# Engineering Multifunctionality in Hybrid Polyoxometalates: Aromatic Sulfonium Octamolybdates as Excellent Photochromic Materials and Self-Separating Catalysts for Epoxidation

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# Supporting Information

**ABSTRACT:** Engineering multifunctionality in hybrid polyoxometalates (hybrid POMs) is an interesting but scarcely explored topic. Herein, we set about engineering two important materials properties, viz., photochromism and self-separating catalysis, in a hybrid POM by modulating the counterion motif. A series of six aromatic sulfonium counterions have been developed on the basis of an aromatic sulfonium counterion motif that allows structural and electronic fine-tuning by changing substituents at multiple locations. Using the aromatic sulfonium counterions and sodium molybdate, six new aromatic sulfonium octamolybdate hybrids (1-6) having formulas  $(HPDS)_4[Mo_8O_{26}]$  (1),  $(HMPDS)_4[Mo_8O_{26}]$  (2),  $(MPDS)_4[Mo_8O_{26}]$  (3),  $(APDS)_4[Mo_8O_{26}]$  (4),



 $(MPDS)_4[Mo_8O_{26}]$  (3),  $(APDS)_4[Mo_8O_{26}]$  (4), (AMPDS)<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>] (5), and (MAPDS)<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>] (6) (where HPDS = (4-hydroxyphenyl)dimethylsulfonium, HMPDS = (4-hydroxy-2-methylphenyl)dimethylsulfonium, MPDS = (4-methoxyphenyl)dimethylsulfonium, APDS = (4-(allyloxy)phenyl)dimethylsulfonium, AMPDS = (4-(allyloxy)-2-methylphenyl)dimethylsulfonium and MAPDS = (4(methacryloyloxy)phenyl)dimethylsulfonium) have been synthesized, and their structures were confirmed by single crystal X-ray diffraction and ESI-MS analyses. Hybrids 1–6 acted as good solid-state photochromic materials exhibiting color change from white to purple under UV illumination (350 nm), and we show here that the photochromic properties of hybrids 1–6 could be modulated by changing the substitutions on the counterion motif. A coloration kinetic half-life ( $t_{1/2}$ ) of 0.33 min was achieved with this class of hybrid POMs. Hybrids 1–6 exhibited excellent self-separating catalytic properties toward the epoxidation of olefins, yielding up to 99% epoxide product with good selectivity in short time. The substituents on the aromatic sulfonium counterions helps to fine-tune the electronic, lipophilic, and solubility properties of the hybrids and thereby their catalytic properties. Moreover, we used ESI-MS analyses to understand the mechanism of catalysis exhibited by octamolybdates 1–6 in the presence of H<sub>2</sub>O<sub>2</sub>, and we succeeded in identifying a hitherto undetected intermediate, tetraperoxo-octamolybdates, shedding more light on the epoxidation mechanism.

# INTRODUCTION

The design and development of multifunctional materials that exhibit two or more properties of interest are gaining attention in recent years.<sup>1–3</sup> Theranostics, which combine diagnosis and therapy, are examples of multifunctional materials.<sup>4</sup> The different properties of a multifunctional material can be brought in by two different components or a single component, and these properties may simply coexist in the system or interact with each other generating new properties.<sup>5–7</sup> In general, properties which cooperatively interact giving rise to synergistic effects are of considerable interest.<sup>8,9</sup> Multifunctional materials are often built on platforms like metal nanoparticles, metal organic frameworks, polymeric materials, and nanocomposites.<sup>10–13</sup> In addition, simple molecular systems have also been reported as multifunctional materials.<sup>14,15</sup> Polyoxometalates (POMs), discrete, anionic metal oxide clusters of early transition metal ions, represent a vast class of inorganic materials possessing enormous diversity in their size, structure and properties. Because of their unique properties, POMs have been widely used as precursors in the development of materials that are relevant to optical, magnetic, catalytic, biological, and electronic applications.<sup>16–19</sup> Despite their widespread use in materials chemistry, POMs have only scarcely been explored in the development of multifunctional materials.<sup>20</sup>

It is well-known that the properties of a hybrid POM can be engineered by systematically varying its counterions.<sup>21</sup> In the present work, we have attempted to combine two diverse materials properties, viz., photochromism and self-separating catalysis, in a simple hybrid POM through molecular design approach using a new class of electronically and structurally

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tunable aromatic sulfonium counterions. Photochromic materials, which exhibit reversible light-induced switching between two optically distinguishable states, are important in a wide range of technological and marketable applications.<sup>22-25</sup> POMs have already been recognized as an important class of precursors in the development of photochromic materials.<sup>25,26</sup> A majority of the reported photochromic POM-hybrids are organoammonium-POMs;<sup>27-29</sup> however, in recent years, sulfonium-POMs have also been reported as photochromic materials.<sup>30,31</sup> Meanwhile, self-separating catalysts, which combine the properties of homogeneous and heterogeneous catalysts in a single entity, are becoming important in many industrial applications.<sup>32,33</sup> In self-separating catalysis, the catalyst precursor is insoluble in the reaction medium but forms soluble catalytically active species under the action of a reagent.<sup>34</sup> However, when the reagent gets completely used up, the catalyst returns to its original structure and precipitates out of the reaction mixture. The quest for self-separating catalysts is therefore driven by both economic and environmental reasons. Although self-separating catalysts have been developed from a variety of materials, there are only a few reports on POM based self-separating catalysts so far.<sup>34,35</sup> Moreover, to the best of our knowledge, a multifunctional hybrid POM exhibiting photochromism and self-separating catalysis is quite unprecedented. In this regard, we were interested in exploring octamolybdate  $([Mo_8O_{26}]^{4-})$  cluster-based systems, as octamolybdate belongs to an important class of isopolyoxometalates and can exist in a variety of isomeric forms.<sup>36'</sup> Over the last few decades, octamolybdate hybrids have been successfully employed for a variety of applications including photochromism and catalysis.

Herein, we have designed and developed a series of electronically and structurally tunable aromatic sulfonium counterions (a-f) based on a fundamental counterion motif A as shown in Chart 1. We imagined that the introduction of an

Chart 1. Synthesis of Aromatic Sulfonium Counterions



aromatic ring in the counterion motif will provide flexibility to introduce substituents. In these counterions, we have attempted to fine-tune the electron availability on the sulfonium S atom by introducing substituents at two different locations, viz., phenolic oxygen  $(R_1)$  and aromatic ring  $(R_2)$  of the counterion motif A. We have also attempted structural fine-tuning by introducing allyl or methacryl groups in three counterions (d-f) for modulating the solubility, lipophilicity and thereby the catalytic properties of their hybrids. Interestingly, the triflate salts of the counterions a-f were found to act as ionic liquids.<sup>37</sup> The various counterions used in this study are labeled as (a) HPDS, (b) HMPDS, (c) MPDS, (d) APDS, (e) AMPDS, and (f) MAPDS, which, as mentioned earlier, are the cationic units of the respective aromatic sulfonium ionic liquids (ASILs) (i) (4hydroxyphenyl)dimethylsulfoniumtriflate (HPDST), (ii) (4hydroxy-2-methylphenyl)dimethylsulfoniumtriflate (HMPDST), (iii) (4-methoxyphenyl)dimethylsulfoniumtriflate

(MPDST), (iv) (4-(allyloxy)phenyl)dimethylsulfoniumtriflate (APDST), (v) (4-(allyloxy)-2-methylphenyl)dimethylsulfoniumtriflate (AMPDST), and (vi) (4(methacryloyloxy)phenyl)dimethylsulfoniumtriflate (MAPDST), respectively, see Chart 1. The reaction of these counterions (a–f) with the commercially available sodium molybdate in deionized water at pH 4.0 resulted in a series of hybrid POMs, and using these hybrids, we show here that the photochromic and catalytic properties of a hybrid POM can be modulated by tuning the counterion motif.

#### RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization. The ASILs HPDST, APDST, and MAPDST were synthesized and characterized following reported procedures.<sup>30,38</sup> The new ASILs HMPDST, MPDST, and AMPDST were also synthesized following similar synthetic procedures. The <sup>1</sup>H NMR spectrum of AMPDST exhibited a multiplet at  $\delta = 6.12$ – 6.07 ppm due to the allyl \*CH=CH<sub>2</sub> proton. The <sup>1</sup>H NMR spectra of HMPDST, MPDST, and AMPDST exhibited singlet peaks at 3.03, 3.07, and 3.13 ppm, respectively, due to the six methyl protons of the sulfonium moiety. The <sup>19</sup>F NMR spectra of HMPDST, MPDST, and AMPDST showed peaks at  $\delta$  = -79.26, -77.66, and -78.81 ppm, respectively, due to the triflate counterion. ESI-MS spectra of HMPDST, MPDST, and AMPDST exhibited peaks at m/z 169.060, 169.070, and 209.096, respectively, confirming their formation (Figures S1-S8, Supporting Information). The FT-IR spectrum of HMPDST showed a peak at 3255 cm<sup>-1</sup> due to the phenolic -OH group and a few peaks in the range 3110-2900 cm<sup>-1</sup> corresponding to the aromatic C-H vibrations. The IR peaks exhibited by HMPDST, MPDST, and AMPDST at 1221, 1238, and 1240 cm<sup>-1</sup> respectively are assigned to the CF<sub>3</sub> group of the triflate counterion moiety<sup>38</sup> (Figure S9, Supporting Information). The phase transition behaviors of HMPDST, MPDST, AMPDST and MAPDST were analyzed by differential scanning calorimetry (DSC) and polarized optical microscopy techniques; see Figures S10-S11, Supporting Information. The DSC analyses showed melting points of 89, 48, 59, and 97 °C for HMPDST, MPDST, AMPDST, and MAPDST, respectively. Polarized optical microscopy images of HMPDST, MPDST, AMPDST, and MAPDST exhibited ionic liquid textures under a crossed polarizer after 24 h at room temperature. DSC and polarized optical microscopy studies therefore show that the behaviors of the ASILs HMPDST, MPDST, AMPDST, and MAPDST are quite similar to those of the previously reported ASILs HPDST and APDST.<sup>30</sup>

Treatment of the ASILs HPDST, HMPDST, MPDST, APDST, AMPDST, and MAPDST (1.5 equiv) with sodium molybdate (1 equiv) in deionized water at pH 4.0 led to the formation of a new series of aromatic sulfonium octamolybdates (HPDS)<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>] (1), (HMPDS)<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>] (2), (MPDS)<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>] (3), (APDS)<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>] (4), (AMPDS)<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>] (5), and (MAPDS)<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>] (6), respectively. The hybrids 1–6 were characterized by IR, NMR, ESI-MS, and single-crystal X-ray diffraction analyses. The IR spectra of hybrids 1–6 showed bands at 3100–2900 cm<sup>-1</sup> due to C–H stretching vibrations and bands at 1590, 1497, and 1420 cm<sup>-1</sup> due to the aromatic rings of the counterions. Hybrids 1 and 2 showed IR bands at 3510 and 3503 cm<sup>-1</sup> respectively due to the phenolic –OH group. Hybrid 6 exhibited an IR band at 1744 cm<sup>-1</sup> due to the C==O group of the MAPDS counterion. The IR bands observed at

938, 902, 835, 718, 662, 556, 520, and 443 cm<sup>-1</sup> for hybrids 1– 6 are assigned to the Mo–O–Mo and Mo=O vibrations of the cluster<sup>27</sup> (Figure S12, Supporting Information). Hybrids 1–6 exhibited <sup>1</sup>H NMR peaks at 3.19, 3.17, 3.22, 3.22, 3.21, and 3.28 ppm, respectively, due to the methyl protons of the sulfonium moieties. Hybrids 1 and 2 exhibited <sup>1</sup>H NMR peaks at 10.73 and 10.67 ppm, respectively, due to the phenolic –OH group of the counterions. Hybrid 3 exhibited a singlet at 3.86 ppm due to the –OCH<sub>3</sub> protons. The allylic protons of the hybrids 4 and 5 appeared in the range of 6.06–6.00 ppm, see Figures S13–S18, Supporting Information.

**ESI-MS Analyses.** For ESI-MS analyses, samples were prepared by dissolving small quantities of the hybrids **1**–**6** in minimum amounts of dimethylformamide followed by dilution with acetonitrile (MeCN). The spectra were recorded in negative-ion mode. The most important peak envelope observed for hybrids **1**–**6** correspond to the "half cluster" moiety, { $Mo_4O_{13}$ }.<sup>39</sup> For example, the mass peaks observed for hybrids **1**–**6** at m/z values 746.6167, 761.6451, 761.4343, 786.6593, 801.4933, and 815.4375 can be assigned to the corresponding "half-cluster" moieties [ $Mo_4O_{13}(HPDS)$ ]<sup>1–</sup>, [ $Mo_4O_{13}(HPDS)$ ]<sup>1–</sup>, [ $Mo_4O_{13}(MPDS)$ ]<sup>1–</sup>, [ $Mo_4O_{13}(MPDS)$ ]<sup>1–</sup>, and [ $Mo_4O_{13}(MAPDS)$ ]<sup>1–</sup>, respectively. In addition, all the major peaks observed in the mass spectra of hybrids **1**–**6** could be satisfactorily assigned to the corresponding molecular formulas with varying combinations of counterions. The negative-ion mode ESI-MS spectrum of a representative hybrid, hybrid **2**, is given in Figure 1. Here, the major peaks observed at m/z values



**Figure 1.** Negative-ion mode ESI-mass spectrum of hybrid **2**. The spectrum was recorded in MeCN at a concentration  $\sim 10^{-6}$  M. The inset is an expansion of the peak centered at 761.6451 to show the 1<sup>-</sup> charge state.

592.5720, 614.5535, 761.6451, 929.7102, and 1400.1745 are assigned to the formulas  $[Mo_4O_{13}H]^{1-}$ ,  $[Mo_4O_{13}Na]^{1-}$ ,  $[Mo_4O_{13}(HMPDS)]^{1-}$ ,  $[Mo_4O_{13}(HMPDS)_2]^{1-}$ , and  $[Mo_8O_{26}(HMPDS)(Na)_2]^{1-}$ , respectively, see Figure 1. Mass spectral data for the remaining hybrids are presented in Figures S19–S29 and Tables S1–S6 of Supporting Information. The ESI-MS data of hybrids 1–6 show the existence of some reduced clusters as well in the samples.<sup>40,41</sup>

Single-Crystal X-ray Diffraction Analyses. The single crystals of hybrids 1–6 were grown from dimethylformamide (DMF) or DMF:dimethylsulfoxide(DMSO) (1:1, v/v) solvent mixture by slow evaporation method. The crystal and structure refinement data for the hybrids 1–6 are presented in Table S7, Supporting Information. Hybrids 1, 3 and 6 crystallized in monoclinic  $P2_1/C$  space group, while hybrids 2, 4, and 5 crystallized in triclinic *P*-1 space group. Single-crystal XRD data revealed that the hybrids 1–6 contain octamolybdate cluster

surrounded by four units of the corresponding aromatic sulfonium counterions as expected. The octamolybdate cluster exists in  $\beta$ -isomeric form<sup>42</sup> in all the hybrids 1–6, see Figure 2.



**Figure 2.** Crystal structures of the hybrids: (a) hybrid 1; (b) hybrid 2; (c) hybrid 3; (d) hybrid 4; (e) hybrid 5; (f) hybrid 6. Thermal ellipsoids are shown at 50% probability level. Solvent molecules are omitted for clarity. Color code:  $MoO_6$  – purple octahedra; S – yellow; O – red; C – gray; H – dark gray.

The asymmetric unit (ASU) of hybrid 1 consists of half of the  $[\beta$ -Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> cluster, two HPDS counterions, one DMF molecule and one water molecule. The ASU of hybrid 2 contains half of the  $[\beta$ -Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> cluster surrounded by two HMPDS counterions and one DMSO molecule. In the case of hybrid 3, the ASU consists of half of the  $[\beta$ -Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> cluster surrounded by two MPDS counterions and one water molecule. The ASU of hybrid 4 contains half of the [ $\beta$ - $Mo_8O_{26}$ ]<sup>4-</sup> cluster and two APDS counterions. In the case of hybrid 5, the ASU consists of a  $[\beta$ -Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> cluster and four AMPDS counterions. Finally, the ASU of hybrid 6 consists of half of the  $[\beta$ -Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> cluster and two MAPDS counterions. The Mo–O bond distances in hybrids **1–6** are comparable to those reported for  $[\beta$ -Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> based hybrids.<sup>41</sup> The average S-C distances and C-S-C bond angles of the sulfonium counterions of the hybrids 1-6 are in the ranges of 1.783(5)-1.793(5) Å, 103.3(3)-101.6(3)°; 1.772(5)-1.790(5) Å,  $102.4(3)-103.2(3)^{\circ}$ ;  $1.763(5)-1.786(7)^{\circ}$ Å,  $100.5(3)-104.5(3)^{\circ}$ ;  $1.778(6)-1.785(8)^{\circ}$ Å,  $102.8(4)-103.5(4)^{\circ}$ ; 1.790(1)-1.821(8) Å, 100.6(5)-103.3(5)°; and 1.764(5)-1.789(6) Å, 100.6(3)-103.5(3)°, respectively. The C-S-C bond angles in hybrids 1-6 are less than  $109^\circ$ , which reveal

that the sulfonium centers of these hybrids are in trigonal pyramidal geometry.<sup>30</sup> Thermal ellipsoidal plots and some representative crystal packing diagrams of hybrids 1-6 are given in Supporting Information, Figures S30–S31.

Solid-State Photochromism. The solid-state photochromic properties of hybrids 1-6 were evaluated under ambient conditions using diffused reflectance spectroscopy (DRS). White microcrystalline powders of hybrids 1-6 exhibited optical band gaps of 3.60, 3.58, 3.31, 3.41, 3.45, and 3.56 eV respectively in their ground state following the order 1 > 2 > 6> 5 > 4 > 3, see Figure S32, Supporting Information. Under UV excitation at 350 nm, the hybrids 1-6 exhibited color change from white to purple accompanied by the growth of two broad absorption bands at around  $\lambda_{\rm max}$  values 560 and 472 nm. Hybrids 2-5 exhibited faster photoresponse showing a visual color change within 10 s of UV irradiation, while the hybrid 1 took comparatively longer time,  $\sim 30$  s, to display a visual color change. At the same time, a visual color change occurred in hybrid 6 only after 8 min of UV irradiation. The absorption band of a representative hybrid, hybrid 3, is shown in Figure 3a



**Figure 3.** (a) K-M-transformed reflectivity of hybrid 3 after irradiation with 350 nm UV lamp at various time intervals. Inset: the color of the hybrid corresponding to the time shown in minutes; (b)  $1/R(t) - R(\infty)$  vs time plots for hybrids 1–6.

and similar spectra for other hybrids are presented in Figure S33, Supporting Information. The absorption spectra of the photoirradiated samples of hybrids 1-6 matched very well with those of the similar compounds reported earlier.<sup>27,31</sup> In the case of hybrids 1-5, the absorbance saturation were attained within

 ${\sim}100$  min of irradiation while hybrid 6 took  ${\sim}160$  min to attain the absorbance saturation.

**EPR Analysis.** The color changes observed in hybrids 1-6 upon UV irradiation are assumed to be due to the photoreduction of the Mo<sup>6+</sup> (d<sup>0</sup>) sites of the octamolybdate cluster to Mo<sup>5+</sup> (d<sup>1</sup>).<sup>28</sup> The photoreduction of Mo<sup>6+</sup> sites in hybrids 1-6 is evidenced by EPR spectroscopy. The EPR spectra of the UV-irradiated samples of hybrids 1-6 exhibited characteristic EPR spectra of Mo<sup>5+</sup> (4d<sup>1</sup>) with *g* values 1.925, 1.908, 1.920, 1.912, 1.922, and 1.919, respectively, see Figure 4. The EPR results observed for hybrids 1-6 are in good agreement with the literature reports on similar systems.<sup>30,31</sup>



**Figure 4.** Powder X-band EPR spectra (recorded at 150 K) of (a) hybrid **1**, (b) hybrid **2**, (c) hybrid **3**, (d) hybrid **4**, (e) hybrid **5**, and (f) hybrid **6** after irradiation with 350 nm UV lamp at 9.199, 9.196, 9.195 9.179, 9.180, and 9.178 GHz spectrometer frequencies, respectively.

**Kinetics of Coloration.** The photocoloration kinetics of hybrids 1–6 were calculated by analyzing their reflectance vs irradiation time (R(t) vs t) plots. Kinetics studies showed that in all the cases, the reflectance value decreases sharply at the beginning and eventually gets flattened out. This behavior is expected based on the depletion of the Mo<sup>6+</sup> sites in the reaction medium with time, following a pseudo second order kinetics law,  $R(t) = (a/bt + 1) + R(\infty)$ .<sup>31</sup> The R(t) vs time plots of hybrids 1–6 are given in Figure S34 and the parameters related to the coloration kinetics are listed in Table S8, Supporting Information. The coloration kinetics half-life ( $t_{1/2}$ ) values calculated for hybrids 1–6 were 1.48, 0.83, 0.33, 0.64, 0.69, and 15.26 min, respectively, which show that the speed of the photoinduced color change in these hybrids follow the order 3 > 4 > 5 > 2 > 1 > 6.

It is well-known that for two hybrid POMs, i and j, having the same type of POM cluster and same photogenerated absorption bands, the ratio of their photocoloration rate constants,  $k_i/k_i$  can be calculated from the ratio of the slopes  $(B_i/B_i)$  of their respective  $1/[R(t) - R(\infty)]$  vs time plots (Figure 3b) in order to compare their photocoloration speeds.<sup>28</sup> The photocoloration rate constant ratios of hybrids 1–5 calculated against that of hybrid 6 were 4.79 for  $k_1/k_{61}$  5.86 for  $k_2/k_6$ , 18.71 for  $k_3/k_6$ , 9.62 for  $k_4/k_6$ , and 8.63 for  $k_5/k_6$  (see Table S8, Supporting Information). These values clearly show the faster rate of photocoloration in hybrids having MPDS, APDS, AMPDS, HMPDS, and HPDS counterions compared to hybrid 6 having MAPDS counterions. Hybrid 3 with MPDS counterion exhibited fastest photocoloration compared to other hybrids and its photocoloration speed was 18.71 times higher than that of hybrid 6. Similarly, hybrid 4 with APDS counterion exhibited a photocoloration speed 9.62 times higher than that of hybrid 6. The ratio of the photocoloration rate constants of hybrid 3 and 4  $(k_3/k_4)$  is 1.94, suggesting that the photocoloration of hybrid 3 is  $\sim$ 2 times faster than that of hybrid 4. A number of factors such as the type of the POM unit, properties of the organic moiety, nature of the interaction between the POM and the organic units, experimental conditions etc. may affect the rate of the photocoloration exhibited by a hybrid POM. As all the hybrids 1-6 contain the same cluster,  $[\beta - Mo_8O_{26}]^{4-}$ , the type of the POM cluster is not a variable in the present case. Similarly, all the hybrids contain the same number of counterions per cluster and the nature of the interaction between the cluster and the counterions are also same in hybrids 1-6. The analyses of the crystal packing diagrams of the hybrids 1-6 show that in all these hybrids, the sulfur atoms of the sulfonium counterions are oriented toward the cluster and the positioning of the sulfur atoms with respect to the cluster are comparable in the series. The sulfonium sulfur to the cluster oxygen distances (S…O distances) in hybrids 1-6 vary in the range 2.841-3.252 Å, which are shorter than or close to the sum of the van der Waals radii of O and S atoms (3.32 Å).<sup>43</sup> Considering all these, we believe that the electronic properties of the counterions a-f, which in turn affect the electron availability to the cluster on photoexcitation, is a dominant factor in determining the photochromic behaviors of the hybrids 1-6.

Role of Counter lons in Photochromism. Dessapt et al. have reported the mechanism of the photochromism exhibited by sulfonium-POM hybrids.<sup>31</sup> According to that mechanism, the UV irradiation causes excitation of an electron from the oxo ligand to the Mo<sup>6+</sup> site of the octamolybdate cluster in hybrids 1-6. Concurrently, a lone-pair electron on the sulfonium S atom gets strongly polarized toward the POM cluster to stabilize the electron deficient oxo ligand. Thus, the photogenerated hole on the POM cluster partially moves onto the sulfonium S atom of the counterion, while the POM cluster exhibits color due to the photoreduced Mo sites. The hybrid maintains the color even after switching-off the UV source due to charge segregation. Therefore, the electron availability on the sulfonium S atom to stabilize the photoexcited POM cluster is very crucial in determining the photochromic behavior of a sulfonium-POM hybrid (see Figure S36, Supporting Information for a suggested mechanism for the observed photochromism).

The observed order (3 > 4 > 5 > 2 > 1 > 6) of the photoinduced color change exhibited by hybrids 1-6 may be explained based on the substituent effect of their counterions. Hybrid 3 with MPDS counterion exhibited the lowest  $t_{1/2}$  value in the series. In this case, a  $-CH_3$  substitution on the phenolic oxygen (as  $R_1$  substituent on the counterion motif A, see Chart

1) is expected to increase the electron availability on the sulfonium S atom, enhancing the photochromic behavior of the hybrid. Hybrid 6 exhibited the highest  $t_{1/2}$  value in the series probably due to the presence of an ester group at the para position of the sulfonium center, which has poor electron donating ability compared to -OH or -OR functional groups. The  $t_{1/2}$  values exhibited by hybrids 2 and 3 (0.83 and 0.33) respectively) reveal that a  $-CH_3$  substituent on the phenolic oxygen of the counterion motif A (as  $R_1$  substituent) is more effective than a  $-CH_3$  substituent at the ortho position of the aromatic ring (as R<sub>2</sub> substituent), see the structure of HMPDS and MPDS in Chart 1. The  $t_{1/2}$  values of hybrids 4 and 5 were somewhat similar, 0.64 and 0.69 min, respectively, which show that the presence of an additional  $-CH_3$  group as  $R_2$ substituent in AMPDS (see Chart 1) plays only a marginal role in the photochromic behavior of the hybrid. However, in the case of hybrids 1 and 2 with HPDS and HMPDS counterions respectively, an additional -CH<sub>3</sub> substituent at R<sub>2</sub> position of the counterion (Chart 1) leads to a considerable improvement in the photocoloration speeds (1.48 and 0.83 min, respectively). The  $t_{1/2}$  values exhibited by hybrids 1 and 4 were 1.48 and 0.64 min, respectively, which suggest that an alkyl substituent at  $R_1$  position of the counterion motif A (-OR group) is more effective than a -H substituent at the same position (-OH group). Based on the  $t_{1/2}$  values exhibited by hybrids 1, 2, 4, and 5, we can assume that  $-CH_3$  group as  $R_1$ substituent has a dominant role compared to the same group as R<sub>2</sub> substituent in controlling the photochromic behaviors of a hybrid. However, in the absence of  $R_1$  substituent, the effect of R<sub>2</sub> substituent dominates.

A comparison of the best  $t_{1/2}$  values reported so far for various hybrid POMs are given in Table S9, Supporting Information. According to this table, the best  $t_{1/2}$  values reported for organoammonium-{Mo<sub>12</sub>} cluster hybrids<sup>27</sup> are in the range 51.81-5.44 min; while that for organoammonium- $\{Mo_8O_{27}\}^{28}$  hybrids are in the range 37.0–0.8 min. Using aliphatic sulfonium counterions,  $t_{1/2}$  values of 4.84 and 30 min have been achieved for clusters  $\{MO_3O_8\}$  and  $\{MO_8O_{26}\}$ respectively.<sup>31</sup> The lowest  $t_{1/2}$  value reported so far for an aromatic sulfonium-POM hybrid is 1.01 min, reported for (APDS)<sub>4</sub>[SiMo<sub>12</sub>O<sub>40</sub>].<sup>30</sup> However, using the same APDS counterion, a better  $t_{1/2}$  value of 0.64 min is achieved in the present study for  $(APDS)_4[Mo_8O_{26}]$  (hybrid 4). This reveals that the choice of the POM cluster is very crucial in deciding the photochromic properties of a hybrid POM. To the best of our knowledge, the best  $t_{1/2}$  value achieved so far for a POMhybrid is 0.37 min, reported for an organoammonium-{Mo<sub>6</sub>} hybrid.<sup>29</sup> In the present study, we could achieve a  $t_{1/2}$  value of 0.33 min for an aromatic sulfonium octamolybdate, which reveals the potential of the counterion motif A (Chart 1) in controlling the photochromic behavior of a hybrid POM. The power of the UV source used in our experiments was 8 W, which is lower than those used (12 W) in some of the examples cited above. The photochromic behavior exhibited by hybrids 1-6 are reversible in nature, however, the observed color fading over time is relatively slow. The observed color fading can be correlated with the reoxidation of the Mo<sup>5+</sup> centers by atmospheric oxygen. It has been reported earlier that in sulfonium-based POM hybrids, the electron-pair donation from sulfonium S to the photoexcited cluster is stabilized even under dark conditions and because of this reason, the lone pair of electrons are not able to come back to their original position, hence slowing down the bleaching processes.<sup>31</sup> We expect the

same reason behind the sluggish reoxidation behavior exhibited by photoreduced hybrids 1-6 as well.

**Catalytic Epoxidation.** Some of the hybrid POMs are known to act as oxidation catalysts.<sup>44,45</sup> Therefore, we decided to test the catalytic properties of hybrids **1–6** using the epoxidation of olefin as a model reaction. Epoxides are important precursors for a variety of industrially relevant materials including glycols, glycol ethers, alkanol-amines, and polymers.<sup>46</sup> Although various POM-hybrids are reported to act as epoxidation catalysts, reports on octamolybdates as epoxidation catalysts are rare in the literature.<sup>35,47</sup>

The epoxidation reactions were carried out in MeCN at 60 °C using 30%  $H_2O_2$  as the oxidant and cyclooctene as the substrate, see Scheme 1. Powdered samples of catalysts 1–6

# Scheme 1. cis-Cyclooctene Epoxidation with $H_2O_2$ Catalyzed by Hybrids 1-6



were insoluble in the reaction medium initially; however, on addition of 1.5 mmol of  $H_2O_2$  reagent to the reaction mixture, the catalysts changed color from white to yellow and became soluble yielding a homogeneous yellow solution, see Figure 5.



**Figure 5.** (a) *cis*-Cyclooctene in MeCN; (b) white powder of hybrid **6** added to the reaction mixture; (c) reaction mixture after addition of  $H_2O_2$  (homogeneous mixture); (d) beginning of the self-precipitation of hybrid **6** from the reaction medium; (e) self-separated hybrid **6** after completion of the reaction.

The dissolution of the catalyst and the formation of a yellow clear solution indicate the formation of some reactive intermediates, which could be the real catalytic species of the reaction.<sup>35</sup>

The progress of the catalytic reactions were monitored by gas chromatography (GC) at various time intervals, and the results are summarized in Figure 6. The reaction having hybrid 6 as the catalyst yielded 69% epoxide product within 5 min and >99% yield within 90 min. Similarly, catalysts 1-5 also yielded epoxide product, and the results are summarized in Figure 6 and Table 1. Interestingly, it was observed that the catalysts start to precipitate out of the reaction mixture within 15 min of the start of the reaction and the precipitation gets completed by  $\sim$ 1.5 h in all the cases. IR analyses showed that the white powders thus obtained are indeed of the respective catalysts used. Therefore, the hybrids 1-6 undergo solid-liquid-solid phase transfer during the catalysis reaction and hence act as self-separating catalysts. The catalytic reaction gets completed by  $\sim 1.5$  h, and at the end of the reaction, the self-separated catalysts 1-6 can be separated by simple filtration. The selfseparated catalysts 1-6 could be reused at least 5 times without any significant loss in activity, see Figure S44, Supporting



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Figure 6. Time-dependent yields of cyclooctene oxide catalyzed by hybrids 1-6 at 60 °C with 1.5 mol % of  $H_2O_2$ .

Table 1.	Epoxidation	of	cis-Cyclooctene	Catalyzed	by
Hybrids	1-6				

entry <sup>a</sup>	catalyst <sup>b</sup>	yield <sup>c</sup> (%)
1	hybrid-1	87
2	hybrid-2	73
3	hybrid-3	82
4	hybrid-4	93
5	hybrid-5	97
6	hybrid-6	99

<sup>*a*</sup>Reaction conditions: *cis*-cyclooctene (0.3 mmol); MeCN (3 mL);  $n(H_2O_2):n(cyclooctene) = 1.5$ ; Time = 1.5 h at 60 °C; <sup>*b*</sup>Catalyst (0.003 mmol); <sup>o</sup>Yields (%) were calculated from GC.

Information. Therefore, the current catalytic system possesses the advantages of both homogeneous and heterogeneous catalysis. We believe that the aromatic sulfonium counterions play a crucial role in regenerating the catalysts after the consumption of the oxidant  $H_2O_2$  and also in protecting the catalytic system from oxidative damages.<sup>48</sup>

Our studies showed that the hybrids 1-6 exhibit excellent selectivity in catalysis as they did not yield any diol products along with the epoxide product, as revealed by GC and NMR analyses. Hybrids 4-6 in general gave higher yields (>90%) compared to hybrids 1-3. Hybrid 6 exhibited the best catalytic activity among all the hybrids tested, as it yielded >99% conversion within 1.5 h with excellent selectivity. A control experiment conducted in the absence of the catalyst did not yield considerable amount of the product. Similarly, control experiments performed using commercially available (NH)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O as the catalyst yielded only 10% epoxide product even after 6 h. These control experiments therefore highlight the importance of the aromatic sulfonium-POM hybrids 1-6 in the observed catalysis.

We were interested in analyzing the reaction products of hybrids 1-6 with  $H_2O_2$  in MeCN using ESI-MS analysis for identifying the catalytic intermediates. The results of these analyses are discussed in detail for hybrid 6 here, which exhibited the best catalytic performance among all the hybrids tested. The negative-ion mode ESI-MS spectrum of the clear yellow solution obtained on addition of 30%  $H_2O_2$  to a suspension of hybrid 6 in MeCN at 60 °C is shown in Figure 7. The spectrum shows the species  $[Mo(O)(O_2)_2]$  at m/z = 176.8612 that has already been identified in similar catalytic reactions.<sup>35</sup> Interestingly, in addition to this known species, we



Figure 7. Negative-ion mode ESI-MS of the yellow solution obtained by reacting hybrid 6 with 30% H<sub>2</sub>O<sub>2</sub> in MeCN.

could observe peaks at m/z = 1438.5207, 1729.5622, and 1837.4060, that could be satisfactorily assigned to the formulas  $[Mo_8O_{22}(O_2)_4(C_8H_{14})Na_2H]^{1-}$ ,  $[Mo_8O_{22}(O_2)_4(H_2O)_2(C_8H_{14})-(MAPDS)_2H]^{1-}$ , and  $[Mo_8O_{22}(O_2)_4(H_2O)_2(C_8H_{14})-(MAPDS)_2H]^{1-}$ , respectively. Observation of these peaks indicate the formation of tetraperoxo-octamolybdate intermediates in the reaction medium from octamolybdate catalyst and  $H_2O_2$  reagent. To the best of our knowledge, identification of such tetraperoxo-octamolybdate intermediates in octamolybdate based catalysis is unprecedented. Interestingly, two out of the three tetraperoxo-octamolybdate intermediates identified in this study have cyclooctene unit  $(C_8H_{14})$  in their formulas, resembling the intermediates proposed by Sharpless et al.<sup>49</sup> in the case of oxo-diperoxo Mo(VI) catalysts, see Figure S38, Supporting Information.

There have only been a couple of attempts earlier to identify the active intermediates of the epoxidation reaction using octamolybdate catalysts. An intermediate tetraperoxo-octamolybdate with the formula  $(Hdmpz)_4[Mo_8O_{22}(O_2)_4(dmpz)_2]$ . 2H<sub>2</sub>O had been reported during the preparation of the oxodiperoxo species  $[MoO(O_2)_2(dmpz)_2]$ , where dmpz = 3,5-dimethylpyrazol.<sup>50</sup> Another reported peroxo-octamolybdate is  $[NH_4]_4[Mo_8O_{24}(O_2)_2(H_2O)_2] \cdot 4H_2O \cdot 5^1$  Recently, Zhou et al. had identified oxo-diperoxomolybdenum,  $[MoO(O_2)_2]$ , as the possible active itermediate in the epoxidation reaction using ESI-MS analyses. However, they did not observe any peroxooctamolybdates in their ESI-MS studies.<sup>35</sup> In the present study, for the first time, we were able to identify the species tetraperoxo-octamolybdate in a catalytic epoxidation reaction formed by the reaction between octamolybdate catalyst and H2O2 reagent. We believe that, in addition to the oxodiperoxomolybdenum species  $[MoO(O_2)_2]$ , the newly identified tetraperoxo-octamolybdate could also be playing significant roles in the catalysis exhibited by the octamolybdates in the presence of  $H_2O_2$ . The reaction products of hybrids 1-5 with H<sub>2</sub>O<sub>2</sub> in MeCN also exhibited similar ESI-MS spectra; the details are given in Figures S39-S43 and Tables S10-S14, Supporting Information. The tetraperoxo-octamolybdate intermediates were also detected in these cases.

We have also recorded the FT-IR spectrum of the yellow reaction product of hybrid **6** and  $H_2O_2$  in MeCN and compared it with the spectra of hybrid **6** before and after catalysis, see Figure 8. Hybrid **6** exhibited Mo=O and Mo-O-Mo vibrations at 940 and 652–903 cm<sup>-1</sup> respectively, see Figure 8a. However, after reaction with  $H_2O_2$ , the intensity of the Mo-O-Mo peak at 903 cm<sup>-1</sup> was reduced, and a new



Figure 8. (a) FT-IR spectra of pure hybrid 6; (b) hybrid 6 after reaction with  $H_2O_2$  (active species); (c) recycled hybrid 6.

band appeared at 582 cm<sup>-1</sup> corresonding to the Mo(O<sub>2</sub>)<sub>2</sub> species, <sup>52</sup> see Figure 8b.

These results suggest the disintegration of some of the clusters upon reaction with  $H_2O_2$ . The reaction mixture also showed a new band at 860 cm<sup>-1</sup> corresponding to (O–O) vibrations<sup>33</sup> and another band at 626 cm<sup>-1</sup>, probably due to the tetraperoxo-octamolybdate<sup>50</sup> intermediates. The FT-IR results therefore corroborate very well with the ESI-MS results and confirm the formation of intermediates such as  $MoO(O_2)_2$  and peroxo-octamolybdates in the catalytic reaction medium. The recycled hybrid exhibited spectral features similar to that of the original hybrid, see Figure 8c, confirming the regeneration of the octamolybdate hybrid in the reaction medium after the complete comsumption of the reagent  $H_2O_2$ .

Furthermore, control experiments were performed to check if the  $H_2O_2$  reagent has any effect on the alkenyl group and/or on the sulfonium sulfur of the counterions during catalysis. The mass and <sup>1</sup>H NMR spectra of the recovered hybrid 6 catalyst showed no change compared to those of the original hybrid 6, confirming that the oxidant H<sub>2</sub>O<sub>2</sub> has no effect on the sulfonium counterions, see Figures S45-S48 and Table S16, Supporting Information. The differences in the catalytic activities exhibited by hybrids 1-6 may be explained on the basis of the differences in their counterions.<sup>34,48</sup> Hybrids 4-6exhibited better catalytic performances compared to hybrids 1-3, probably because of the presence of relatively long allyl/ methacryl groups as R<sub>1</sub> substituents, that are more lipophilic compared to -H and -CH<sub>3</sub> groups. These long carbon chain groups may also help in solubilizing the active species in MeCN at a faster rate compared to the hybrids 1-3.

Inorder to check if the photochromic and catalytic properties can coexist in hybrids 1-6, the recoverd catalysts were subjected to photochromic studies again. A similar color change from white to purple on UV exposure was observed in all the cases. Similarly, the photoreduced purple hybrids were tested again as catalysts. The purple hybrids become white under experimental conditions and behave quite similar to the original hybrids.<sup>53</sup> These studies confirm that the catalysis and photochromism can coexist in these hybrids, see Figure S49, Supporting Information for a model DRS spectrum of the recovered catalyst.

Epoxidation of Bioderived Olefins. We were interested in checking the applicability of hybrids 1-6 as self-separating catalysts for the epoxidation of bioderived olefins<sup>54,55</sup> as well. This is because, the fatty acid alkyl esters (FAAE) have a wide range of industrial applications as plasticizers/stabilizers in the production of polyvinyl chlorides (PVC) and have relevance as intermediates in the production of biodegradable lubricants.<sup>56,57</sup> The industrially used process (Prileshajev reaction) for the epoxidation of unsaturated plant oils is known to have certain drawbacks such as the formation of byproducts, corrosion of the equipment and the necessity of a neutralization processes downstream.<sup>57</sup> The use of high-valent transitionmetal-ion-based catalysts is perceived as a solution to prevent such drawbacks.<sup>54</sup> We tested hybrid 6 as a model catalyst for the epoxidation of bioderived olefins using methyl oleate (MO) or ethyl oleate (EO) as the substrates; see Scheme 2.

Scheme 2. Epoxidation of Bioderived Olefins ( $R = CH_3$  and  $C_2H_5$ ) Catalyzed by Hybrid 6

$$\overset{O}{\operatorname{RO}^{(CH_2)_7}} \overset{CH_3}{\longrightarrow} \overset{Hybrid 6}{\operatorname{MeOH}, H_2O_2, 60 \ ^\circ C} \overset{O}{\operatorname{RO}^{(CH_2)_7}} \overset{O}{\longleftarrow} \overset{O}{\operatorname{(CH_2)_7}} \overset{O}{\longleftarrow} \overset{O}{\operatorname{(CH_2)_7}} \overset{O}{\longrightarrow} \overset{O}{\longrightarrow}$$

The reaction was monitored by TLC analyses, which revealed complete consumption of the starting materials within 6 h of the reaction. The catalyst was precipitated out of the reaction mixture during this time, which was separated out and the products thus obtained were subjected to <sup>1</sup>H NMR and ESI-MS analyses. The <sup>1</sup>H NMR spectra of MO and its epoxidation product are given in Figure 9a,b, respectively.



Figure 9. <sup>1</sup>H NMR spectra: (a) methyl oleate (MO); (b) MO after epoxidation; (c) ethyl oleate (EO); (d) EO after epoxidation.

Comparison of these spectra reveals that the peak observed at 5.33 ppm for MO due to the -HC=CH- protons is shifted to 3.36-3.39 ppm in the product. Similarly, the peak due to the  $-CH_2$  protons adjacent to the alkene group of MO was shifted from 1.99 to 1.43 ppm in the product. The <sup>13</sup>C NMR spectral analyses showed that the alkene carbon peak of MO at 129 ppm is shifted to 58 ppm in the product, confirming the formation of the epoxide, see Figure S50 of the Supporting Information. ESI-MS analyses of the reaction products

confirmed the formation of the epoxide product of MO, see Figure S51, Supporting Information. NMR analyses did not show the formation of any side products in this reaction. Similarly, the <sup>1</sup>H NMR, <sup>13</sup>C NMR, and ESI-MS analyses of EO and its epoxidation products also revealed the selective formation of the expected epoxide product, see Figure 9c,d and Figures S52–S53, Supporting Information. These studies therefore show the potential of hybrids 1–6 to act as self-separating catalysts for the epoxidation of bioderived olefins.

# CONCLUSIONS

In this study, electronically and structurally tunable aromatic sulfonium counterions have been used to engineer multifunctionality in hybrid POMs. Electronic and structural properties of a series of aromatic sulfonium octamolybdates have been systematically fine-tuned by introducing appropriate substitutions on the counterion motif, which in turn helped to control the overall photochromic and catalytic properties of the hybrids. In this way, we could achieve a  $t_{1/2}$  value of 0.33 min for one of the aromatic sulfonium-octamolybdate, which is among the best  $t_{1/2}$  values reported so far for any POM based photochromic material. The aromatic sulfonium octamolybdates reported here combine the properties of homogeneous and heterogeneous catalysts in a single entity and act as good self-separating catalysts for the epoxidation of olefins. The catalytic properties of these hybrids could be fine-tuned by introducing lipophilic substituents on the counterion motif, and the catalysts could be reused for at least 5 times without any significant loss of activity. Moreover, the photochromic and catalytic properties are shown to coexist in these hybrids. ESI-MS analyses performed on the reaction mixture of aromatic sulfonium octamolybdates and  $H_2O_2$  revealed a hitherto undetected intermediate, tetraperoxo-octamolybdate, shedding more lights on the epoxidation mechanism of octamolybdates. Aromatic sulfonium counterions play significant roles in protecting the catalytic species from oxidative damages during the epoxidation reaction and also in the regeneration of the catalyst after the reaction. In short, a new approach to develop multifunctional POM-organic hybrids using tunable counterions has been successfully explored in this study. Currently, we are in the process of developing new multifunctional POM materials using the concepts delineated in this study.

## EXPERIMENTAL SECTION

Materials and Methods. 4-methylmercaptophenol and 3-methyl-4-(methylthio)phenol were purchased from Alfa Aesar. 4-Methoxyphenyl(methyl)sulfane, silver trifluoromethanesulfonate, allyl bromide, *cis*-cyclooctene, and cyclooctene oxide were purchased from Sigma-Aldrich. Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O was purchased from Merck. Methyl oleate and ethyl oleate were purchased from TCI India. All the solvents used were of spectroscopic grade. Acetonitrile was distilled over CaH<sub>2</sub> and stored over 4 Å molecular sieves prior to the use.

**Physical Measurements.** FT-IR spectra were recorded on Agilent Technologies Cary 600 Series instrument. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were recorded on Jeol-JNM 500 MHz NMR spectrometer using  $CDCl_3/D_2O/CD_3CN/DMSO-d_6$  solvents and TMS as internal standard. ESI-MS spectra were recorded on Bruker HD compact instrument. DRS spectra were recorded on PerkinElmer UV/vis/NIR Lambda 750 spectrophotometer. Differential scanning calorimetry (DSC) experiments were performed on a Netzsch (Model STA 449 F1 JUPITER) instrument at a heating rate of 5 °C/min under N<sub>2</sub> atmosphere. Polarized optical microscopy images of the ASILs were recorded on Nikon ECLIPSE LV 100 POL microscope. Luzchem photoreactor model LZC-4 V with lamp LZC-UVA ( $\lambda_{exc} = 350$  nm, P = 8 W) was used for the photoirradiation of POM hybrids. The X-

band electron paramagnetic resonance (EPR) spectra were recorded at 150 K on JEOL Model JES FA200 instrument.

**X-ray Crystallography.** Single crystal X-ray diffraction data of hybrids **1–6** were collected on an Agilent Super Nova diffractometer, equipped with multilayer optics, monochromatic dual source (Cu and Mo) and Eos CCD detector, using Mo K $\alpha$  (0.71073 Å) radiation at 293 K (for hybrid 1) and at 150 K (for hybrids **2–6**). Data acquisition, reduction and analytical face-index based absorption correction were performed by using CrysAlisPRO program.<sup>58</sup> The structure was solved with ShelXS and refined on  $F^2$  by full matrix least-squares techniques using ShelXL program provided in Olex<sup>2</sup> (v.1.2) program package.<sup>59,60</sup> Anisotropic displacement parameters were applied for all the atoms, except hydrogen atoms and some less intensely scattered carbon atoms. Data CCDC: **1536033–1536038** contain the supplementary crystallographic data of hybrids **1–6** respectively.

In general, hybrids 1-6 are crystalline in nature; however, due to their weakly diffracting nature, the quality of data were poor in some cases. As a result of this, the probabilities of finding less intensely scattered atoms, especially those from the solvent or counterion moieties, were less and such atoms had to be refined isotropically. Because of this, Checkcif alerts of "isotropic non-H atoms in main residue(s)" were generated in some cases. Other Checkcif alerts like "short interaction D...A contacts", "Large Hirshfeld Difference", "Solvent Accessible Void" etc. might have arisen due to disorders in the structure. "Short contacts" between disordered fragments are to be expected. Due to the poor quality of diffraction data and small unresolved disorders, alerts like "high "MainMol" Ueq as compared to neighbors", and high "ADP max/min Ratio", were generated in hybrid 6. In addition, "ADDSYM" suggested possible pseudo/new space group for hybrid 5, but our attempts to refine and solve the structure in the suggested space group were unsuccessful.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/ cifdata.

**Gas Choromatography (GC) Analyses.** Gas chromatograms were recorded on an Agilent 7890A series gas chromatograph system equipped with a HP-5 column. Flame ionization detector (FID) and  $N_2$  carrier gas were used for the sample analyses. Agilent open lab control panel software A.01.05 (1.3.19.115) was used to analyze the results and to operate the GC system.

Synthesis and Characterisations of Aromatic Sulfonium Ionic Liquids (ASILs). Synthesis of HMPDST. To an ice-cooled and stirred solution of 3-methyl-4-(methylthio)phenol (0.50 g, 3.24 mmol) and AgOTf (1.25 g, 4.86 mmol) in anhydrous acetonitrile was added methyl iodide (0.30 mL, 4.86 mmol) under N<sub>2</sub> atmosphere. The stirring was continued at 0 °C for 2 h. Subsequently, the stirring was stopped for 30 min to settle down the silver iodide (AgI). The AgI was filtered off and the solvent was removed under reduced pressure to afford HMPDST as a viscous solid. Yield: 0.81 g, 78%. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  ppm 8.61 (s, -OH), 7.74 (d, 1H, J = 8.95 Hz, ArH), 7.00 (dd, 1H,  $J^1 = 2.75$  and  $J^2 = 8.90$  Hz, ArH), 6.89 (d, 1H, J =2.75 Hz, ArH), 3.03 (s, 6H, -S(CH<sub>3</sub>)<sub>2</sub>), 2.49 (s, 3H, ArCH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN): δ ppm 163.01, 144.81, 131.24, 119.23, 117.40, 114.00, 29.69, 19.93. <sup>19</sup>F NMR (470 MHz, CD<sub>3</sub>CN):  $\delta$  ppm -79.26 (3F, s, -CF<sub>3</sub>). ESI-MS: calcd for C<sub>9</sub>H<sub>13</sub>OS<sup>+</sup> [M]<sup>+</sup>, 169.069; found, 169.0607. FT-IR (cm<sup>-1</sup>): 3255 (vs), 3026 (sh), 2910 (w), 1610 (w), 1513 (sh), 1488 (w), 1420 (w), 1221 (vs), 1160 (sh), 1021 (sh).

*Synthesis of MPDST*. MPDST was synthesized using a procedure similar to that used for HMPDST. Yield: 0.83 g, 80%. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN): *δ* ppm 7.84 (d, 2H, *J* = 9.6 Hz, ArH), 7.21 (d, 2H, *J* = 6.90 Hz, ArH), 3.89 (s, 1H, ArOCH<sub>3</sub>), 3.07 (s, 6H,  $-S(CH_3)_2$ ). <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN): *δ* ppm 165.43, 133.01, 118.37, 117.32, 56.86, 29.96. <sup>19</sup>F NMR (470 MHz, CD<sub>3</sub>CN): *δ* ppm -77.66 (3F, s,  $-CF_3$ ). ESI-MS: calcd for  $C_9H_{13}OS^+$  [M]<sup>+</sup>, 169.069; found, 169.070. FT-IR (cm<sup>-1</sup>): 3102 (m), 3032(sh), 2910 (w), 1590 (sh), 1503 (sh), 1470 (w), 1428 (w), 1238 (vs), 1158 (sh), 1023 (sh).

Synthesis of (4-(Allyloxy)-2-methylphenyl)(methyl)sulfane. (4-(Allyloxy)-2-methylphenyl)(methyl)sulfane was synthesized by adopting a published procedure.<sup>30</sup> To a stirred solution of 3-methyl-4-(methylthio)phenol (0.50 g, 3.24 mmol) and cesium carbonate (1.58 g, 4.86 mmol) in dry THF was added commercially available allyl bromide (0.42 mL, 4.86 mmol) at 65 °C. Stirring was continued at the same temperature for 12 h. After completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure to yield a residue. The residue was dissolved in EtOAc (15 mL) and washed with a saturated solution of ammonium chloride. The organic layer was dried over anhydrous Na2SO4 and concentrated under reduced pressure. Purification by silica gel column chromatography using a gradient solvent system of 0.5-1% ethyl acetate in hexane yielded (4-(allyloxy)-2-methylphenyl)(methyl)sulfane as colorless oil. Yield: 0.57 g, 90%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ ppm 7.18 (d, 1H, J = 8.25 Hz, ArH), 6.78 (d, 1H, J = 2.75 Hz, ArH), 6.75 (dd, 2H), 6.1H,  $J^1 = 2.75$  Hz,  $J^2 = 8.25$  Hz, ArH), 6.07–6.01 (m, 1H, CH<sub>2</sub>–  $CH^* = CH_2$ ), 5.40 (dd, 1H,  $J^1 = 17.17$  Hz,  $J^2 = 1.40$  Hz,  $CH = CH_2^*$ (trans)), 5.28 (dd, 1H,  $J^1 = 11.00$  Hz,  $J^2 = 1.40$  Hz, CH=CH<sub>2</sub>\* (cis)), 4.51 (d, 2H, J = 5.45 Hz, -OCH2), 2.40 (s, 3H,  $-SCH_3$ ), 2.37 (s, 3H, -ArCH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ ppm 156.91, 138.87, 133.22, 129.03, 128.23, 117.60, 116.78, 112.66, 68.83, 20.43 17.84. ESI-MS: calcd for C<sub>10</sub>H<sub>12</sub>OS [M]<sup>+</sup>, 194.077; found, 194.100.

Synthesis of AMPDST. AMPDST was synthesized using a procedure similar to that used for HMPDST. Yield: 0.97 g, 70%. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O):  $\delta$  ppm 7.83 (d, 1H, J = 8.95 Hz, ArH), 7.14 (dd, 1H, J<sup>1</sup> = 2.75 nad J<sup>2</sup> = 8.90 Hz, ArH), 7.03 (d, 1H, J = 2.75 Hz, ArH), 6.12–6.07 (m, 1H, CH<sub>2</sub>–CH\*=CH<sub>2</sub>), 5.42 (d, 1H, J = 17.15, –C=CH<sub>2</sub>\* (trans)), 5.34 (d, 1H, J = 11 –C=CH<sub>2</sub>\* (cis)), 4.67 (d, 2H, J = 5.5 Hz, –OCH<sub>2</sub>), 3.13 (s, 6H, –S(CH<sub>3</sub>)<sub>2</sub>), 2.53 (s, 3H, ArCH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O):  $\delta$  ppm 162.13, 143.49, 131.68, 129.35, 120.87, 118.36, 117.53, 117.36, 115.81, 114.61, 69.10, 28.34, 18.90. <sup>19</sup>F NMR (470 MHz, D<sub>2</sub>O):  $\delta$  ppm –78.81 (3F, s, –CF<sub>3</sub>). ESI-MS: calcd for C<sub>9</sub>H<sub>13</sub>OS<sup>+</sup> [M]<sup>+</sup>, 209.100; found, 209.096. FT-IR (cm<sup>-1</sup>): 3107 (w), 3028(sh), 2932 (m), 1583 (sh), 1495 (sh), 1456 (m), 1421 (m), 1240 (vs), 1158 (sh), 1026 (sh).

*Synthesis of MAPDST.* MAPDST was synthesized according to a literature procedure.<sup>38</sup> Yield: 0.74 g, 83%. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O):  $\delta$  ppm 8.04 (d, 2H, *J* = 8.20 Hz, ArH), 7.52 (d, 2H, *J* = 8.90 Hz, ArH), 6.41 (s, 1H,  $-C=CH_2^*$  (trans)), 5.95 (s, 1H,  $-C=CH_2^*$  (cis)), 3.25 (s, 6H,  $-S(CH_3)_2$ ), 2.03 (s, 3H,  $-CH_3$ ). <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O):  $\delta$  ppm 167.60, 155.05, 134.88, 131.32, 129.48, 124.58, 122.44, 28.64, 17.26. <sup>19</sup>F NMR (470 MHz, D<sub>2</sub>O):  $\delta$  ppm -79.22 (3F, s,  $-CF_3$ ). ESI-MS: calcd for C<sub>9</sub>H<sub>13</sub>OS<sup>+</sup> [M]<sup>+</sup>, 223.079; found, 223.081. FT-IR (cm<sup>-1</sup>): 3102 (w), 3032 (sh), 2928 (w), 1732 (sh), 1636 (w), 1584(sh), 1500 (sh), 1430 (w), 1248 (sh), 1168 (m), 1029 (sh).

General Procedure for the Synthesis of Hybrids 1–6. Hybrids 1–6 were synthesized by using a general procedure as follows:  $Na_2MoO_4 \cdot 2H_2O$  (0.50 g, 2.06 mmol) was dissolved in 5 mL of water, and the pH of the reaction mixture was adjusted to 4.0 with 4 M HCl. Aromatic sulfonium counterion (3.09 mmol), which was dissolved in 5 mL of water, was added dropwise to the reaction mixture with continuous stirring for 30 min. The white precipitates of hybrids 1–6 thus obtained were collected through filtration and washed successively with cold  $H_2O$ , EtOH, acetone, and diethyl ether followed by air drying. The single crystals of hybrids 1–6 were obtained from DMF or DMSO/DMF (1:1, v/v) solvent mixture via slow evaporation method.

 $(HPDS)_4[Mo_8O_{26}]$  (Hybrid 1). Yield: 62% based on Mo. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  ppm 10.73 (1H, s, ArOH), 7.88 (2H, d, J = 8.25 Hz, ArH), 7.03 (2H, d, J = 8.95 Hz, ArH), 3.19 (6H, s,  $-S(CH_3)_2$ ). FT-IR (cm<sup>-1</sup>): HPDS<sup>+</sup> cation, 3516 (sh), 3084 (w), 3012 (sh), 2935 (w), 1585 (sh), 1497 (sh), 1423 (w), 1285 (sh), 1242 (sh), 1172, 1093, 1044,  $\nu$ (Mo=O, Mo–O–Mo), 944 (sh), 902 (vsh), 838 (sh), 707 (m), 657(br), 556 (m), 520 (m), 450 (w).

(*HMPDS*)<sub>4</sub>[*M*0<sub>8</sub>O<sub>26</sub>] (*Hybrid* **2**). Yield: 72% based on Mo. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  ppm 10.67 (1H, s, ArOH), 7.96 (1H, d, J = 8.90 Hz, ArH), 6.94 (1H, dd,  $J^1$  = 2.40 and  $J^2$  = 8.60 Hz, ArH), 6.83 (1H, d, J = 2.75 Hz, ArH), 3.17 (6H, s,  $-S(CH_3)_2$ ), 2.48 (3H, s, ArCH<sub>3</sub>). FT-IR (cm<sup>-1</sup>): HMPDS<sup>+</sup> cations, 3509 (sh), 3155(w), 3012 (sh), 2921 (w), 1598 (sh), 1575 (sh), 1425 (w), 1314 (sh), 1046 (m),  $\nu$ (Mo=O, Mo–O–Mo), 943 (sh), 903 (vsh), 842 (sh), 702 (sh), 651 (br), 544 (m), 521 (m), 445 (w).

 $(MPDS)_4[Mo_8O_{26}]$  (Hybrid 3). Yield: 67% based on Mo. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  ppm 8.01 (d, 2H, J = 9.60 Hz, ArH), 7.26 (d, 2H, J = 8.95 Hz, ArH), 3.86 (s, 3H, ArOCH<sub>3</sub>), 3.22 (s, 6H,  $-S(CH_3)_2$ ). FT-IR (cm<sup>-1</sup>): APDS<sup>+</sup> cations, 3090 (w), 3016 (sh), 2923 (w), 1594 (sh), 1494 (sh), 1423 (w), 1315 (w), 1177 (m),  $\nu$ (Mo=O, Mo-O-Mo), 940 (sh), 900 (v, sh), 831 (sh), 698 (m), 662 (br), 552 (m), 520 (sh), 443 (w).

 $(APDS)_4[Mo_8O_{26}]$  (Hybrid 4). Yield: 68% based on Mo. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  ppm 8.01 (d, 2H, J = 8.90 Hz, ArH), 7.27 (d, 2H, J = 8.95 Hz, ArH), 6.06–6.00 (m, 1H, –CH<sub>2</sub>–CH\*=CH<sub>2</sub>), 5.41 (dd, 1H, J<sup>1</sup> = 1.70, J<sup>2</sup> = 18.90 Hz, –CH=CH<sub>2</sub>\* (trans)), 5.29 (dd, 1H, J<sup>1</sup> = 1.63 and J<sup>2</sup> = 10.65 Hz, –CH=CH<sub>2</sub>\* (cis)), 4.70 (d, 2H, J = 5.5 Hz, ArOCH<sub>2</sub>), 3.22 (s, 6H, –S(CH<sub>3</sub>)<sub>2</sub>). FT-IR (cm<sup>-1</sup>): APDS<sup>+</sup> cations, 3095 (w), 3012 (sh), 2927 (w), 1590 (sh), 1497 (sh), 1426 (w), 1332 (w), 1176 (m),  $\nu$ (Mo=O, Mo–O–Mo), 938 (sh), 906 (v, sh), 830 (sh), 704 (w), 656 (b), 551 (m), 521 (m), 443 (w).

(AMPDS)<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>] (Hybrid 5). Yield: 63% based on Mo. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  ppm 8.08 (d, 2H, J = 8.90 Hz, ArH), 7.19 (d, 1H, J = 8.95 Hz, ArH), 7.08 (s, 1H, ArH), 6.06–6.00 (m, 1H,  $-CH_2-CH^*=CH_2$ ), 5.40 (dd, 1H,  $J^1 = 1.37$  and  $J^2 = 17.17$  Hz,  $-CH=CH_2^*$  (trans)), 5.28 (d, 1H, J = 10.35 Hz,  $-CH=CH_2^*$  (cis)), 4.68 (d, 2H, J = 4.8 Hz, ArOCH<sub>2</sub>), 3.21 (s, 6H,  $-S(CH_3)_2$ ), 2.55 (s, 3H, ArCH<sub>3</sub>). FT-IR (cm<sup>-1</sup>): APDS<sup>+</sup> cations, 3088 (w), 3027 (sh), 2929 (w), 1597 (sh), 1484 (sh), 1423 (w), 1298 (sh), 1183 (m),  $\nu$ (Mo=O, Mo–O–Mo), 938 (sh), 903 (v, sh), 837 (sh), 707 (sh), 652 (br), 552 (m), 515 (m), 449 (w).

(*MAPDS*)<sub>4</sub>[*Mo*<sub>8</sub>*O*<sub>26</sub>] (*Hybrid* **6**). Yield: 60% based on Mo. <sup>1</sup>H NMR (500 MHz, DMSO-*d*6):  $\delta$  ppm 8.15 (d, 2H, *J* = 8.95 Hz, ArH), 7.58 (d, 2H, *J* = 8.90 Hz, ArH), 6.32 (s, 1H,  $-C=CH_2^*$  (trans)), 5.96 (s, 1H,  $-C=CH_2^*$  (cis)), 3.28 (s, 6H,  $-S(CH_3)_2$ ), 2.01 (s, 3H,  $-CH_3$ ). FT-IR (cm<sup>-1</sup>): APDS<sup>+</sup> cations, 3104 (w), 3027 (sh), 2927 (w), 1631 (w), 1581 (m), 1494 (m), 1415 (m), 1317 (sh), 1169 (sh),  $\nu$ (Mo=O, Mo–O–Mo), 940 (sh), 903 (v, sh), 835 (sh), 718 (sh), 652 (br), 549 (m), 516 (sh), 443 (w).

Catalytic Activities of Hybrids 1–6 toward the Epoxidation of *cis*-Cyclooctene. Three milliliters of an acetonitrile (MeCN) solution of *cis*-cyclooctene (0.30 mmol) containing 0.003 mmol of catalysts (hybrid 1/2/3/4/5 or 6) and 0.45 mmol of H<sub>2</sub>O<sub>2</sub> was stirred in a round-bottom flask equipped with a reflux condenser at 60 °C. Conversion of the reaction was monitored by GC analyses using internal standard method (phenyl bromide).<sup>61</sup> Aliquots (30  $\mu$ L) were withdrawn after 5, 30, 60, and 90 min time intervals for timedependent product analyses. Each time, the aliquots were diluted with 1 mL of MeCN and dried over sodium sulfate. Internal standard (2.0  $\mu$ L) was added to the resulting solution, filtered through a nylon-6 filter (0.22  $\mu$ m), and subjected to gas chromatography (GC) analyses.

**Reuse of the Catalyst.** The recovered catalyst was washed successively with ethanol, acetone, and diethyl ether and finally dried in an oven at 40 °C. The resulting catalyst was characterized by IR spectroscopy, NMR, and HRMS analyses. The catalyst was reused up to 5 catalytic cycles. The catalyst was found to be robust after each cycle and the yields obtained in consecutive cycles are given in Figure S44. The NMR and mass spectrum of the recovered catalyst hybrid **6** are given in Figures S45–S48 and Table S16, Supporting Information.

General Procedure for the Epoxidation of Fatty Acid Alkyl Ester (FAAE). MO/EO (0.5 mmol) was dissolved in 3 mL of MeOH. To this solution, 0.005 mmol of hybrid 6 as catalyst was added followed by the addition of 1.5 equiv of 30%  $H_2O_2$ . The catalyst gets dissolved in the reaction mixture, and the color becomes yellow. The reaction mixture was stirred at 60 °C for 6 h, and the reaction dynamics were monitored from time to time using TLC measurements revealed complete consumption of the starting material within 6 h. Subsequently, the self-separated catalyst was filtered out. The reaction mixture was dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated under reduced pressure, and the product was extracted with hexane (3 × 5 mL). Hexane was removed under reduced pressure to afford the epoxide product of MO/EO. The product was analyzed by NMR and ESI-MS techniques.

(a). Epoxidation of MO: Yield – 144 mg (92%).

(b). Epoxidation of EO: Yield – 146 mg (89%).

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01143.

Characterization details of the compounds reported in this study (PDF)

#### **Accession Codes**

CCDC 1536033–1536038 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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