Supporting Information

Two novel supramolecular structures of Evans-Showell type polyoxometalate for heterogeneous and efficient catalytic conversion of different sulfides

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CONTENTS

Section I. Supplementary Experimental Section

1.1 Material Preparation

$(NH_4)_6[Co_2Mo_{10}H_4O_{38}]\cdot 7H_2O$ was synthesized based on the literature method with slight modifications,[1] of which structure was also confirmed by FT-IR spectroscopy experiments. FT-IR(KBr pellet, cm^{-1}): 1612(m), 1401(vs), 939(vs), 908(vs) , 847(s), 735(s), 689(s), 631(s), 521(m).

$[Co(bpy)_3]_2[Co_2Mo_{10}O_{38}H_4]\cdot 6H_2O$ (**1**)

In a typical synthetic procedure, $CoCl_2\cdot 6H_2O$ (0.6mmol, 143mg) and polyoxometalate precursor (~0.1mmol, 200mg) were dissolved in 5 ml deionized water, respectively. They were mixed after thorough stirring and 2,2'-bipyridine (0.2mmol, 32mg) was added to the resulting solution. After stirring for 5 hours, the pH of the solution was adjusted to 3.0 using 1M HNO_3 and 2M KOH. The solution was kept stirring for another hour and the pH was finely adjusted to ensure consistency with expectation. The suspension was transferred to Teflon-lined hydrothermal synthesis reactor and heated at 85°C for 4 days. After 48 hours of natural cooling, the resulting product was washed thoroughly in the ultrasonic cleaner sequentially with water and ethanol to obtain green crystals in flakes.

$C_{60}H_{64}N_{12}Co_4Mo_{10}O_{44}$(2852.33) , Found (Calcd)%: C, 24.98 (25.27); H, 2.19 (2.26); N, 5.27 (5.89).

FT-IR(KBr Pellet, cm^{-1}): 1638(m), 1604(s), 1568(w), 1500(m), 1467(m), 1449(s), 1317(m), 1246(m), 1178(w), 1076(w), 1037(m), 939(vs), 912(vs), 855(vs), 769(vs), 723(s), 687(vs), 522(s).

$[Cu_3(bpy)_3(H_2O)_6][Co_2Mo_{10}O_{38}H_4]\cdot 5H_2O$ (**2**)

The synthesis path for the hybrid with copper as a bridging atom is similar to that of cobalt, except that $CoCl_2\cdot 6H_2O$ is replaced by $CuCl_2\cdot 2H_2O$ (0.2mmol, 34mg). The amount of polyoxometalate precursor is 0.1 mmol while the amount of ligand is twice as much. The green crystals in flakes were obtained optimized quality under pH=2.5.

$C_{30}H_{50}N_6Cu_3Co_2Mo_{10}O_{49}$ (2546.63), Found (Calcd)%: C, 14.20 (14.15); H, 1.89 (1.98); N, 3.21 (3.30).

FT-IR(KBr Pellet, cm^{-1}): 1600(m), 1566(w), 1495(w), 1472(m), 1442(m), 1315(w), 1247(w), 1157(w), 1023(w), 947(vs), 909(vs), 859(s), 772(s), 728(s), 690(s), 523(s).

One can easily notice that the ratio of copper or cobalt hydrate in the precursors to the other raw materials is not equal when obtaining the best quality crystals in the synthesis of above-mentioned compounds. Some parallel experiments have demonstrated that copper hydrate is indeed needed in much smaller amounts to obtain high-quality crystals and excess amount leads to massive growth of cracks on the crystal surface. For compound **1**, when the amount of cobalt hydrate was reduced, the size of the crystal became so small that it was very unfavorable to collect diffraction test data.

1.2 Characterization

The X-ray single crystal diffraction were collected by Bruker D8 Venture single crystal diffractometer with Mo-Kα radiation. 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 Bruker D8 Advanced X-ray diffractometer with Cu-Kα radiation ($\lambda = 0.154$ nm) and 2θ transforming from 5 to 50°. The EDS were determined using a JSM-7610F Plus scanning electron microscope at an accelerating voltage of 10 kV. Energy-dispersive spectroscopy (EDS) mapping was employed to examine the element mapping of compounds **1** & **2**. Elemental analyses (H, C and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer; Liquid UV-vis spectrum was measured from 200 to 400 nm on Techcomp UV1000 spectrophotometer. The products in catalytic experiments were detected by gas chromatography with SE-54 capillary column (Techcomp GC 7900II) and gas chromatography-mass spectroscopy (Trace ISQ). The thermal weight loss curves of the two compounds were recorded by TA Q500 thermogravimetric analyzer.

1.3 X-Ray Crystallography

The crystal data of **1** and **2** were collected at 193 K or 302 K with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å). The crystal structures were solved and refined by full matrix least-squares methods against F^2 by using SHELXTL programs.[2] 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. Crystallographic data, structure refinements and CCDC reference numbers for **1** and **2** are listed in Table S1.

Section II. Structures and Characterization

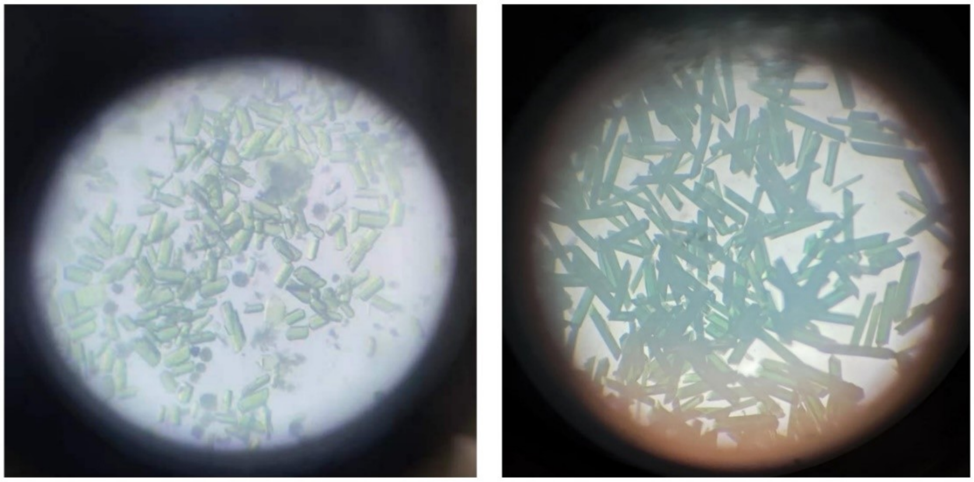

Fig. S1 The crystal photos of compound **1** (left) and compound **2** (right) under the microscope.

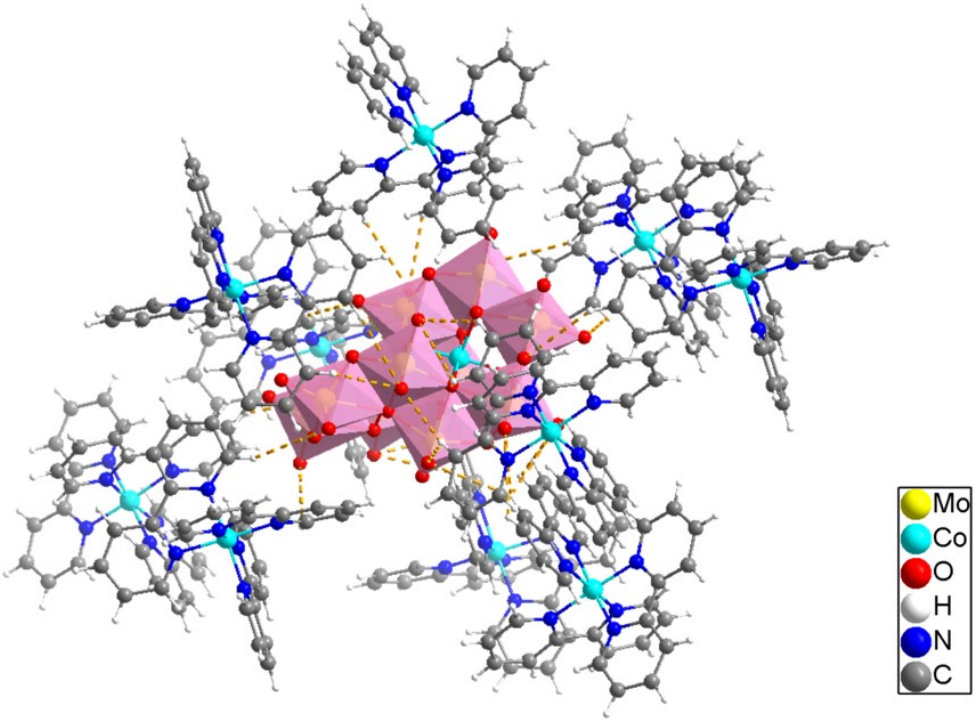

Fig. S2 The C−H···O hydrogen bonds between $[Co(bpy)_3]^{3+}$ and $[Co_2Mo_{10}O_{38}H_4]^{6-}$ in compound **1**.

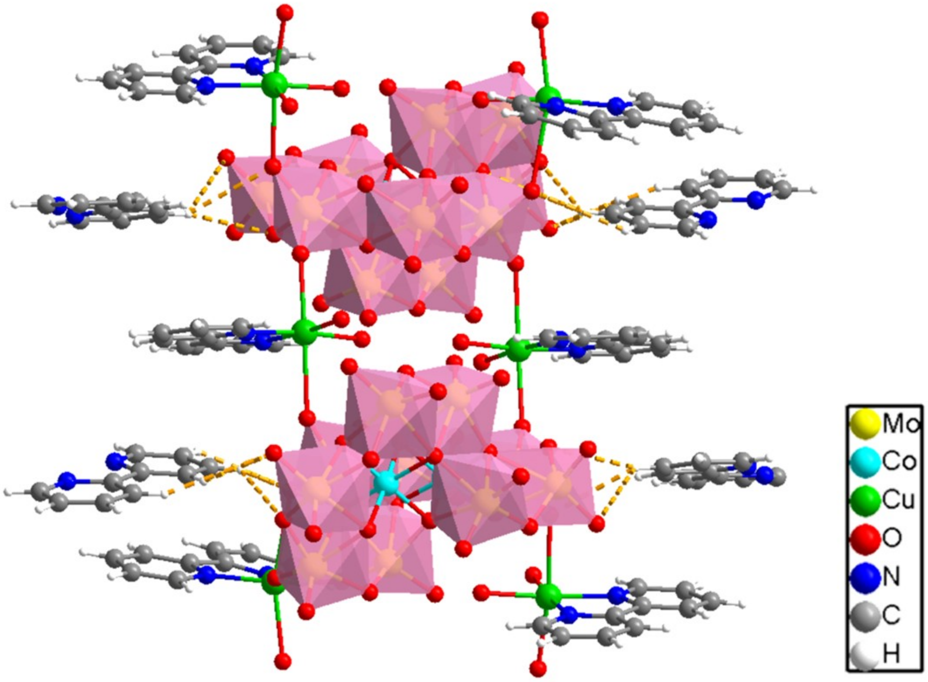

Fig. S3 The C−H···O hydrogen bonds between $[Cu(bpy)]^{2+}$ and $[Co_2Mo_{10}O_{38}H_4]^{6-}$ in compound **2**.

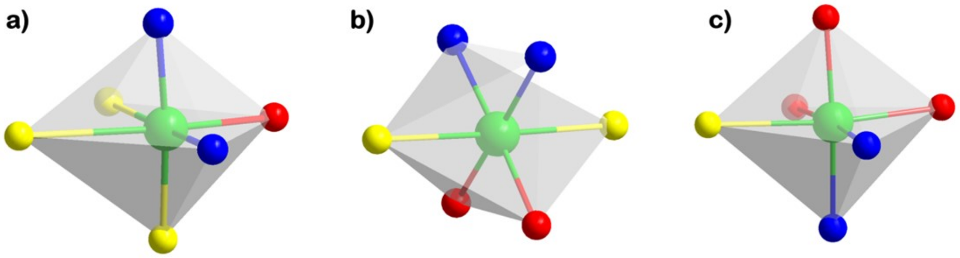

Fig. S4 The respective coordination spheres of different Cu atoms in **2**. (a) Cu1. (b) Cu2. (c) Cu3. green: Cu atom, blue: N atom on ligand, red: O atom on water, yellow: O atom on POM skeleton.

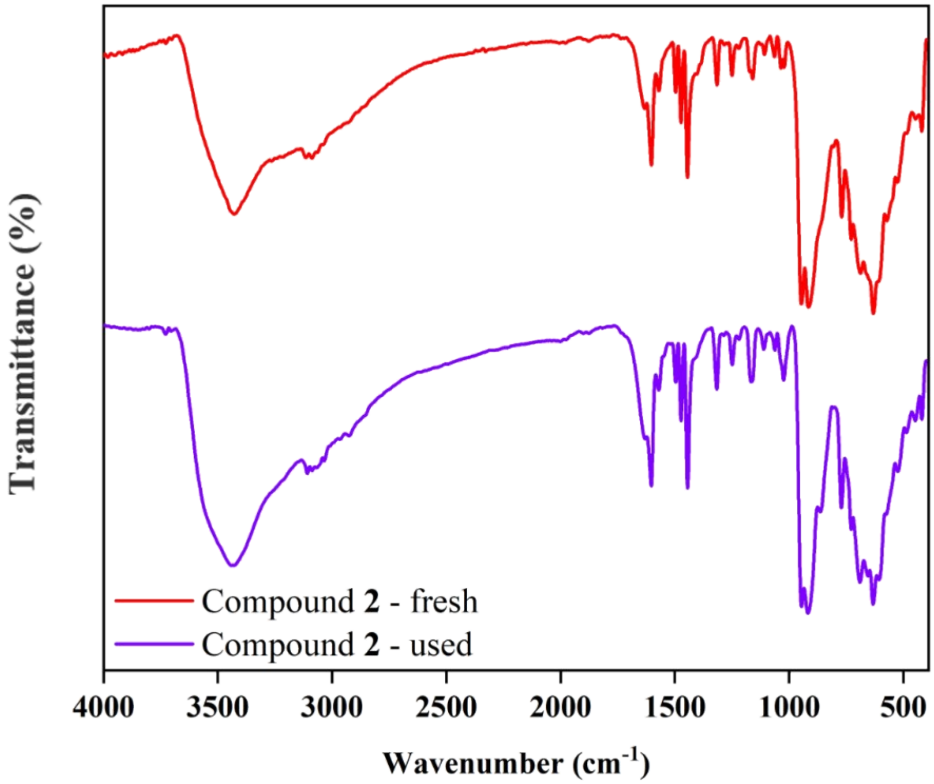

Fig. S5 FT-IR spectra of compound **2** before and after catalytic reaction.

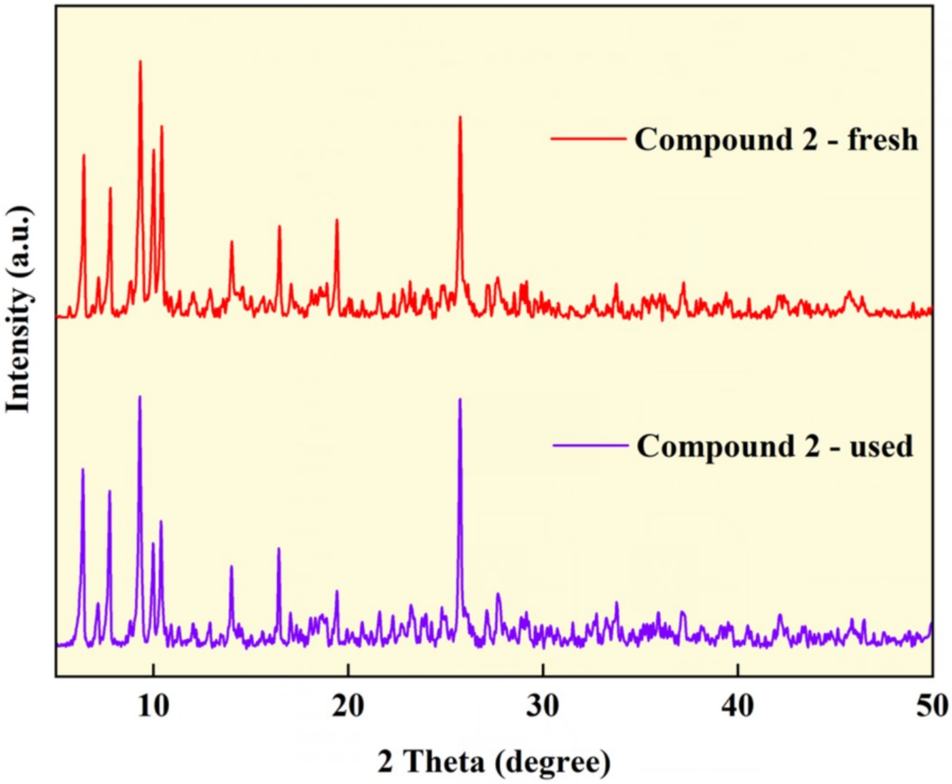

Fig. S6 Experimental PXRD patterns of compound **1** before and after catalytic reaction.

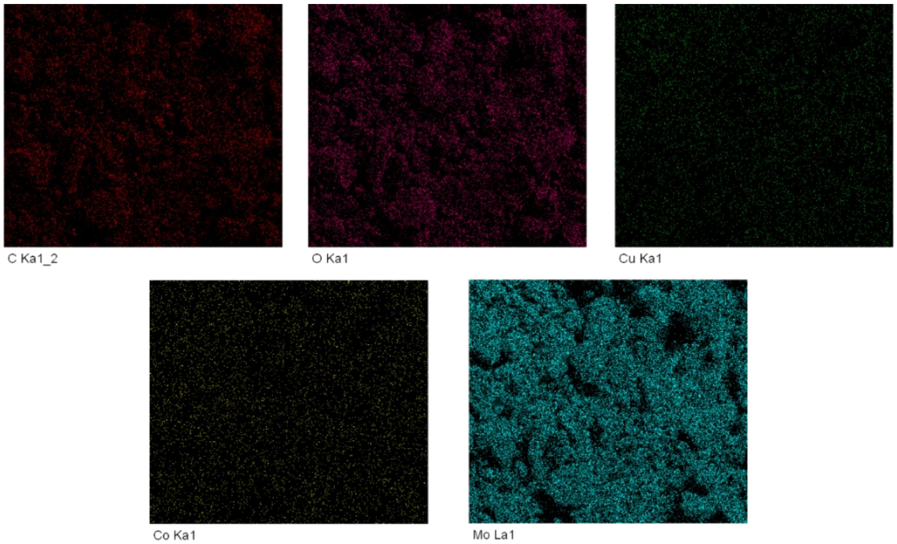

Fig. S7 EDS elemental mapping images for C, O, Cu, Co and Mo of compound **2**.

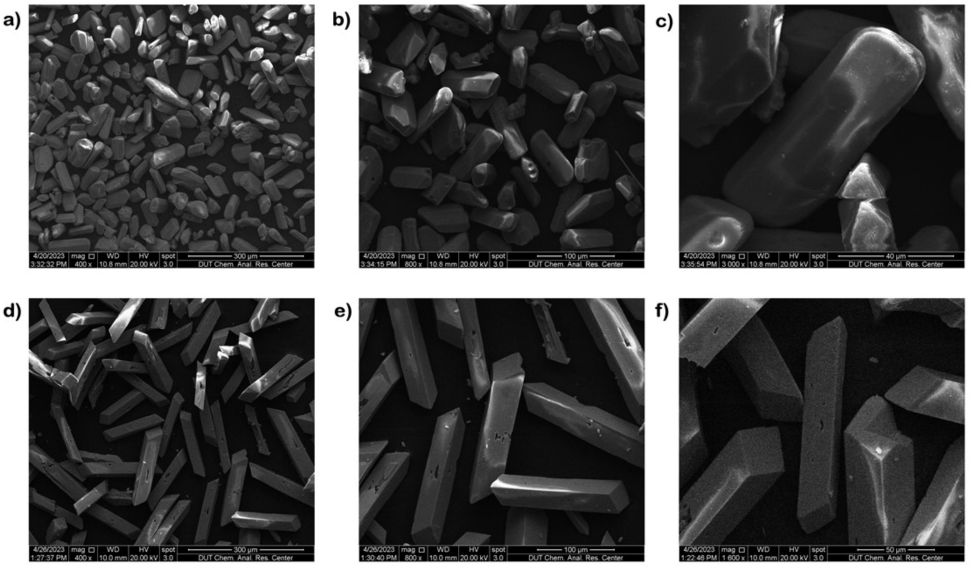

Fig. S8 SEM images of compound **1** (a-c) and **2** (d-f).

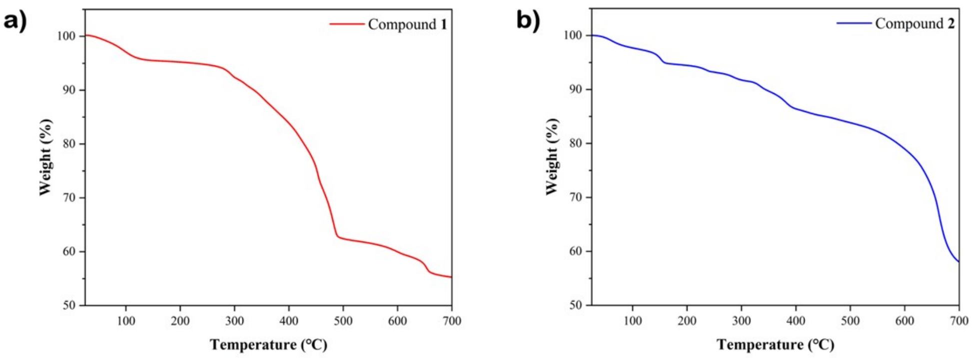

Fig. S9 Thermogravimetric curves of compound **1** (left) and compound **2** (right).

Section III. Supplementary Reaction Characterization

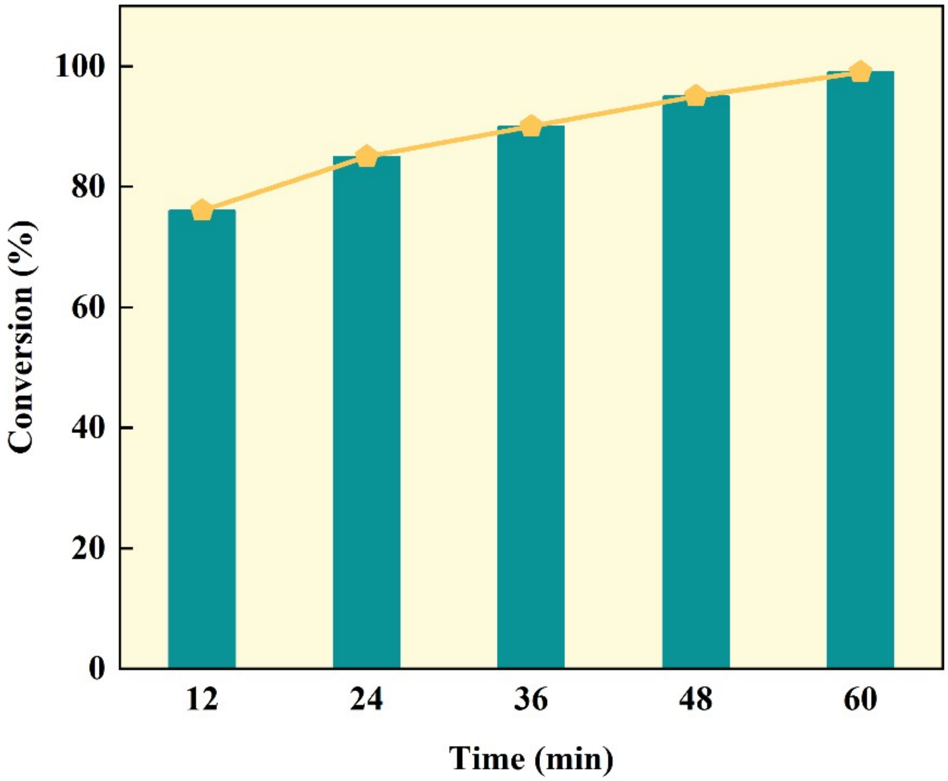

Fig. S10 Time-sharing graph in 60 minutes of MPS oxidation using compound **2** to monitor the reaction process under optimal conditions.

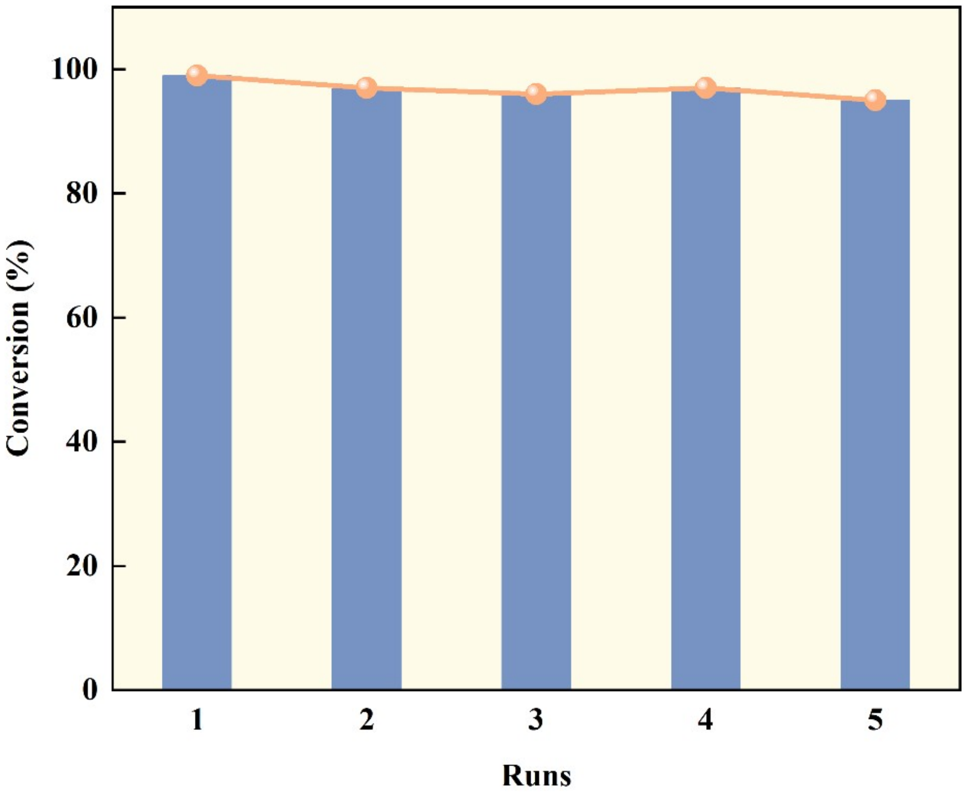

Fig. S11 Performance stability test for compound **2** under working conditions.

Section IV. Crystal Data

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

Compound	**1**	**2**
CCDC	2250421	2250422
Empirical formula	$C_{60}H_{64}N_{12}Co_4Mo_{10}O_{44}$	$C_{30}H_{50}N_6Cu_3Co_2Mo_{10}O_{49}$
Formula weight	2852.33	2546.63
Temperature (K)	193	302
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	Monoclinic
Space group	C2/c	$P2_1/n$
a (Å)	12.7136(5)	16.0443(6)
b (Å)	32.3882(11)	20.4432(10)
c (Å)	20.7077(8)	20.5811(9)
α (°)	90	90
β (°)	106.411(2)	106.9253(13)
γ (°)	90	90
Volume ($Å^3$)	8179.4(5)	6458.1(5)
Z	4	4
Density (g/cm^3)	2.313	2.619
F(000)	5536	4900
Theta range for data collection (°)	4.812 to 54.978	2.245 to 24.999
Index ranges	-16<=h<=16, -41<=h<=42, -26<=h<=26	-18<=h<=19, -24<=k<=24, -24<=l<=20
Reflections collected	114209	42083
Independent reflections	9380 [Rint = 0.0955]	11347 [Rint = 0.0469]
Completeness	0.997	0.998
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	9380/18/607	11347/12/891
Goodness-of-fit on F^2	1.087	1.015
Final R indices [I>2σ(I)]	R1 = 0.0281, wR_2 = 0.0627	R1 = 0.0360, wR_2 = 0.0768
R indices (all data)	R1 = 0.0401, wR_2 = 0.0730	R1 = 0.0592, wR_2 = 0.0866
Largest diff. peak and hole	1.03/-0.55	1.367/-0.795

Table S2 Hydrogen-bond geometry (Å, deg.) for **1**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(11)-H(11)...O(4)#3	0.95	2.51	3.275(4)	137.7
C(11)-H(11)...N(1)	0.95	2.51	3.031(5)	114.3
C(30)-H(30)...O(8)#4	0.95	2.6	3.164(4)	118.6
C(30)-H(30)...N(2)	0.95	2.51	3.022(5)	113.6
C(21)-H(21)...N(3)	0.95	2.48	2.985(5)	113.3
C(27)-H(27)...O(9)#5	0.95	2.27	3.204(5)	169
C(12)-H(12)...O(1)#3	0.95	2.4	3.144(5)	135.2
C(1)-H(1)...N(5)	0.95	2.49	2.998(5)	113.2
C(1)-H(1)...O(25^b)#5	0.95	2.63	3.275(15)	125.7
C(7)-H(7)...O(18)#6	0.95	2.29	3.227(5)	167.6
C(20)-H(20)...N(6)	0.95	2.48	2.992(5)	113.8
C(20)-H(20)...O(23)#5	0.95	2.47	3.195(5)	133.5
C(2)-H(2)...O(10)#7	0.95	2.65	3.471(5)	145.4
C(9)-H(9)...O(19)#1	0.95	2.28	3.202(5)	164.1
C(10)-H(10)...O(21)	0.95	2.48	3.292(4)	143.2
C(10)-H(10)...N(4)	0.95	2.49	3.001(5)	113.7
C(29)-H(29)...O(7)#4	0.95	2.44	3.226(5)	139.5
C(24)-H(24)...O(9)#5	0.95	2.09	3.037(4)	178.6
O(24^a)-H(24B^a)...O(22)#8	0.87	2.01	2.695(14)	135

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2, #2 -x,y,-z+1/2, #3 -x+2,-y+1,-z+1, #4 -x+1,-y+1,-z+1, #5 +1/2,y+1/2,z, #6 x,-y+1,z+1/2, #7 x+1,-y+1,z+1/2, #8 x+1/2,-y+1/2,z+1/2

Table S3 Hydrogen-bond geometry (Å, deg.) for compound **2**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1)-H(1A)...OW5	0.93	2.13	2.64(3)	113.3
C(2)-H(2A)...O(5W)	0.93	2.49	3.013(11)	115.5
C(6)-H(6A)...O(6W)	0.93	2.5	3.035(9)	116.8
C(6)-H(6A)...O(13)	0.93	2.49	3.318(10)	147.8
C(9)-H(9A)...O(4W)	0.93	2.61	3.119(11)	114.7
C(9)-H(9A)...O(9)	0.93	2.39	3.238(9)	152.4
C(11)-H(11A)...O(2)#1	0.93	2.46	3.310(10)	152.8
C(11)-H(11A)...O(2W)	0.93	2.54	3.055(10)	115.5
C(12)-H(12A)...O(11)	0.93	2.51	3.003(8)	113.2
C(16)-H(16A)...OW4#2	0.93	2.57	3.489(14)	170.3
C(18)-H(18A)...O(4)#2	0.93	2.47	3.112(12)	126.1
C(26)-H(26A)...O(3W)#3	0.93	2.57	3.251(9)	130.7
C(27)-H(27A)...O(24)#4	0.93	2.56	3.152(9)	121.5
C(29)-H(29A)...O(32)	0.93	2.55	3.038(9)	112.8

Symmetry transformations used to generate equivalent atoms:

#1 -x-1/2,y-1/2,-z+3/2, #2 x-1/2,-y+3/2,z+1/2, #3 x+1,y,z, #4 x-1,y,z

Section V. Reference

1 G. A. Tsigdinos, PhD thesis, Boston University, 1961.

2 G. M. Sheldrick, SHELXS97 and SHELXL97. Program for Crystal Structure Solution and Refinement, University of Göttingen, Göttingen, Germany, 1997