Supporting Information

POM-based porous supramolecular framework for the efficient sulfide-sulfoxide transformation with low molar O/S ratio

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Section I. Supplementary experimental section

1.1 Materials and instrumentation.

2-(pyridinium-4-yl)-1H-imidazole-4,5-dicarboxylic acid was synthesized based on the literature method,^{1,2} which can be proved by IR spectra. Other reagents and solvents were used as received from commercial suppliers without further purification. 1H NMR spectra were recorded on a Bruker DRX spectrometer operating at 400 MHz. Elemental analyses (H, C and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR spectra were recorded in the range 4000-400 cm⁻¹ on a Nexus Euro FT/IR Spectrophotometer using KBr pellets. The powder X-ray diffraction (PXRD) patterns of the as-prepared products were carried out by using Rigaku Smart Lab X-ray diffractometer with Cu-K α radiation ($\lambda = 0.154$ nm) and 2 θ transforming from 5 to 50°. The X-ray single crystal diffraction of the as-prepared products were collected by Bruker D8 Venture single crystal diffractometer with Mo-K α radiation. Liquid UV-vis spectra were measured from 200 to 800 nm on Techcomp UV1000 spectrophotometer. The products in catalytic experiments were determined by gas chromatography with SE-54 capillary column (Techcomp GC 7900II) and gas chromatography-mass spectroscopy (Trace ISQ).

1.2 X-Ray crystallography.

The crystal data of **1** and **2** were collected at 295(2) K and 150(2) K with graphite monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). The crystal structures were solved and refined by full matrix least-squares methods against F^2 by using SHELXTL-2018 programs.^{3,4} All non-hydrogen atoms were refined with anisotropic temperature parameters. All hydrogen atoms associated with C and N atoms were placed in geometrically idealized positions using a riding model. For compound **1**, the contribution of partial solvent electron densities was removed by the SQUEEZE routine in PLATON program.⁵ Crystallographic data, structure refinements and CCDC reference numbers for **1** and **2** are listed in Table S1.

1.3 Calculations of efficiency of hydrogen peroxide in the sulfoxidation reaction system.

The reaction mixture was vigorously stirred under preset conditions, and was quickly filtered with a syringe filter to remove the catalysts. The residual H_2O_2 concentration of the supernatant was determined by titration with 0.002 M Ce(NH₄)₂(NO₃)₆ solution. The titration indicator, Ferroin (0.025 mol·L⁻¹), was prepared with 1,10-phenanthroline and FeSO₄·7H₂O based on a 3:1 stoichiometric relationship. And according to the color of the mixture solution from nacarat to blue the titration end-point was determined.

• The H₂O₂ utilization efficiency was calculated according to the following formula (Assuming that one mol of oxidant reacts with one mol of substrate):

$$H_2O_2$$
 efficiency (%) = 100 x
mol of H_2O_2 consumed in the formation of sulfoxides
mol of H_2O_2 converted

- <u>Part I:</u> The calculations are shown with oxidation of methyl phenyl sulfide (MPS) to methyl phenyl sulfoxide (MPSO), with catalysts 1 and 2.
 - ♦ For catalyst 1: (i) H₂O₂ (mmol) consumed in the formation of sulfoxide (yield: >99%) from 0.25 mmol sulfides = **0.25 mmol**. (ii) The titrated value was found to be: 0.02304 mmol. Since 0.30 mmol H₂O₂ has been originally used for the reaction. Therefore, total mol of H₂O₂ converted = (0.30-0.02304) mmol = **0.27696 mmol**. Thus, H₂O₂ efficiency = $100 \times [0.25/0.27696] = 90.3\%$.
 - ♦ For catalyst 2: (i) H_2O_2 (mmol) consumed in the formation of sulfoxide (yield: >99%) from 0.25 mmol sulfides = 0.25 mmol. (ii) The titrated value was found to be: 0.02056 mmol. Since 0.30 mmol H_2O_2 has been originally used for the reaction. Therefore, total mol of H_2O_2 converted = (0.30-0.02056) mmol =

0.27944 mmol. Thus, H_2O_2 efficiency = $100 \times [0.25/0.27944] = 89.5\%$

- <u>Part II:</u> The calculations are shown with oxidation of 2-chloroethyl ethyl sulfide (CEES) to 2-chloroethyl ethyl sulfoxide (CEESO), with catalysts 1 and 2.
 - For catalyst 1: (i) H₂O₂ (mmol) consumed in the formation of CEESO (yield: >99%) from 0.25 mmol CEES = 0.25 mmol. (ii) The titrated value was found to be: 0.03552 mmol. Since 0.30 mmol H₂O₂ has been originally used for the reaction. Therefore, total mol of H₂O₂ converted = (0.30-0.03552) mmol = 0.26448 mmol Thus, H₂O₂ efficiency = 100 × [0.25/0.26448] = 94.5%
 - ♦ For catalyst 2: (i) H_2O_2 (mmol) consumed in the formation of CEESO (yield: >99%) from 0.25 mmol CEES = 0.25 mmol. (ii) The titrated value was found to be: 0.03022 mmol. Since 0.30 mmol H_2O_2 has been originally used for the reaction. Therefore, total mol of H_2O_2 converted = (0.30-0.03022) mmol = 0.26978 mmol. Thus, H_2O_2 efficiency = $100 \times [0.25/0.26978] = 92.7\%$.



Scheme S1. Schematic diagram of ligands conversion in-situ.



Fig. S1. Asymmetric unit of compound **1**. Counter cations and hydrogen atoms are omitted for clarity.



Fig. S2. The coordination modes of Zn ions in compound 1.

(a) Zn1, (b) Zn2, (c) Zn3 and (d) Zn4. Symmetry transformations used to generate equivalent atoms: #5: 1/4-y, 3/4+x, -1/4+z.



Fig. S3. The 3D space-filling framework of compound 1.



Fig. S4. Porous framework viewed from different directions in compound **1**. *TOP*: viewed from c-axis. *Bottom left*: viewed from a-axis. *Bottom right*: viewed from b-axis.



Fig. S5. Asymmetric unit of compound **2**. Counter cations and hydrogen atoms are omitted for clarity.



Fig. S6. The coordination modes of Zn ions in compound **2**. (a) Zn1, (b) Zn2, (c) Zn3 and (d) Zn4.



Fig. S7. 2D layer of compound **2**. *TOP*: viewed from c-axis. *Bottom*: viewed from b-axis.



Fig. S8. The 3D space-filling framework of compound 2.

Section III. Supplementary physical characterizations

IR spectra of **1** and **2** are shown in Fig. S9, the signatures of P–O, Mo=O and Mo–O–Mo vibrations of the inorganic skeleton of the ε -Keggin POM are around 1070 cm⁻¹, 965 cm⁻¹, 935 cm⁻¹, 903 cm⁻¹, 815 and 784 cm⁻¹, respectively. Obviously, in the high-wavenumber region (v > 1100 cm⁻¹), the signatures of C=C, C=N, C–H and N–H vibrations of the organic ligand are around 1140–1622 cm⁻¹ and 2870–3571 cm⁻¹.



Fig. S9. IR spectra for **1**, **2**, and Ligands. L: 2-(pyridinium-4-yl)-1H-imidazole-4,5-dicarboxylic acid.

The measured powder X-ray diffraction (PXRD) spectra of 1 and 2 are consistent with the simulated XRD spectra of X-ray structure analysis, indicating that they have good phase purity. (Fig. S10).



Fig. S10. Experimental and simulated powder X-ray diffraction patterns of 1 and 2.



Fig. S11. The UV-vis spectra of MPS oxidation catalyzed by 1 and 2.

(A) the UV-vis spectra of filtrate after reaction for 10-15 min under the optimal conditions without substrate; (B) the UV-vis spectra of pure MPS; (C) the UV-vis spectra of filtrate before reaction; (D) the UV-vis spectra of filtrate after reaction 3 min for 1 and 5 min for 2; (E) the UV-vis spectra of filtrate after reaction 10 min for 1 and 15 min for 2; (F) the UV-vis spectra of pure MPSO.



Fig. S12. Hot filtration and catalytic activity stability experiment of 2 in MPS oxidation. (a) Hot filtration experiment for MPS oxidation over 2. (b) The recycle test of the oxidation of MPS was carried out with the recovered 2. (c) The continuous recycle test for the oxidation of MPS using 2.



Fig. S13. Hot filtration and catalytic activity stability experiment of 1 in CEES oxidation. (a) Hot filtration experiment for CEES oxidation over 1. (b) The recycle test of the oxidation of CEES was carried out with the recovered 1. (c) The continuous recycle test for the oxidation of CEES using 1.



Fig. S14. Hot filtration and catalytic activity stability experiment of 2 in CEES oxidation. (a) Hot filtration experiment for CEES oxidation over 2. (b) The recycle test of the oxidation of CEES was carried out with the recovered 2. (c) The continuous recycle test for the oxidation of CEES using 2.



Fig. S15. The IR spectra and PXRD patterns of fresh and spent 2.



Fig. S16. Kinetic profiles of oxidation of MPS catalyzed by 1 at 50 °C.





(a) The kinetic profiles of the oxidation of MPS catalyzed by compound 1 at 40 °C, 45 °C and 50 °C. (b) The Arrhenius–Eyring plot (lnk = -(Ea/RT) + lnA).



Fig. S18. Kinetic profiles of oxidation of CEES catalyzed by 1 at room temperature.



Fig. S19. Kinetic profiles of oxidation of CEES catalyzed by 2 at room temperature.



Fig. S20. UV-vis spectra of 2 before and after treatment with H_2O_2 .



Fig. S21. Raman spectra of 1 before and after treatment with H_2O_2 .

Section IV. Supplementary tables

	Compound 1	Compound 2
CCDC number	2120945	2120946
Formula	$C_{41}H_{89}Mo_{12}N_8O_{42}PZn_4\\$	$C_{33}H_{56}KMo_{12}N_{10}O_{40}PZn_4\\$
Formula weight	2809.93	2715.70
<i>T</i> (K)	295(2) K	150(2) K
Crystal system	Tetragonal	Monoclinic
Space group	$I4_{I}/a$	$P2_{1}/n$
<i>a</i> (Å)	33.2771(7)	14.2512(4)
<i>b</i> (Å)	33.2771(7)	17.3920(4)
<i>c</i> (Å)	32.1701(11)	26.0369(7)
α (°)	90	90
β (°)	90	96.7360(10)
γ (°)	90	90
$V(Å^3)$	35624.1(19)	6408.9(3)
Ζ	16	4
μ (mm ⁻¹)	2.780	3.920
	-39<=h<=39	-16<=h<=16
Index ranges	-39<=k<=34	-20<=k<=20
	-37<=l<=38	-30<=1<=30
Reflections collected	104422	46781
Independent reflections	15677	11261
R _{int}	0.1029	0.0678
Data/restraints/parameters	15677/50/797	11261/574/911
GOF on F^2	1.036	1.033
$R_1, wR_2 [I > 2\sigma(I)]$	0.0888, 0.1932	0.0405, 0.0946
R_1 , wR_2 (all data)	0.1242, 0.2042	0.0705, 0.1066

 Table S1. Crystal data and structure refinement for 1 and 2.

 $R_{I} = \Sigma ||F_{\rm o}| - |F_{\rm c}|| / \Sigma |F_{\rm o}|. \ wR_{2} = \Sigma [w(F_{\rm o}^{2} - F_{\rm c}2)^{2}] / \Sigma [w(F_{\rm o}^{2})^{2}]^{1/2}$

Cada	Compound 1				Compound 2		
Code	BVS	Selected bond	Bond lengths (Å)	BVS	Selected bond	Bond lengths (Å)	
Mo1	5.29			5.41			
Mo2	5.33	Mo(1)-Mo(12)	2.6324(19)	6.01	Mo(1)-Mo(10)	2.6222(10)	
Mo3	5.27			6.12			
Mo4	6.02			5.33			
Mo5	5.22	Mo(2)-Mo(6)	2.639(2)	5.20	Mo(2)-Mo(8)	3.1814(9)	
Mo6	5.45			6.04			
Mo7	6.18			5.37			
Mo8	6.06	Mo(3)-Mo(11)	2.6368(19)	6.04	Mo(3)-Mo(6)	3.1949(9)	
Mo9	5.33			5.31			
Mo10	6.12			5.28			
Mo11	5.42	Mo(4)-Mo(10)	3.1817(18)	5.24	Mo(4)-Mo(5)	2.6361(11)	
Mo12	5.38			5.25			
P1	4.70			4.78			
Zn1	2.02	Mo(5)-Mo(9)	2.629(2)	2.00	Mo(7)-Mo(12)	2.6238(11)	
Zn2	2.03			1.98			
Zn3	2.03	Mo(7)-Mo(8)	3 174(2)	1.98	$M_{0}(9)-M_{0}(10)$	2 6077(10)	
Zn4	2.00	1410(7)-1410(8)	5.1/4(2)	1.97		2.0077(10)	

Table S2. The BVS calculations of Mo, P and Zn and selected bonds for 1 and 2.

Table S3. The molecular sizes of MPS, CEES, and their oxidation products^a.



^aThese molecular sizes are calculated based on the Corey-Pauling-Koltun (CPK) model.

catal.	oxid.	O/S^a	temp. (°C)	time (min)	conv. (%)	sel. (%) ^c	TOF $(h^{-1})^b$	ref.
Catalyst 1	H_2O_2	1.2	50	10	>99	>99	1200	c
Catalyst 2	H_2O_2	1.2	50	15	>99	>99	800	c
Mo ₁₃₂	H_2O_2	2	rt	45	100	100	13333.3	6
Mo ₁₃₂	H_2O_2	2	rt	45	100	100^{d}	666.7	6
Cu ₈ (Mo ₈) ₂	TBHP	1.6	50	30	99	99	198	7
Tb ₃ (Mo ₈) ₂	H_2O_2	2	50	60	100	99.7 ^d	277.8	8
(Zn ₄ PMo ₁₂) ₂	H_2O_2	1.08	50	30	>99	>99	400	9
Cu ₆ PMo ₁₂	TBHP	3.75	40	180	99	100	25.9	10
Co(PMo ₆) ₂	H_2O_2	1.2	rt	20	99.5	98	298.5	11
Mn(PMo ₆) ₂	H_2O_2	1.2	rt	20	96.3	97.1	288.9	11
Ni(PM0 ₆) ₂	H_2O_2	1.2	rt	20	98.3	97.6	294.9	11
Zn(PMo ₆) ₂	H_2O_2	1.2	rt	20	97.3	97.4	291.9	11
CuTeMo ₆	TBHP	1.1	40	60	97	99	1616.7	12
Cu ₃ Co ₂ Mo ₁₀	TBHP	2	40	240	99	100	16.5	13
$Cu_2Co_2Mo_{10}$	TBHP	2	40	240	98.4	95.2	16.4	13
$Cu_3(Co_2Mo_{10})_2$	TBHP	2	40	240	94.8	95.1	15.8	13
Cu(Co ₂ Mo ₁₀) ₂	TBHP	2	40	240	96.7	96.3	16.1	13
(Ti ₇ SbW ₉) ₂	H_2O_2	2.8	50	60	100	100^{d}	1000	14
Zr ₂₄ Ge ₆ W ₅₆	H_2O_2	3	60	60	99	16	99	15
$Zr_8B_2Si_4W_{40}$	H_2O_2	3	80	180	86	78^d	57.3	16
$Zr_4P_5Sb_6W_{26}$	H_2O_2	2.4	45	60	100	100^{d}	1000	17
AsNi ₁₆ Si ₄ W ₃₆	H_2O_2	5	70	120	100	100^{d}	250	18
Ce ₂ Se ₃ W ₃₁	H_2O_2	3	40	60	100	100^{d}	500	19
Nd ₄ Se ₄ W ₃₆	H_2O_2	3	35	10	100	100 ^c	3000	20
$Ru_3As_4W_{42}$	H_2O_2	1.2	40	60	95.1	99	317	21
$Ru_3As_2W_{21}$	H_2O_2	1.2	40	60	68.2	99	227.3	21
$Ru_2As_4W_{40}$	H_2O_2	2.5	50	60	97.4	87	608.8	22
Ru ₂ As ₄ W ₄₀	H ₂ O ₂	2.5	50	60	100	100 ^d	625	22
V ^{IV} ₈	TBHP	33	40	240	100		2.8	23
V ^{IV} ₈	TBHP	0.67	rt	480	90	97.8	33.8	24
V ^V ₁₇ V ^{IV} ₁₂	TBHP	2	rt	60	98	91	326.7	25
CoV ₂	TBHP	1.5	50	15	98	98	653.3	26
NiV ₂	TBHP	1.5	50	15	100	99	666.7	26
CuV ₂	H_2O_2	1.1	40	240	98.7	100	7.3	27
NiV ₄	H_2O_2	2.5	40	60	100	100^{d}	20	28
MnV ₁₀	H_2O_2	1.2	50	240	97.5	98.5	7.6	29
Co ₂ V ₄	TBHP	2.5	50	240	99	100	49.5	30
Ni_2V_4	H_2O_2	1.2	45	240	96.8	98.7	6.9	31
Cu_2V_4	H_2O_2	1.2	45	240	98.8	96.5	7.1	31
Co ₄ V ₈	H_2O_2	1.2	45	240	98.2	96.8	7.0	31
Se ₄ V ₁₀	TBHP	3	rt	60	53.8	100	269	32
NiSe ₈ V ₂₀	TBHP	3	rt	60	96.4	100	482	33
$Mn_4Se_8V_{20}$	TBHP	3	rt	60	96.3	100	481.5	32
								18

 Table S4. Summary of the MPS oxidation over different catalyst systems.

C04Se8V20	TBHP	3	rt	60	98.9	100	494.5	32
$Zn_4Se_8V_{20}$	TBHP	3	rt	60	97.9	100	489.5	32
Mn ₆ Se ₈ V ₂₀	TBHP	3	rt	60	96.2	97.8	481	34
Co ₆ Se ₈ V ₂₀	TBHP	3	rt	60	98.8	97.9	494	34
$Zn_6Se_8V_{20}$	TBHP	3	rt	60	96.5	97.8	482.5	34

 ${}^{a}O/S =$ the molar ratio of oxidant to substrate. ${}^{b}Selectivity$ to MPSO. ${}^{c}Turnover$ frequency (TOF) = (mol of MPS consumed)/(mol of the catalyst used × reaction time). ${}^{c}This$ work. ${}^{d}Selectivity$ to MPSO₂.

entry	solvent	con. (%) ^{<i>b</i>}	sel. (%) ^c	TOF $(h^{-1})^d$	TOF (h ⁻¹) ^e
1	МеОН	>99	>99	1200	1200
2	EtOH	94.2	97.0	1130.4	1096.5
3	i-PrOH	90.0	>99	1080	1080
4	n-BuOH	96.0	96.3	1152	1109.4
5	Cyclohexanol	>99	96.1	1200	1153.2
6	Acetone	85.0	>99	1020	1020
7	MeCN	86.5	98.0	1038	1017.2
8	DMF	45.7	>99	548.4	548.4
9	DMSO	37.2	>99	446.4	446.4

Table S5. The effect of solvent on MPS oxidation catalyzed by compound 1^a.

^{*a*}Reaction conditions: 0.25 mmol of MPS, 0.5 mol% of compound **1**, 1.2 equivalents of H_2O_2 , 0.5 mL of solvent, 50 °C, 10 min. ^{*b*}Results determined by GC using naphthalene as internal standard. ^{*c*}Selectivity to MPSO. ^{*d*}Turnover frequency (TOF) = (mol of MPS consumed)/(mol of the catalyst used × reaction time). ^{*e*}Turnover frequency (TOF) = (mol of MPSO generated)/(mol of the catalyst used × reaction time).

	$k (\mathrm{min}^{-1})$			$E_{\rm a}$	ΔH^{\neq}	ΔS^{\neq}
	40 °C	45 °C	50 °C	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$	$(J \cdot mol^{-1} \cdot K^{-1})$
1	0.1294	0.2160	0.4493	95.16	92.47	6.56
2	0.0901	0.1514	0.2981	100.64	97.95	20.09

Table S6. Formula required for kinetic study.

^{*a*}All results are based on the first-order kinetic simulation curve. Except for the rate constant (*k*), the calculation of other parameters is based on the optimal conditions. The meaning of some variables and constants in the following formulas (the unit or constant value are listed in parentheses). c_0 : the initial TMP concentrations (mol·L⁻¹). c_t : the TMP concentration at the specified time (mol·L⁻¹). k_t : rate constant (min⁻¹). E_a : activation energy (kJ·mol⁻¹). *R*: gas constant (8.314 J·mol⁻¹·K⁻¹). *T*: reaction temperature (K). *A*: preexponential factor. ΔH^{\neq} : activation enthalpy (kJ·mol⁻¹). ΔS^{\neq} : activation entropy (J·mol⁻¹·K⁻¹). k_B : Boltzmann constant (1.38 × 10⁻²³ J·K⁻¹). *h*: Planck constant (6.62 × 10⁻³⁴ J·s = 1.10 × 10⁻³⁵ J·min). c° : substrate concentration (mol·L⁻¹). *n*: order of reaction.

$$ln(\frac{C_{\rm t}}{C_0}) = -kt$$
 Eq. S1

$$lnk = -\frac{E_a}{RT} + lnA$$
 Eq. S2

$$\triangle H^{\neq} = E_{a} - RT \qquad \qquad \text{Eq. S3}$$

$$k = -\frac{k_{\rm a}T}{h} (c^{\Theta})^{1-n} exp\left[-\frac{\bigtriangleup r^{\neq} H_m(c^{\Theta})}{RT}\right] exp\left[-\frac{\bigtriangleup r^{\neq} S_m(c^{\Theta})}{R}\right] \quad \text{Eq. S4}$$

 Table S7. Characterization of partially oxidation products catalyzed by compound 1.

products	m/z	¹ H NMR (ppm) ^a
methyl phenyl sulfoxide	140(M ⁺), 125, 109, 97, 77, 65, 51	2.64 (s, 3H), 7.49 (m, 2h), 7.53 (m, 1H), 7.54 (d, 2H)
methyl <i>p</i> -tolyl sulfoxide	154(M ⁺), 139, 123, 91, 77, 65, 51, 49, 35	2.43 (s, 3H), 2.61 (s, 3H), 7.30 (d, 2H), 7.44 (d, 2H)
4-methoxyphenyl methyl sulfoxide	170(M ⁺), 155, 139, 123, 110, 96, 77, 63	2.66 (s, 3H), 3.82 (s, 3H), 6.99 (d, 2H), 7.56 (d, 2H)
4-bromophenyl methyl sulfoxide	220(HM ⁺), 218, 205, 203, 175, 155, 139, 108, 96	2.67 (s, 3H), 7.48 (d, 2H), 7.62 (d, 2H)
2-pyridyl methyl sulfoxide	141(M ⁺), 124, 93, 78, 51	2.99 (s, 3H), 7.66 (m, 1H), 7.66 (m, 1H), 8.10 (m, 1H), 8.64 (q, 1H)
3-methanesulfinyl-2-methylfuran	144(M ⁺), 116, 85, 59, 45	2.30 (s, 3H), 2.52 (s, 3H), 6.42 (d, 1H), 7.58 (d, 1H)
(phenylsulfinyl)cyclopropane	166(M ⁺), 125, 117, 97, 78, 62	0.81-1.06 (m, 2H), 1.27 (m, 2H), 7.53 (m, 1H), 7.49 (m, 2H), 7.54 (m, 2H)
phenyl sulfoxide	202(M ⁺), 186, 185, 173, 154, 141, 125, 109, 97, 77, 65, 51, 39	7.64 (m, 4H), 7.49 (m, 6H)
dibutyl sulfoxide	162(M ⁺), 146, 106. 88, 61, 56, 41, 29	0.89 (t, 6H), 1.30 (m, 4H), 1.39 (m, 4H), 2.55 (t, 4H)
2-chloroethyl ethyl sulfoxide	124(M ⁺), 75, 61, 47, 29	1.16 (t, 3H), 2.61 (q, 2H), 2.85 (t, 2H), 3.72 (t, 2H)

^{*a*}400 MHz and DMSO as solvent.

Section V. References

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