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Supporting Information

Synthesis of two New Copper-Sandwiched Polyoxotungstates and their Catalytic Activity of Hydrogen Evolution Influenced by Nuclear Number

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Table S1. Crystallographic data and structure refinements for **1** and **2**.

	1	**2**
formula	$[Cu(dap)_2]_2[\{Cu_8(dap)_4(H_2O)_2\}(SiW_9O_{34})_2]\cdot 7H_2O$	$[Cu(dap)_2(H_2O)]_2[Cu(dap)_2]_2[\{Cu_6(dap)_2\}(SiW_9O_{34})_2]\cdot 8H_2O$
Formula weight	5743.74	5938.27
crystal size[mm^3]	0.18×0.10×0.08	0.20×0.12×0.10
Crystal color	dark blue	dark green
crystal system	monoclinic	triclinic
space group	P 21/c	P -1
a [Å]	13.6402(10)	12.4480(5)
b [Å]	31.703(2)	14.3192(5)
c [Å]	12.2361(9)	17.1822(7)
α [°]	90	98.959(3)
β [°]	114.901(2)	110.639(4)
γ [°]	90	104.727(3)
Volume [$Å^3$]	4799.5(6)	2668.2(2)
Z	2	1
Dcalc. [$mg\cdot m^{-3}$]	3.974	3.696
μ[mm^{-1}]	32.365	24.32
F_{000}	5128.0	2674.0
θ range[°]	3.534 to 58.994	6.766 to 53
Reflections collected	63281	22326
Independent reflections	13332	11032
R(int)	0.0481	0.0537
Completeness	0.998	0.997
Data/restraints/parameters	13332/51/641	11032/132/702
Goodness-of-fit on F^2	1.209	1.067
Final *R* indices [I>2sigma(I)]	$R_1 = 0.0466$, $wR_2 = 0.0927$	$R_1 = 0.0425$, $wR_2 = 0.0942$
R indices (all data)	$R_1 = 0.0584$, $wR_2 = 0.0965$	$R_1 = 0.0594$, $wR_2 = 0.1052$
Largest diff. peak and hole/e.$Å^{-3}$	2.32/-3.19	4.45/-3.62

Table S2. Bond valence sum (BVS) calculations of all Cu and W atoms in **1** and **2**.

1-BVS		**2**-BVS	
Cu1	2.11	Cu1	2.16
Cu2	2.12	Cu2	2.17

Cu3	2.00	Cu3	2.19
Cu4	2.15	Cu4	2.24
Cu5	2.14	Cu5	2.47
W1	6.19	Cu6	2.01
W2	6.05	W1	6.24
W3	6.20	W2	6.28
W4	6.14	W3	6.09
W5	6.19	W4	6.13
W6	6.10	W5	6.23
W7	6.01	W6	6.13
W8	6.09	W7	6.10
W9	6.08	W8	6.20
		W9	5.99

Table S3. Quantum yields of H_2 production for **1** and **2** under different conditions in 10 hours.

QY (%)				
Compound **1**	$[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM) TEOA (0.25 M)	Catalyst **1** (mg)	1	0.016
			2	0.051
			4	0.093
	Catalyst **1** (2 mg) TEOA (0.25 M)	$[Ir(ppy)_2(dtbbpy)][PF_6]$ (mM)	0.1	0.021
			0.4	0.057
	Catalyst **1** (2 mg) $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM)	TEOA (M)	0.05	0.022
			0.15	0.035
Compound **2**	$[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM) TEOA (0.25 M)	Catalyst **2** (mg)	1	0.028
			2	0.036
			4	0.083
	Catalyst **2** (2mg) TEOA (0.25 M)	$[Ir(ppy)_2(dtbbpy)][PF_6]$ (mM)	0.1	0.011
			0.4	0.053
	Catalyst **2** (2mg) $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM)	TEOA(M)	0.05	0.015
			0.15	0.025

Table S4. Elemental analysis for **1** and **2**.

Elemental analysis		calcd (%)	Found (%)
Compound **1**	C	5.11	5.35
	N	3.97	4.21
Compound **2**	C	6.16	5.82
	N	4.79	4.75

Table S5. Major bond lengths and bond angles for POM **1** and **2**.

1		**2**	
Bond lengths (Å)		Bond lengths (Å)	
Cu1-N	1.965(13)-1.971(11)	Cu1-O	1.922(7)-2.318(6)
Cu1-O	1.976(8)-2.427(8)	Cu2-O	1.920(7)-2.300(7)
Cu2-O	1.939(8)-2.437(11)	Cu3-N	1.960(9)-1.969(9)
Cu3-N	1.983(15)-2.029(14)	Cu3-O	1.991(7)-2.339(7)
Cu3-O	1.993(8)-2.359(8)	Cu4-N	1.979(11)-2.016(12)
Cu4-O	1.953(7)-2.358(7)	Cu4-O	2.489 (4)-2.583 (3)
Cu5-N	1.972(18)-2.022(18)	Cu5-N	1.89(2)-1.997(19)
Si1-O	1.620(8)- 1.642(8)	Cu5-O	3.137(2)-3.147(3)
W1-O	1.721(8)- 2.381(7)	Cu6-N	2.007(11)-2.015(12)
W2-O	1.707(9)-2.425(7)	Cu6-O	3.232(6)
W3-O	1.708(9)- 2.386(7)	Si1-O	1.625(7)-1.635(7)
W4-O	1.725(8)-2.348(7)	W1-O	1.705(8)-2.391(7)
W5-O	1.706(8)-2.373(7)	W2-O	1.713(7)-2.391(7)
W6-O	1.727(9)-2.289(7)	W3-O	1.728(8)- 2.410(7)
W7-O	1.724(9)-2.368(7)	W4-O	1.718(7)-2.363(6)
W8-O	1.725(9)- 2.355(7)	W5-O	1.715(7)-2.306(7)
W9-O	1.710(8)-2.316(7)	W6-O	1.715(7)-2.376(7)
		W7-O	1.715(7)-2.420(7)
		W8-O	1.718(7)-2.285(7)
		W9-O	1.730(7)-2.351(6)
Bond angles(°)		Bond angles(°)	
N-Cu1-N	84.3(6)	O-Cu1-O	75.0(3)-87.3(3)
N-Cu1-O	91.6(5)-174.2(5)	O-Cu2-O	83.1(3)-176.2(3)
O-Cu1-O	72.6(3)-90.6(3)	N-Cu3-N	84.2(2)
O-Cu2-O	84.8(3)-173.6(4)	N-Cu3-O	91.9(0)-171.0(2)
N-Cu3-N	85.9(6)	O-Cu3-O	85.4(3)-175.6(3)
N-Cu3-O	89.3(5) -168.6(5)	N-Cu4-N	83.7(6)-178.3(5)
O-Cu3-O	75.5(3)-86.7(3)	N-Cu4-O	87.2(2)-95.8(1)
O-Cu4-O	83.4(3)-176.1(3)	O-Cu4-O	175.5(8)
N-Cu5-N	82.3(7)-176.7(7)	N-Cu5-N	85.7(8)-180.0
N-Cu5-O	77.9(8)-100.3(8)	N-Cu5-O	66.7(4)-113.2(6)

O-Cu5-O	173.0(0)	O-Cu5-O	180.0
O-Si1-O	107.6(4)-112.6(4)	N-Cu6-O	79.6(5)-100.3(4)
O-W1-O	73.1(3)-170.3(4)	O-Cu6-O	180.0
O-W2-O	72.5(3)-172.1(4)	O-Si1-O	107.8(4)- 111.4(4)
O-W3-O	74.9(3)-170.9(4)	O-W1-O	72.4(3)-169.2(3)
O-W4-O	72.6(3)-167.6(4)	O-W2-O	73.1(3) -172.0(3)
O-W5-O	73.0(3)-168.4(4)	O-W3-O	73.1(3)-171.2(3)
O-W6-O	74.0(3)-170.7(4)	O-W4-O	74.6(3)-172.8(3)
O-W7-O	74.1(3)-173.3(4)	O-W5-O	73.6(3)- 169.7(3)
O-W8-O	74.4(3)-170.0(4)	O-W6-O	71.8(3)-166.9(3)
O-W9-O	73.7(3)-169.7(4)	O-W7-O	71.3(3)-167.3(3)
		O-W8-O	72.7(3)-168.4(3)
		O-W9-O	72.8(3)- 166.9(3)

The description for the DFT computational model.

The atomic valence electronic configuration considered as H:$1s^1$, C: $2s^22p^2$, N: $2s^22p^3$, O: $2s^22p^4$, Si: $3s^23p^2$, Cu: $3d^{10}4s^1$ and W: $5d^46^2$.

Model: A single molecule of **1** and **2** is placed in a box with 25 × 25 ×25 Å to avoid periodic interactions. To meet the experimental configuration, the experimental structure of **1** and **2** were employed to investigate the electronic structure rather than the geometric optimization by DFT. The total system is net neutral.

The charge, spin and fractional coordination (including the information of crystal lattice) are shown in Table S6-S11.

Table S6. The charge of **1**.

Atom	s	p	d	total
1C	0.873	1.572	0	2.445
2C	0.843	1.797	0	2.64
3C	0.86	1.567	0	2.426
4C	0.854	1.56	0	2.414
5C	0.844	1.615	0	2.458
6C	0.844	1.749	0	2.593
7C	0.873	1.572	0	2.445
8C	0.843	1.797	0	2.64
9C	0.859	1.567	0	2.426

10C	0.853	1.561	0	2.414
11C	0.844	1.615	0	2.459
12C	0.844	1.75	0	2.594
13N	1.273	2.377	0	3.65
14N	1.314	2.193	0	3.507
15N	1.318	2.167	0	3.485
16N	1.285	2.263	0	3.547
17N	1.273	2.376	0	3.649
18N	1.314	2.194	0	3.508
19N	1.318	2.166	0	3.484
20N	1.284	2.263	0	3.548
21O	1.586	3.566	0	5.152
22O	1.602	3.491	0	5.093
23O	1.597	3.452	0	5.049
24O	1.581	3.6	0	5.18
25O	1.598	3.463	0	5.062
26O	1.582	3.608	0	5.19
27O	1.595	3.623	0	5.218
28O	1.597	3.503	0	5.1
29O	1.601	3.482	0	5.084
30O	1.597	3.526	0	5.123
31O	1.595	3.518	0	5.113
32O	1.603	3.488	0	5.091
33O	1.602	3.486	0	5.088
34O	1.596	3.458	0	5.055
35O	1.601	3.489	0	5.09
36O	1.607	3.444	0	5.051
37O	1.603	3.477	0	5.08
38O	1.6	3.457	0	5.056
39O	1.594	3.52	0	5.115
40O	1.602	3.485	0	5.087
41O	1.601	3.491	0	5.093
42O	1.58	3.603	0	5.183
43O	1.595	3.603	0	5.198
44O	1.599	3.472	0	5.071
45O	1.593	3.626	0	5.219
46O	1.605	3.484	0	5.089
47O	1.589	3.651	0	5.24
48O	1.595	3.627	0	5.221
49O	1.598	3.617	0	5.215
50O	1.595	3.512	0	5.107
51O	1.596	3.514	0	5.11
52O	1.584	3.674	0	5.258

53O	1.591	3.651	0	5.242
54O	1.619	3.416	0	5.035
55O	1.586	3.566	0	5.151
56O	1.603	3.486	0	5.089
57O	1.596	3.452	0	5.049
58O	1.581	3.599	0	5.18
59O	1.598	3.464	0	5.062
60O	1.583	3.608	0	5.191
61O	1.595	3.622	0	5.216
62O	1.596	3.515	0	5.111
63O	1.601	3.482	0	5.084
64O	1.597	3.518	0	5.116
65O	1.595	3.518	0	5.113
66O	1.603	3.489	0	5.092
67O	1.603	3.484	0	5.087
68O	1.597	3.456	0	5.053
69O	1.601	3.489	0	5.09
70O	1.607	3.443	0	5.05
71O	1.603	3.477	0	5.08
72O	1.599	3.458	0	5.057
73O	1.595	3.52	0	5.114
74O	1.601	3.484	0	5.085
75O	1.603	3.491	0	5.094
76O	1.58	3.602	0	5.182
77O	1.595	3.603	0	5.198
78O	1.599	3.472	0	5.071
79O	1.593	3.626	0	5.219
80O	1.604	3.486	0	5.09
81O	1.586	3.656	0	5.242
82O	1.594	3.629	0	5.223
83O	1.598	3.616	0	5.214
84O	1.595	3.513	0	5.108
85O	1.596	3.511	0	5.107
86O	1.585	3.673	0	5.258
87O	1.589	3.655	0	5.245
88O	1.619	3.417	0	5.035
89Si	0.672	1.011	0	1.682
90Si	0.672	1.011	0	1.682
91Cu	0.324	0.37	9.212	9.906
92Cu	0.325	0.343	9.256	9.924
93Cu	0.4	0.396	9.145	9.941
94Cu	0.351	0.35	9.196	9.897
95Cu	0.324	0.37	9.213	9.907

96Cu	0.325	0.343	9.257	9.925
97Cu	0.399	0.396	9.146	9.941
98Cu	0.351	0.35	9.196	9.897
99W	0.749	1.067	4.313	6.129
100W	0.755	1.077	4.342	6.174
101W	0.749	1.071	4.319	6.138
102W	0.753	1.101	4.347	6.201
103W	0.742	1.069	4.342	6.152
104W	0.748	1.08	4.313	6.142
105W	0.746	1.085	4.329	6.16
106W	0.752	1.069	4.352	6.173
107W	0.761	1.07	4.416	6.247
108W	0.748	1.066	4.321	6.135
109W	0.755	1.078	4.341	6.174
110W	0.748	1.068	4.328	6.144
111W	0.749	1.102	4.334	6.185
112W	0.741	1.072	4.328	6.141
113W	0.748	1.081	4.311	6.141
114W	0.748	1.083	4.349	6.179
115W	0.753	1.071	4.344	6.168
116W	0.761	1.07	4.415	6.246
117H	0.643	0.041	0	0.684
118H	0.639	0.041	0	0.681
119H	0.637	0.042	0	0.68
120H	0.645	0.044	0	0.688
121H	0.641	0.041	0	0.682
122H	0.645	0.042	0	0.686
123H	0.637	0.042	0	0.68
124H	0.639	0.041	0	0.681
125H	0.643	0.041	0	0.684
126H	0.645	0.042	0	0.687
127H	0.641	0.041	0	0.682
128H	0.645	0.044	0	0.689
129H	0.564	0.106	0	0.67
130H	0.524	0.093	0	0.618
131H	0.594	0.114	0	0.709
132H	0.554	0.103	0	0.657
133H	0.542	0.099	0	0.641
134H	0.592	0.117	0	0.709
135H	0.592	0.111	0	0.703
136H	0.63	0.074	0	0.704
137H	0.563	0.105	0	0.668
138H	0.524	0.093	0	0.618

139H	0.561	0.106	0	0.667
140H	0.597	0.116	0	0.712
141H	0.554	0.104	0	0.658
142H	0.542	0.098	0	0.64
143H	0.593	0.117	0	0.709
144H	0.591	0.113	0	0.704
145H	0.631	0.075	0	0.705
146H	0.561	0.106	0	0.667
147H	0.632	0.045	0	0.678
148H	0.636	0.043	0	0.679
149H	0.633	0.046	0	0.678
150H	0.636	0.043	0	0.68

Table S7. The magnetic configuration (spin) of **1**.

Atom	s	p	d	total
1C	0.001	-0.003	0	-0.002
2C	0	-0.002	0	-0.002
3C	0.01	0.065	0	0.075
4C	0.001	-0.018	0	-0.017
5C	-0.003	-0.021	0	-0.024
6C	0.002	0.007	0	0.008
7C	0.001	-0.002	0	-0.001
8C	0	-0.002	0	-0.002
9C	0.01	0.066	0	0.076
10C	0.001	-0.017	0	-0.016
11C	-0.003	-0.022	0	-0.025
12C	0.002	0.007	0	0.008
13N	0	-0.015	0	-0.014
14N	0.01	0.31	0	0.32
15N	0.01	0.273	0	0.283
16N	0.005	0.074	0	0.079
17N	0	-0.013	0	-0.012
18N	0.01	0.314	0	0.323
19N	0.01	0.276	0	0.286
20N	0.005	0.074	0	0.079
21O	-0.003	-0.054	0	-0.057
22O	0	-0.006	0	-0.006
23O	-0.003	-0.021	0	-0.024
24O	0	-0.001	0	-0.001
25O	-0.002	-0.018	0	-0.02
26O	0	-0.001	0	-0.001
27O	0	0	0	0

28O	-0.001	-0.012	0	-0.013
29O	0	0.001	0	0.002
30O	0	-0.007	0	-0.007
31O	0	0	0	0
32O	0	-0.005	0	-0.005
33O	0	0.006	0	0.006
34O	0.001	0	0	0.001
35O	0	0.008	0	0.008
36O	0	-0.001	0	0
37O	0	0.01	0	0.011
38O	0	0.001	0	0.001
39O	0	-0.005	0	-0.005
40O	0	-0.001	0	-0.001
41O	0	-0.002	0	-0.002
42O	0	-0.002	0	-0.002
43O	0	0.001	0	0.002
44O	0	-0.001	0	-0.001
45O	0	0.005	0	0.005
46O	0	0.005	0	0.005
47O	0.001	0.014	0	0.015
48O	0.001	0.002	0	0.003
49O	0	0.004	0	0.004
50O	0	-0.002	0	-0.002
51O	0	-0.001	0	-0.001
52O	0	0.004	0	0.004
53O	0.003	0.015	0	0.018
54O	0	0	0	0
55O	-0.003	-0.055	0	-0.058
56O	0	-0.005	0	-0.005
57O	-0.003	-0.022	0	-0.025
58O	0	-0.001	0	-0.001
59O	-0.002	-0.018	0	-0.02
60O	0	-0.001	0	-0.001
61O	0	0.002	0	0.002
62O	0	-0.005	0	-0.005
63O	0	0.002	0	0.002
64O	0	-0.006	0	-0.006
65O	0	0	0	0
66O	0	-0.006	0	-0.006
67O	0	-0.001	0	-0.001
68O	0	-0.007	0	-0.007
69O	0	0.009	0	0.01
70O	0	-0.003	0	-0.002

71O	0	0.009	0	0.01
72O	0	0.007	0	0.007
73O	0	-0.004	0	-0.005
74O	0	0.003	0	0.003
75O	0	-0.005	0	-0.006
76O	0	-0.001	0	-0.001
77O	0	0	0	0
78O	0	0	0	0
79O	0	0.006	0	0.006
80O	0	0.009	0	0.009
81O	0.001	0.008	0	0.009
82O	0	0	0	0
83O	0	0.006	0	0.006
84O	0	-0.003	0	-0.003
85O	0	-0.004	0	-0.004
86O	0.001	0.016	0	0.017
87O	0.002	0.01	0	0.012
88O	0	0.001	0	0.001
89Si	0	-0.001	0	-0.001
90Si	0	-0.001	0	-0.001
91Cu	0.001	0.001	-0.313	-0.311
92Cu	0	0	-0.019	-0.018
93Cu	-0.003	0.009	0.148	0.154
94Cu	0	0.001	0.047	0.047
95Cu	0.001	0.001	-0.312	-0.31
96Cu	0	0	-0.019	-0.019
97Cu	-0.003	0.009	0.147	0.152
98Cu	0	0.001	0.048	0.049
99W	0	-0.001	0.022	0.02
100W	0.001	0.001	0.028	0.03
101W	0	0	0	0
102W	0.003	0.007	0.169	0.179
103W	0.004	0.007	0.291	0.303
104W	0	0	0.061	0.061
105W	0.001	0.001	0.065	0.067
106W	0.002	0.002	0.108	0.111
107W	0	0	0.002	0.002
108W	0	-0.001	0.048	0.048
109W	0	0	0.014	0.014
110W	0.001	0.001	0.037	0.038
111W	0.001	0.003	0.114	0.119
112W	0.004	0.006	0.222	0.232
113W	0	0	0.061	0.061

114W	0.002	0.006	0.143	0.151
115W	0.001	0.001	0.062	0.064
116W	0	0	0.003	0.004
117H	0.002	0	0	0.002
118H	0	0	0	0
119H	-0.001	0	0	-0.001
120H	-0.001	0	0	-0.001
121H	0.002	0	0	0.002
122H	0	0	0	0
123H	-0.001	0	0	-0.001
124H	0	0	0	0
125H	0.002	0	0	0.002
126H	0	0	0	0
127H	0.002	0	0	0.002
128H	-0.002	0	0	-0.002
129H	0	0	0	0
130H	0.002	0	0	0.002
131H	0.006	0	0	0.006
132H	0.003	0	0	0.003
133H	0	0.001	0	0
134H	0.001	0	0	0.001
135H	0.012	0	0	0.012
136H	0	0	0	0
137H	0.002	0	0	0.001
138H	0.001	0	0	0.001
139H	0.001	0.001	0	0.001
140H	0.004	0	0	0.004
141H	0.001	0	0	0.001
142H	0.001	0.001	0	0.001
143H	0.003	0	0	0.003
144H	0.009	0	0	0.008
145H	0	0	0	0
146H	0	0.001	0	0.001
147H	0	0	0	0
148H	-0.002	0.001	0	-0.001
149H	0	0	0	0
150H	-0.002	0.001	0	-0.001

Table S8. The charge of **2**.

Atom	s	p	d	total
1C	0.863	1.66	0	2.523
2C	0.86	1.666	0	2.526

3C	0.842	1.797	0	2.64
4C	0.862	1.661	0	2.523
5C	0.86	1.666	0	2.526
6C	0.843	1.797	0	2.64
7N	1.289	2.248	0	3.537
8N	1.302	2.236	0	3.538
9N	1.288	2.25	0	3.538
10N	1.302	2.236	0	3.538
11O	1.601	3.489	0	5.09
12O	1.593	3.51	0	5.103
13O	1.602	3.479	0	5.081
14O	1.597	3.499	0	5.096
15O	1.596	3.516	0	5.112
16O	1.597	3.512	0	5.108
17O	1.607	3.431	0	5.037
18O	1.598	3.466	0	5.064
19O	1.605	3.445	0	5.05
20O	1.609	3.449	0	5.058
21O	1.594	3.519	0	5.113
22O	1.598	3.488	0	5.087
23O	1.608	3.436	0	5.044
24O	1.601	3.484	0	5.084
25O	1.601	3.489	0	5.09
26O	1.597	3.465	0	5.061
27O	1.581	3.597	0	5.178
28O	1.582	3.612	0	5.194
29O	1.595	3.623	0	5.218
30O	1.597	3.621	0	5.218
31O	1.595	3.513	0	5.108
32O	1.579	3.589	0	5.169
33O	1.586	3.572	0	5.158
34O	1.601	3.493	0	5.094
35O	1.602	3.474	0	5.077
36O	1.603	3.485	0	5.087
37O	1.602	3.498	0	5.1
38O	1.589	3.652	0	5.241
39O	1.592	3.648	0	5.24
40O	1.59	3.66	0	5.25
41O	1.589	3.655	0	5.244
42O	1.59	3.639	0	5.23
43O	1.595	3.601	0	5.196
44O	1.587	3.672	0	5.259
45O	1.601	3.491	0	5.091

46O	1.593	3.508	0	5.102
47O	1.602	3.481	0	5.083
48O	1.596	3.507	0	5.103
49O	1.597	3.509	0	5.105
50O	1.597	3.511	0	5.108
51O	1.606	3.434	0	5.04
52O	1.598	3.466	0	5.064
53O	1.605	3.444	0	5.049
54O	1.609	3.447	0	5.056
55O	1.594	3.519	0	5.114
56O	1.599	3.488	0	5.086
57O	1.608	3.438	0	5.046
58O	1.602	3.481	0	5.083
59O	1.602	3.488	0	5.09
60O	1.597	3.465	0	5.062
61O	1.581	3.597	0	5.178
62O	1.582	3.614	0	5.196
63O	1.595	3.623	0	5.218
64O	1.596	3.625	0	5.221
65O	1.595	3.512	0	5.107
66O	1.58	3.59	0	5.17
67O	1.586	3.572	0	5.158
68O	1.601	3.494	0	5.095
69O	1.601	3.479	0	5.079
70O	1.603	3.483	0	5.086
71O	1.601	3.504	0	5.106
72O	1.587	3.657	0	5.244
73O	1.59	3.652	0	5.242
74O	1.59	3.659	0	5.25
75O	1.59	3.652	0	5.242
76O	1.591	3.639	0	5.23
77O	1.595	3.602	0	5.197
78O	1.589	3.669	0	5.258
79Si	0.674	1.017	0	1.691
80Si	0.674	1.017	0	1.691
81Cu	0.325	0.366	9.231	9.922
82Cu	0.408	0.407	9.132	9.947
83Cu	0.331	0.372	9.26	9.963
84Cu	0.325	0.366	9.233	9.923
85Cu	0.408	0.408	9.134	9.95
86Cu	0.332	0.373	9.261	9.965
87W	0.748	1.075	4.381	6.204
88W	0.742	1.066	4.314	6.121

89W	0.747	1.064	4.356	6.167
90W	0.757	1.085	4.348	6.19
91W	0.758	1.078	4.364	6.2
92W	0.733	1.058	4.312	6.103
93W	0.76	1.095	4.381	6.236
94W	0.763	1.114	4.377	6.254
95W	0.754	1.076	4.336	6.166
96W	0.752	1.074	4.379	6.205
97W	0.739	1.065	4.315	6.119
98W	0.741	1.066	4.352	6.158
99W	0.757	1.087	4.339	6.183
100W	0.758	1.076	4.367	6.202
101W	0.737	1.057	4.315	6.11
102W	0.76	1.095	4.384	6.239
103W	0.764	1.113	4.384	6.262
104W	0.753	1.074	4.342	6.169
105H	0.636	0.041	0	0.677
106H	0.641	0.041	0	0.682
107H	0.641	0.041	0	0.682
108H	0.639	0.043	0	0.682
109H	0.637	0.041	0	0.678
110H	0.639	0.041	0	0.679
111H	0.642	0.042	0	0.684
112H	0.639	0.043	0	0.683
113H	0.561	0.105	0	0.666
114H	0.598	0.116	0	0.714
115H	0.593	0.11	0	0.703
116H	0.591	0.114	0	0.706
117H	0.599	0.112	0	0.711
118H	0.593	0.115	0	0.709
119H	0.545	0.1	0	0.645
120H	0.598	0.115	0	0.712
121H	0.522	0.092	0	0.614
122H	0.542	0.098	0	0.64
123H	0.595	0.115	0	0.71
124H	0.521	0.092	0	0.613
125H	0.56	0.104	0	0.664
126H	0.6	0.117	0	0.717
127H	0.597	0.112	0	0.709
128H	0.591	0.114	0	0.705
129H	0.595	0.111	0	0.705
130H	0.593	0.114	0	0.707

Table S9. The magnetic configuration (spin) of **2**

Atom	s	p	d	total
1C	0.005	0.068	0	0.073
2C	0.002	0.017	0	0.019
3C	0	0	0	0
4C	0.005	0.07	0	0.075
5C	0.002	0.019	0	0.021
6C	0	0	0	0.001
7N	0.007	0.145	0	0.152
8N	0.009	0.255	0	0.265
9N	0.007	0.157	0	0.164
10N	0.009	0.256	0	0.265
11O	0	0.004	0	0.005
12O	0	-0.003	0	-0.003
13O	0	-0.002	0	-0.002
14O	0	-0.01	0	-0.011
15O	0	-0.005	0	-0.005
16O	-0.001	-0.017	0	-0.018
17O	0	0	0	0
18O	0.001	0.001	0	0.002
19O	0	-0.002	0	-0.001
20O	0	-0.001	0	-0.001
21O	0	-0.001	0	-0.001
22O	0	0.004	0	0.004
23O	-0.002	-0.013	0	-0.015
24O	0	0.003	0	0.003
25O	0	-0.005	0	-0.006
26O	-0.002	-0.017	0	-0.019
27O	0.001	0.003	0	0.004
28O	0	-0.001	0	-0.001
29O	0.001	0.003	0	0.004
30O	0.001	0.007	0	0.008
31O	0	-0.005	0	-0.006
32O	0	-0.002	0	-0.002
33O	-0.002	-0.038	0	-0.04
34O	0	-0.001	0	-0.001
35O	0	0.002	0	0.002
36O	0	-0.009	0	-0.009
37O	0	0.004	0	0.004
38O	0	0.004	0	0.004

39O	0.003	0.015	0	0.018
40O	0	0.002	0	0.002
41O	0	0.001	0	0.001
42O	0.003	0.013	0	0.016
43O	0.001	0.004	0	0.005
44O	0.001	0.01	0	0.011
45O	0	0.004	0	0.004
46O	0	-0.004	0	-0.004
47O	0	-0.004	0	-0.004
48O	0	-0.006	0	-0.006
49O	0	-0.008	0	-0.009
50O	-0.001	-0.018	0	-0.019
51O	0	-0.001	0	-0.002
52O	0.001	0.003	0	0.004
53O	0	0	0	0.001
54O	0	0.002	0	0.002
55O	0	-0.001	0	-0.001
56O	0	0.004	0	0.004
57O	-0.002	-0.014	0	-0.016
58O	0	0.003	0	0.003
59O	0	-0.004	0	-0.004
60O	-0.002	-0.016	0	-0.018
61O	0	-0.002	0	-0.002
62O	0	-0.001	0	-0.001
63O	0.001	0.004	0	0.005
64O	0.001	0.006	0	0.007
65O	0	-0.005	0	-0.005
66O	0	0.002	0	0.003
67O	-0.002	-0.038	0	-0.04
68O	0	-0.001	0	0
69O	0	0.001	0	0.001
70O	0	-0.005	0	-0.006
71O	0	0.001	0	0.001
72O	0	0.005	0	0.005
73O	0.003	0.017	0	0.019
74O	0	0.004	0	0.004
75O	0	0.001	0	0.002
76O	0.003	0.013	0	0.016
77O	0.001	0.003	0	0.004
78O	0.001	0.009	0	0.01
79Si	0	-0.001	0	-0.001
80Si	0	-0.001	0	-0.001
81Cu	0.001	0.001	-0.233	-0.231

82Cu	-0.006	0.01	0.123	0.127
83Cu	0	0	-0.01	-0.009
84Cu	0.001	0.001	-0.237	-0.235
85Cu	-0.006	0.011	0.124	0.129
86Cu	0	0	-0.012	-0.011
87W	0	0	0.016	0.016
88W	0.001	0.001	0.034	0.035
89W	0.004	0.008	0.285	0.297
90W	0.001	0.001	0.088	0.09
91W	0.001	0.002	0.055	0.058
92W	0.004	0.01	0.297	0.311
93W	0	-0.001	0.035	0.034
94W	0.002	0.003	0.134	0.138
95W	0.001	0.002	0.081	0.084
96W	0.001	0.001	0.032	0.033
97W	0.001	0	0.042	0.043
98W	0.004	0.011	0.282	0.297
99W	0	0	0.061	0.061
100W	0.001	0.002	0.066	0.069
101W	0.005	0.008	0.29	0.303
102W	0	0	0.046	0.046
103W	0.003	0.004	0.145	0.151
104W	0.002	0.002	0.099	0.102
105H	0.001	0	0	0.001
106H	0	0	0	0
107H	0.003	0	0	0.003
108H	-0.002	0.001	0	-0.001
109H	0	0	0	0
110H	0.003	0	0	0.003
111H	0.001	0	0	0.001
112H	-0.002	0.001	0	-0.001
113H	0.002	0	0	0.002
114H	0	0	0	0
115H	0.014	0	0	0.013
116H	0.001	0	0	0.001
117H	0.014	0	0	0.013
118H	0.005	0	0	0.005
119H	0.001	0.001	0	0.002
120H	0.001	0	0	0.001
121H	0.004	0	0	0.005
122H	0.002	0.001	0	0.003
123H	0	0	0	0
124H	0.004	0.001	0	0.004

125H	0.003	0	0	0.003
126H	0	0	0	0
127H	0.013	0	0	0.013
128H	0.001	0	0	0.001
129H	0.013	0	0	0.013
130H	0.006	0	0	0.006

Table S 10. The information of **1** geometric configuration

Crystal lattice:

cell_length_a	25.00000
cell_length_b	25.00000
cell_length_c	25.00000
cell_angle_alpha	90.000000
cell_angle_beta	90.000000
cell_angle_gamma	90.000000

Atom	x	y	z
1C	0.30075	0.53454	0.32154
2C	0.77967	0.57025	0.39587
3C	0.704	0.54554	0.33458
4C	0.73885	0.5285	0.3821
5C	0.27103	0.50559	0.35898
6C	0.26467	0.44525	0.34258
7C	0.69925	0.46546	0.67846
8C	0.22033	0.42975	0.60413
9C	0.296	0.45446	0.66542
10C	0.26115	0.4715	0.6179
11C	0.72897	0.49441	0.64102
12C	0.73534	0.55475	0.65742
13N	0.35974	0.51177	0.31725
14N	0.69943	0.51711	0.42563
15N	0.30237	0.50896	0.41158
16N	0.65487	0.51399	0.32831
17N	0.64026	0.48823	0.68275
18N	0.30057	0.48289	0.57437
19N	0.69763	0.49104	0.58842
20N	0.34513	0.48601	0.67169
21O	0.50109	0.45517	0.47275
22O	0.36776	0.30567	0.48113
23O	0.38752	0.45338	0.46446
24O	0.45007	0.3646	0.49815
25O	0.61477	0.45588	0.46947
26O	0.55578	0.36737	0.49994
27O	0.39487	0.39076	0.28913

28O	0.45479	0.26686	0.43463
29O	0.36294	0.38724	0.54786
30O	0.55826	0.26998	0.43695
31O	0.50116	0.36289	0.60219
32O	0.64084	0.31031	0.48691
33O	0.41865	0.30177	0.57477
34O	0.56334	0.45903	0.36914
35O	0.50597	0.3943	0.30549
36O	0.44347	0.44972	0.57806
37O	0.64003	0.39336	0.55252
38O	0.44522	0.45448	0.36563
39O	0.61842	0.37542	0.40296
40O	0.45379	0.30905	0.33736
41O	0.56069	0.31252	0.33785
42O	0.50461	0.36833	0.40716
43O	0.40273	0.3796	0.65257
44O	0.55573	0.45167	0.5815
45O	0.70879	0.39607	0.46419
46O	0.58665	0.30488	0.57835
47O	0.40646	0.20801	0.51585
48O	0.61636	0.3986	0.29244
49O	0.29651	0.38974	0.46062
50O	0.38832	0.37019	0.39868
51O	0.50354	0.26366	0.52515
52O	0.60317	0.21118	0.52176
53O	0.51031	0.21476	0.35157
54O	0.5982	0.38222	0.65577
55O	0.49891	0.54483	0.52725
56O	0.63224	0.69433	0.51887
57O	0.61248	0.54662	0.53554
58O	0.54993	0.6354	0.50185
59O	0.38523	0.54412	0.53053
60O	0.44422	0.63263	0.50006
61O	0.60513	0.60924	0.71087
62O	0.54521	0.73314	0.56537
63O	0.63706	0.61276	0.45214
64O	0.44174	0.73002	0.56305
65O	0.49884	0.63711	0.39781
66O	0.35916	0.68969	0.51309
67O	0.58135	0.69823	0.42523
68O	0.43666	0.54097	0.63086
69O	0.49403	0.6057	0.69451
70O	0.55653	0.55028	0.42194

71O	0.35997	0.60664	0.44748
72O	0.55478	0.54552	0.63437
73O	0.38158	0.62458	0.59704
74O	0.54621	0.69095	0.66264
75O	0.43931	0.68748	0.66215
76O	0.49539	0.63167	0.59284
77O	0.59727	0.6204	0.34743
78O	0.44427	0.54833	0.4185
79O	0.29121	0.60393	0.53581
80O	0.41335	0.69512	0.42165
81O	0.59354	0.79199	0.48415
82O	0.38364	0.6014	0.70756
83O	0.70349	0.61026	0.53938
84O	0.61168	0.62981	0.60132
85O	0.49646	0.73634	0.47485
86O	0.39683	0.78882	0.47824
87O	0.48969	0.78524	0.64843
88O	0.4018	0.61778	0.34423
89Si	0.50328	0.38975	0.46863
90Si	0.49672	0.61025	0.53137
91Cu	0.55914	0.5008	0.5017
92Cu	0.49757	0.49753	0.61077
93Cu	0.62992	0.49055	0.39979
94Cu	0.37706	0.48771	0.39289
95Cu	0.44086	0.4992	0.4983
96Cu	0.50243	0.50247	0.38923
97Cu	0.37008	0.50945	0.60021
98Cu	0.62294	0.51229	0.60711
99W	0.36368	0.38313	0.47104
100W	0.42888	0.37911	0.58869
101W	0.43763	0.38454	0.34302
102W	0.43077	0.2718	0.50627
103W	0.50916	0.27666	0.38047
104W	0.64108	0.38712	0.47419
105W	0.57876	0.2738	0.51073
106W	0.57143	0.38932	0.3433
107W	0.57541	0.38212	0.59159
108W	0.63632	0.61687	0.52896
109W	0.57112	0.62089	0.41131
110W	0.56237	0.61546	0.65698
111W	0.56923	0.7282	0.49373
112W	0.49084	0.72334	0.61953
113W	0.35892	0.61288	0.52581

114W	0.42124	0.7262	0.48927
115W	0.42857	0.61068	0.6567
116W	0.42459	0.61788	0.40841
117H	0.81268	0.57177	0.3667
118H	0.79716	0.56375	0.43577
119H	0.75971	0.60942	0.39648
120H	0.3051	0.42867	0.33875
121H	0.2436	0.44046	0.30406
122H	0.24196	0.42272	0.37278
123H	0.24071	0.39096	0.60038
124H	0.20027	0.43808	0.56581
125H	0.18928	0.42598	0.63519
126H	0.75884	0.57703	0.62772
127H	0.75523	0.55928	0.69658
128H	0.69508	0.5719	0.66035
129H	0.37591	0.42457	0.28035
130H	0.38572	0.41284	0.66965
131H	0.39119	0.18997	0.54686
132H	0.63632	0.43288	0.28742
133H	0.28127	0.42561	0.45001
134H	0.60185	0.17845	0.54255
135H	0.53178	0.19867	0.32309
136H	0.61764	0.45918	0.70168
137H	0.62374	0.57518	0.71978
138H	0.61423	0.58712	0.3304
139H	0.27383	0.56883	0.54256
140H	0.58321	0.82604	0.46846
141H	0.36342	0.56739	0.71281
142H	0.7188	0.57427	0.54963
143H	0.39017	0.81507	0.4504
144H	0.51296	0.80437	0.67327
145H	0.38228	0.54098	0.29857
146H	0.72623	0.43112	0.4574
147H	0.29077	0.56813	0.29543
148H	0.71558	0.57505	0.30412
149H	0.70919	0.43182	0.70449
150H	0.2844	0.42494	0.69585

Table S 11. The information of **2** geometric configuration

Crystal lattice:

cell_length_a	25.00000
cell_length_b	25.00000
cell_length_c	25.00000

cell_angle_alpha	90.000000
cell_angle_beta	90.000000
cell_angle_gamma	90.000000

Atom	x	y	z
1C	0.24407	0.47297	0.41317
2C	0.27181	0.47725	0.36489
3C	0.25286	0.45501	0.31249
4C	0.75593	0.52703	0.58683
5C	0.72819	0.52275	0.63511
6C	0.74714	0.54499	0.68751
7N	0.27179	0.49739	0.45959
8N	0.33004	0.48113	0.37183
9N	0.72821	0.50261	0.54041
10N	0.66996	0.51887	0.62817
11O	0.33735	0.62913	0.58139
12O	0.48125	0.64613	0.63107
13O	0.39805	0.70964	0.59993
14O	0.43108	0.73353	0.45533
15O	0.53526	0.73094	0.4568
16O	0.48384	0.74086	0.54596
17O	0.41199	0.56219	0.60979
18O	0.35687	0.55406	0.50959
19O	0.39545	0.45547	0.49791
20O	0.45442	0.4635	0.5895
21O	0.4023	0.37576	0.56705
22O	0.52028	0.41027	0.65581
23O	0.53609	0.55692	0.60748
24O	0.62096	0.69393	0.50931
25O	0.57132	0.31989	0.63353
26O	0.58347	0.45994	0.58447
27O	0.46527	0.36324	0.46992
28O	0.51825	0.37126	0.56031
29O	0.26907	0.62244	0.49305
30O	0.62946	0.40702	0.67101
31O	0.63646	0.37199	0.56599
32O	0.57329	0.3593	0.4717
33O	0.52186	0.45207	0.49208
34O	0.37953	0.38331	0.42061
35O	0.34412	0.70361	0.50683
36O	0.56539	0.70331	0.60174
37O	0.53635	0.67746	0.36611
38O	0.38252	0.64027	0.68374

39O	0.58208	0.7932	0.54135
40O	0.5777	0.62575	0.68207
41O	0.40976	0.41024	0.67526
42O	0.38915	0.80096	0.53659
43O	0.30763	0.38989	0.50595
44O	0.48643	0.7755	0.36821
45O	0.66265	0.37087	0.41861
46O	0.51875	0.35387	0.36893
47O	0.60195	0.29036	0.40007
48O	0.56892	0.26647	0.54467
49O	0.46474	0.26906	0.5432
50O	0.51616	0.25914	0.45404
51O	0.58801	0.43781	0.39021
52O	0.64313	0.44594	0.49041
53O	0.60455	0.54453	0.50209
54O	0.54558	0.5365	0.4105
55O	0.5977	0.62424	0.43295
56O	0.47972	0.58973	0.34419
57O	0.46391	0.44308	0.39252
58O	0.37904	0.30607	0.49069
59O	0.42868	0.68011	0.36647
60O	0.41653	0.54006	0.41553
61O	0.53473	0.63676	0.53008
62O	0.48175	0.62874	0.43969
63O	0.73093	0.37756	0.50695
64O	0.37054	0.59298	0.32899
65O	0.36354	0.62801	0.43401
66O	0.42671	0.6407	0.5283
67O	0.47814	0.54793	0.50792
68O	0.62047	0.61669	0.57939
69O	0.65588	0.29639	0.49317
70O	0.43461	0.29669	0.39826
71O	0.46365	0.32254	0.63389
72O	0.61748	0.35973	0.31626
73O	0.41792	0.2068	0.45865
74O	0.4223	0.37425	0.31793
75O	0.59024	0.58976	0.32474
76O	0.61085	0.19904	0.46341
77O	0.69237	0.61011	0.49405
78O	0.51357	0.2245	0.63179
79Si	0.51976	0.38734	0.49793
80Si	0.48024	0.61266	0.50207
81Cu	0.52858	0.50371	0.55247

82Cu	0.347	0.51285	0.44176
83Cu	0.40557	0.51114	0.55251
84Cu	0.47142	0.49629	0.44753
85Cu	0.653	0.48715	0.55824
86Cu	0.59443	0.48886	0.44749
87W	0.45133	0.3999	0.62148
88W	0.40675	0.6328	0.61963
89W	0.5581	0.72969	0.53268
90W	0.58655	0.39408	0.61947
91W	0.37578	0.38501	0.49695
92W	0.40995	0.73544	0.52948
93W	0.55388	0.62468	0.61799
94W	0.48563	0.71751	0.40358
95W	0.33666	0.62516	0.5063
96W	0.54867	0.6001	0.37852
97W	0.59325	0.3672	0.38037
98W	0.4419	0.27031	0.46732
99W	0.41345	0.60592	0.38053
100W	0.62422	0.61499	0.50305
101W	0.59005	0.26456	0.47052
102W	0.44612	0.37532	0.38201
103W	0.51437	0.28249	0.59642
104W	0.66334	0.37484	0.4937
105H	0.25284	0.41092	0.31391
106H	0.27976	0.46731	0.2799
107H	0.21195	0.46799	0.30239
108H	0.204	0.45616	0.41905
109H	0.7645	0.58513	0.68183
110H	0.77832	0.52008	0.70642
111H	0.71338	0.54822	0.71548
112H	0.79593	0.54399	0.58092
113H	0.2512	0.58832	0.48293
114H	0.36886	0.61774	0.71229
115H	0.61915	0.80428	0.54773
116H	0.59555	0.59986	0.70511
117H	0.40667	0.83552	0.53159
118H	0.50599	0.79269	0.33931
119H	0.35085	0.55789	0.3268
120H	0.60844	0.55851	0.31034
121H	0.71291	0.57569	0.50333
122H	0.64831	0.44278	0.67259
123H	0.39424	0.38595	0.70144
124H	0.28683	0.42421	0.49678

125H	0.74867	0.41178	0.51721
126H	0.63447	0.37967	0.28767
127H	0.43199	0.17058	0.46261
128H	0.404	0.40018	0.29527
129H	0.64743	0.18519	0.46555
130H	0.53343	0.2095	0.66177

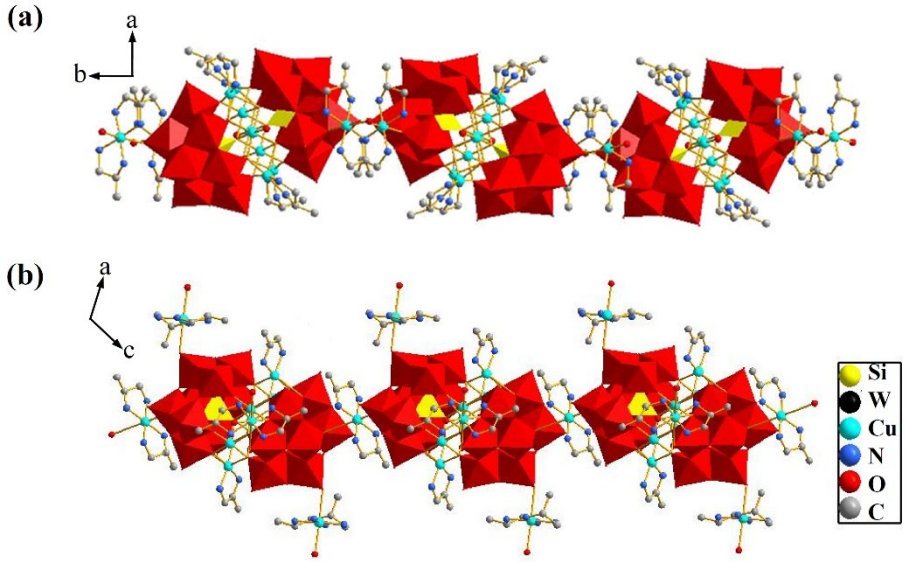

Fig. S1. Views of compound **1** along the c axis and compound **2** along the b axis.

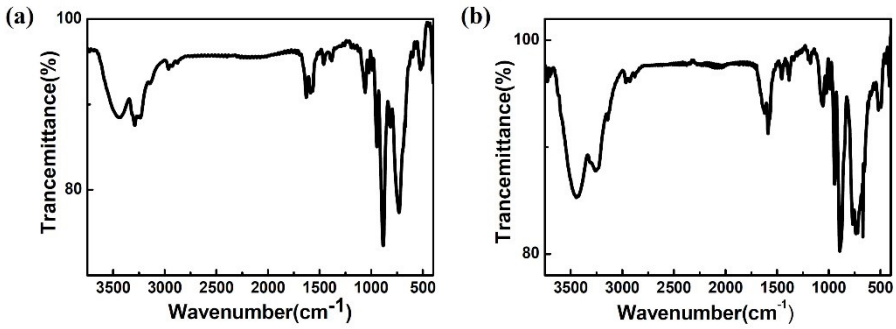

Figure S2. IR spectra of **1** and **2,** exhibiting an intense band at 1040 cm^{-1}, attributed to the feature of $\nu_{P\text{-}O}$, and bands at 940 cm^{-1} due to $\nu_{W=O}$, bands at 850, 790, and 710 cm^{-1} due to $\nu_{M\text{-}O\text{-}M}$ (M = W or Ni). The characteristics of the -NH_2 and -CH_2 groups are fallen in the 1400 and 3100-3300 cm^{-1} region.

1: 3439(m), 3291(m), 1627(m), 1460(w), 1388(w), 1062(m), 1022(w), 988(w), 947(m), 884(s), 726(s), 521(w).

2: 3439(s), 3262(m), 2979(w), 1627(m), 1590(m), 1455(w), 1383(w), 1172(w), 1062(w), 984(s), 942(s), 904(s), 779(s), 737(s), 660(s), 640(m), 521(w), 492(w).

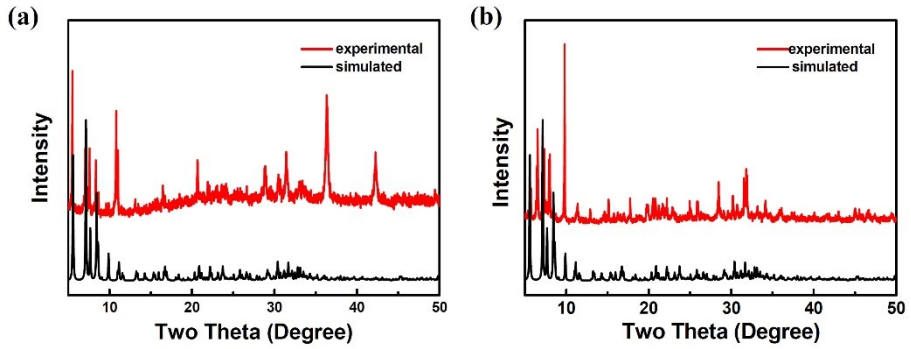

Figure S3. The simulated and experimental PXRD patterns of compounds **1** (a) and **2** (b).

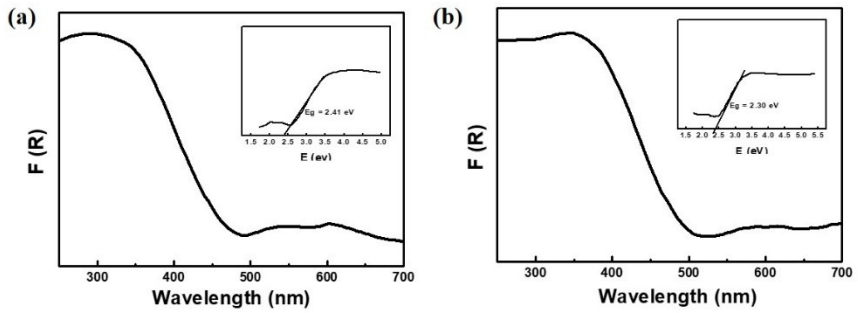

Figure S4. UV/Vis-NIR diffuse reflectance spectrum of **1** (a) and **2** (b).

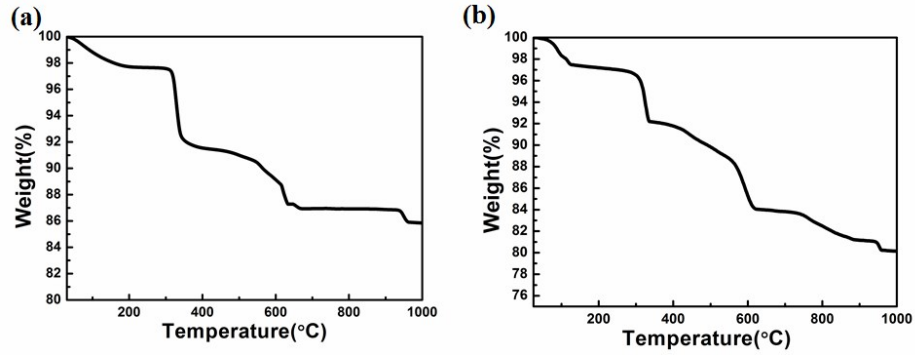

Figure S5. The TG curves of **1** (a) and **2** (b).

The thermogravimatric behaviors of **1** and **2** were investigated in the flowing air atmosphere from 25 to 1000 °C (Figure S5).

For **1**, the first weight loss of 2.30% from 25 to 240 °C is assigned to release of 7 lattice water molecules (calcd. 2.20%). From 240 to 480 °C, the weight loss of 6.49% corresponds to release of 2 $Cu(dap)_2$ groups (calcd. 6.68%). From 480 to 960 °C, the weight loss of 5.32% corresponds to release of 2 coordination water molecules and 4 dap ligands (calcd. 5.08%). For **2**, the first weight loss of 3.0% from 25 to 270 °C is assigned to release of 8 lattice water molecules and 2 coordination water molecules

(calcd. 3.0%). From 270 to 650 °C, the weight loss of 12.96% corresponds to release of 4 $Cu(dap)_2$ groups (calcd. 12.93%).

Formula for calculating H_2 production

We choose CH_4 as standard gas. And we can get the standard curve between H_2 and CH_4 : y=1.8458x (x is the rate of the peak area of H_2 and CH_4, y is the volume of hydrogen production) by GC. And we can get the volume of hydrogen production by testing the peak area of H_2 and CH_4 by GC. Finally, we can get the $n(H_2)$ by $n=V/V_m$.

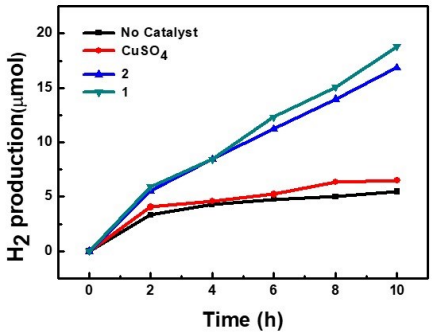

Fig. S6. Photocatalytic of **1** (4 mg), **2** (4 mg)**,** CuSO4 (4 mg) and without catalyst. Conditions: LED light (450 nm), $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM), 3mL CH_3CN/DMF (1/3), H_2O (2 M) deaerated with Ar.

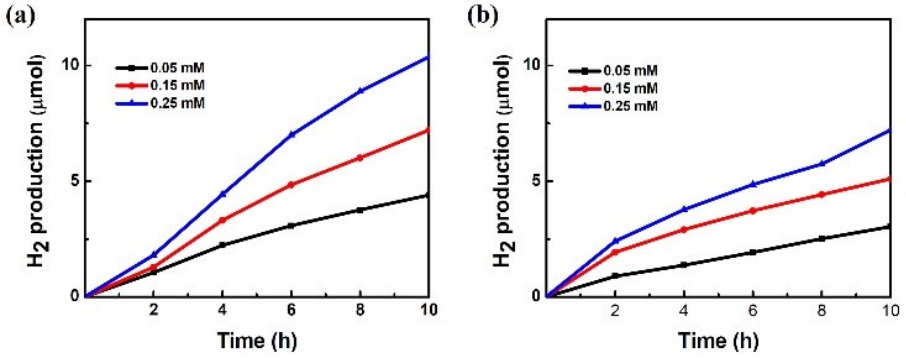

Fig. S7. Photocatalytic at different amount of TEOA for **1** (a) and **2** (b). Conditions: LED light (450 nm), $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM), 3mL CH_3CN/DMF (1/3), H_2O (2 M) deaerated with Ar/CH_4 (4:1).

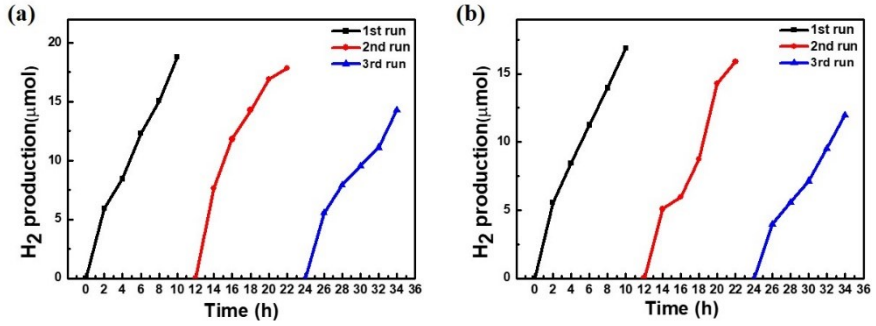

Fig. S8. Photocatalytic of **1** (a) and **2** (b) of the first run, second run and third run. Conditions: LED light (450 nm), $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM), 3mL CH_3CN/DMF (1/3), H_2O (2 M) deaerated with Ar/CH_4 (4:1).

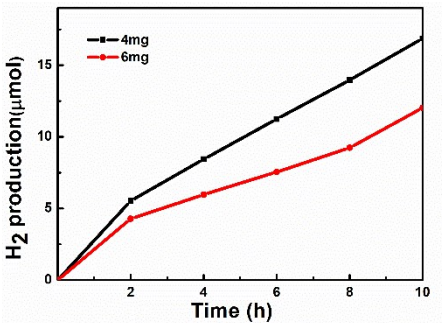

Fig. S9. Photocatalytic of **2** for 4 mg and 6 mg. Conditions: LED light (450 nm), $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM), 3mL CH_3CN/DMF (1/3), H_2O (2 M) deaerated with Ar/CH_4 (4:1).

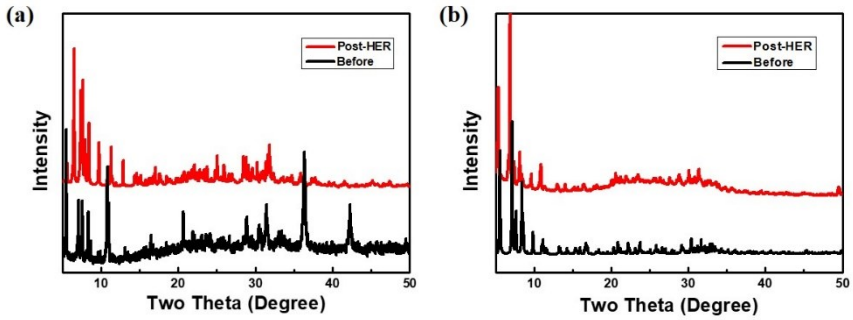

Fig. S10. The before and post-HER PXRD patterns of **1** (a) and **2** (b).