Supplementary Information

Two novel Dawson-like type tungstoantimonates with difunctional properties of photocatalysis and magnetism

Lin Shi , Xiao-mei Gao,Ting-Yu Liu, Xiao-Hui Huang , Zhi-Hui Gong , Yi-Ping Chen * ,Yan-Qiong Sun

College of chemistry, Fuzhou University, 350108 Fuzhou, PR China.

† Electronic Supplementary Information (ESI) available: Crystallographic, IR, UV-DRS, TGA, 2D-IR, and PXRD data.

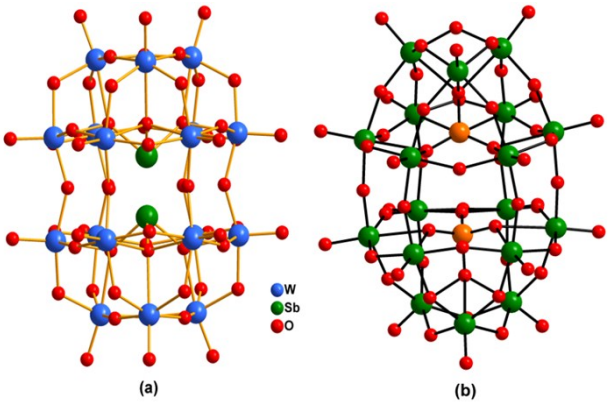

Fig. S1 Crystal structure and polyhedrons diagram of Dawson-like $[SbW_{18}O_{60}]^{9-}$ polyanion

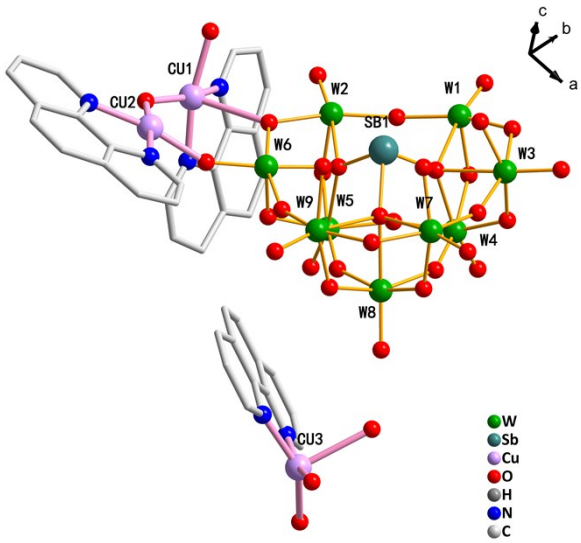

Fig. S2 The basic crystallographic unit of compound **2**, Sb atom and Cu(3) complex existing with site half-occupancy.

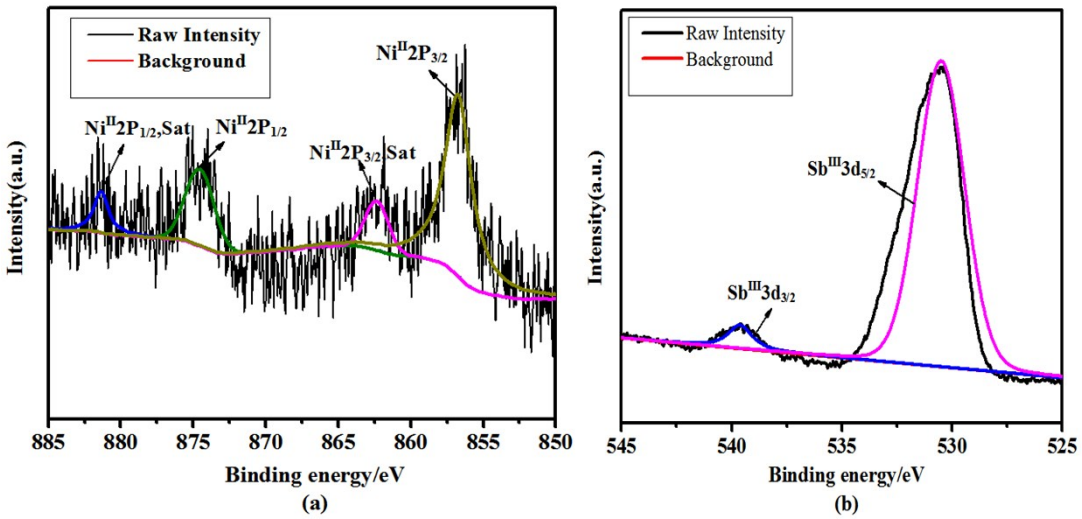

Fig. S3 High resolution the XPS of Ni and Sb for compound **1**.

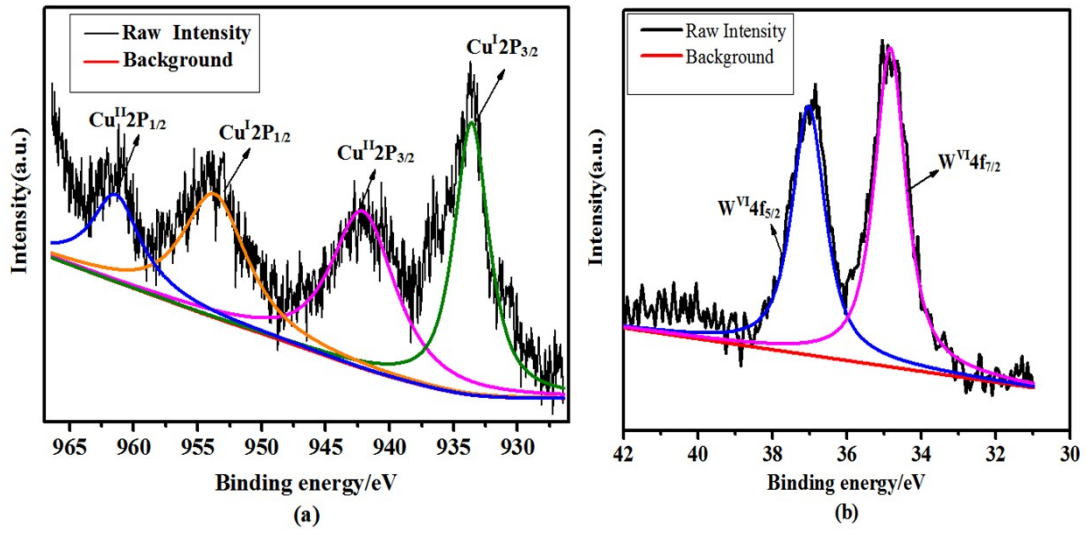

Fig. S4 High resolution the XPS of Cu and W for compound **2**.

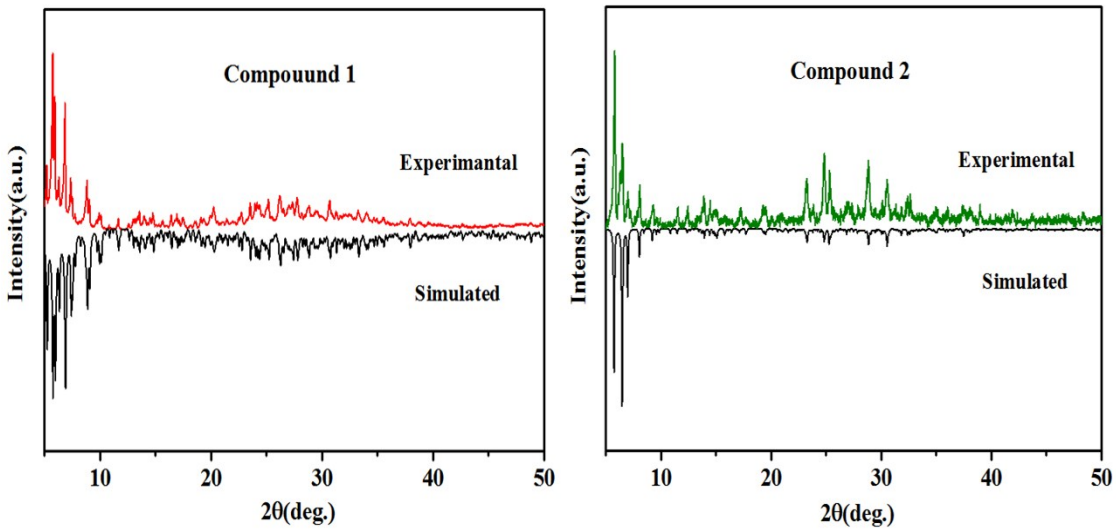

Fig. S5 Simulated and experimental X-ray power diffraction graph of compounds **1** and **2**

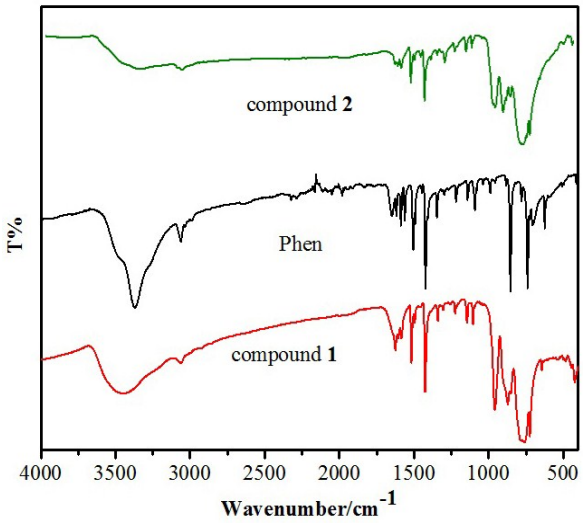

Fig. S6 IR spectra of compound **1** and **2** and ligand phen

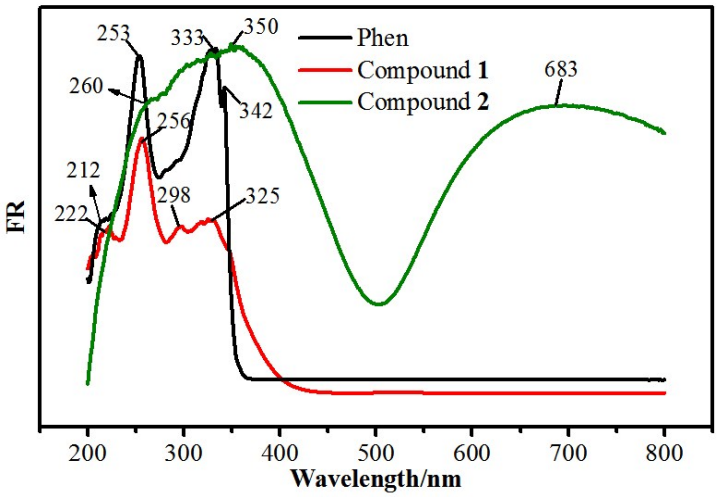

Fig. S7 UV-Vis DRS spectra of compounds **1-2** and Phen ligand

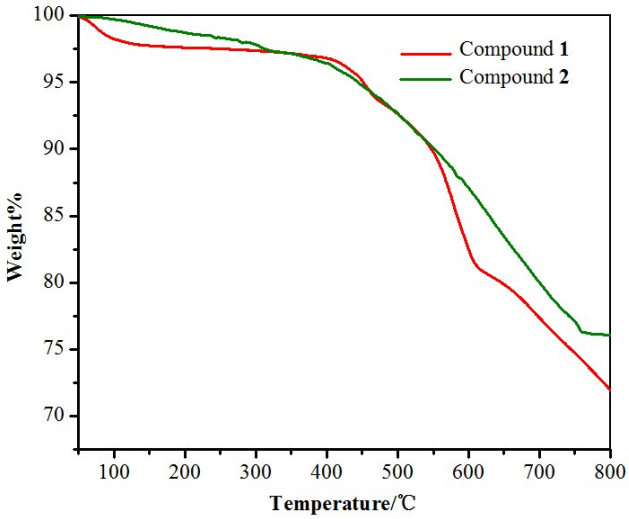

Fig. S8 TG curves of compounds **1** and **2**

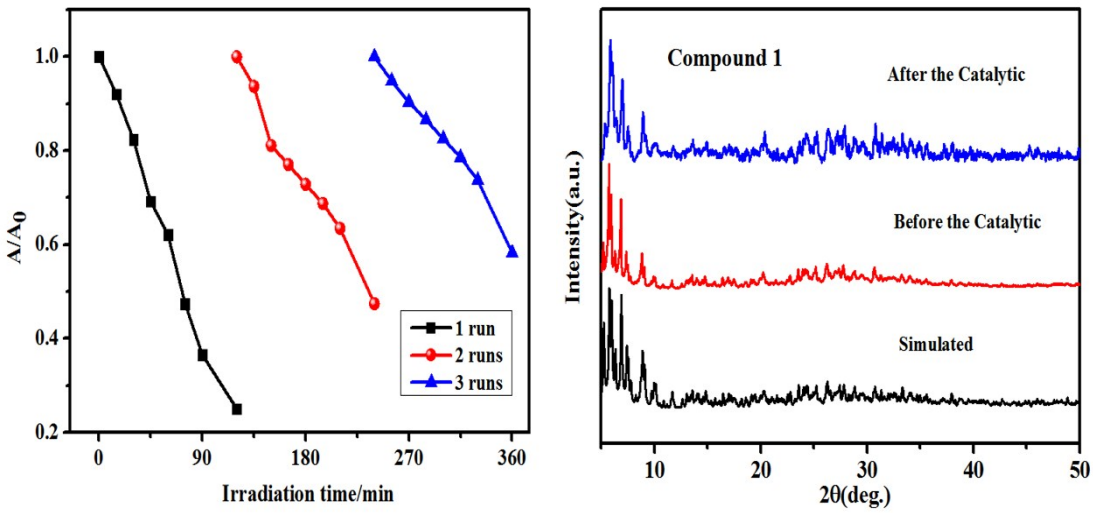

Fig. S9 (a)Three runs of the RhB degradation test by compound **1**;(b) The experimental and after three runs of photocatalysis PXRD patterns of compound **1**.

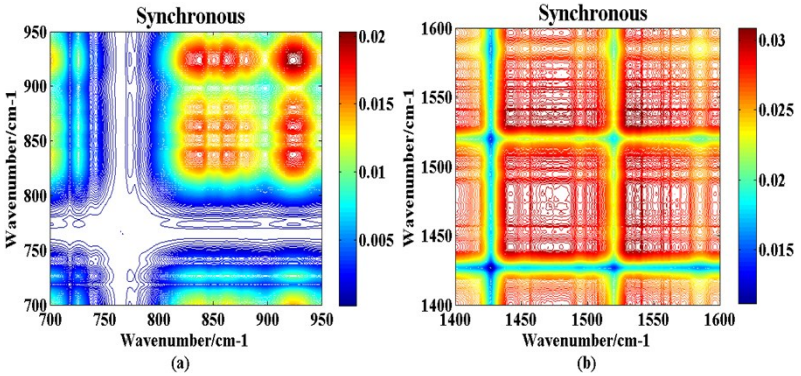

Fig. S10 Synchronous correlation 2D-IR spectra of **2** over a magnetic intensity of 5-50 mT.

Tab. S1 Crystallographic Data for compounds

Compound reference	**1**	**2**
Chemical formula	$C_{107}H_{79}N_{18}Ni_3O_{60}SbW_{18}$	$C_{60}H_{78}Cu_5N_{10}O_{69}SbW_{18}$
Molecular formula	$\{Ni(Phen)_3\}_3[SbW_{18}O_{60}]\cdot 7H_2O$	$[Cu^{I}(Phen)(H_2O)_3][\{[Cu^{II}_2(Phen)_2(H_2O)_2]_2[SbW_{18}O_{60}]\}\cdot 2H_2O$
Formula Mass	6253.02	5792.07
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	***P*Error!**
a/Å	13.8933(12)	12.800(3)
b/Å	33.825(3)	13.810(3)
c/Å	30.729(3)	15.700(3)
α/°	90.00	97.50(3)
β/°	91.3890(10)	96.85(3)
γ/°	90.00	92.83(3)
Unit cell volume/Å^3	14436(2)	2725.9(9)
Temperature/K	293(2)	298(2)
Z	4	1
F(000)	11308.0	2588
Limiting indices	-16<=h<=16, -40<=k<=32, -36<=l<=32	-16 ≤ h ≤ 15,-17 ≤ k ≤ 12 -20 ≤ l ≤ 20
Reflections collected	62488	21674
Independent reflections	25365	11798
R_{int}	0.0439	0.0970
Goodness of fit on F^2	1.066	1.032
Theta range for data collection	1.32 to 27.99	3.20 to 27.50
Data / restraints / parameters	25365 / 1 / 1371	11798 / 4 / 542
Absorption coefficient/mm^-1	15.117	20.195
Final *R* factors ($I>2\sigma$ *(I)*)	R_1[a] =0.0616 ,wR_2[b]= 0.1890	R1 = 0.1020, wR2 = 0.2722
R indices (all data)	R_1 =0.0866,wR_2=0.2094	R1 = 0.1082, wR2 = 0.2800
$\triangle\rho_{max}$ /$\triangle\rho_{min}$ (e Å^{-3})	5.114 and -10.288	8.627 and -6.153

[a]$R1=\sum||Fo|-|Fc||/\sum|Fo|$,[b]$wR2=\{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table. S2 Hydrogen bond lengths (Å) and angles(°) of compound **1** and **2**

	D—H…A	D--H	H…A	D…A	<DHA	Symmetry codes
compound **1**	O(5W)-H(5WA)···O(36)	0.85	2.30	2.9124	129	
	O(1W)-H(1WA)···O(40)	0.85	2.33	2.9187	127'	1+x,y,z
	O(7W)-H(7WA)···O(23)	0.85	2.21	3.0480	167	1+x,y,z
	C(1)-H(1)···O(13)	0.93	2.60	3.2814	131	1+x,y,z
	C(2)-H(2)···O(6W)	0.93	2.56	3.3918	149	
	C(3)-H(3)···O(45)	0.93	2.57	3.4480	158	
	C(6)-H(6)···O(46)	0.93	2.34	3.2383	162	
	C(11)-H(11)···O(19)	0.93	2.34	2.9512	123	x,1/2-y,1/2+z
	C(22)-H(22)···O(15)	0.93	2.34	3.0241	130	1+x,y,z
	C(34)-H(34)···O(59)	0.93	2.38	3.1194	138	1-x,-1/2+y,1/2-z
	C(39)-H(39)···O(46)	0.93	2.34	3.2709	166	x,1/2-y,-1/2+z
	C(59)-H(59)···O(34)	0.93	2.57	3.3573	143	1-x,-1/2+y,1/2-z
	C(85)-H(85)···O(11)	0.93	2.23	2.9686	136	
	C(86)-H(86)···O(2)	0.93	2.56	3.2887	135	
	C(86)-H(86)···O(12)	0.93	2.51	3.3341	147'	
	C(91)-H(91)···O(51)	0.93	2.53	3.3864	153	-x,-1/2+y,1/2-z
	C(97)-H(97)···O(52)	0.93	2.25	3.0831	149	1-x,-1/2+y,1/2-z
	C(106-H(106)···O(20)	0.93	2.52	3.2767	139	x,1/2-y,1/2+z
	C(107)-H(107)···O(21)	0.93	2.42	3.0903	129	x,1/2-y,1/2+z

	X-H···π	H···Cg	X···Cg	∠X-H···Cg	Symmetry Code
	C(14)-H(14) > Cg(1)	2.62	3.4488	159	x,1/2-y,1/2+z
	C(74)-H(74)> Cg(2)	2.62	3.4831	154	x, y, z
	C(78)-H(78)> Cg(1)	2.61	3.3412	154	x, y, z
	C(79)-H(79)> Cg(1)	2.82	3.4535	127	x, y, z

	D—H…A	D--H	H…A	D…A	<DHA	Symmetry codes
compound **2**	O(31)-H(31B)···O(17)	0.91	2.47	3.132(15)	130	1+x,y,z
	O(31)-H(31B)···O(18)	0.91	2.49	3.29(2)	146	1-x,1-y,1-z
	O(31)-H(31B)···O(20)	0.91	2.29	3.040(16)	139	1-x,1-y,1-z
	O(32)-H(32B)···O(34)	0.91	2.21	3.189(12)	139	-x,1-y,1-z
	C(1)-H(1)···O(7)	0.95	2.50	3.38(4)	155	1+x,y,z
	C(5)-H(5)···O(34)	0.95	2.57	3.49(2)	165	x,y,1+z
	C(10)-H(10)···O(9)	0.95	2.31	3.24(4)	166	-x,1-y,2-z
	C(14)-H(14)···O(30)	0.95	2.46	3.38(3)	163	-1+x,y,z
	C(20)-H(20)···O(18)	0.95	2.44	3.34(3)	159	-x,-y,1-z
	C(21)-H(21)···O(5)	0.95	2.56	3.42(3)	150	-1-x,-y,1-z
	C(23)-H(23)···O(1)	0.95	2.41	3.13(3)	132	-x,-y,1-z
	C(26)-H(26)···O(3)	0.95	2.25	3.194(15)	171	-x,-y,1-z
	C(35)-H(35)···O(12)	0.95	2.37	3.235(16)	152	x,y,-1+z

	Two planes		Center-to-Center Distance	Symmetry Code
π-π stacking	Cg(1)-Cg(1)	3.4514	3.836	
	Cg(2)-Cg(2)	3.4916	3.786	-x,-y,-z

Compound **1:** Cg(1):C49,C50,C51,C52,C53,C54,C55,C56,C57,C58,C59,N9,N10.

Cg(2): C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,C11,C12,N1,N2.

Compound **2** :Cg(1):C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,C11,C12,N1,N2.

Cg(2):C13,C14,C15,C16,C17,C18,C19,C20,C21,C22,C23,C24,N3,N4.

Explanation of checkcif

1.PLAT202_ALERT_3_A Isotropic non-H Atoms in Anion /Solvent.
C atoms were not executed anisotropy of 1.

2.PLAT602_ALERT_2_A VERY LARGE Solvent Accessible VOID(S) in Structure. Adjacent ligand had major voids in stratiform structure of 1.