

Supporting information

Two hybrid materials assembled from transition metal mono-substituted Keggin polyoxoanions as photocatalyst under visible light

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S1. Materials and Measurements

Chemicals were purchased from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) was carried out with an X-ray diffractometer of Rigaku, Rint 2000. The C, H, and N elemental analyses were conducted on a Perkin-Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer TG-7 analyzer heated from room temperature to 800 $^{\circ}\text{C}$ at a ramp rate of 5 $^{\circ}\text{C}/\text{min}$ under nitrogen. UV-Visible spectral measurements were carried out using a Varian Cary 500 spectrometer.

S2. Synthesis

The ligand tris(4-pyridyl)triazine (tpt) and 4,4'-bipyridine- N,N' -dioxide (dpdo) were prepared following the method as described in the literatures.¹

$\{[\text{Zn}(\text{H}_2\text{tpt})_2(\text{dpdo})_{0.5}(\text{H}_2\text{O})_2][\text{Zn}_{0.5}(\text{H}_2\text{O})]\text{PW}_{11}\text{Zn}(\text{tpt})\text{O}_{39}\} \cdot 11\text{H}_2\text{O}$ (1): A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.29 g, 1 mmol), $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ (0.432 g, 0.15 mmol), tpt (0.156 g, 0.5 mmol) and dpdo (0.047 g, 0.025 mmol) was suspended in 15 mL of distilled water. The mixture was stirred for 5 hours at room temperature. When the pH of the mixture was adjusted about 6-7 with 1 M HCl and 1 M NaOH, the suspension was put into a 25mL Teflon-lined stainless-steel autoclave and kept under autogenous pressure at 135 $^{\circ}\text{C}$ for 3 days. After slow cooling to room temperature, colorless block crystals were filtered and washed with distilled water (58.54 % yield based on W).
Elemental analysis (%) calcd (found) for
 $\{[\text{Zn}(\text{H}_2\text{tpt})_2(\text{dpdo})_{0.5}(\text{H}_2\text{O})_2][\text{Zn}_{0.5}(\text{H}_2\text{O})]\text{H}_2\text{PW}_{11}\text{Zn}(\text{tpt})\text{O}_{39}\} \cdot 11\text{H}_2\text{O}$ **1**: C 8.25(8.27), N 2.75(2.81), H 1.03(1.10).

$\{[\text{Co}(\text{H}_2\text{tpt})_2(\text{dpdo})_{0.5}(\text{H}_2\text{O})_2][\text{Co}_{0.5}(\text{H}_2\text{O})]\text{PW}_{11}\text{Co}(\text{tpt})\text{O}_{39}\} \cdot 11\text{H}_2\text{O}$ (2): Compound **2** was synthesized following the procedure for **1** except for the replacing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.291 g, 1 mmol). Reddish brown block crystals were filtered and washed with distilled water (58.54 % yield based on W).
Elemental analysis (%) calcd (found) for

$\{[\text{Co}(\text{H}_2\text{tpt})_2(\text{dpdo})_{0.5}(\text{H}_2\text{O})_2][\text{Co}_{0.5}(\text{H}_2\text{O})]\text{PW}_{11}\text{Co}(\text{tpt})\text{O}_{39}\} \cdot 11\text{H}_2\text{O}$ **2**: C 8.28(8.30), N 2.76(2.80), H 1.04(1.08).

S3. Photocatalytic degradation experiments

The photochemical experiment was performed in a 250mL Pyrex reactor with a xenon lamp as a light source. 420-800 nm cutoff filters were placed before the vessel to ensure the irradiation of the RhB/cat. system occurred only by visible light. H₂O₂ (1.5 mmol/L, 1 mL) and powder of compound **1** (0.6g) were added to the RB solution (15mg/L, pH = 6-7) with continuous shaking at room temperature. The photocatalytic experiments were carried out under visible light irradiation with regular intervals. The photocatalytic activities were monitored by UV-vis measurements of the absorbency of the solution with a Lambda35 spectrophotometer (Perkin-Elmer, USA) after given time intervals. The decolorization rate of RB solution was calculated by the following formula:

$$D = (A_0 - A_1) / A_0 \times 100\%$$

where D is decolorization rate, A_0 and A_1 are the characteristic absorbency of RB solutions in adsorption equilibrium before and after irradiation, respectively.

S4. X-ray crystallography

Single-crystal X-ray diffraction data were recorded on a Bruker Apex CCD diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71069 \text{ \AA}$) at 293K. Absorption corrections were applied using multi-scan technique. All the structures were solved by Direct Method of SHELXS-97² and refined by full-matrix least-squares techniques using the SHELXL-97 program³ within WINGX.⁴ Non-hydrogen atoms were refined with anisotropic temperature parameters except for the special atoms in which different refinements were used. For **1**, the restraint command 'ISOR' is used to refine C3, C6. Atoms O2W, O13W, O14W, had been refined as isotropic; For **2**, the command 'omit -3 50' was used to omit the weak reflection above 50 degree, and the restraint command 'ISOR' is used to refine the non-H atoms with ADP problems. These atoms are as follows: N19 C25 N8 O12W. For both cases of **1** and **2**, The H atoms on water molecules cannot be found from the residual peaks and the Calc-OH program in the WinGX suite was used to help to

determine the hydrogen positions of the water molecules. For some water molecules, one hydrogen atom of the two hydrogen atoms has been deleted because of the failure of forming reasonable H-bond network. The detailed crystallographic data and structure refinement parameters for **1** and **2** are summarized in Table S1. Selected bond lengths and angles for complexes **1** and **2** are given in Table S2 and Table S3, respectively. Crystallographic data for the structure reported in this paper have also been deposited with the CCDC as deposition no. CCDC 1004589-1004590 (available free of charge, on application to the CCDC, 12 Union Rd., Cambridge CB2 1EZ, U.K.; e-mail deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinements for compound **1** and **2**

Identification code	1	2
Formula	C ₅₉ H ₇₀ N ₁₉ O ₅₄ PW ₁₁ Zn _{2.5}	C ₅₉ H ₇₀ N ₁₉ O ₅₄ PW ₁₁ Co _{2.5}
Formula weight	4126.08	4109.98
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	15.049(5)	15.078(5)
<i>b</i> (Å)	15.269(5)	15.311(5)
<i>c</i> (Å)	22.867(5)	22.730(5)
α (°)	75.758(5)	76.136(5)
β (°)	72.920(5)	72.873(5)
γ (°)	70.938(5)	70.769(5)
<i>V</i> (Å ³)	4681(2)	4675(2)
<i>Z</i>	2	2
<i>D</i> _{calcd.} [g cm ⁻³]	2.927	2.919
<i>F</i> (000)	3786	3771
Reflections collected	29633 / 20862	21656 / 15862
<i>R</i> (int)	0.0370	0.0322
Goodness-of-fit on <i>F</i> ²	0.990	1.015
<i>R</i> _I ^a [<i>I</i> > 2σ (<i>I</i>)]	0.0465	0.0465

wR_2^b	0.0829	0.1100
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$$^aR_1 = \sum |F_o| - |F_c| / \sum |F_o|, \quad ^b wR_2 = \frac{|\sum w(|F_o|^2 - |F_c|^2)|}{\sum w(F_o^2)^2}^{1/2}$$

Table S2. Selected bond lengths (Å) for **1**

Zn(1)-O(3W)	2.088(8)	W(6)-O(22)	1.765(7)
Zn(1)-O(4W)	2.104(8)	W(6)-O(21)	1.945(7)
Zn(1)-O(28)	2.104(8)	W(6)-O(18)	1.949(7)
Zn(1)-O(23)	2.140(8)	W(6)-O(19)	2.051(7)
Zn(1)-N(14)	2.155(10)	W(6)-O(1)	2.460(7)
Zn(1)-N(13)	2.172(10)	W(7)-O(23)	1.737(7)
Zn(2)-O(80)	2.011(7)	W(7)-O(24)	1.773(7)
Zn(2)-O(24)	2.031(7)	W(7)-O(21)	1.900(7)
Zn(2)-O(8)	2.045(8)	W(7)-O(25)	1.930(8)
Zn(2)-N(19)#1	2.052(8)	W(7)-O(26)	2.027(6)
Zn(2)-O(22)	2.067(8)	W(7)-O(1)	2.333(6)
Zn(2)-O(1)	2.489(6)	W(8)-O(27)	1.697(7)
Zn(3)-O(12W)#2	2.100(8)	W(8)-O(7)	1.899(7)
Zn(3)-O(12W)	2.100(8)	W(8)-O(25)	1.900(8)
Zn(3)-N(1)	2.134(8)	W(8)-O(48)	1.906(7)
Zn(3)-N(1)#2	2.134(8)	W(8)-O(15)	1.931(8)
Zn(3)-O(10)	2.145(7)	W(8)-O(3)	2.445(6)
Zn(3)-O(10)#2	2.145(7)	W(9)-O(29)	1.709(7)
W(1)-O(5)	1.717(7)	W(9)-O(26)	1.856(7)
W(1)-O(8)	1.772(8)	W(9)-O(48)	1.903(7)
W(1)-O(9)	1.929(7)	W(9)-O(30)	1.943(7)
W(1)-O(7)	1.952(7)	W(9)-O(31)	1.953(7)
W(1)-O(6)	2.046(7)	W(9)-O(4)	2.440(6)
W(1)-O(3)	2.454(6)	W(10)-O(32)	1.701(7)
W(2)-O(10)	1.739(7)	W(10)-O(19)	1.820(7)
W(2)-O(80)	1.746(7)	W(10)-O(30)	1.908(7)
W(2)-O(9)	1.913(7)	W(10)-O(17)	1.928(7)
W(2)-O(11)	1.937(7)	W(10)-O(33)	1.974(7)
W(2)-O(12)	2.024(7)	W(10)-O(4)	2.432(7)
W(2)-O(2)	2.423(6)	W(11)-O(81)	1.700(7)
W(3)-O(13)	1.711(8)	W(11)-O(12)	1.852(7)
W(3)-O(6)	1.840(7)	W(11)-O(16)	1.901(8)
W(3)-O(15)	1.911(7)	W(11)-O(60)	1.910(7)
W(3)-O(60)	1.912(7)	W(11)-O(34)	1.951(6)
W(3)-O(14)	1.944(7)	W(11)-O(2)	2.499(7)
W(3)-O(3)	2.446(7)	W(12)-O(47)	1.724(7)
W(5)-O(50)	1.702(8)	W(12)-O(34)	1.881(7)

W(5)-O(18)	1.880(7)	W(12)-O(33)	1.885(8)
W(5)-O(17)	1.904(7)	W(12)-O(14)	1.896(7)
W(5)-O(11)	1.913(7)	W(12)-O(31)	1.908(7)
W(5)-O(16)	1.933(8)	W(12)-O(4)	2.412(7)
W(5)-O(2)	2.437(7)	N(19)-Zn(2)#1	2.052(8)
W(6)-O(20)	1.696(8)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1;
#2 -x+1,-y,-z+1; #3 -x,-y+1,-z

Table S3. Selected bond lengths (Å) for **2**

Co(1)-O(34)	2.058(7)	W(5)-O(10)	1.890(7)
Co(1)-O(10W)	2.090(9)	W(5)-O(19)	1.902(7)
Co(1)-O(38)	2.106(6)	W(5)-O(16)	1.925(7)
Co(1)-O(9W)	2.127(7)	W(5)-O(20)	1.945(6)
Co(1)-N(18)	2.160(9)	W(5)-O(32)	2.430(6)
Co(1)-N(12)	2.200(9)	W(6)-O(39)	1.712(7)
Co(2)-O(11W)	2.076(7)	W(6)-O(22)	1.816(7)
Co(2)-O(11W)#1	2.076(7)	W(6)-O(21)	1.913(6)
Co(2)-O(9)#1	2.116(7)	W(6)-O(12)	1.920(6)
Co(2)-O(9)	2.116(7)	W(6)-O(1)	1.971(7)
Co(2)-N(5)#2	2.153(8)	W(6)-O(31)	2.428(6)
Co(2)-N(5)#3	2.153(8)	W(7)-O(38)	1.731(6)
Co(3)-O(5)	2.007(6)	W(7)-O(24)	1.779(7)
Co(3)-O(30)	2.042(7)	W(7)-O(23)	1.899(6)
Co(3)-O(24)	2.051(6)	W(7)-O(19)	1.937(6)
Co(3)-O(17)	2.055(7)	W(7)-O(11)	2.051(7)
Co(3)-N(6)	2.101(9)	W(7)-O(33)	2.351(6)
Co(3)-O(33)	2.342(7)	W(8)-O(25)	1.701(7)
W(1)-O(35)	1.722(7)	W(8)-O(15)	1.850(7)
W(1)-O(3)	1.893(7)	W(8)-O(20)	1.901(6)
W(1)-O(1)	1.895(6)	W(8)-O(37)	1.906(6)
W(1)-O(2)	1.901(6)	W(8)-O(3)	1.941(7)
W(1)-O(4)	1.906(6)	W(8)-O(32)	2.440(6)
W(1)-O(31)	2.435(6)	W(9)-O(26)	1.685(7)
W(2)-O(9)	1.732(7)	W(9)-O(27)	1.872(7)
W(2)-O(5)	1.751(7)	W(9)-O(6)	1.900(7)
W(2)-O(8)	1.912(6)	W(9)-O(21)	1.912(7)
W(2)-O(6)	1.936(6)	W(9)-O(28)	1.951(7)
W(2)-O(7)	2.023(7)	W(9)-O(41)	2.446(6)
W(2)-O(41)	2.403(7)	W(10)-O(40)	1.701(7)
W(3)-O(14)	1.718(6)	W(10)-O(7)	1.858(7)
W(3)-O(11)	1.836(7)	W(10)-O(28)	1.915(6)
W(3)-O(10)	1.919(6)	W(10)-O(37)	1.931(6)
W(3)-O(12)	1.932(6)	W(10)-O(2)	1.931(7)
W(3)-O(4)	1.955(6)	W(10)-O(41)	2.506(6)

W(3)-O(31)	2.430(6)	W(11)-O(29)	1.686(7)
W(4)-O(18)	1.715(7)	W(11)-O(30)	1.766(8)
W(4)-O(17)	1.754(7)	W(11)-O(23)	1.949(6)
W(4)-O(16)	1.946(6)	W(11)-O(27)	1.955(6)
W(4)-O(8)	1.947(6)	W(11)-O(22)	2.053(7)
W(4)-O(15)	2.033(7)	W(11)-O(33)	2.466(6)
W(4)-O(32)	2.461(7)	N(5)-Co(2)#5	2.153(8)
W(5)-O(36)	1.696(6)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+2,-y,-z+1$; #2 $x,y-1,z$; #3 $-x+2,-y+1,-z+1$; #4 $-x+1,-y+1,-z$ #5 $x,y+1,z$

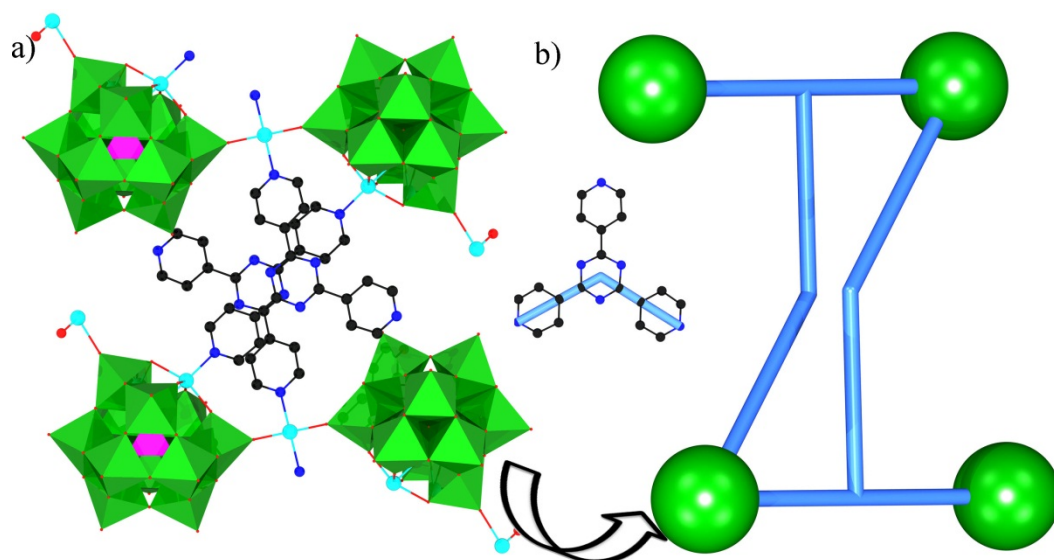


Fig. S1 a) Subunit formed from four [PW₁₁ZnO₃₉] connected by two V-shaped μ₂-tpt ligands. The μ₁-tpt ligands arrayed along the two sides of the subunit have been omitted for clarity. b) Schematic view of the formation of the subunit in a). The green balls represents [PW₁₁ZnO₃₉], and V-shaped blue lines represents the μ₂-tpt ligands. Water molecules and hydrogen atoms have been omitted for clarity.

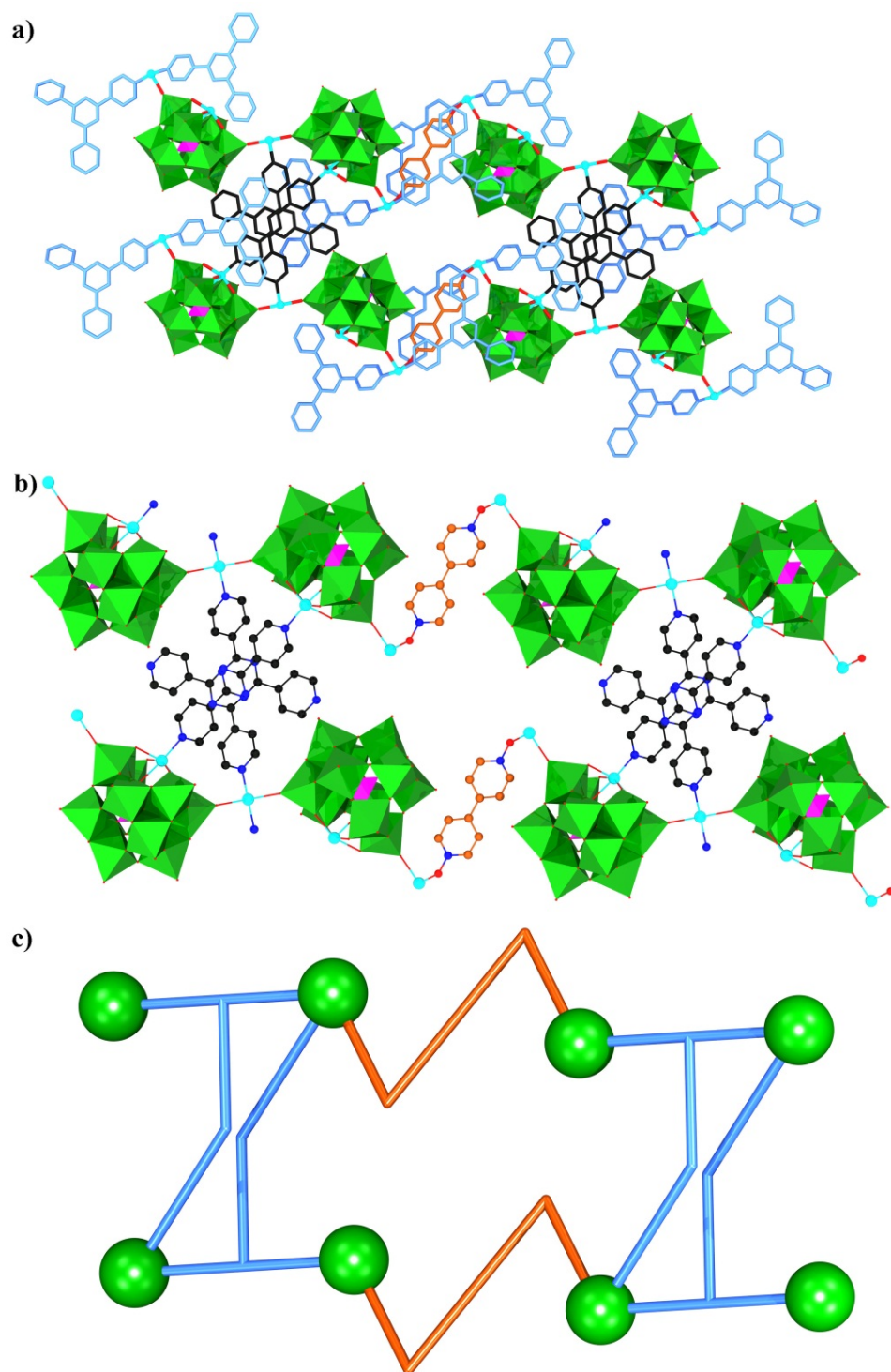


Fig. S2 a) The subunits formed by four [PW₁₁ZnO₃₉] are further connected by dpdo into a 2D layer. b) The 2D is presented without the μ₁-tpt ligands. c) Schematic view of the formation of the 2D layer. Water molecules and hydrogen atoms have been omitted for clarity.

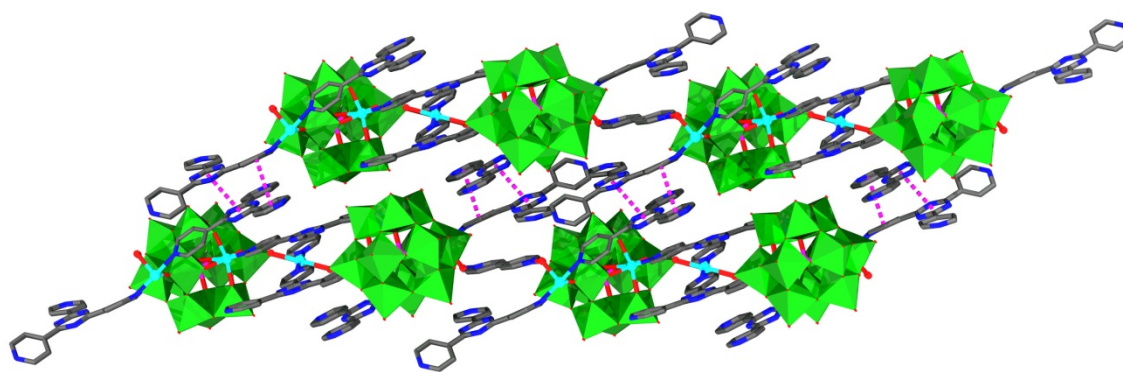
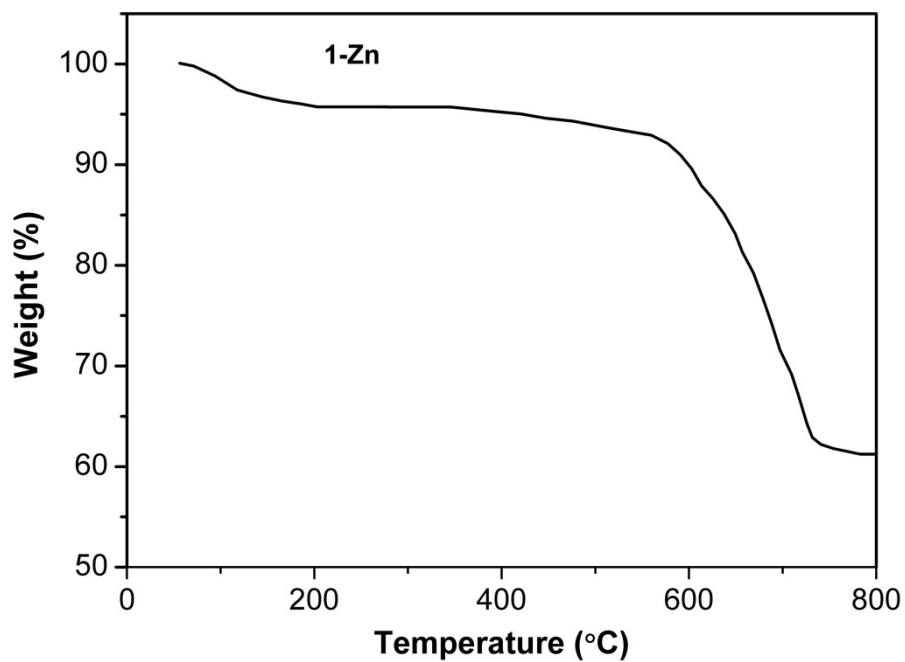


Fig. S3 The whole 3D structure formed by the strong π - π stacking interactions between two μ_1 -tpt ligands from two different 2D layers. Water molecules and hydrogen atoms are omitted for clarity.



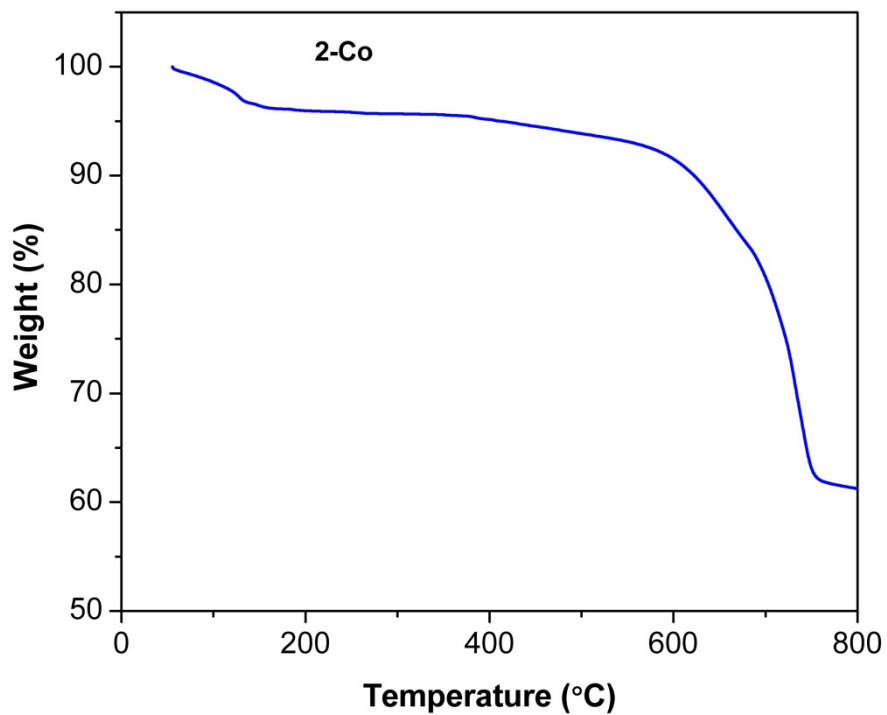
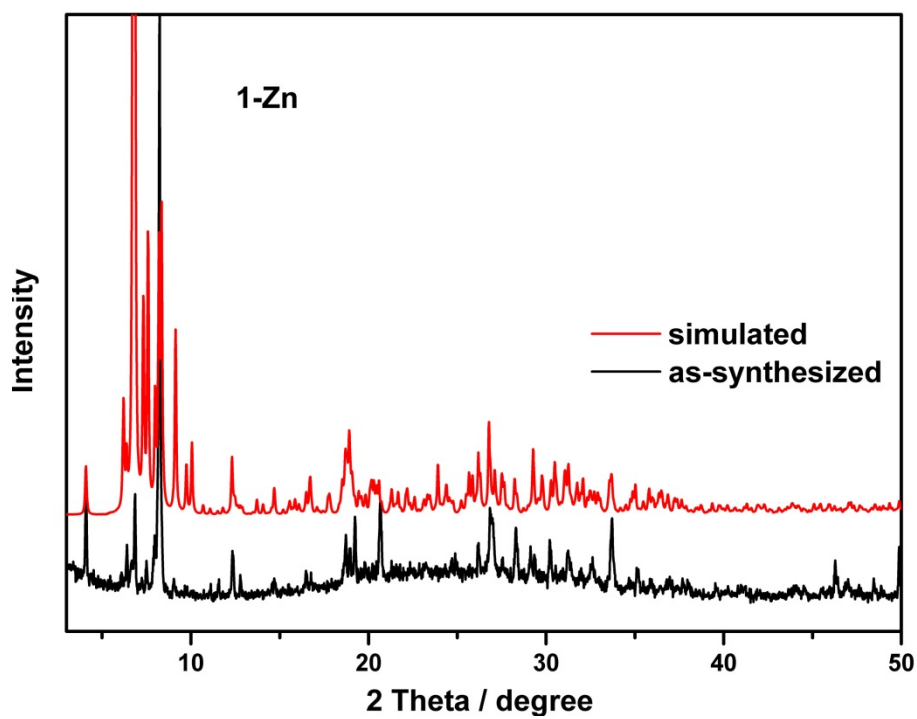


Fig. S4 Thermal gravimetric curve of compound 1 and 2.



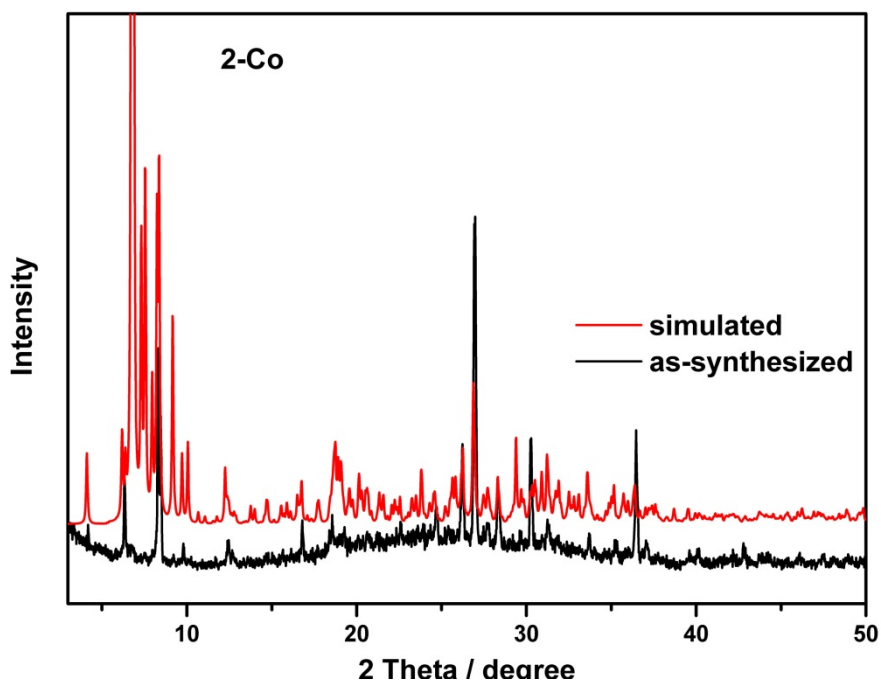


Fig. S5 PXRD profiles of compound 1 and 2.

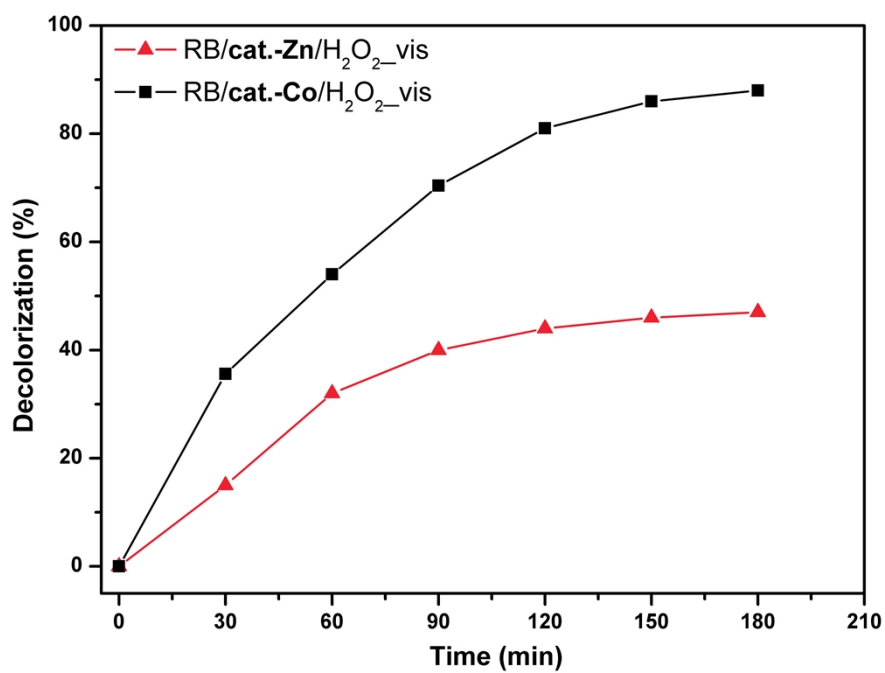


Fig.S6 Decolorization rates of RB when **cat.-Zn** or **cat.-Co** was used as the photocatalyst in the same reaction systems: RB (15 mg L⁻¹), photocatalyst (0.6 g L⁻¹), H₂O₂ (1.5 mmol L⁻¹).

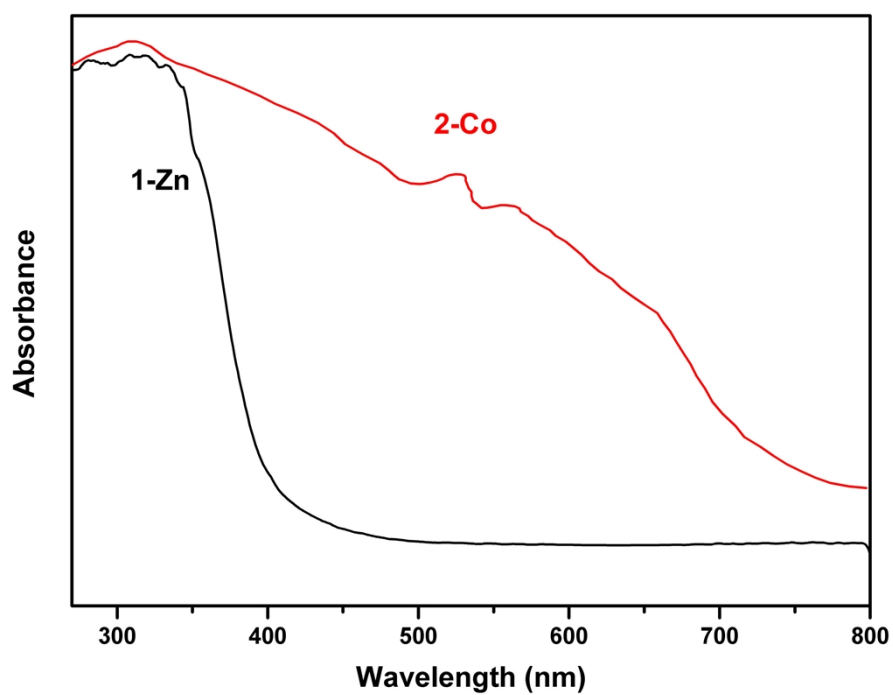


Fig. S7 The UV-vis spectrum of the crystal of compound 1 and 2.

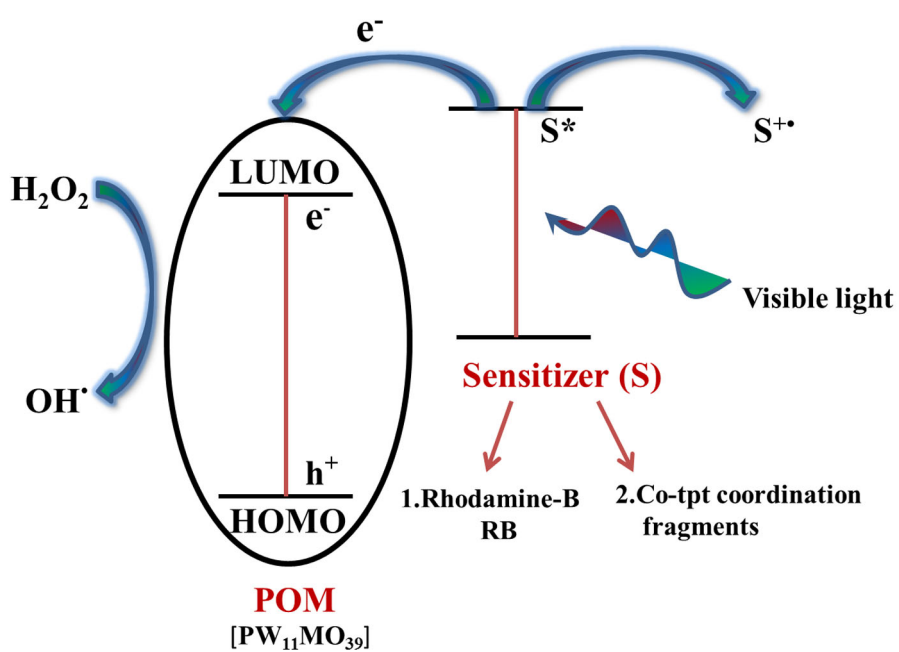


Fig. S8 Proposed photodegradation mechanism⁵.

References

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