# **Inorganic Chemistry**

### A Polyoxovanadate–Resorcin[4]arene-Based Porous Metal–Organic Framework as an Efficient Multifunctional Catalyst for the Cycloaddition of CO<sub>2</sub> with Epoxides and the Selective Oxidation of Sulfides

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**S** Supporting Information

**ABSTRACT:** In this work, we report a new polyoxovanadate– resorcin[4]arene-based metal–organic framework (PMOF),  $[Co_2L_{0.5}V_4O_{12}]$ ·3DMF·5H<sub>2</sub>O (1), assembled with a newly functionalized wheel-like resorcin[4]arene ligand (L). 1 features an elegant porous motif and represents a rare example of PMOFs composed of both a resorcin[4]arene ligand and polyoxovanadate. Remarkably, 1 shows open V sites in the channel, which makes 1 an efficient heterogeneous Lewis acid catalyst for the cycloaddition of carbon dioxide to epoxides with high conversion and selectivity. Strikingly, 1 also exhibits high catalytic activity for the heterogeneous oxidative desulfurization of sulfides. Particularly, the heterogeneous catalyst 1 can be easily separated and reused with good catalytic activity.

#### **INTRODUCTION**

Carbon dioxide  $(CO_2)$ , as the main greenhouse gas, is suspected of causing global warming as well as subsequent climate changes in the past few decades.<sup>1-4</sup> As a result, considerable attention has been devoted to the development of CO<sub>2</sub> sequestration technologies, which would positively reduce the greenhouse emissions and satisfy human demand for raw chemical materials.<sup>5-9</sup> Thus far, quite a lot of effort has been made to convert  $CO_2$  into highly valuable chemical products.<sup>10-12</sup> In this domain, the coupling reaction of  $CO_2$ with epoxides is regarded as one of the most popular routes for CO2 conversion because of the high atom efficiency and important application of cyclic carbonates.<sup>13–17</sup> In terms of the cycloaddition of CO2 with epoxides, various homogeneous catalysts have been employed for the catalytic generation of cyclic carbonates.<sup>18–21</sup> Nevertheless, homogeneous catalytic systems suffer from the inherent limitations of the separation of the product and catalyst recycling.<sup>22,23</sup> To overcome these limitations, heterogeneous catalysts including zeolites, metal oxides, and functional polymers have been well developed.<sup>24-1</sup> Very recently, the emerging metal-organic frameworks (MOFs) or polyoxometalate (POM)-based MOFs (PMOFs), as promising heterogeneous candidate catalysts, have attracted increasing interest.<sup>29-34</sup>

In general, organic linkers have an important role in the design and synthesis of PMOF catalysts because of their tunable structural features.<sup>35–41</sup> In this context, calixarene, as a well-known macrocyclic compound, has been actively studied in supramolecular chemistry.<sup>42,43</sup> In this regard, resorcin[4]-arenes are particularly attractive because of their variable



structures adjusted by different functionalized moieties.<sup>44–47</sup> However, studies on the coordination chemistry of the functionalized resorcin[4]arenes as versatile linkers to construct MOFs are limited.<sup>48–51</sup> Particularly, decorating POM into resorcin[4]arene-based MOFs remains almost unknown.<sup>52–55</sup>

Over the past several years, we have performed an investigation on resorcin[4]arene-based metal-organic motifs featuring elegant structures and properties.<sup>56-58</sup> In this work, we designed a newly functionalized wheel-like resorcin[4]arene ligand (L) with eight powerful chelating 2-(2-pyridyl)imidazole substituents (Scheme 1). By utilizing the new resorcin[4]arenefunctionalized L ligand, a new PMOF, [Co<sub>2</sub>L<sub>0.5</sub>V<sub>4</sub>O<sub>12</sub>]·3DMF·  $5H_2O(1)$ , which features a porous architecture with 1D open channels, has been synthesized under solvothermal conditions. To our knowledge, 1 represents an exceedingly rare PMOF composed of both resorcin[4]arene ligand and polyoxovanadate (POV). Most strikingly, the open V sites in the pores make 1 an efficient Lewis acid catalyst for the cycloaddition of CO<sub>2</sub> with epoxides into cyclic carbonates. Remarkably, 1 also exhibits high catalytic activity for the heterogeneous oxidative desulfurization of different sulfides.

#### RESULTS AND DISCUSSION

**Crystal Structure of 1.** Crystals of 1 were synthesized by using  $Co(NO_3)_2 \cdot 6H_2O$ ,  $NH_4VO_3$ , and L under solvothermal conditions. Single-crystal X-ray diffraction analysis reveals that 1 crystallizes in the triclinic system with space group  $P\overline{1}$ . During

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Scheme 1. Synthetic Route for the L Ligand Used in This Work





**Figure 1.** (a) Coordination environments of the Co<sup>II</sup> and V<sup>V</sup> cations in 1. (b) View of the  $[V_4O_{12}]^{4-}$  cycle. (c) Coordination mode of the L ligand. (d) Inorganic–organic hybrid layer structure of 1. (e) View of the porous packing structure of 1. H atoms are omitted for clarity. Symmetry codes: #1, -x + 1, -y + 1, -z; #2, -x + 4, -y + 2, -z + 1; #3, -x + 3, -y + 1, -z + 1.

the refinement, the SQUEEZE routine in PLATON was employed because of the highly disordered solvents.<sup>59</sup> In each unit cell, there exist three free  $N_iN'$ -dimethylformamide (DMF) and five lattice water molecules, established by thermogravimentric analysis (TGA), elemental analysis, and electron diffraction density (Figure S1). As shown in Figure 1a, the asymmetric unit of 1 consists of two unique Co<sup>II</sup> cations (Co1 and Co2), a half of a L ligand, and two halves of a  $[V_4O_{12}]^{4-}$  unit. Each  $Co^{II}$  cation was surrounded by two Oatoms from one  $[V_4O_{12}]^{4-}$  unit and four N atoms from two 2-(2-pyridyl)imidazole groups of the same L ligand in an octahedral geometry. V1 and V2 and their symmetry-related species share corner O atoms to yield a  $[V_4O_{12}]^{4-}$  cycle, as illustrated in Figure 1b. In the  $[V_4O_{12}]^{4-}$  cycle, each V center exhibits a VO4 tetrahedral coordination sphere. As depicted in Figure 1c, every L ligand bridges four Co<sup>II</sup> cations via its eight chelating 2-(2-pyridyl)imidazole moieties to produce a  $[Co_4L]$ secondary building unit (SBU). Further, adjacent [Co<sub>4</sub>L] SBUs are linked by  $[V_4O_{12}]^{4-}$  cycles to result in a charming inorganic-organic hybrid layer with an open channel along the *a* axis (ca. 9.6 Å  $\times$  15.2 Å; Figure 1d). Neighboring hybrid layers are stacked on each other to yield a highly porous supramolecular architecture (Figure 1e). The solvent-accessible volume is about 45.5% of the unit cell volume (5686.0  $Å^3$ ), calculated by the PLATON program.<sup>5</sup>

**Cycloaddition of CO**<sub>2</sub> with Epoxides. Given the high porosity, together with the exposed V sites, the catalytic performance of the Lewis acid catalyst 1 was evaluated for the cycloaddtion of CO<sub>2</sub> with epoxides at 1 and 20 atm, respectively. As shown in Scheme 2, 2-(butoxymethyl)oxirane

## Scheme 2. Schematic Representation of CO<sub>2</sub> Cycloaddition to Epoxides



was first chosen as a model substrate for the  $CO_2$  cycloaddtion to investigate the optimum reaction conditions. During the cycloaddtion of  $CO_2$  with epoxides, the catalytic products were certified by <sup>1</sup>H NMR data (Figures S2–S9), and the conversion of the cyclic carbonate was calculated by gas chromatography (GC; Figures S10 and S11). As illustrated in Table 1, only a

Table 1. Cycloaddition of CO2 with 2-(Butoxymethyl)oxirane at Different Conditions

entry	catalyst 1 (mmol)	<i>n</i> -Bu <sub>4</sub> NBr (mmol)	time (h)	temperature (°C)	$(\%)^b$
1	0.01	0	6	80	trace
2	0	0.25	6	80	47
3	0.01	0.25	6	25	25
4	0.01	0.25	6	50	76
5	0.01	0.25	6	80	>99

<sup>*a*</sup>Reaction conditions: 1 (0.01 mmol based on V), epoxide (5 mmol), and *n*-Bu<sub>4</sub>NBr (0.25 mmol);  $CO_2$  (1 atm). <sup>*b*</sup>Isolated yields were calculated by GC.

trace of the catalytic product was achieved without n-Bu<sub>4</sub>NBr or catalyst 1 at 80 °C and CO<sub>2</sub> pressure of 1 atm (Figure S10a,b). Noticeably, when 1 and n-Bu<sub>4</sub>NBr were employed as cocatalysts, conversion of 2-(butoxymethyl)oxirane was drastically enhanced (Figure S10e, entry 5). With increasing temperatures from 25 to 80 °C, conversion of 2-(butoxymethyl)oxirane increases from 25% to the final >99% after 6 h of catalytic reaction (Figure S10c-e, entries 3-5). On the basis of the above catalytic conditions, the following catalytic experiments were performed with 1 and n-Bu<sub>4</sub>NBr as cocatalysts at 80 °C and 1 atm.

To further explore the catalytic generality of catalyst 1, the substrates were extended to other epoxides under the optimized catalytic conditions. As shown in Table 2, the corresponding conversion of epichlorohydrin can reach 92% after 6 h of the catalytic reaction (entry 1). The substrates 2-(butoxymethyl)oxirane, 1,4-butanediol diglycidyl ether, benzyl glycidyl ether, and glycidyl phenyl ether can be fully converted to the corresponding cyclic carbonates within 6 h (Figures S5, S6, S8, and S9, entries 4, 5, 7, and 8). The much higher catalytic conversions of the substrates mainly account for the electronwithdrawing groups in their structures.<sup>60</sup> In contrast, only 72% of the overall 1,2-epoxyethylbenzene was converted to the catalytic product at the same time (Figure S7). When the reaction time was further prolonged to 12 h, almost all of the substrates were fully converted to the corresponding cyclic carbonates (Figure S11), except the electron-donor 1,2epoxyethylbenzene (Figure S11e, entry 6).

To further investigate the reaction kinetics, the substrates with electron-withdrawing groups, namely, 1,4-butanediol diglycidyl ether, glycidyl phenyl ether, 2-(butoxymethyl)oxirane, and benzyl glycidyl ether, were selected to couple with  $CO_2$  at 1 atm. As shown in Figure 2, the conversions are more than 80% for 1,4-butanediol diglycidyl ether, glycidyl phenyl ether, and 2-(butoxymethyl)oxirane within 2 h, and the conversion of benzyl glycidyl ether is only up to 70% at the same time. Finally, these substrates are almost fully converted to the catalytic product within 6 h.

Moreover, catalyst 1 can be easily separated from the reaction mixture through centrifugation and filtration. The separated samples were washed with dichloromethane, dried in air, and then reused for at least five cycles with catalytic activity without obvious change (Figures 3 and S12). The result demonstrates that catalyst 1 shows good stability and recyclability.<sup>61-63</sup>

We also conduct the high-pressured cycloaddtion of  $CO_2$  to epoxides with 1 as the catalyst in a microreactor at 80 °C and a  $CO_2$  pressure of 20 atm. In the presence of *n*-Bu<sub>4</sub>NBr (1 mmol) and catalyst 1 (0.01 mmol based on V), most of the substrates could be converted to the cyclic carbonates at a high conversion rate of more than 90% after 4 h of catalytic reaction (Table 3 and Figure S14). In particular, conversion of epichlorohydrin and glycidyl phenyl ether can reach 98% with a high turnover number (TON) of 1960 within 4 h (entries 1 and 8). Notably, 1,2-epoxyethylbenzene only can be converted to the cyclic carbonates in a relatively low conversion rate of 80% because of its electron-donor effect (entry 6).<sup>64,65</sup> The results indicate that the catalytic activity and selectivity of catalyst 1 toward the substrates at 20 atm are similar to those demonstrated at 1 atm.

The catalytic reaction dynamic was further explored in the presence of the substrate 1,2-epoxyethylbenzene with 1 (0.01 mmol based on V) and n-Bu<sub>4</sub>NBr (1 mmol) as cocatalysts at 80

Table 2. Syntheses of	Cyclic Carbonates fr	rom CO <sub>2</sub> and Epoxid	les Catalyzed by 1'
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Easter :	Enovidos	Draduota	Time	Yields	Time	Yields
Епиу	Epoxides	Products	(h)	(%)	(h)	(%) <sup>b</sup>
1	CI	CI	6	92	12	99
2	$\sim$		6	82	12	99
3	$\sqrt[n]{2}$	p~~~cl	6	88	12	98
4		~~~~ť	6	99	12	99
5	<sub>₹</sub>	gy-on-off	6	99	12	99
6	C) <sup>&amp;</sup>	O <sup>L</sup>	6	72	12	87
7	Q_o_A	Q	6	99	12	99
8			6	99	12	99

"Reaction conditions: 1 (0.01 mmol based on V), epoxide (5 mmol), and *n*-Bu<sub>4</sub>NBr (0.25 mmol); CO<sub>2</sub> (1 atm), 80 °C, 12 h. <sup>b</sup>Isolated yields were calculated by GC.



Figure 2. Conversion curves of the differently substituted epoxides coupled with  $CO_2$  along with increasing reaction time.

°C and a CO<sub>2</sub> pressure of 20 atm. As shown in Figure 4, conversion of 1,2-epoxyethylbenzene increases with increasing reaction time. Finally, a total conversion of 99% is achieved after 8 h and the TON is close to 2000 (Figures S15 and S14f), which are much higher than those at 1 atm, demonstrating that the high pressure supports the cycloaddition of CO<sub>2</sub> with epoxides to produce cyclic carbonates.<sup>66</sup> This TON for the CO<sub>2</sub> cycloaddition with epoxides is close to the recent values found in the nanotube-based MOF catalyst<sup>67</sup> but is much higher than most of the related heterogeneous MOF catalysts.<sup>68–70</sup> Notably, conversion of 2-(butoxymethyl)oxirane still remains more than 95% after five runs (Figures 5 and S16).



Figure 3. Recycling catalytic experiments with 1 and n-Bu<sub>4</sub>NBr as cocatalysts at a CO<sub>2</sub> pressure of 1 atm.

A possible synergistic catalytic mechanism for the cycloaddition of CO<sub>2</sub> to epoxide was proposed, as shown in Scheme 3. In the initial step, the O atom of the epoxide interacts with the Lewis acid V sites of  $1.^{71,72}$  The epoxide ring was activated and then opened by nucleophilic attack of the Br<sup>-</sup> anion, forming the metal-coordinated bromoalkoxide I.<sup>73</sup> After that, CO<sub>2</sub> coupled with the O atom of the intermediate I to yield the metal carbonate II. Then the O atom of II attacks its C atom to release Br<sup>-</sup>, producing the final cyclic carbonate.<sup>74</sup> It could be deduced that the synergistic effects of the V sites and *n*-Bu<sub>4</sub>NBr as cocatalysts play a crucial role in promoting the catalytic performance effectively.

Table 3. Syntheses of	Cyclic Carbonates fro	m CO <sub>2</sub> and Epoxides	Catalyzed by 1 <sup><i>a</i></sup>
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Entry	Epoxides	Products	Conversion(%) <sup>b</sup>	TON
1		a, L	98	1960
2		~~~l	97	1940
3	$\sqrt[n]{2}$	p~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	93	1860
4			95	1900
5	₹~o~~o~A	growell	91	1820
6			80	1600
7		Quit	92	1840
8	C <sup>a A</sup>	or the	98	1960

"Reaction conditions: epoxide (20 mmol), 1 (0.01 mmol based on V), and n-Bu<sub>4</sub>NBr (1 mmol); CO<sub>2</sub> (20 atm), 80 °C, 4 h. <sup>b</sup>Isolated yields were calculated by GC.



Figure 4. Conversion curve of 1,2-epoxyethylbenzene coupled with  $CO_2$  at different reaction times.

**Catalytic Oxidative Desulfurization.** POMs as environmentally friendly redox catalysts have received considerably attention in recent years.<sup>75–80</sup> Here, the catalytic sulfoxidation reactions were investigated by using 1 as the heterogeneous catalyst.<sup>81</sup> A preliminary investigation on oxidation of the model methyl phenyl sulfide (MBT) was carried out to achieve optimum reaction conditions using 1 as the catalyst (0.002 mmol) and 70% *tert*-butyl hydroperoxide (TBHP) as the oxidant (1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> at 50 °C (Scheme 4). The corresponding oxidized sulfoxide and sulfone products were confirmed by Fourier transform infrared (FT-IR) spectroscopy<sup>82</sup> (Figure S17), and the conversions were detected by highperformance liquid chromatography (HPLC) analysis (Figure



Figure 5. Recycling catalytic experiments with 1 and n-Bu<sub>4</sub>NBr as cocatalysts at a CO<sub>2</sub> pressure of 20 atm.

S18). As illustrated in Table 4, when the reaction was carried out without oxidant, no catalytic products were achieved (Figure S18e, entry 1). Notably, the conversion of MBT is very low when TBHP was replaced by  $H_2O_2$  as the oxidant (Figure S18f, entry 2).<sup>83</sup> Thus, we can deduce that the oxidant TBHP has an important role in the catalytic reaction.<sup>84</sup> Once the reaction was conducted without catalyst 1, conversion only reaches 35% within 4 h (Figure S18g, entry 3). Using 1 as the catalyst and TBHP as the oxidant, conversion of MBT gradually increased from 38% to 99% along with prolonging the reaction time from 1 to 4 h (Figure S18a–d, entries 4–7). Thus, the following catalytic reactions were conducted in the presence of both catalyst 1 and TBHP at 50 °C for 4 h.

Scheme 3. Proposed Catalytic Mechanism for the Cycloaddition of  $CO_2$  to Epoxide Using 1 and *n*-Bu<sub>4</sub>NBr as Cocatalysts



Scheme 4. Schematic Representation of Sulfoxidation Reaction with Catalyst 1 and TBHP



Table 4. Results of Sulfoxidation Reactions Catalyzed by 1 at Different Conditions  $a^{a}$ 

entry	catalyst	oxidant	time (h)	conversion $(\%)^b$
1	1	none	4	trace
2	1	$H_2O_2$	4	trace
3	none	TBHP	4	35
4	1	TBHP	1	38
5	1	TBHP	2	72
6	1	TBHP	3	91
7	1	TBHP	4	99

<sup>*a*</sup>Reaction conditions: substrate (0.4 mmol), **1** (0.002 mmol), TBHP (1 mmol), and  $CH_2Cl_2$  (5 mL). <sup>*b*</sup>Isolated conversions were calculated by HPLC.

To evaluate the catalytic generality of catalyst 1, a series of substrates were selected under the optimized reaction conditions. As shown in Table 5, when diphenyl sulfide was utilized as the substrate, the catalytic oxidation conversion of diphenyl sulfide reaches more than 99% within 4 h (Figure S19a, entry 2). However, for sulfur-containing aromatic substrates such as dibenzothiophene (Figure S19b, entry 3), 4,6-dimethyldibenzothiophene (4,6-DMDBT; Figure S19c, entry 4), and benzothiophene (Figure S19d, entry 5), 93%, 88%, and 75% conversions were achieved after 12 h of catalytic reactions, respectively. The results indicate that the catalytic oxidation of the thiophene substrates is more difficult than that of the sulfur ethers during sulfoxidation reactions.<sup>85–87</sup>

Further, the catalytic reaction dynamics of 4,6-DMDBT were explored at the same conditions. Conversion of 4,6-DMDBT was detected every 2 h (Figures 6 and S20). In the initial reaction, conversions of 4,6-DMDBT was drastically enhanced, reached 76% within 8 h, and then slowly increased from 76% to 88% in the next 4 h. The results demonstrate that the reaction is nearly accomplished at the beginning of 8 h. Although we

have tried to further prolong the reaction time, conversion of 4,6-DMDBT cannot be promoted effectively.

Exploratory experiments on the reusability of 1 were performed using model sulfoxidation of MBT. Conversion of MBT was calculated by GC (Figures S21 and S22). After catalysis, the samples of catalyst 1 were separated from the reaction mixture through centrifugation and filtration. Then the separated catalyst 1 was reused for at least five cycles with good catalytic activity, as shown in Figure 7.

The POM-based MOFs have been widely used for catalytic oxidative desulfurization.<sup>88–93</sup> It is proposed that a peroxyvanadic acid complex was generated in the presence of the oxidant TBHP. Then the sulfur-containing aromatic substrate engages in a nucleophilic attack on the peroxo moiety and achieves one O atom from the active species of the peroxyvanadic acid complex. As a result, the sulfur-containing substrate was oxidized to sulfoxide and sulfone.<sup>94,95</sup>

#### CONCLUSION

In summary, we have synthesized a newly functionalized wheellike resorcin[4]arene ligand, and subsequently it has been utilized for the construction of a 2D POV–resorcin[4]arenebased porous PMOF (1). The resulting 1 represents an exceedingly rare example of PMOFs composed of both resorcin[4]arene and POVs. The constructed PMOF 1 exhibits exposed V sites in the channel and then was exploited as a heterogeneous catalyst for the  $CO_2$ –epoxide coupling reaction and oxidative desulfurization of sulfides with high conversion and selectivity. Significantly, the heterogeneous catalyst 1 can be easily separated and reused with no obvious decrease in the catalytic activity.

#### EXPERIMENTAL SECTION

Materials and Methods. All chemicals were commercially available and were employed without further purification. FT-IR spectra were conducted on a Mattson Alpha Centauri spectrometer. Elemental analyses were recorded on a PerkinElmer 240 CHN elemental analyzer. TGA measurement was carried out on a PerkinElmer model TG-7 analyzer. PXRD patterns were measured on a Rigaku Dmax 2000 X-ray diffractometer with graphitemonochromatized Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm). <sup>1</sup>H NMR spectra were determined on a Varian 500 MHz. The catalytic products for the cycloaddtion of CO2 were determined by GC equipment with a capillary (30 m long × 0.25 mm i.d., WondaCAP 17) and a flame ionization detector (GC-2014C, Shimadzu, Japan). Sulfoxidation products were detected by HPLC with a UV-vis detector at  $\lambda$  = 254 nm using an Inertsil (5  $\mu$ m, 4.6  $\times$  150 mm) ODS C18 column (Agilent-1220). A mass spectrometry (MS) spectrum for L was recorded on a Bruker AutoflexIII Smartbeam matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometer. High-resolution MS spectra for the catalytic products were recorded on a Bruker MicroTOF spectrometer.

**X-ray Crystallography.** Crystallographic data of 1 were collected on an Oxford Diffraction Gemini R CCD diffractometer with graphitemonochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least squares using the *SHELXS-2014* crystallographic software package.<sup>96–98</sup> During the refinement, the *SQUEEZE* function in *PLATON* was applied because of the highly disordered solvents in the channel.<sup>59</sup> All non-H atoms were refined with anisotropic temperature parameters except disordered solvent molecules. The H atoms attached to C atoms were generated geometrically. Crystallographic data are listed in Table S1.

**Synthesis of L.** A mixture of sodium methoxide (19.5 g, 0.36 mol), resorcinol (20.0 g, 0.18 mol), methanol (200 mL), and 1-bromo-3-chloropropane (171.9 g, 1.09 mol) was stirred at 80 °C for 12 h. The

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Entry	Epoxides	Time (h)	Yields (%) <sup>b</sup>
1	€ S S S S S S S S S S S S S S S S S S S	4	>99
2		4	>99
3		12	93
4	L-s-L	12	88
5	$\left( \right) $	12	75

Table 5.	Results	of	Sulfoxidation	Reactions	Catalyzed	l by 1	l Using	TBHP	as the	Oxidant <sup>a</sup>

"Reaction conditions: substrate (0.4 mmol), 1 (0.002 mmol), TBHP (1 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (5 mL). <sup>b</sup>Isolated conversions were calculated by HPLC.



Figure 6. Dynamic conversion curve of 4,6-DMDBT catalyzed by 1.



Figure 7. Recycling experiments of sulfoxidation reactions of MBT using 1 as the catalyst and TBHP as the oxidant.

mixture was then filtered, and the liquor was collected. The solvent and excess 1-bromo-3-chloropropane were removed under reduced pressure to give a yellow oil residue. The product was further washed using NaOH (1 mol  $L^{-1}$ ) and water. The precursor I was achieved in a 64% yield after drying with anhydrous sodium sulfate and evaporation of the solvent (Scheme 1).

Further,  $BF_3 \cdot OEt_2$  (5.68 g, 0.04 mmol) was added dropwise to a mixture of the precursor I (2.76 g, 0.02 mmol), benzaldehyde (5.26 g, 0.02 mol), and anhydrous dichloromethane (200 mL) under an ice bath and then stirred for 48 h at room temperature. The reaction mixture was washed three times with water, and then the organic layer was dried with anhydrous sodium sulfate. The raw product was achieved after the solvent was evaporated. The precursor II was obtained in 53% yield after acetone was added to the raw product (Scheme 1).

A mixture of the precursor II (22.48 g, 0.016 mol), 2-(2pyridyl)imidazole (27.84 g, 0.192 mol), 60% NaH (6.4 g, 0.16 mol), and DMF (100 mL) was stirred for 48 h at 120 °C. After the reaction finished, the solvent was evaporated, and washed with 0.1 M NaOH and water. The milk-white L was achieved in 85% yield. IR data (KBr, cm<sup>-1</sup>): 3434 (w), 2928 (w), 2872 (w), 1609 (w), 1587 (s), 1489 (s), 1463 (s), 1408 (m), 1298 (s), 1192 (s), 1157 (w), 1094 (s), 1034 (m), 792 (m), 744 (m), 706 (s), 623 (w), 593 (w). <sup>1</sup>H NMR (DMSO):  $\delta$ 8.45-8.50 (m, 8H, Ar-H), 7.99-8.08 (m, 8H, Ar-H), 7.78-7.83 (m, 8H, Ar-H), 7.20-7.32 (m, 8H, Ar-H), 6.91-6.98 (m, 16H, N-CH), 6.79-6.81 (S, 4H Ar-H), 6.70-6.78 (m, 8H, Ar-H), 6.63-6.69 (m, 8H, Ar-H), 6.20-6.47 (m, 8H, Ar-H), 5.77-5.78 (m, 4H, CH), 4.25-4.49 (m, 8H, OCH2), 4.08-4.18 (m, 8H, OCH2), 3.33-3.97 (m, 16H, CH<sub>2</sub>N), 1.80-2.08 (m, 16H, CH<sub>2</sub>). MALDI-TOF-MS. Calcd for  $C_{140}H_{128}O_8N_{24}$  ([M – e]<sup>-</sup>): m/z 2274.0. Found: m/z 2274.0 (Figure S23).

**Synthesis of**  $[Co_2L_{0.5}V_4O_{12}]$ **·3DMF·5H**<sub>2</sub>**O (1).** A mixture of NH<sub>4</sub>VO<sub>3</sub> (0.02 g, 17 mmol), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.023 g, 0.8 mmol), L (0.023 g, 0.1 mmol), DMF (4 mL), H<sub>2</sub>O (4 mL), and 1 M HCl (2 drops) was sealed in a 15 mL Teflon reactor and heated at 130 °C for 3 days. The red crystals were achieved in 41% yield. Anal. Calcd for  $C_{79}H_{95}N_{15}O_{24}Co_2V_4$  ( $M_r$  = 1960.32): C, 48.36; H, 4.85; N, 10.71. Found: C, 47.28; H, 4.78; N, 11.45. IR data (KBr, cm<sup>-1</sup>): 3365 (m), 3113 (m), 2929 (m), 2876 (m), 1655 (m), 1604 (s), 1474 (s), 1408 (m), 1379 (w), 1074 (w), 1053 (w), 1040 (w), 789 (s), 417 (w).

**Cycloaddtion of CO<sub>2</sub> to Epoxides at 1 atm.** The cycloaddtion of CO<sub>2</sub> with epoxides was performed in a 10 mL round-bottomed flask at 1 atm. Typically, epoxide (5 mmol), *n*-Bu<sub>4</sub>NBr (80 mg, 0.25 mmol), and catalyst 1 (4.9 mg, 0.0025 mmol) were added to the round-bottomed flask at a CO<sub>2</sub> pressure of 1 atm and then stirred for 12 h at 80 °C. The catalytic products were certified by <sup>1</sup>H NMR data, and the yields were calculated by GC.

**Cycloaddtion of CO<sub>2</sub> to Epoxides at 20 atm.** Catalyst 1 (4.9 mg, 0.0025 mmol), *n*-Bu<sub>4</sub>NBr (322 mg, 1 mmol), and epoxide (20 mmol) were placed in a 25 mL stainless steel high-pressure reactor at a CO<sub>2</sub> pressure of 20 atm and stirred for 4 h at 80 °C. <sup>1</sup>H NMR data were used to certify the catalytic products. The yields of the products were calculated by GC.

**Catalytic Oxidative Desulfurization.** In a typical procedure, catalyst 1 (7.8 mg, 0.004 mmol), TBHP (90 mg, 1 mmol), and MBT (50 mg, 0.4 mmol) were added to  $CH_2Cl_2$  (5 mL) in a round-bottomed flask and heated at 50 °C for 4–12 h with stirring. The products were identified by FT-IR spectroscopy, and the yields were detected by HPLC and GC. All analyses were conducted with the mobile phase of  $CH_3CN$  and  $H_2O$  (9:1) at an operating flow rate of 1 mL min<sup>-1</sup>.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01685.

TGA curve, GC, FT-IR, MALDI-TOF-MS, HPLC, and <sup>1</sup>H NMR spectra, PXRD patterns, and tables (PDF)

#### **Accession Codes**

CCDC 1556497 contains 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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