Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

The first 3D host-guest structure based on three-fold interpenetrated Ag-pz coordination polymer network and Keggin-type aluminumtungstates with photo-/electro-catalytic properties

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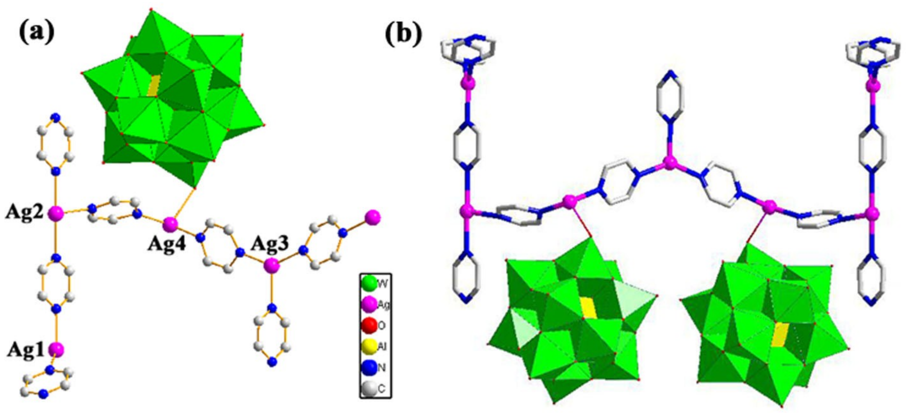

Figure S1 (a) Polyhedral and ball-stick representation of the symmetric unit of compound **1**. The H atoms are omitted for clarity. Codes: yellow tetrahedron, $\{AlO_4\}$; green octahedron, $\{WO_6\}$. (b) "double ball" unit.

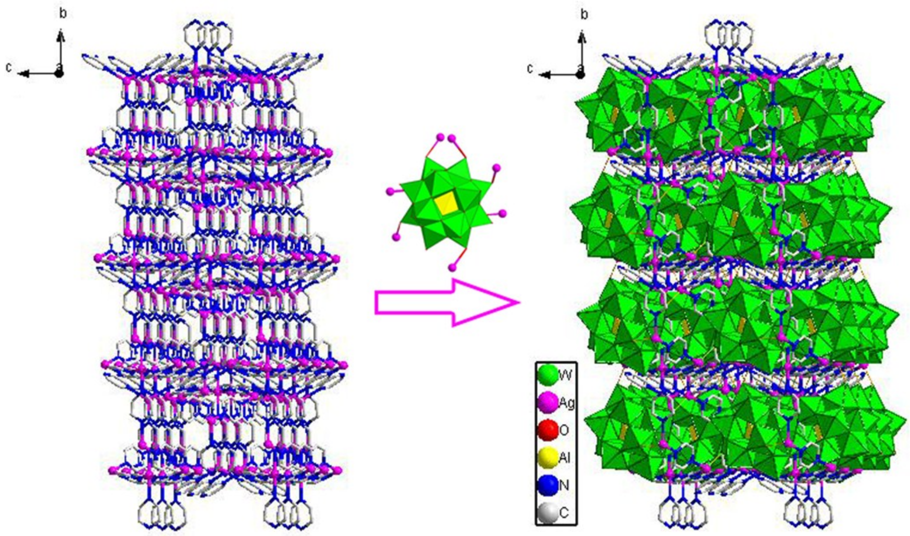

Figure S2 The 3D POMOF network of compound **1** based on Keggin polyanions $[AlW_{12}O_{40}]^{5-}$ and Ag-pz network.

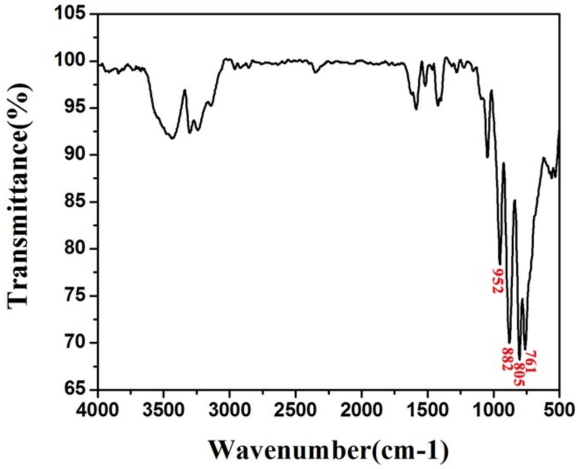

Figure S3 IR spectra of compound **1**

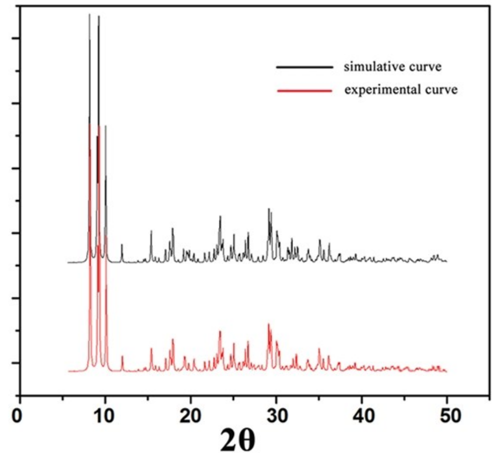

Figure S4 The XRD patterns for compound **1**

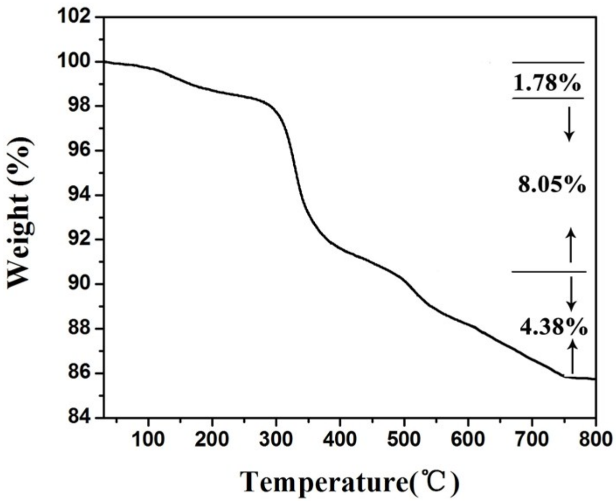

Figure S5 TG curve of compound **1.**

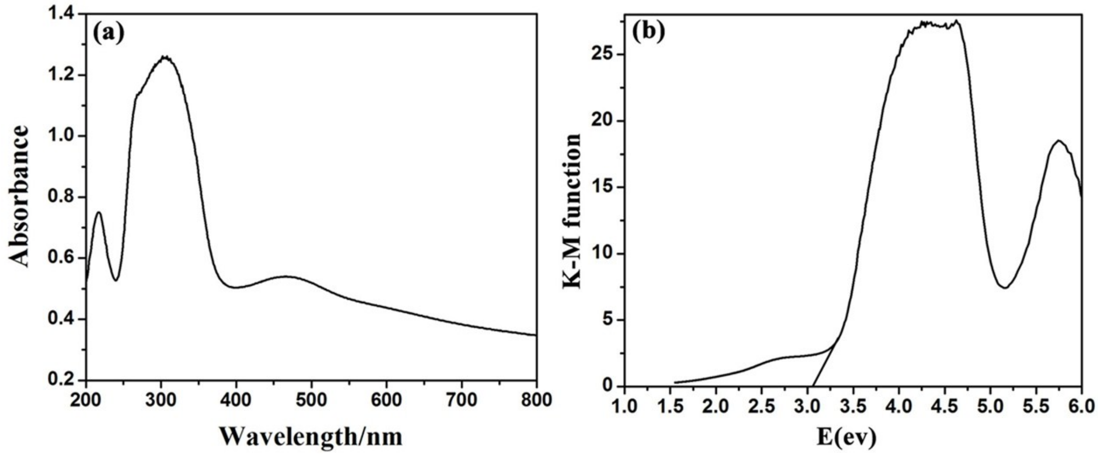

Figure S6 (a) Solid state UV-vis spectra and, (b) the diffuse reflectance spectra of compound **1.**

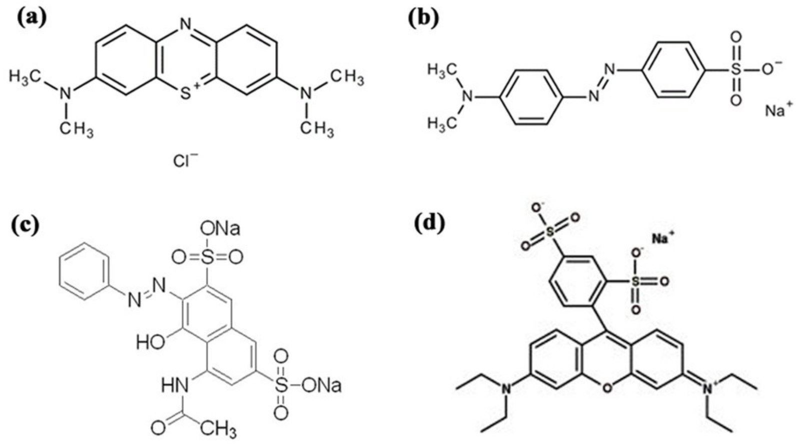

Figure S7 The structures of MB (a), MO (b), AP (c), RhB (d).

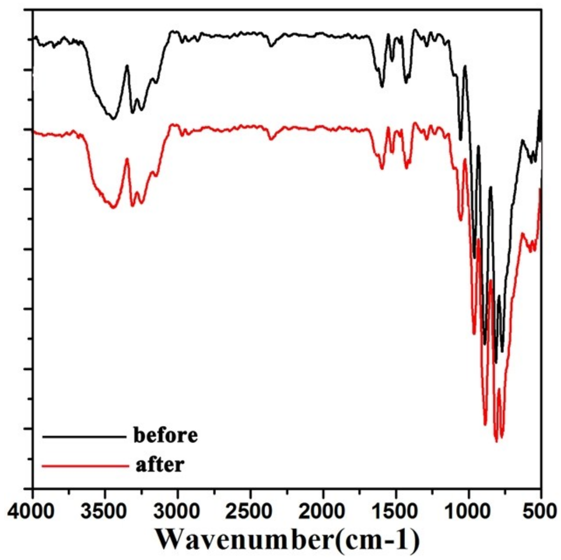

Figure S8 IR spectra of compound **1** before and after photocatalytic reaction.

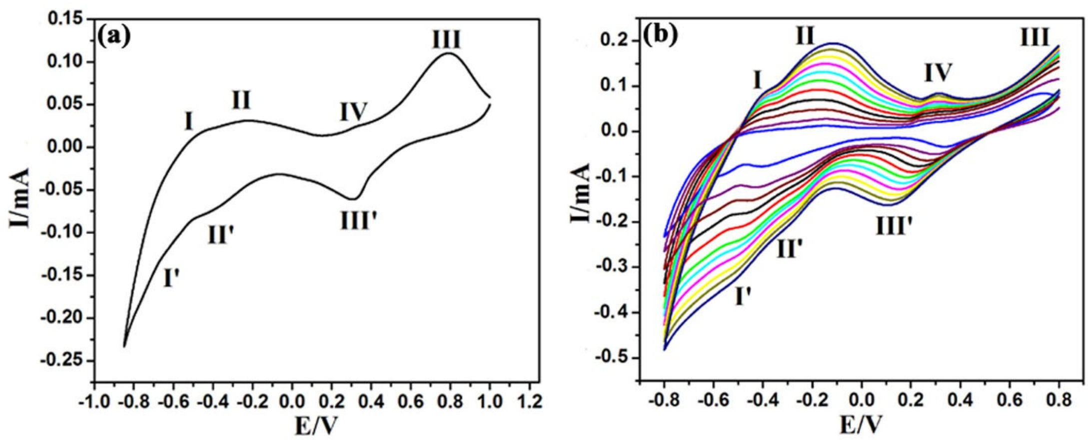

Figure S9 (a) Cyclic voltammograms of **1**-CPE in 1 M H_2SO_4 aqueous solution. Potentials vs.SCE. Scan rate: 20mVs^{-1}. (b) Cyclic voltammograms of **1**-CPE in 1M H_2SO_4 solution at different scan rates (from inner to outer:20,50,80,110,140,170,200,230,260,290,320mV.s^{-1}).

Table S1. The summarization of known POTA-based hybrid compounds.

NO.	Compounds	References
1	$[Cu(2,2'\text{-bipy})_2]\{AlW^{VI}_{11}W^{V}O_{40}[Cu(2,2'\text{-bipy})_2]_2\}\cdot 2H_2O$	[1]
2	$H_{3.5}[Ni(2,2'\text{-bipy})_3]_3\{[AlW_{12}O_{40}Ni(2,2'\text{-bipy})_2(H_2O)]_2Na_{0.5}\}$	[2]
3	$\{Ag_3(2,2'\text{-bipy})_2(4,4'\text{-bipy})_2\}\{Ag(2,2'\text{-bipy})_2\}\{Ag(2,2'\text{-bipy})\}[AlW_{12}O_{40}]\cdot H_2O$	[3]
	$[Ag(phen)_2]_3[Ag(phen)_3][AlW_{12}O_{40}]\cdot H_5O_2$	
	$\{Co(2,2'\text{-bipy})_3\}_3\{Co(H_2O)(2,2'\text{-bipy})_2[AlW_{12}O_{40}]\}_2\cdot H_2O$	
4	$[Cu(en)_2(H_2O)]\{[Cu(bpp)]_3[AlW_{12}O_{40}]\}\cdot H_2O$	[4]
5	$\{[Cu(2,2'\text{-bipy})_2]_2(Hbpy)[\alpha\text{-}AlW_{12}O_{40}]\}\cdot H_2O$	[5]
	$\{[H_2en][Cu^{I}(4,4'\text{-bipy})]_3(a\text{-}AlW_{12}O_{40})\}\cdot 4H_2O$	
6	$[AlCu_3W_{12}O_{40}(C_2H_8N_2)_6(H_2O)_3]$,	[6]
7	$[Ni_2(H_2O)_2(bipy)_4(Hbipy)][AlW_{12}O_{40}]\cdot 7H_2O$	[7]
8	$K_2(H_2O)_4Ln(H_2O)_7[Ln(H_2O)_3HAlW_{11}O_{39}]$. nH2O (Ln：Pr 1, Nd 2, Sm 3, Eu 4, Gd 5, Tb 6; for 1, n=8; for 2,4,5,6, n=7; for 3, n=9),	[8]
9	$[Ag(2\text{-MMIZ})_2]_6\{[Ag(2\text{-MMIZ})_2]_2[Ag(2\text{-MMIZ})]_2[AlW_{12}O_{40}]_2\}$	[9]
	$[Ag(2\text{-MMIZ})_2]_5[AlW_{12}O_{40}]$	
10	$[Co(Hbztpy)_2]H[AlW_{12}O_{40}]\cdot 3H_2O$	[10]

Table S2 Selected bond lengths (Å) and bond angles (º) of compound **1**

W(1)-O(11)	1.662(17)	W(1)-O(4)	1.877(18)	W(1)-O(13)	1.90(2)
W(1)-O(3)	1.86(2)	W(1)-O(20)#1	1.88(2)	W(1)-O(17)	2.262(18)
W(1)-O(19)	2.26(2)	W(2)-O(7)	1.69(2)	W(2)-O(15)	1.86(2)
W(2)-O(20)	1.87(2)	W(2)-O(2)	1.89(2)	W(2)-O(14)	1.91(2)
W(2)-O(16)#1	2.26(2)	W(2)-O(19)#1	2.34(4)	W(3)-O(10)	1.680(19)

W(3)-O(1)	1.85(2)	W(3)-O(12)#1	1.90(2)	W(3)-O(22)	1.92(2)
W(3)-O(4)	1.93(2)	W(3)-O(21)	2.27(3)	W(3)-O(17)	2.42(2)
W(4)-O(5)	1.689(15)	W(4)-O(2)	1.84(3)	W(4)-O(18)#1	1.87(2)
W(4)-O(22)	1.90(3)	W(4)-O(3)#1	1.91(3)	W(4)-O(21)	2.26(2)
W(4)-O(19)#1	2.37(2)	W(5)-O(14)	1.87(2)	W(5)-O(18)	1.91(2)
W(5)-O(21)#1	2.32(4)	W(5)-O(16)#1	2.41(2)	W(5)-O(6)	1.92(2)
W(5)-O(8)	1.671(18)	W(5)-O(12)	1.85(3)	W(6)-O(9)	1.64(2)
W(6)-O(6)	1.86(2)	W(6)-O(13)	1.88(2)	W(6)-O(1)	1.90(2)
W(6)-O(15)	1.92(2)	W(6)-O(16)#1	2.27(3)	W(6)-O(17)	2.35(2)
Al(1)-O(17)	1.690(19)	Al(1)-O(17)#1	1.69(2)	Al(1)-O(19)#1	1.72(3)
Al(1)-O(19)	1.72(3)	Al(1)-O(16)	1.75(3)	Al(1)-O(16)#1	1.75(3)
Al(1)-O(21)	1.81(4)	Al(1)-O(21)#1	1.81(4)	Ag(1)-N(4)	2.21(3)
Ag(1)-N(5)#2	2.273(19)	Ag(1)-N(5)	2.273(19)	Ag(2)-N(11)	2.31(4)
Ag(2)-N(7)	2.34(3)	Ag(2)-N(7)#2	2.34(3)	Ag(2)-N(3)	2.42(4)
Ag(3)-N(6)	2.24(3)	Ag(3)-N(6)#3	2.24(3)	Ag(3)-N(10)	2.27(7)
Ag(4)-N(1)	2.14(4)	Ag(4)-N(2)	2.23(3)	Ag(4)-O(10)	2.56(5)
Ag(3)-O(9)	2.69(9)				
O(11)-W(1)-O(3)	101.6(13)	O(11)-W(1)-O(4)	98.3(13)	O(11)-W(1)-O(20)#1	105.9(12)
O(11)-W(1)-O(13)	97.4(12)	O(11)-W(1)-O(17)	152.7(11)	O(11)-W(1)-O(19)	159.9(12)
O(7)-W(2)-O(15)	100.1(14)	O(7)-W(2)-O(20)	101.0(12)	O(7)-W(2)-O(2)	103.4(12)
O(7)-W(2)-O(14)	100.1(14)	O(7)-W(2)-O(16)#1	155.1(11)	O(7)-W(2)-O(19)#1	154.1(11)
O(10)-W(3)-O(1)	102.3(11)	O(10)-W(3)-O(12)#1	101.6(15)	O(10)-W(3)-O(22)	99.8(14)
O(10)-W(3)-O(4)	99.5(11)	O(10)-W(3)-O(21)	153.2(13)	O(10)-W(3)-O(17)	154.0(9)
O(5)-W(4)-O(2)	103.5(11)	O(5)-W(4)-O(18)#1	99.8(14)	O(5)-W(4)-O(22)	98.2(14)
O(5)-W(4)-O(3)#1	100.6(12)	O(5)-W(4)-O(21)	152.3(13)	O(5)-W(4)-O(19)#1	154.9(10)
O(8)-W(5)-O(12)	101.2(14)	O(8)-W(5)-O(14)	99.8(12)	O(8)-W(5)-O(18)	101.0(13)
O(8)-W(5)-O(6)	100.9(12)	O(8)-W(5)-O(21)#1	152.2(11)	O(8)-W(5)-O(16)#1	153.0(9)
O(9)-W(6)-O(6)	101.3(14)	O(9)-W(6)-O(13)	101.5(11)	O(9)-W(6)-O(1)	100.8(11)
O(6)-W(6)-O(15)	88.7(10)	O(6)-W(6)-O(16)#1	65.1(11)	O(6)-W(6)-O(17)	96.3(13)
O(17)-Al(1)-O(17)#1	179.996(4)	O(17)-Al(1)-O(19)#1	115.6(11)	O(17)-Al(1)-O(19)	64.4(10)
O(17)-Al(1)-O(16)	110.4(11)	O(17)-Al(1)-O(16)#1	69.6(11)	O(17)-Al(1)-O(21)	73.3(11)
O(17)-Al(1)-O(21)#1	106.7(12)	N(4)-Ag(1)-N(5)#2	120.9(6)	N(4)-Ag(1)-N(5)	120.9(6)
N(11)-Ag(2)-N(7)	82.6(7)	N(11)-Ag(2)-N(7)#2	82.6(7)	N(11)-Ag(2)-N(3)	180.000(9)
N(6)-Ag(3)-N(6)#3	140.6(18)	N(6)-Ag(3)-N(10)	109.7(9)	N(1)-Ag(4)-N(2)	116.4(11)
N(1)-Ag(4)-O(10)	95.5(7)	N(2)-Ag(4)-O(10)	113.5(4)		

Table S3 Photocatalytic summary of some classical Keggin structures

Compound	RhB			MB			MO			Reference
	Time /min	Degradation rate/%	Light	Time /min	Degradation rate/%	Light	Time /min	Degradation rate/%	Light	
$[Ag_2(L_1)_4][HPW_{12}O_{40}]$	100	27.94	UV							[1]
$[Cu(H_2tda)(H_2O)_2]_4[SiW_{12}O_{40}]$	360	90	UV							[2]
$[Cu_2(H_2tda)_2(H_2O)_4][SiW_{12}O_{40}]\cdot(TMA)_2$	360	68	UV							
$[Cu(H_2tda)(H_2O)_3][SiW_{12}O_{40}]\cdot(TMA)_3$	360	48	UV							

$[Cu_2(bipy)_2][H_2SiW_{12}O_{40}]$.(bipy)	300	51.3	UV							[3]
$[Cu(bpyb)_2(H_2O)_2][H_2SiW_{12}O_{40}]$.(bpyb)	300	69.7	UV							
$[Cu(bib)][H_2SiW_{12}O_{40}]$.(bib)	300	46.2	UV							
$[Ag_4(H_2pyttz\text{-}I)(H_2pyttz\text{-}II)(Hpyttz\text{-}II)][HSiW_{12}O_{40}]$	150	63.3	UV							[4]
$[Ag_4(H_2pyttz\text{-}II)(Hpyttz\text{-}II)_2][H_2SiW_{12}O_{40}]$	150	81.1	UV							
$[Cu_3(2\text{-}pytz)_2(bipy)_4(H_2O)_6][H_4SiW_{12}O_{40}]_2$	120	70	UV							[5]
$[Cu_2(2\text{-}pytz)(phen)(OH)]_2[SiW_{12}O_{40}]$	120	61	UV							
$[Cd(Htrz)_3]_2[SiW_{12}O_{40}]$	210	71	UV							[6]
$[Ni_2Cl_2(bipy)_3(Hbipy)_2][SiW_{12}O_{40}]$	300	51.1	UV							[7]
$[Ni_2(H_2O)_2(bipy)_4(Hbipy)][AlW_{12}O_{40}]$	300	47.7	UV							
$(H_2bimb)_2SiW_{12}O_{40}$	180	66.8	UV							[8]
$[Cu(bimb)]_2(HPW_{12}O_{40})$	180	72.6	UV							
$(H_2bimb)_3CoW_{12}O_{40}$	180	58.9	UV							
$K_2[Ag_6(pytz)_4][PW_{12}O_{40}]$	360	72	UV							[9]
$[Ni(bix)_2][VW_{12}O_{40}]\cdot(H_2bix)$	420	86.7	UV							[10]
$[Co(bix)_2][VW_{12}O_{40}]\cdot(H_2bix)$	420	91.2	UV							
$\{[Cu(2,2'\text{-}bipy)_2]_2(Hbpy)[\alpha\text{-}AlW_{12}O_{40}]\}$	140	89.66	UV							[11]
$Na[Ag_4(pyttz\text{-}I)_2](H_2PMo_{12}O_{40}]$	150	75.98	UV							[12]
$[Cu_7(2\text{-}ptz)_8(OH)_2(H_2O)_2(HPMo^{VI}_{10}Mo^{V}_2O_{40})]$	150	86.1	UV							[13]
$[Cu_5(2\text{-}ptz)_6\text{-}(HPMo^{VI}_{10}Mo^{V}_2O_{40})(H_2O)_4$	150	58.7	UV							

]										
$[Ag_6(4\text{-}ptz)_4(H_2SiMo_{12}O_{40})]$	150	82.1	UV							
$[Ag_5(4\text{-}ptz)_4(H_2PMo_{12}O_{40})]$	150	60.3	UV							
$[CuPTCP(H_2O)_{2.5}]_2[SiW_{12}O_{40}]$	270	68.68	visible light							[14]
$[Cu_3(2,2'\text{-}bpy)_3(inic)(\mu_2\text{-}OH)(H_2O)][SiW_{12}O_{40}]$	360	36.5	visible light							[15]
$[Cu_6(phen)_6(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_2Cl_2(inic)_2][SiW_{12}O_{40}]$	360	36.8	visible light							
$[Cu_2(hnic)(2,2'\text{-}bpy)_2Cl]_2[H_2SiW_{12}O_{40}]$	360	42.3	visible light							
$[Cu_2(nic)(phen)_2Cl_2]_2[SiW_{12}O_{40}]$	360	42.8	visible light							
$[Cu_2(pic)(2,2'\text{-}bpy)_2Cl]_2[SiW_{12}O_{40}]$	360	31.7	visible light							
$[Cu^{II}_3Cl(BBTZ)_5(BW_{12}O_{40})(H_2O)_2]$	45	94.1	UV							[16]
$[Cu^{I}_3Cu^{II}(BBTZ)_5(BW_{12}O_{40})(H_2O)]$	45	93.8	UV							
$[Cu_3(4,4'\text{-}bpy)_3](HSiW_{12}O_{40}].(C_3H_4N_2)$	390	53.2	UV							[17]
$[Cu_3(4,4'\text{-}bpy)_3](PMo_{12}O_{40}].(C_5H_6N_2)$	390	47.7	UV							
$[Cu_2(4,4'\text{-}bpy)_2](HPMo_{12}O_{40}].(C_5H_6N_2)$	390	35.0	UV							
$[Cu(Phen)(4,4'\text{-}bpy)(H_2O)]_2(PW_{12}O40].(4,4'\text{-}bpy)$	390	58.8	UV							
$[Yb(O)(HL)_2(H_2L)_{0.5}(H_2O)_3][SiMo_{12}O_{40}].2.5CH_3CN$	90	91.72	UV							[18]
$[Ca(HL)_2(L)_{0.5}(H_2O)_4][SiMo_{12}O_{40}].5CH_3CN$	90	91.75	UV							
$[Ag_3(pytz)_2(H_2O)]_2.[HAgGe\text{-}Mo_{12}O_{40}]$	150	80.3	UV							[19]
$[Cu_3(L)_3(PMo_{12}O_{40})_2]$	165	94.2	UV							[20]
$[Cu_3(L)_3(PW_{12}O_{40})_2]$	330	93.7	UV							

$Na[Ag_6(pyttz)_2(H_2O)][PMo_{12}O_{40}]$	150	70.1	UV							[21]
$K[Ag_{14}(pyttz)_4(H_2O)_2][PW_{12}O_{40}]_2 \cdot (OH)$	150	70.6	UV							[22]
$K[Ag_{14}(pyttz)_4(H_2O)_4][HSiW_{12}O_{40}]$	150	59.1	UV							
$(4,4'\text{-}bipyH)_4[SiW_{12}O_{40}](4,4\text{-}bipy)$	210	96	visible-light/ H_2O_2							[23]
$[Ag_5(btp)_4][PW^{VI}_{10}W^{V}_2O_{40}]$	180	59.0	UV							[24]
$[Mn(salen)(CH_3OH)_2]_3[PMo_{12}O_{40}]$	300	91.3	UV							[25]
$[Mn(salen)(CH_3OH)_2]_3[PW_{12}O_40]$	300	60.3	UV							
$[Cu_3(4\text{-}atrz)_8(PMo_{12}O_{40})_2(H_2O)_2]$	180	93.72	UV	35	96.52	UV				[26]
$[Cu_2(4\text{-}atrz)_6(SiW_{12}O_{40})(H_2O)]$	180	28.76	UV	60	98.22	UV				
$[K_2Ag_{15}(L_1)_{10}(H_2O)_2][H(PMo_{11}^{VI}Mo^{V}O_{40})_2]$	100	64.5	UV	100	71.0	UV				[27]
$[Ag_7(L_1)_4][PW_{12}O_{40}]$	100	77.4	UV	100	75.6	UV				
$Ag_{10}(L_2)_8(H_2O)][PW_{12}O_{40}]$	100	86.7	UV	100	77.3	UV				
$[Ag_4(Hpyttz)_2(H_2pyttz)][HVW_{12}O_{40}]$	210	60	UV	210	42	UV				[28]
$[Cu_3(\mu_2\text{-}OH)(pdon)_3(pca)(H_2O)_3][SiW_{12}O_{40}]$				140	80	UV				[29]
$[(H_2toym)_2(SiW_{12}O_{40})]$				120	80.36	UV				[30]
$[Ag(phen)_2]_2(Agphen)_2SiW_{12}O_{40}$				210	70.25	UV				[31]
$[Cd(3\text{-}Hptz)_4(CH_3O)_2](H_3PMo_{12}O_{40})$				120	66.4	UV				[32]
$[Cd(4\text{-}Hptz)_4(CH_3O)_2](H_3PMo_{12}O_{40})_2$				120	59.9	UV				
$\{[Ni_3(4\text{-}ptz)_2(4\text{-}Hptz)_2(\mu_3\text{-}O)(H_2O)_2](HPMo_{12}O_{40})\}_2$				120	72.5	UV				

$[Ag_3(bpz)_2(pz)(H_4SiW_{12}O_{40})]$				120	68.5	UV				[33]
$[Ag_5(bpz)_4\text{-}(H_{5/2}PMo_{12}O_{40})_2]\cdot 6H_2O$				120	54.4	UV				
$[Ag_3(3\text{-}bpo)_4(PMo_{12}O_{40})]$				120	82.6	UV				[34]
$[Ag_4(3\text{-}bpo)_2(CH_3CN)_2(SiW_{12}O_{40})]$				120	94.2	UV				
$[Cu_2L_{2\text{-}}(PMo^{VI}{}_{11}Mo^{V}O_{40})(H_2O)_2]$				210	35.9	UV				[35]
$[Cu_2L_2(PW^{VI}{}_{11}W^{V}O_{40})(H_2O)_6]$				210	93.7	UV				
$[Cu_2L_2(SiW_{12}O_{40})(H_2O)_6]$				210	90.6	UV				
$[Cu_2(SiW_{12}O_{40})L^1(phen)_2(H_2O)]$				240	84	UV				[36]
$[Cu_2(SiW_{12}O_{40})L^2(phen)_2(H_2O)_4]$				240	78	UV				
$Cu_2(SiW_{12}O_{40})L^3(phen)_2(H_2O)_4]$				240	83	UV				
$[Co^{II}(HBBTZ)(BBTZ)_{2.5}][PMo_{12}O_{40}]$				90	93.6	UV				[37]
$[Cu^{I}\text{-}(BBTZ)]_5[BW_{12}O_{40}]$				90	90.9	UV				
$[Cu^{II}\text{-}(BBTZ)]_3[AsW^{V}{}_3W^{VI}{}_9O_{40}]$				90	90.8	UV				
$(SiMo_{12}O_{40})(H_2bipy)_2$				60	81.9	UV				[38]
$\{[Zn(phen)_2(H_2O)]_2[VW_{12}O_{40}]\}$				90	90	UV				[39]
$[Ag_6(ptz)_4(H_2O)_2][HPMo_{12}O_{40}]$				180	42.7	UV				[40]
$[Cu^{II}{}_2(biz)_8(HPMo^{VI}{}_{10}Mo^{V}{}_2O_{40})(H_2O)_2]$				160	95.4	UV				[41]
$[Cu^{I}{}_4(biz)_8(SiW_{12}O_{40})]$				160	92.8	UV				
$[Ag_8(btp)_4(H_2O)_2(HPW^{VI}{}_{10}W^{V}{}_2O_{40})_2]$				75	81	UV				[42]
$[Ag_4(btb)_2(HPW^{VI}{}_{10}W^{V}{}_2O_{40})]$				75	82.4	UV				
$[(btb)(H_3PW_{12}O_{40})].6H_2O$				75	78.8	UV				
$[Ag_5(btx)_4(PW^{VI}{}_{10}W^{V}{}_2O_{40})]$				75	90.6	UV				

$[Ag_6Cl_2(mmt)_4(H_4SiMo_{12}O_{40})(H_2O)_2]$				75	60	UV				[43]
$[Cu^I_8(BTA)_4(HBTA)_8(SiMo_{12}O_{40})]$				140	91.5	UV				[44]
$[Cu^{II}_6(OH)_4(BTA)_4(SiW_{12}O_{40})(H_2O)_6]$				140	96.5	UV				
$[Cu(pz)]_3[PW_{12}O_{40}]$							210	29.45	UV	[45]

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