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#### Article

# Efficient Catalytic Oxidative Desulfurization toward Thioether and Sulfur Mustard Stimulant by Polyoxomolybdate–Resorcin[4]arene-Based Metal–Organic Materials

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**ABSTRACT:** The design and synthesis of effective and recyclable oxidative desulfurization catalysts is of great importance in view of environmental protection and human health. Herein, a family of polyoxomolybdate-based inorganic–organic hybrid materials, namely,  $[Mn(TMR4A)(H_2O)_4]$ - $[Mo_6O_{19}]\cdot 0.5CH_3CH_2OH\cdot H_2O$  (1),  $[Ni(TMR4A)(H_2O)_4][Mo_6O_{19}]\cdot 0.5CH_3CH_2OH\cdot H_2O$  (2),  $[Zn(TMR4A)(H_2O)_4][Mo_6O_{19}]\cdot 0.5CH_3CH_2OH\cdot H_2O$  (2),  $[Zn(TMR4A)(H_2O)_4][Mo_6O_{19}]\cdot 0.5CH_3CH_2OH$ . H<sub>2</sub>O (3), and  $[Co_2(TMR4A)_2(H_2O)_4(\beta-Mo_8O_{26})]\cdot CH_3CN\cdot 12H_2O$  (4), were assembled by the functionalized resorcin[4] arene ligand (TMR4A) with polyoxomolybdate and metal ions under solvothermal conditions. In isostructural 1–3, the  $[M(TMR4A)(H_2O)_4]^{2+}$  species (M = Mn<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup>) and  $[Mo_6O_{19}]^{2-}$  anions are held together via C–H…O hydrogen bonds to give a 3D supramolecular architecture. In 4, two  $[Co(TMR4A)(H_2O)_2]^{2+}$  cations were linked by one  $[\beta-Mo_8O_{26}]^{4-}$  anion to produce an attractive



molecular dimer. Remarkably, 1-4, as recyclable heterogeneous catalysts, exhibit efficient catalytic oxidation desulfurization activities toward thioethers. Particularly, 1, as a representative example, features selective catalytic oxidation for sulfur mustard simulant. Moreover, their electrochemical properties were also studied.

# INTRODUCTION

The effective removal of sulfur-based compounds from petroleum remains a serious environmental problem owing to the negative influence on the atmosphere and human health arising from their combustions.<sup>1,2</sup> As a result, it is an important process for desulfurization of transportation fuels in the case of safeguarding the environments. $^{3-6}$  In this regard, hydrodesulfurization (HDS) is considered to be the most commonly used industrial process for removing sulfur diesels,<sup>7-10</sup> while this technique is usually carried out under severe operating conditions with low desulfurization efficiencies.<sup>11-14</sup> Recently, alternative desulfurization approaches have been developed including oxidative desulfurization (ODS),15-19 adsorption, 20-22biodesulfurization, etc. Among them, ODS is regarded as the most promising technique for deep desulfurization of fuel.<sup>23–25<sup>1</sup></sup>In particular, the ODS method is greatly efficient for the removal of refractory aromatic sulfurbased species relative to HDS.<sup>25</sup>

On the other hand, sulfur mustard (mustard gas), used as one of the most typical and toxic chemical warfare agents (CWAs) in World War I, is a major threat to human health.<sup>26-32</sup> The ODS technique is the most popular method to selectively oxidize sulfur mustard to nontoxic sulfoxide rather than sulfone in the presence of suitable catalysts.<sup>33-36</sup>

In this facet, polyoxometalates (POMs), one of the most popular types of catalysts,<sup>37–40</sup> demonstrate remarkable ODS

activity.<sup>41–47</sup> Nevertheless, POMs are easily soluble in solvents, which limits their application as recycled catalysts. POM-based metal–organic materials, assembled with POMs, organic ligands, and metal ions, feature structural diversity and stability.<sup>48</sup> Thus, they were used as heterogeneous catalysts in various catalytic reactions.<sup>37,49,50</sup> Moreover, the organic ligands play an important role in the assembly of the target POM-based metal–organic catalysts.

Resorcin[4]arenes are excellent organic ligand candidates for the construction of POM-based metal-organic materials because of their bowl-shaped aromatic cavities and easily modified structure features.<sup>51-53</sup> Usually, the target structures of the resorcin[4]arenes can be achieved by well modifying their upper rims with different functional groups.<sup>54-56</sup> In this facet, the mercaptopyridine *N*-oxide groups possess strong and flexible coordination ability with metal ions. In particular, the substituted 2-mercaptopyridine *N*-oxide groups on the modified resorcin[4]arenes tend to chelate metal ions to produce stable structures.<sup>57</sup> Thus, the 2-mercaptopyridine *N*-

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oxide group-functionalized resorcin[4]arenes are potential organic ligand candidates for constructing POM-based metal–organic catalysts.<sup>58–60</sup>

Herein, we successfully synthesized four new inorganicorganic hybrid materials, namely,  $[Mn(TMR4A)(H_2O)_4]$ - $[Mo_6O_{19}]\cdot 0.5CH_3CH_2OH\cdot H_2O$  (1),  $[Ni(TMR4A)(H_2O)_4]$ - $[Mo_6O_{19}]\cdot 0.5CH_3CH_2OH\cdot H_2O$  (2),  $[Zn(TMR4A)(H_2O)_4]$ - $[Mo_6O_{19}]\cdot 0.5CH_3CH_2OH + H_2O$  (3), and  $[Co_2(TMR4A)_2(H_2O)_4(\beta-Mo_8O_{26})]\cdot CH_3CN\cdot 12H_2O$  (4), with a functionalized resorcin[4]arene ligand (TMR4A), metal ions, and POMs. These hybrid materials exhibit structural diversities adjusted by POMs and TMR4A (Scheme 1). Markedly, 1-4 feature efficient catalytic oxidation

### Scheme 1. Structure of TMR4A



desulfurization activity toward thioethers as stable and recyclable heterogeneous catalysts. More importantly, 1, as a representative example, exhibits selective catalytic oxidation for the sulfur mustard simulant 2-chloroethyl ethyl sulfide (CEES). Moreover, their electrochemical properties were also investigated.

#### EXPERIMENTAL SECTION

The materials and characterizations used in this work are given in the Supporting Information. The organic ligand TMR4A was prepared by following the literature.<sup>57</sup> Quantities of catalysts 1–4 were achieved by using a large number of Teflon reactors (15 mL) under hydrothermal conditions.

Synthesis of [Mn(TMR4A)(H<sub>2</sub>O)<sub>4</sub>][Mo<sub>6</sub>O<sub>19</sub>]-0.5CH<sub>3</sub>CH<sub>2</sub>OH-H<sub>2</sub>O (1). A mixture of MnCl<sub>2</sub>·4H<sub>2</sub>O (0.008 g, 0.04 mmol), TMR4A (0.011 g, 0.01 mmol), [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>] (0.023 g, 0.01 mmol), ethanol (5 mL), and deionized water (3 mL) was placed in a Teflon reactor (15 mL) and heated at 100 °C for 6 days. After cooling to room temperature, yellow-green rod crystals were achieved in 40% yield. Anal. Calcd for C<sub>61</sub>H<sub>65</sub>MnMo<sub>6</sub>N<sub>4</sub>O<sub>36.5</sub>S<sub>4</sub> ( $M_r$  = 2196.99): C, 33.35; H, 2.98; N, 2.55. Found: C, 32.57; H, 3.12; N, 2.52. IR data (KBr, cm<sup>-1</sup>): 3733 (w), 3419 (w), 3108 (m), 2970 (w), 1591 (w), 1557 (w), 1472 (s), 1426 (m), 1375 (w), 1280 (w), 1252 (m), 1220 (m), 1149 (m), 1096 (m), 1049 (w), 1018 (m), 960 (s), 800 (s), 756 (s), 708 (m), 688 (m), 646 (m), 578 (m), 501 (m), 438 (m).

Synthesis of [Ni(TMR4A)(H<sub>2</sub>O)<sub>4</sub>][Mo<sub>6</sub>O<sub>19</sub>] $\cdot$ 0.5CH<sub>3</sub>CH<sub>2</sub>OH $\cdot$ H<sub>2</sub>O (2). A mixture of NiCl<sub>2</sub>·6H<sub>2</sub>O (0.010 g, 0.04 mmol), TMR4A (0.011 g, 0.01 mmol), [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>] (0.023 g, 0.01 mmol),



**Figure 1.** (a) Coordination sphere of Mn<sup>II</sup>. (b) Hydrogen-bonding interactions formed by one  $[Mn(TMR4A)(H_2O)_4]^{2+}$  cation with six  $[Mo_6O_{19}]^{2-}$  anions. (c) Hydrogen-bonding interactions formed by one  $[Mo_6O_{19}]^{2-}$  anion with six  $[Mn(TMR4A)(H_2O)_4]^{2+}$  cations. (d) 3D architecture constructed by  $[Mo_6O_{19}]^{2-}$  anions and  $[Mn(TMR4A)(H_2O)_4]^{2+}$  cations via hydrogen bonds. Symmetry codes: #1, *x*, -*y*, *z*; #2, -*x* + 1, *y*, -*z*.

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**Figure 2.** (a) Coordination sphere of Co<sup>II</sup>. (b) Dimeric structure of 4. (c-d) 3D supramolecular framework constructed by the  $[\beta$ -Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> anions and  $[Co(TMR4A)(H_2O)_2]^{2+}$  cations through hydrogen-bonding interactions. Symmetry code: #1, -x + 1, -y, -z.

ethanol (6 mL), and deionized water (2 mL) was sealed in a Teflon reactor (15 mL) and heated at 100 °C for 6 days. After cooling to room temperature, green rod crystals were collected in 32% yield. Anal. Calcd for  $C_{61}H_{65}Mo_6N_4NiO_{36.5}S_4$  ( $M_r$  = 2200.76): C, 33.29; H, 2.98; N, 2.55. Found: C, 31.88; H, 3.09; N, 2.50. IR data (KBr, cm<sup>-1</sup>): 3733 (w), 3421 (w), 3112 (w), 2970 (w), 1592 (w), 1557 (w), 1473 (s), 1427 (m), 1281 (w), 1250 (w), 1218 (m), 1150 (w), 1096 (m), 1051 (w), 1019 (m), 961 (s), 801 (s), 757 (s), 709 (m), 688 (m), 579 (m), 502 (w), 441 (m).

**Synthesis of [Zn(TMR4A)(H<sub>2</sub>O)<sub>4</sub>][Mo<sub>6</sub>O<sub>19</sub>]·0.5CH<sub>3</sub>CH<sub>2</sub>OH·H<sub>2</sub>O (3). 3 was prepared with a method similar to that of 2 except that NiCl<sub>2</sub>·6H<sub>2</sub>O (0.010 g, 0.04 mmol) was replaced by Zn(NO<sub>3</sub>)<sub>2</sub> (0.012 g, 0.04 mmol) and 1.2 M HCl (1 drop) was used. Green rod crystals were obtained in 30% yield. Anal. Calcd for C\_{61}H\_{65}Mo\_6N\_4O\_{36.5}S\_4Zn (M\_r = 2207.42): C, 33.20; H, 2.97; N, 2.54. Found: C, 32.89; H, 3.00; N, 2.38. IR data (KBr, cm<sup>-1</sup>): 3564 (w), 3110 (w), 2969 (w), 1591 (w), 1557 (w), 1473 (s), 1427 (m), 1281 (w), 1250 (m), 1219 (m), 1150 (m), 1096 (m), 1050 (w), 1019 (m), 961 (s), 801 (s), 756 (s), 708 (m), 688 (m), 578 (m), 501 (m), 437 (m).** 

**Synthesis of [Co<sub>2</sub>(TMR4A)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>][β-Mo<sub>8</sub>O<sub>26</sub>]·CH<sub>3</sub>CN·12H<sub>2</sub>O (4). A mixture of TMR4A (0.011 g, 0.01 mmol), CoCl<sub>2</sub>·6H<sub>2</sub>O (0.010 g, 0.04 mmol), [(n-C\_4H\_9)\_4N]\_4[Mo\_8O\_{26}] (0.023 g, 0.01 mmol), acetonitrile (3 mL), and deionized water (5 mL) was sealed in a 15 mL Teflon reactor at 100 °C for 3 days. After cooling to room temperature, pink rod crystals were obtained in 25% yield. Anal. Calcd for C<sub>122</sub>H<sub>139</sub>Co<sub>2</sub>Mo<sub>8</sub>N<sub>9</sub>O<sub>66</sub>S<sub>8</sub> (M\_r = 3929.27): C, 37.29; H, 3.57; N, 3.21. Found: C, 37.32; H, 3.29; N, 3.14. IR data (KBr, cm<sup>-1</sup>): 3733 (w), 3356 (m), 2972 (m), 1634 (w), 1594 (w), 1559 (w), 1472 (s), 1426 (m), 1339 (w), 1300 (w), 1250 (m), 1212 (m), 1151 (m), 1093**  (m), 1054 (m), 1020 (m), 981 (s), 903 (s), 837 (m), 756 (m), 720 (s), 580 (m), 414 (m).

#### RESULTS AND DISCUSSION

Structures of 1–3. Compounds 1–3 were prepared in the mixed solutions of ethanol and water. Noticeably, the precursor [Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> was transformed to [Mo<sub>6</sub>O<sub>19</sub>]<sup>2-</sup> during the hydrothermal syntheses.<sup>61</sup> Isostructural 1-3 crystallize in the monoclinic C2/m space group (Table S1). Thus, the crvstal structure of 1 will be described (Figures S1 and S2). The asymmetric unit of 1 contains half of a TMR4A ligand, half of a  $\rm Mn^{II}$  cation, half of a  $\rm [Mo_6O_{19}]^{2-}$  anion, a quarter of a free ethanol molecule, two coordination water molecules, and half of a free water molecule. Each Mn<sup>II</sup> cation exhibits an octahedral coordination sphere, completed by two oxygen atoms of one TMR4A ligand (O6 and O6<sup>#1</sup>) and four oxygen atoms of four water molecules (O1W, O2W, O3W, and O3W<sup>#1</sup>) with Mn-O distances of 2.079(7)-2.199(7) Å (Figure 1a). Noticeably, the  $[Mo_6O_{19}]^{2-}$  anion is free and balances the positive charge of the  $[Mn(TMR4A)(H_2O)_4]^{2+}$ unit. Remarkably, each  $[Mn(TMR4A)(H_2O)_4]^{2+}$  cation interacts with six  $[Mo_6O_{19}]^{2-}$  anions (Figure 1b), and each  $[Mo_6O_{19}]^{2-}$  anion is interlinked by six  $[Mn(TMR4A)-(H_2O)_4]^{2+}$  cations (Figure 1c) through C–H…O hydrogen bonds (Table S2), yielding a 3D supramolecular architecture (Figure 1d).



Figure 3. PXRD patterns of 1 in different organic solvents (a) and different pH values (b).

Structure of 4. Compound 4 was synthesized in the mixed solution of acetonitrile and water. In the refinement of 4, the SQUEEZE routine was employed to remove the disordered solvents.<sup>62</sup> Elemental analysis, the electron diffraction density, and thermogravimentric analysis (TGA) suggest that there exist half of a free CH<sub>3</sub>CN and six free water molecules in each unit cell (Figure S3). As illustrated in Figure 2a, each Co<sup>II</sup> is six-coordinated by six oxygen atoms from one TMR4A ligand (O9 and O10), two water molecules (O1W and O2W), and two  $[\beta$ -Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> anions, with Co–O distances ranging from 2.028(7) to 2.123(6) Å (Table S3). Markedly, two [Co- $(TMR4A)(H_2O)_2]^{2+}$  cations are held together by one [ $\beta$ - $Mo_8O_{26}$ ]<sup>4-</sup> anion to produce an elegant dimer (Figure 2b). Adjacent dimers are further joined by weak C-H-O hydrogen bonds to give a 3D supramolecular framework (Table S2 and Figure 2c,d).

During the syntheses of 1–4, we find that their crystallinities are highly dependent on the solvent systems used. Isostructural 1–3 always crystallize in the mixture of ethanol and water, while the crystals of 4 are only obtained in the mixed solution of acetonitrile and water. Clearly, the different solvent systems influenced the complex crystal nucleation and growth.<sup>61</sup> Besides, the  $[Mo_8O_{26}]^{4-}$  anions were transformed to the free  $[Mo_6O_{19}]^{2-}$  anions in 1–3 and the large  $[\beta$ -Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> anions in 4, which may also account for the different solvent systems used under the hydrothermal conditions.<sup>63</sup>

**Stability.** Chemical stability is a key prerequisite for the property study of the compounds.<sup>64</sup> In this study, **1** as a representative example was used to explore the stability. The samples of **1** were soaked in different organic solvents or aqueous solutions (pH = 0, 2, 4, 6, 8, 10, and 12) for 12 h. To gain full interaction between the acid—base and compound, the soaking time of the sample was prolonged to 12 h. Afterward, the samples were filtered and washed with methanol. The dried samples in air were then used for powder X-ray diffraction (PXRD) measurements. As described in Figure 3, their PXRD patterns correspond to the simulated one, indicating structural integrity.

**Catalytic Oxidation for CEES.** CWAs have caused extremely serious damage to humankind, and therefore it is greatly necessary to find effective catalysts for the oxidation or degradation of CWAs. In this regard, the POM-based metal–organic materials are effective catalyst candidates.<sup>65,66</sup> Here,

considering the high toxicity of CWAs, CEES, featuring chemical properties and structures similar to those of CWAs, was chosen as the simulant molecule (Scheme 2). The catalytic

Scheme 2. Catalytic Oxidation of CEES to CEESO and CEESO<sub>2</sub> Catalyzed by 1 Using  $3\% H_2O_2$ 



oxidative reaction for CEES was conducted in methanol (4 mL) with 1 as the catalyst (1.25  $\mu$ mol) and 3% H<sub>2</sub>O<sub>2</sub> as the oxidant (1 mmol). The catalytic oxidative reaction was monitored by <sup>1</sup>H NMR data (Figures 4 and S4). Noticeably, in the absence of catalyst 1, only 12% of CEES was transformed into the corresponding CEESO and CEESO<sub>2</sub> at 40 °C within 25 min (entry 1, Table 1). When 1 was used as the catalyst, the conversions of CEES reach 93% and 99% at 30 and 40 °C within 25 min, respectively (Table 1). Further, the catalytic oxidative dynamics toward CEES were also studied. The conversion of CEES was monitored every 5 min. As shown in Figure 5, the conversion rapidly reached 73% within 10 min and gradually increased to 99% when the reaction time was prolonged to 25 min.

Remarkably, the catalytic oxidation activity of **1** toward CEES is comparable to those of the reported POM-based metal–organic catalysts.<sup>67–70</sup> For example, the conversion of CEES catalyzed by **1** is up to 99% with a CEESO selectivity of 97% at 40 °C within 25 min (entry 2, Table 1). For the known PW<sub>12</sub>@NU-1000 catalyst, a similar conversion (98%) of CEES was achieved under the similar conditions, but the selectivity of CEESO is only up to 57%.<sup>70</sup> The result indicates that **1** features a superior catalytic performance and high selectivity toward CEES.

**Catalytic ODS.** Catalytic ODS of 1 toward sulfur-based compounds was also studied. Methyl phenyl sulfide (MBT) was selected as a model substrate (Scheme 3).<sup>42</sup> The catalytic oxidative reaction was carried out in CH<sub>3</sub>OH (5 mL) by using



**Figure 4.** <sup>1</sup>H NMR data for the catalytic products of CEES at 40 °C and different reaction times using 1 as the catalyst and  $H_2O_2$  as the oxidant and without a catalyst at 25 min in CDCl<sub>3</sub>. Peaks used for calculations were labeled (the signals between 1.5 and 2.5 ppm were generated from water and methanol).

Table 1. Catalytic ODS of CEES Catalyzed by 1<sup>a</sup>

entry	catalyst	temperature (°C)	oxidant	time (min)	conversion (%) <sup>b</sup>	selectivity (%) <sup>c</sup>
1	none	40	$H_2O_2$	25	12	98
2	1	40	$H_2O_2$	25	99	97
3	1	30	$H_2O_2$	25	93	99

<sup>*a*</sup>Reaction conditions: 1, 1.25  $\mu$ mol; H<sub>2</sub>O<sub>2</sub>, 1 mmol; substrate, 0.25 mmol; CH<sub>3</sub>OH, 4 mL. <sup>*b*</sup>Isolated conversion was determined by <sup>1</sup>H NMR. <sup>*c*</sup>Selectivity for CEESO.



Figure 5. Catalytic oxidative dynamics of CEES catalyzed by 1.

Scheme 3. Catalytic Desulfurization of MBT to MBTO and MBTO<sub>2</sub> by 1 in  $CH_2Cl_2$  at 40 °C



1 (2  $\mu$  mol) and 3% H<sub>2</sub>O<sub>2</sub> (1 mmol) at 40 °C. Gas chromatography (GC) was applied to determine conversion of the substrate. The conversion of MBT was only up to 68%

within 1 h by using 1 as the catalyst and  $H_2O_2$  as the oxidant (entry 1, Table 2). When 3%  $H_2O_2$  and methanol were

#### Table 2. Catalytic Desulfurization of MBT with 1<sup>a</sup>

entry	catalyst	oxidant	temperature (°C)	solvent	time (h)	conversion (%) <sup>b</sup>
1	1	$H_2O_2$	40	CH <sub>3</sub> OH	1	68
2	1	TBHP	40	$CH_2Cl_2$	0.5	91
3	1	TBHP	40	$CH_2Cl_2$	1	>99
4	none	TBHP	40	$CH_2Cl_2$	1	22
5	1	TBHP	30	$CH_2Cl_2$	1	92
<sup><i>a</i></sup> Reaction conditions: substrate, 0.4 mmol; TBHP, 1 mmol; 1, 2 $\mu$ mol; solvent, 5 mL <sup><i>b</i></sup> GC was used to determine the conversion.						

replaced by 70% *tert*-butyl hydroperoxide (TBHP) and dichloromethane, respectively, a satisfactory conversion was achieved, as illustrated in Table 2. The conversion of MBT reaches 91% within 0.5 h in the presence of TBHP and dichloromethane (entry 2). Under the same conditions, almost all MBT was oxidized by extending the reaction time to 1 h (entry 3). When the reaction temperature was reduced under the same conditions, the conversion decreases as well (entry 5). Noticeably, only 22% conversion of MBT was obtained in the absence of catalyst (entry 4). Thus, the catalytic ODS was measured in the presence of 1 mmol of TBHP, 2  $\mu$ mol of catalyst, and 5 mL of CH<sub>2</sub>Cl<sub>2</sub> at 40 °C for 1 h.

Further, different sulfur-based compounds were employed as substrates to explore the catalytic behavior of 1. As listed in Table 3, the monophenyl thioether substrates with electronwithdrawing or -donor groups could be completely converted into sulfoxides and sulfones at 40  $^{\circ}$ C within 1 h (entries 1–6). For the diphenyl sulfide substrate, the steric hindrance has no obvious influence on the catalytic performance of 1 (entry 7). However, for thiophene sulfides, it will take prolonged time to be completely oxidized under the same conditions. For example, almost all of dibenzothiophene (DBT) was oxidized within 5 h (entry 8). Owing to the steric hindrance and electron density around the sulfur atoms on the thiophene sulfides, the conversions of benzothiophene and 4,6dimethyldibenzothiophene (4,6-DMDBT) reached to 92% and 98%, respectively, within 10 h (entries 9 and 10). Moreover, the catalytic behaviors of 2-4 toward DBT and 4,6-DMDBT were also investigated under the same conditions (entries 11-16). Compounds 2-4 exhibit similar catalytic activities for the oxidation of different thioethers.

The catalytic dynamic behaviors of 4,6-DMDBT and DBT were studied with 1 as the catalyst. As depicted in Figure 6, the catalytic oxidation conversions of the substrates were monitored at different time intervals. Only 42% of DBT was transformed into the corresponding oxidation products within 1 h, and the catalytic reaction finished after 5 h. For the catalytic oxidation of 4,6-DMDBT, the conversion was significantly enhanced (56%) within 2 h (Figures 7 and S5). Afterward, the conversions slowly reached 98% after 10 h. Meanwhile, no obvious catalytic reaction activity for the remaining filtrate was observed when the catalyst was removed after 3 h (Figure 7). Moreover, the inductively coupled plasma (ICP) analysis demonstrates that no  $Mn^{II}$  cations were leached in the filtrate, suggesting the heterogeneity of the catalytic reaction.

To examine the reusability of catalyst 1, a series of recycling experiments for the oxidation of MBT were performed. As

# Table 3. Catalytic Oxidation of Various Thioethers by 1-4 Using TBHP as the Oxidant<sup>a</sup>

Entry	Catalyst	Substrates	Time (h)	Conversions (%) <sup>b</sup>
1	1	S S	1	>99
2	1	0.N S	1	>99
3	1	S S	1	>99
4	1	H-CO	1	>99
5	1	njeo Solo	1	>99
6	1	ſŢ, s∽	1	>99
7	1		1	>99
8	1	s s	1	42
0	1		5	>99
9	1	s s	1	13
			10	92
10	1	s	1	30
			10	>98
11	2		5	>99
12	3		5	>99
13	4		5	>99
14	2		10	91
15	3		10	85
16	4		10	94

<sup>*a*</sup>Reaction conditions: CH<sub>2</sub>Cl<sub>2</sub>, 5 mL; catalyst, 2  $\mu$ mol; substrate, 0.4 mmol; TBHP, 1 mmol; 40 °C. <sup>*b*</sup>High-performance liquid chromatography was used to determine the conversion.



Figure 6. Dynamic curve for the catalytic oxidation of DBT by 1.



Figure 7. Conversion curves of 4,6-DMDBT with the reaction time catalyzed by 1 (red) and by filtrate after 3 h of catalytic reaction (blue).

illustrated in Figure 8, the catalytic activity of 1 was wellmaintained after four runs of the catalytic reaction. In addition,



Figure 8. Recycling experiments for the oxidation of MBT with 1.

the Fourier transform infrared (FT-IR) spectra and PXRD patterns further indicate that catalyst 1 still retains structural stability after four cycles of catalytic reactions (Figures 9 and 10).

It is well established that the POMs usually act as catalytic active sites.<sup>36,41,42</sup> For instance, the substrate MBT was completely transformed to catalytic products with 1 as the catalyst at 40 °C within 1 h (entry 3, Table 2). In contrast, the conversion of MBT was only up to 28% in the presence of



**Figure 9.** PXRD patterns of **1** for simulated (black), experimental (red), and recycled data after 4 runs of the catalytic oxidation of MBT (blue).



Figure 10. FT-IR spectra of 1 before (black) and after four cycles of the catalytic oxidation reaction (red).

CuCl<sub>2</sub> when the reaction time was prolonged to 4 h (entry 1, Table S4). Moreover, in the presence of NiCl<sub>2</sub>·6H<sub>2</sub>O and TMR4A, only 25% MBT was converted to the products at 50 °C for 1 h (entry 2, Table S4). In addition, the typical polyoxomolybdate,  $[Mo_8O_{26}]^{4-}$  anion, featured remarkable catalytic activity (82.3% conversion) toward DBT at 30 °C within 1.5 h (entry 3, Table S4). The result further indicates that polyoxomolybdates in 1–4 are the main catalytic active species for the catalytic oxidation reactions.<sup>40,49</sup>

On the other hand, the catalytic ODS performances of 1 are comparable to those of the related POM-based catalysts (Table S5). For instance, MBT was completely converted to catalytic products, with 1 as the catalyst at 40 °C within 1 h. When the POM-based  $[Co_2L_{0.5}V_4O_{12}]$ ·3DMF·5H<sub>2</sub>O (L = 2-(2-pyridyl)imidazole-functionalized resorcin[4]arene) and  $(en)[Cu_3(ptz)_4(H_2O)_4][Co_2Mo_{10}H_4O_{38}]\cdot 24H_2O$  [en = ethylenediamine; ptz = 5-(4-pyridyl)-1H-tetrazole] were used as catalysts, the overall conversions of MBT were accomplished within 4 h under similar conditions (Table S5).<sup>42,49</sup> In addition, the catalytic oxidation of DBT by 1 finished within 5 h (entry 8, Table 3), while the similar conversions were achieved by using  $[Co^{II}(HBBTZ)(BBTZ)_{2.5}][PMo_{12}O_{40}]$ [BBTZ = 4,4'-bis(1,2,4-triazol-1-ylmethyl)benzene] and [Co- $(BBPTZ)_{3}$ [HPMo<sub>12</sub>O<sub>40</sub>]·24H<sub>2</sub>O [BBPTZ = 4,4'-bis(1,2,4triazol-1-ylmethyl)biphenyl] within the prolonged reaction

time (9 and 8 h).<sup>43</sup> The result demonstrates that 1 is an efficient potential heterogeneous catalyst for ODS.

# CONCLUSIONS

In summary, we have successfully synthesized a series of POM-resorcin[4]arene-based metal-organic catalysts through a solvothermal method. These hybrid materials exhibit structural diversities tuned by POMs as well as TMR4A. Markedly, they are very stable in different organic solvents as well as different pH values. Importantly, 1 features an effective oxidation degradation for toxic representative CEES. In particular, they feature efficient catalytic activities for catalytic ODS as recycled catalysts. These materials are also potentials for the oxidation of ascorbic acid and the reduction of NaBrO<sub>3</sub>.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00225.

Experimental details, crystallographic data, structural figures, TGA and cyclic voltammetry curves, <sup>1</sup>H NMR, FT-IR, GC, high-performance liquid chromatography, PXRD patterns, and tables (PDF)

# **Accession Codes**

CCDC 1909233–1909235 and 1909237 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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