Supplementary Information (SI) for New Journal of Chemistry.

Supporting Information

Synthesis and sulfide oxidation catalytic activity of copper monosubstituted Keggin-type polyoxometalate-based supramolecular compound

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1. Materials and Instrumentations.

Materials and Instrumentations. Except for $K_5PW_{11}Cu(H_2O)O_{39}$, which is synthesized according to literature,[1] all experimental reagents are purchased commercially, and the purity is analytical pure and not further purified; the water used is distilled. Powder X-ray diffraction (PXRD) measurements were performed on a Smartlab instrument with Cu Ka radiation (λ = 1.5418 Å, 2θ = 5°-50°, scan rate = 10° min^{-1}). Fourier transform infrared (FT-IR) spectra were collected on an Agilent Technologies Cary 630FT-IR spectrophotometer in the range 400–4000 cm^{-1}. Thermal gravimetric analysis (TGA) was conducted on a TGA 5500 of TA instruments under a nitrogen atmosphere with a heating rate of 10 ºC min^{-1} to 800 ºC. ^{1}H-NMR spectra were recorded on a Bruker Advance 600 (1H: 600 MHz) at ambient temperature. The reactant conversion and product selectivity were monitored by Agilent GC-7820A gas chromatograph. Single-crystal X-ray diffraction (SCXRD) data of compound **1** was collected on the Bruker diffractometer with Mo Kα radiation (λ=0.071073 nm) at 293 K. Crystal data and structure refinement are summarized in Table S1. The CCDC number for **1** is 2395457, it can be obtained free of charge from The Cambridge Crystallographic Data Centre.

2. Supplemental Figures and Tables

Table S1 Crystallographic data and structure refinement of **1**.

Compound	**1**
Empirical formula	$C_{144}H_{108}Cu_{10}N_{24}O_{166}P_4W_{44}$
Formula weight	13681.62
Temperature (K)	293(2)
Crystal system	triclinic
Space group	P-1
a(Å)	11.7259(6)
b(Å)	22.3057(12)
c(Å)	23.4333(13)
α(°)	94.292(5)
β(°)	96.418(5)
γ(°)	98.299(5)
Volume (Å^3)	6001.0(6)
Z, ρ_{calc} (g/cm^3)	1, 3.786
Radiation	Mo Kα (λ = 0.71073)
F (000)	6075.0
2θ range (°)	6.676 to 50
index range	$-13 \leq h \leq 9$ $-24 \leq k \leq 26$ $-27 \leq l \leq 23$
Reflections collected / unique	36977/20284 [Rint =0.0730]
Data / restraints / parameters	20284/2403/1794
Goodness-of-fit on F^2	0.900
R_1, wR_2 [$I > 2\sigma(I)$]	0.0551, 0.0794
R_1, wR_2 [all data]	0.1075, 0.1011
Largest diff. peak and hole (e Å^{-3})	2.40/-1.81

$R_1 = \sum||F_o|-|F_c||/ \sum|F_o|$. $wR_2 = [\sum[w (Fo^2-Fc^2)^2] / \sum[w (Fo^2)^2]]^{1/2}$

Table S2 Selected bond lengths and angles for **1**.

Bond Lengths (Å) and Angles (º)			
Cu1-N9	1.936(5)	Cu2-N3	2.012(4)
Cu1-N10	1.991(4)	Cu2-N4	1.912(4)
Cu1-N11	1.999(5)	Cu3-N5	1.968(5)
Cu1-N12	1.945(5)	Cu3-N6	1.934(5)
Cu2-N1	1.941(4)	Cu3-N7	1.979(5)
Cu2-N2	2.026(5)	Cu3-N8	2.047(5)
Cu2-O3	2.095(13)	Cu3-O43	2.415(12)
N4-Cu2-N3	83.36(14)	N9-Cu1-N12	155.4(3)
N4-Cu2-N2	98.0(2)	N9-Cu1-N11	102.6(2)
N4-Cu2-O3	92.1(5)	N9-Cu1-N10	83.31(17)
N4-Cu2-N1	177.8(2)	N5-Cu3-O43	78.8(4)
N3-Cu2-N2	122.9(2)	N5-Cu3-N8	101.63(16)
N3-Cu2-O3	131.2(6)	N5-Cu3-N7	161.4(3)
N2-Cu2-O3	105.9(6)	N8-Cu3-O43	117.1(4)
N1-Cu2-N3	94.6(2)	N7-Cu3-O43	82.8(3)
N1-Cu2-N2	82.39(17)	N7-Cu3-N8	84.32(15)
N1-Cu2-O3	89.8(5)	N6-Cu3-O43	89.6(4)
N12-Cu1-N11	84.65(15)	N6-Cu3-N5	82.26(16)
N12-Cu1-N10	101.3(2)	N6-Cu3-N8	153.4(3)
N10-Cu1-N11	152.2(3)	N6-Cu3-N7	100.4(2)

Table S3 Selected hydrogen bond lengths (Å) and bond angles (°) of compound **1**.

Donor-H···Acceptor	D-H/Å	H···A/Å	D···A/Å	D-H···A/º
C38-H38···O52	0.9308	2.6220	3.4770(134)	152.990
C62-H62···O11	0.9301	2.6646	3.0570(15)	106.161
C46-H46···O17	0.9300	2.6540	3.4896(151)	149.853

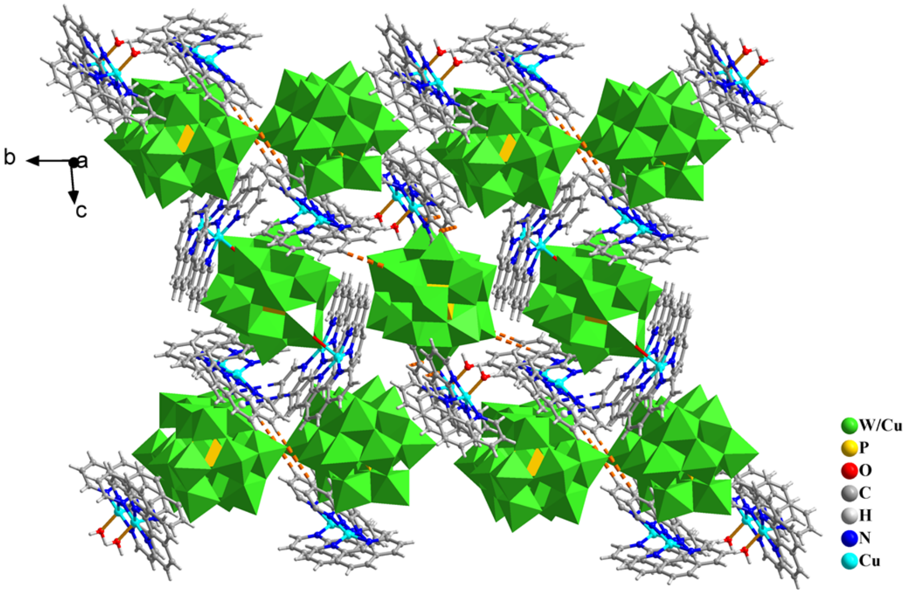

Fig. S1 The 3D supramolecular stacking structure of compound **1**.

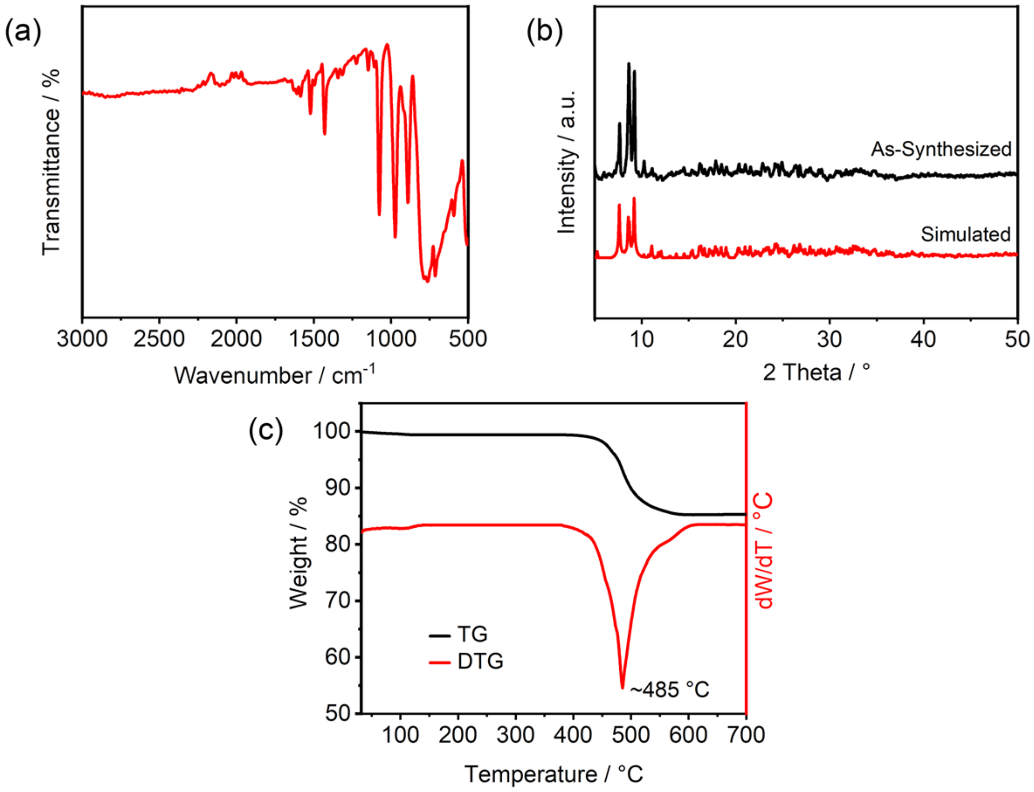

Fig. S2 (a) The FT-IR spectrum of **1**. (b) The PXRD patterns of **1**. (c) The TG-DTG curves of **1**.

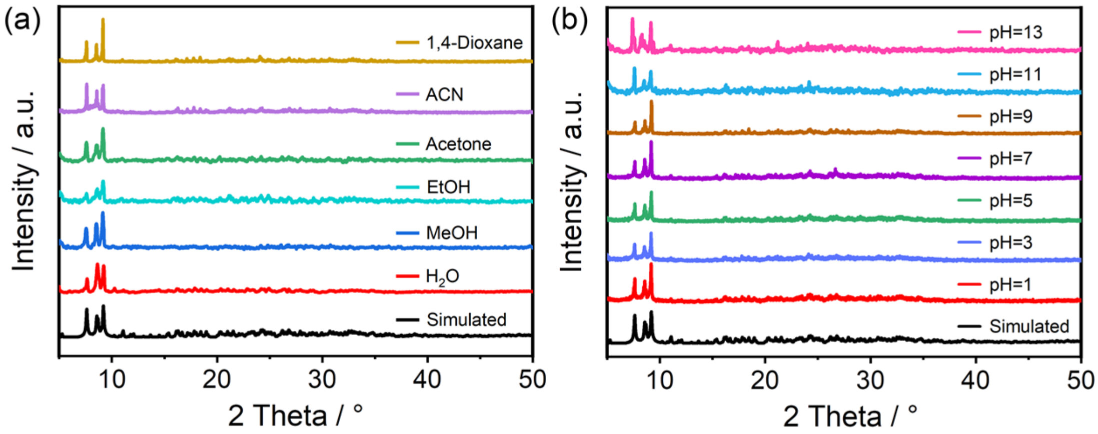

Fig. S3 (a) PXRD patterns of **1** in different organic solvents for 3 days and (b) different pH values aqueous solutions for 24 h.

Table S4 Redox potentials of oxidizing agents and sulfides.

Entry	electric pair	E^θ/V
1	O_2/H_2O	1.229
2	H_2O_2/H_2O	1.776
3	MPS/MPSO	1.52
4	RSH/RSSR	0.15

E^θ is the redox potential of the oxidizer and sulfide relative to the standard hydrogen electrode.[2]

Table S5 The performance of different catalytic system in the oxidation of MPS.

Entry	Catalyst	Conv.(%)	Sel.(%)
1	**1**	>99	96
2	—	42	73
3	phen	46	75
4	$K_5PW_{11}Cu(H_2O)O_{39}$	90	87
5	$H_3PW_{12}O_{40}$	84	45
6	$Cu(NO_3)_2$	75	88
7	$Cu(NO_3)_2$ with IPA	44	—
8	$Cu(NO_3)_2$+phen+$K_5PW_{11}Cu(H_2O)O_{39}$	92	89

Reaction conditions: MPS (0.2 mmol)，30 % H_2O_2 (0.6 mmol)，MeOH (2 mL)，catalyst (2.5 mol%)，50°C，2h.

Table S6 Effect of Radical Scavengers on the Oxidation of MPS Catalyzed by **1**.

Radical scavengers	Time(h)	Conv.(%)
—	2	>99
p-BQ ($\cdot O_2$- /$\cdot O_2H$)	2	98
IPA($\cdot$OH)	2	97.5

Reaction conditions: MPS (0.2 mmol), H_2O_2 (0.6 mmol), **1** (2.5 mol%), radical scavengers (0.2 mmol), MeOH (2 mL), 50°C.

Table S7 The performance of different catalytic system in the oxidation of mercaptan.

Entry	Catalyst	Conv.(%)
1	-	<2
2	**1**	>99
3	$Cu(NO_3)_2$	60
4	$H_3PW_{12}O_{40}$	6
5	$K_5PW_{11}Cu(H_2O)O_{39}$	56
6	phen	<1
7	$K_5PW_{11}Cu(H_2O)O_{39}$+$Cu(NO_3)_2$	71

Reaction conditions: 2-hydroxy-1-ethanethiol (0.2 mmol), O_2, ACN (3 mL), Catalyst (4 mol%), 50 °C, 6 h.

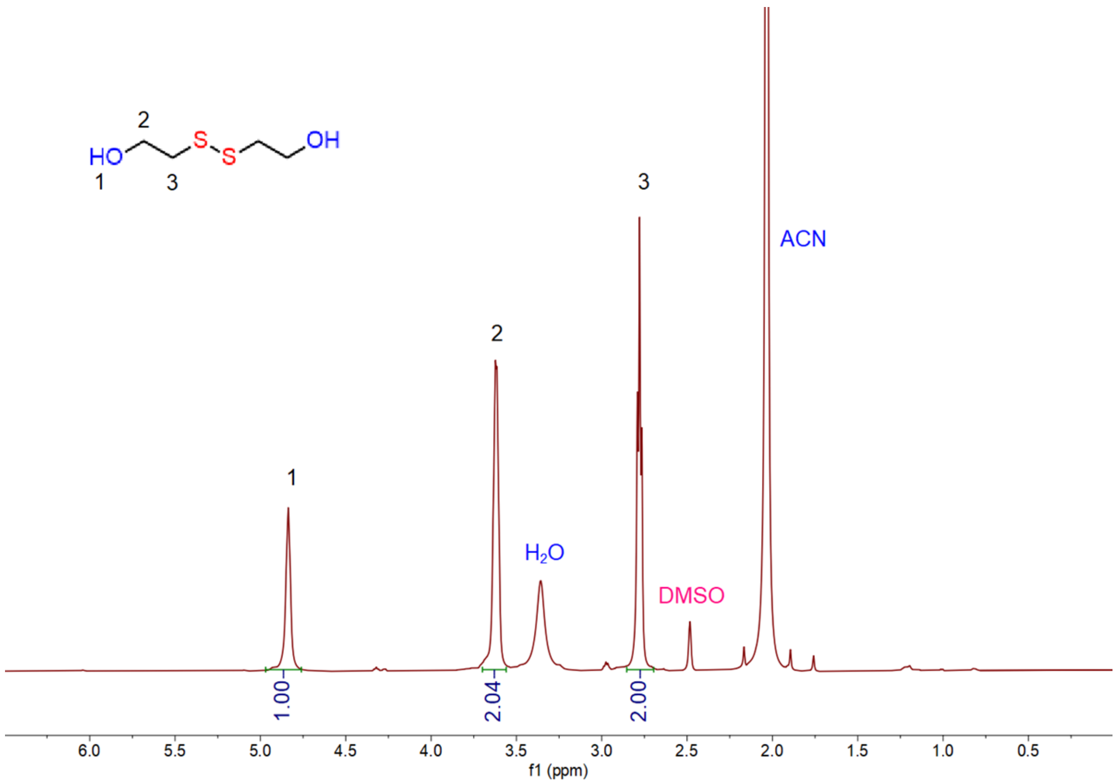

Fig. S4 ^{1}H-NMR spectra of 2-hydroxyethyl disulfide, the oxidation product of 2-hydroxy-1-ethanethiol.

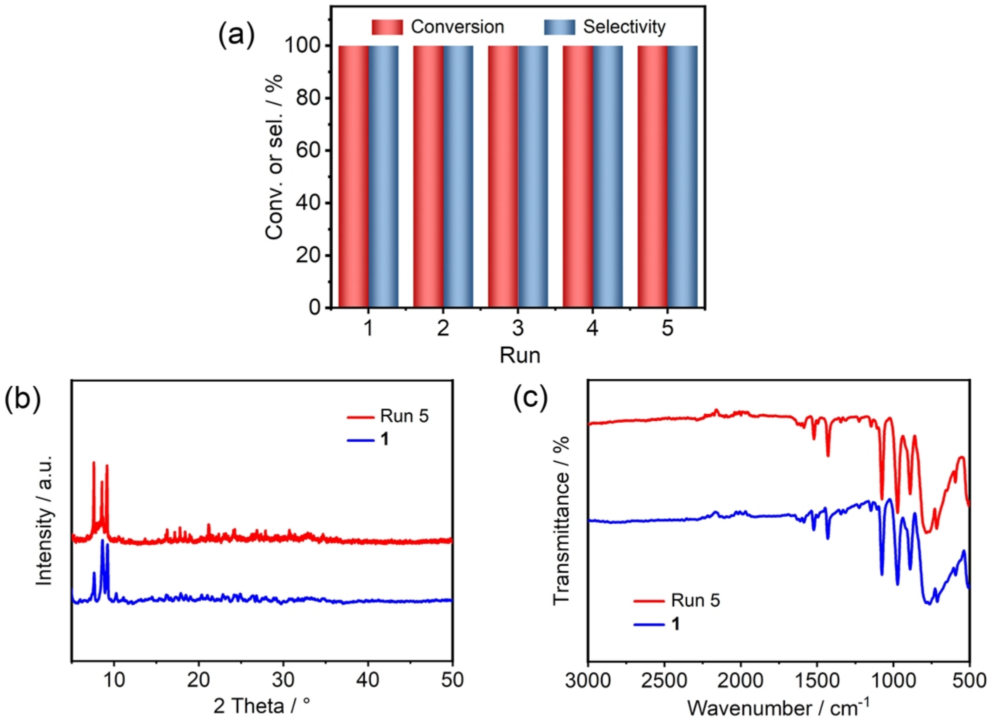

Fig. S5 (a) Cyclic experiments of mercaptan oxidation catalyzed by **1**. (b) PXRD pattern of **1** before and after cycling. (c) FT-IR spectra of **1** before and after cycling.

Reference

1. C. M. Tourné, G. F. Tourné, S. A. Malik and T. J. R. Weakley, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3875-3890.
2. R. D. Gall, M. Faraj and C. L. Hill, *Inorg. Chem.*, 1994, **33**, 5015-5021.