Supporting Information

A 4,4-conected 2D POM-based complex with synergistic mixed-valence Cu^{I}/Cu^{II} for mild and efficient catalytic oxidation of phenols

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Materials and instruments

The ligand Hcmbcbpy was synthesized according to the reported literature[1], and other reagents and solvents used in the synthesis process were purchased from commercial sources and used without further purification. FT-IR spectra were recorded using a Magna FT-IR 560 spectrometer (KBr tablets) with a test range of 4000-400 cm^{-1}. Powder X-ray diffraction (PXRD) patterns were performed using an Ultima IV with D/teX Ultra diffractometer at 40 kV, 40 mA with Cu Ka radiation. Thermogravimetric analysis (TGA) was performed using a Pyris Diamond TG instrument. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha spectrometer with an Al Kα X-ray source. EPR spectra were recorded on a BrukerEMXplus-6/1. Raman spectra were recorded on a HORIBA LabRAM odyssey. The conversion and selectivity of the reaction mixtures were monitored using Shimadzu Techcomp GC-7900 gas chromatograph.

Catalytic oxidation procedure

The oxidation of 2,3,6-TMP was carried out in a 5 mL thick-walled pressure tube with TBHP as the oxidant in an isothermal oil bath. The typical reaction mixture consists of catalyst **1** powder, 0.25 mmol of 2,3,6-TMP, TBHP and 1.0 mL of dichloromethane. The oil bath pot is preheated to the specified temperature in advance, and placed in a thick-walled pressure tube containing the mixture for heating and stirring. After the completion of the reaction, the mixture was cooled in ice water and filtered using a syringe with a filter membrane (pore size : 0.2 μm) to obtain a test sample. The catalytic activity was monitored by Shimadzu Techcomp GC-7900 gas chromatograph with naphthalene as internal standard. Qualitative analysis was performed by the peak position of the real product sample, and quantitative analysis was performed by the peak area ratio of the reaction product to the internal standard (naphthalene) and the peak area ratio of the real sample to the internal standard. After each reaction, the used catalyst was filtered and thoroughly washed with ethanol. After vacuum drying at 60 °C for 10 h, the recovered catalyst was used for the next cycle under the same reaction conditions.

Table S1 Bond valence sum (BVS) calculations of all Cu and W atoms in complex **1**

Atom	BVS
Cu1	1.21
Cu2	2.26
W1	6.34
W3	6.39
W3	6.33
W4	6.38
W5	6.12
W6	5.88

W7	6.35
W8	6.25
W9	6.20
W10	6.41
W11	5.74
W12	5.77

Table S2 Selected bond lengths [Å] for complex **1**

Complex **1**			
Cu(1)-N(4)#1	1.98(3)	W(6)-O(45)	1.922(13)
Cu(1)-O(2)	1.954(10)	W(6)-O(46)	1.909(12)
Cu(1)-O(19)	2.392(11)	W(6)-O(47)	1.692(12)
Cu(1)-O(3W)	1.964(13)	W(6)-O(48)	2.05(2)
Cu(1)-O(4W)	1.956(13)	W(6)-O(5)	1.86(2)
Cu(2)-N(3)#2	2.005(12)	W(7)-O(6)#3	2.484(18)
Cu(2)-O(3)	1.959(10)	W(7)-O(14)	1.902(11)
Cu(2)-O(12)	2.474(10)	W(7)-O(22)	1.894(12)
Cu(2)-O(1W)	1.951(11)	W(7)-O(23)	1.713(12)
Cu(2)-O(2W)	2.002(10)	W(7)-O(24)	1.894(12)
Cu(2)-O(5W)	2.385(13)	W(7)-O(28)	1.849(13)
W(1)-O(6)#3	2.453(16)	W(7)-O(29)	2.426(18)
W(1)-O(7)	2.470(17)	W(8)-O(8)#4	2.389(15)
W(1)-O(10)#3	1.897(13)	W(8)-O(37)	1.912(13)
W(1)-O(20)	1.886(12)	W(8)-O(39)	1.692(13)
W(1)-O(22)	1.905(12)	W(8)-O(40)	1.901(12)
W(1)-O(25)	1.896(12)	W(8)-O(41)	2.454(17)
W(1)-O(26)	1.673(10)	W(8)-O(45)	1.872(11)
W(2)-O(7)#3	2.519(18)	W(8)-O(49)	1.924(11)
W(2)-O(10)	1.878(13)	W(9)-O(8)#4	2.521(15)
W(2)-O(11)	1.855(13)	W(9)-O(9)	2.424(18)
W(2)-O(12)	1.698(10)	W(9)-O(30)#4	1.905(12)
W(2)-O(13)	1.903(12)	W(9)-O(35)	1.848(14)
W(2)-O(14)	1.916(12)	W(9)-O(36)	1.702(10)
W(2)-O(29)	2.432(16)	W(9)-O(37)	1.884(15)
W(3)-O(7)	2.507(18)	W(9)-O(48)#4	2.04(2)

W(3)-O(13)#3	1.913(12)	W(9)-O(5)#4	1.805(19)
W(3)-O(18)	1.899(14)	W(10)-O(8)	2.471(17)
W(3)-O(19)	1.691(11)	W(10)-O(30)	1.906(11)
W(3)-O(20)	1.921(13)	W(10)-O(31)	1.716(11)
W(3)-O(21)#3	2.487(17)	W(10)-O(32)	1.879(12)
W(3)-O(27)	1.852(11)	W(10)-O(40)#4	1.895(14)
W(4)-O(38)	1.856(12)	W(10)-O(42)#4	2.410(17)
W(4)-O(41)	2.517(17)	W(10)-O(43)	1.865(14)
W(4)-O(42)#4	2.372(17)	W(11)-O(9)	2.446(17)
W(4)-O(43)	1.921(13)	W(11)-O(32)	1.953(13)
W(4)-O(44)	1.676(12)	W(11)-O(33)	1.905(16)
W(4)-O(46)	1.897(11)	W(11)-O(34)	1.750(12)
W(4)-O(49)	1.872(11)	W(11)-O(35)	1.924(13)
W(5)-O(6)	2.475(17)	W(11)-O(38)	1.922(14)
W(5)-O(16)	1.872(12)	W(12)-O(11)	1.915(11)
W(5)-O(17)	1.721(13)	W(12)-O(15)	1.793(17)
W(5)-O(18)	1.903(12)	W(12)-O(16)	1.912(12)
W(5)-O(21)#3	2.47(2)	W(12)-O(21)#3	2.46(2)
W(5)-O(24)#3	1.915(12)	W(12)-O(27)	1.903(12)
W(5)-O(25)#3	1.904(12)	W(12)-O(28)	1.925(13)
W(6)-O(9)#4	2.387(15)	W(12)-O(29)	2.460(18)
W(6)-O(33)#4	1.903(15)		

Symmetry code: #1 – x + 1, - y + 1, - z + 2; #2 – x + 1, - y + 2, - z + 1; #3 – x + 1, - y + 1, - z + 1; #4 - x, - y + 2, - z + 2

Table S3 Selected hydrogen-bonding distance (Å) for complex **1**.

Complex **1**				
D-H···A	D-H	H···A	D···A	D-H···A
O1W-H1WA···O1#2	0.91	1.85	2.677(15)	151.0
O2W-H2WA···O4	0.88	1.82	2.617(16)	149.6
O2W-H2WB···O36#3	0.88	2.00	2.822(15)	156.7
O3W-H3WA···O1	0.85	1.94	2.594(17)	132.7
O3W-H3WB···O32#4	0.85	1.98	2.75(2)	150.6
O4W-H4WA···O32#4	0.92	2.32	2.980(	128.3

			16)	
O4W-H4WB···O40#5	0.88	2.55	3.129(17)	124.1
O5W-H5WB···O4#3	0.88	1.94	2.814(17)	173.4

Table S4 The effect of different solvents on catalytic performance[a]

Entry	Solvent	Conv./%	Sel./%
1	DMF	23	100
2	C_2H_5OH	58	98
3	CH_2Cl	14	100
4	CH_3CN	83	100

[a]Reaction conditions: 0.25 mmol 2,3,6-TMP; 10.0 mg catalyst; 0.25 mmol TBHP; reaction temperature 50 °C; reaction time 13 min.

Table S5 The effect of different solvent ratioes on the catalytic performance of the reaction[a]

Entry	CH_3CN: CH_2Cl	Conv./%	Sel./%
1	1:9	75	100
2	2:8	98	98
3	3:7	98	97
4	4:6	98	97
5	5:5	95	99
6	6:4	91	100
7	7:3	86	100
8	8:2	87	100
9	9:1	50	100

[a]Reaction conditions: 0.25 mmol 2,3,6-TMP; 11.0 mg catalyst; 0.25 mmol TBHP; reaction temperature 50 °C; reaction time 13 min.

Table S6 Effect of catalyst addition on the ccatalytic performance of the reaction[a]

Entry	catalyst	Conv./%	Sel./%
1	7 mg	59	100
2	8 mg	65	100
3	9 mg	69	100
4	10 mg	81	100

5	11 mg	98	98
6	12 mg	80	100
7	13 mg	76	100

[a]Reaction conditions: 0.25 mmol 2,3,6-TMP; 0.25 mmol TBHP; solvent 1.0 mL (acetonitrile/dichloromethane = 2/8); reaction temperature 50 °C; reaction time 13 min.

Table S7 Effect of TBHP addition on the ccatalytic performance of the reaction[a]

Entry	TBHP	Conv./%	Sel./%
1	0.25 mmol	98	98
2	0.5 mmol	69	85
3	0.75 mmol	50	73
4	1 mmol	26	46

[a]Reaction conditions: 0.25 mmol 2,3,6-TMP; 11.0 mg complex **1**; solvent 1.0 mL (acetonitrile/dichloromethane = 2/8); reaction temperature 50 °C; reaction time 13 min.

Table S8 Effect of different temperatures on the catalytic performance of the reaction[a]

Entry	Temperature	Conv./%	Sel./%
1	40 ℃	45	100
2	45 ℃	93	100
3	50 ℃	98	98
4	55 ℃	98	95

[a]Reaction conditions: 0.25 mmol 2,3,6-TMP; 0.25 mmol TBHP; solvent 1.0 mL (acetonitrile/dichloromethane = 2/8); 11.0 mg complex **1**; reaction time 13 min.

Table S9 Effect of different times on the catalytic performance of the reaction[a]

Entry	catalyst	Conv./%	Sel./%
1	8 min	84	100
2	9 min	86	100

3	10 min	90	100
4	11 min	94	100
5	12 min	96	98
6	13 min	98	98
7	14 min	98	97
8	15 min	99	95

[a]Reaction conditions: 0.25 mmol 2,3,6-TMP; 0.25 mmol TBHP; solvent 1.0 mL (acetonitrile/dichloromethane = 2/8); reaction temperature 50 °C; 11.0 mg complex **1**.

Table S10 Comparison of complex **1** with the reported POM-based complex catalytic oxidation of 2,3,6-TMP.

Catalyst	Temp. (˚C)	Time (min)	Oxidant	Conv. [%]	Sele. [%]
$[Bu_4N]_4[PTi(L)W_{11}O_{39}]$[2]	80	30	H_2O_2	90	45
$(n\text{-}Bu_4N)_7H[\{PW_{11}O_{39}Zr(\mu\text{-}OH)\}_2]$[3]	80	60	H_2O_2	90	45
$(n\text{-}Bu_4N)_8[\{PW_{11}O_{39}Zr(\mu\text{-}OH)\}_2]$[3]	80	60	H_2O_2	90	30
$\{Cu_2(HL)_4[H_3BW_{12}O_{40}]_2(HL)\}\cdot 4H_2O$ (Cu-BW)[4]	60	20	TBHP	99	99
$\{Cu_2(HL)_2(H_2O)_2[SiW_{12}O_{40}]\}\cdot 3.5H_2O$ (Cu-SiW)[4]	60	20	TBHP	82.9	99
$H[Cu^{II}(ttb)(H_2O)_3]_2[Cu^{II}(ttb)Cl]_2[PW_{12}O_{40}]\cdot 4H_2O$[5]	60	20	H_2O_2	99	99
Complex **1**	50	13	TBHP	98	99

Table S11 The catalytic performance for the oxidation of 2,3,6-TMP during the cycling experiments.

Cycles	Conv./%	Sel./%
1	96	99
2	97	98
3	96	98
4	95	99

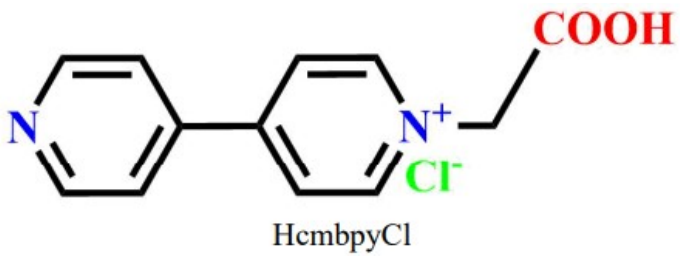
[a]Reaction conditions: 0.25 mmol 2,3,6-TMP; 11.0 mg complex **1**; 0.25 mmol TBHP; solvent 1.0

mL (acetonitrile/dichloromethane = 2/8); reaction temperature 50 °C; reaction time 13 min.

Table S12 The effect of free trapping agents on the performance of selective catalytic oxidation of 2,3,6-TMP[a]

Entry	Deviations from standard conditions	Conv./%	Sel./%
1	BHT	13	100
2	DPA	84	100
3	TEMPO	68	100
4	TBA	50	100

[a]Reaction conditions: 0.25 mmol 2,3,6-TMP; 11.0 mg catalyst; 0.25 mmol TBHP; solvent 1.0 mL (CH_3CN: CH_2Cl = 2:8); reaction temperature 50 °C; reaction time 13 min.



HcmbpyCl

Scheme S1 The structure of HcmbpyCl

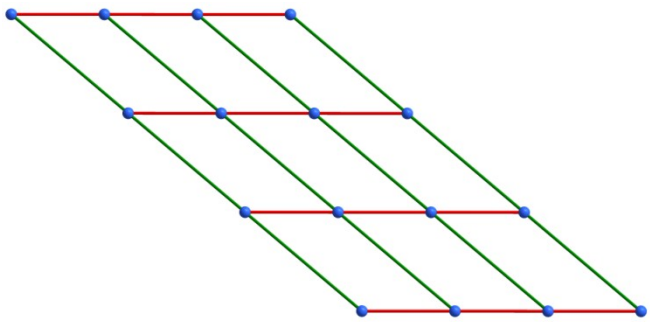


Fig S1 The 2D simplified diagram of complex **1**

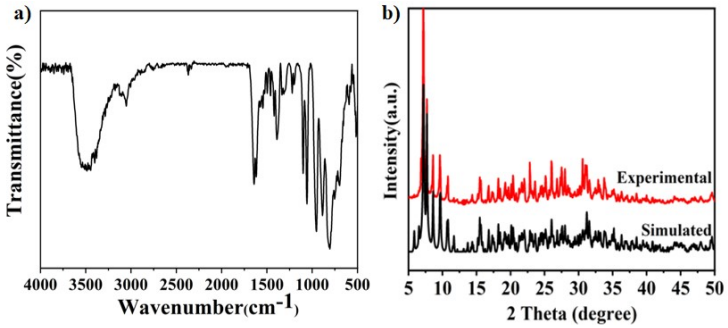


Fig S2 a) The PXRD spectra of complex **1;** b) The IR spectra of complex **1**

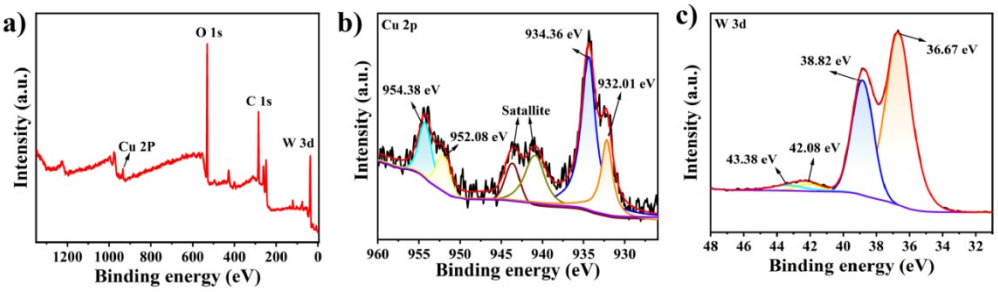


Fig S3 a) The full spectrum of complex **1;** b) Cu 2p**;** c) W 3d

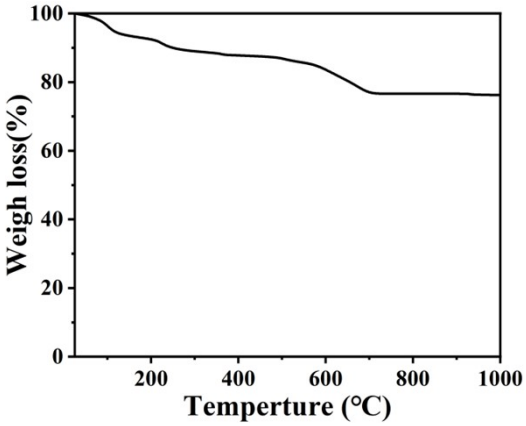


Fig S4 The TG curve of complex **1**

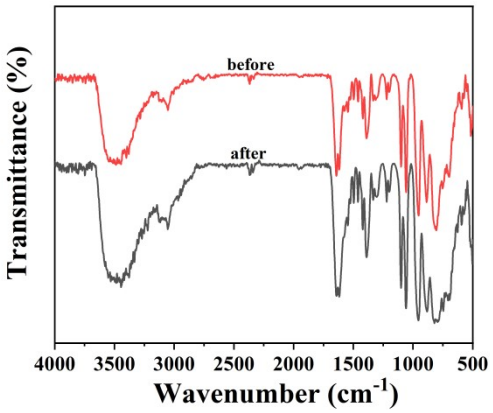


Fig S5 The IR of complex **1** before and after the reaction.

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