 500 recyclability of the supported catalyst makes it better over the non-supported one. 501



- 506
- Scheme 4. Oxidative bromination products of *trans*-stilbene. 507
- 508
- 509
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- 511

#### Table 9 512

Results of oxidative bromination of *trans*-stilbene (0.90 g, 5 mmol) using catalyst PS-[Mo<sup>VI</sup>O<sub>2</sub>(sal-513

514 iah)(MeOH)] (3) after 2 h of reaction time.

Entry	KBr	$H_2O_2$	HClO <sub>4</sub>	Catalyst	CHCl <sub>3</sub> /H <sub>2</sub> O	% Conv.,	% selectivity			
No.	(g, mmol,	(g, mmol,	(g, mmol,	(g)	(V/V, mL)	TOF (h <sup>-1</sup> )	% Mono-	% Di-	%	%
	eq.) <sup>a</sup>	eq.)	eq.)				bromo	bromo	T.S.O. <sup>b</sup>	others
1	2.38, 20, 4	2.27, 20, 4	4.29, 30, 6	0.015	20 /20	97, 727	35.5	56.4	4.3	3.8
2	2.38, 20, 4	2.27, 20, 4	4.29, 30, 6	0.020	20/20	97, 545	39.4	56.3	3.2	1.0
3	2.38, 20, 4	2.27, 20, 4	4.29, 30, 6	0.025	20/20	98, 441	40.8	55.6	2.2	1.5
4	2.38, 20, 4	2.27, 20, 4	1.43, 10, 2	0.015	20/20	57, 427	46.4	50.6	2.6	0.4
5	2.38, 20, 4	2.27, 20, 4	2.86, 20, 4	0.015	20/20	96, 720	49.0	47.5	1.9	1.6
6	2.38, 20, 4	1.13, 10, 2	2.86, 20, 4	0.015	20/20	80, 600	43.7	48.3	4.4	3.6
7	2.38, 20, 4	1.70, 15, 3	2.86, 20, 4	0.015	20/20	81, 607	46.2	36.9	10.6	6.0
8	1.19, 10, 2	2.27, 20, 4	2.86, 20, 4	0.015	20/20	40, 300	55.9	33.1	6.9	4.2
9	1.79, 15, 3	2.27, 20, 4	2.86, 20, 4	0.015	20/20	78, 585	56.5	36.8	3.4	3.3

515

<sup>a</sup> eq. = equivalent amount

<sup>b</sup> T.S.O. = trans-stlbene oxide 516

3.9. Reactivity of  $[Mo^{VI}O_2(sal-iah)(MeOH)](1)$  with  $H_2O_2$  and possible reaction pathway of the 518 catalyst 519

The formation of  $[MoO(O_2)]^{2+}$  intermediate using  $[MoO_2]^{2+}$  complexes has been 520 established in the literature. We have been able to isolate peroxido complex [Mo<sup>VI</sup>O(O<sub>2</sub>)(sal-521 iah)(MeOH)] (2) by the reaction of  $H_2O_2$  and characterize it. Its in-situ formation has also been 522 523 established here by electronic absorption spectroscopy. Thus, the titration of a methanolic solution of 1 (3.64  $\times$  10<sup>-4</sup> M) with 30 % H<sub>2</sub>O<sub>2</sub> (one drop) dissolved in 10 ml of MeOH results in 524 the shift of 380 nm band to 400 nm along with increase in intensity (inset of Fig. 7). The 525 intensities of other bands i.e. bands at 320, 289, 279 and 220 nm in diluted methanolic solution 526  $(7.2 \times 10^{-5} \text{ M})$  increases regularly without shifting (Fig. 7). The shape of final spectrum is 527 similar to the spectrum of peroxide complex 2, thus verifying the formation of similar 528 oxidoperoxido species in solution as well. 529

530

<sup>517</sup> 



532

**Fig. 7.** UV-Vis spectral changes observed during titration of  $[Mo^{VI}O_2(sal-iah)(MeOH)]$  (1) with H<sub>2</sub>O<sub>2</sub>. The spectra recorded after successive addition of one drop portions of dilute H<sub>2</sub>O<sub>2</sub> (1 drop of 30% H<sub>2</sub>O<sub>2</sub> in 10 ml MeOH) to 22 mL of 7.2× 10<sup>-5</sup> M methanolic solution of 1. Inset shows similar spectral changes with 3.64 × 10<sup>-4</sup> M solution of 1 in methanol.

537

It is normally accepted that V-dependent bromoperoxidase enzymes (V-BrPOs) 538 [33,34,40,53,54] in the presence of hydrogen peroxide [55], forms a peroxido intermediate 539 derivative which oxidizes the bromide ion to bromine equivalent intermediate. This intermediate 540 then either brominates an organic substrate or reacts with another molecule of Br to form 541 bromine. The peroxide  $[MoO(O_2)]^{2+}$  intermediate species form here may similarly oxidize the 542 bromide (to Br<sub>2</sub>, Br<sub>3</sub><sup>-</sup> and/or HOBr), which may react with styrene to give bromonium ion as 543 intermediate. The attack of nucleophile Br<sup>-</sup> on the  $\alpha$ -carbon of the intermediate gives 1,2-544 dibromo-1-phenylethane while attack of H<sub>2</sub>O gives 2-bromo-1-phenylethane-1-ol. The 545 nucleophile H<sub>2</sub>O may further attack on the  $\alpha$ -carbon of 2-bromo-1-phenylethane-1-ol to give 1-546 phenylethane-1,2-diol (Scheme 5) [40]. The poor selectivity of dibromo product is possibly due 547 548 to its fast sequential conversion into the mono-bromo derivative, which in turn converts into diol. We have also tested the conversion of monobromo derivative alone under the optimized reaction 549 conditions and observed the formation of 1-phenylethane-1,2-diol (Fig. S5). Thus the formation 550 of good amount of 1-phenylethane-1,2-diol is justified under any experimental conditions 551

552 mentioned in Table 8. The presence of acid in the aqueous phase is possibly promoting the 553 protonation of the peroxido moiety and the presence of KBr is essential to get reasonable amount 554 of brominated product(s).

555 Following similar mechanisms (Scheme 6) may also be proposed for the formation of 556 different products upon oxidative bromination of *trans*-stilbene [40].

557



558

Scheme 5. Proposed mechanisms for the formation of three main products, after the bromoniumion is formed by action of catalytically generated HOBr on styrene.

561



564 **Scheme 6.** Proposed mechanisms for the formation of products, after the bromonium ion is 565 formed by action of catalytically generated HOBr on *trans*-stilbene.

566

563

#### 567 4. Conclusions

Complex  $[Mo^{VI}O_2(sal-iah)(MeOH)]$  (1) with dibasic tridentate ONO donor ligand H<sub>2</sub>saliah (I) derived from salicylaldehyde and indole-3-acetic hydrazide has been prepared which can also be converted, by treatment with H<sub>2</sub>O<sub>2</sub>, to the corresponding peroxido-complex  $[Mo^{VI}O(O_2)(sal-iah)(MeOH)]$  (2). Complex 1 has also been grafted successfully through covalent bonding of the nitrogen of the indole group to chloromethylated polystyrene crosslinked with 5% divinylbenzene {now abbreviated as PS-[[Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)] (3)}.

Oxidative bromination of styrene and *trans*-stilbene has been successfully carried out 574 using 1 and 3 as catalyst precursor. The presence of some of the metal centers on the surface of 575 the polymer in 3 due to insertion of spacer between polymer support and catalyst possibly 576 allowed its better interaction with substrates and oxidant during catalytic reaction, also observed 577 earlier [44], resulting in better performance of the catalyst. Further, the recyclability of 3 over 578 non-polymer analog makes it useful functional model analog of haloperoxidases. A moderate 579 conversions of the substrates in the absence of the catalyst has also been obtained but the 580 selectivity profiles of the reaction products differ significantly. The peroxido species, similar to 581

 $[Mo^{VI}O(O_2)(sal-iah)(MeOH)]$  (2) isolated in the solid state, has also been demonstrated to form in solution which oxidizes bromide, in the presence of acid, which in turn reacts with styrene and *trans*-stilbene to give corresponding bromonium ion as intermediate. This intermediate is responsible for different reaction products of substrates.

586

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592

### 593 Appendix A. Supplementary data

594 CCDC 990876 contains the supplementary crystallographic data for the structure reported 595 in this paper. These data can be obtained free of charge vihttp://www.ccdc.cam.ac.uk/conts/ 596 retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, 597 Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. 598 Supplementary data associated with this article can be found, in the online version, at doi: \$\$\$\$ 599 Fragment of the crystal packing of complex [Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)] (**1**) and <sup>13</sup>C NMR spectra 590 of H<sub>2</sub>sal-iah (**I**) and [Mo<sup>VI</sup>O<sub>2</sub>(sal-iah)(MeOH)] (**1**) are presented in the supporting Information.

601

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- 739 (Graphical Abstract: Text)
- 740 Polymer and non polymer-grafted dioxidomolybdenum(VI) complexes having
- 741 ONO donor ligand and their catalytic activities for the oxidative bromination
- 742 of organic substrates
- 743 Mannar R. Maurya, Naveen Kumar, Fernando Avecilla
- Polymer-grafted dioxidomolybdenum(VI) complex and its catalytic potential for the oxidative
- bromination of styrene and *trans*-stilbene are reported.



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- 754 ONO donor ligand and their catalytic activities for the oxidative bromination
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- 757

### 758 Research Highlights

- 1. Polystyrene grafted and neat dioxidomolybdenum(VI) complexes are reported.
- 760 2. These complexes catalyze the oxidative bromination of styrene and *trans*-stilbene.
- 761 3. Polymer grafted complex is stable and recyclable.
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