Supporting information

Organic-inorganic hybrid photocatalyst based on sandwich-type tetra-Co-substituted Phosphotungstates with high visible light photocatalytic activity

Bai-Qiao Song, Xin-Long Wang*, Chun-Yi Sun, Yu-Teng Zhang, Xue-Song Wu, Liu Yang, Kui-Zhan Shao, Liang Zhao* and Zhong-Min Su*

Institute of Functional Material Chemistry；Key Laboratory of Polyoxometalate Science of Ministry of Education, Northeast Normal University, Changchun, 130024 Jilin, People's Republic of China；E-mail: wangxl824@nenu.edu.cn, zmsu@nenu.edu.cn

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 900 °C at a ramp rate of 5 °C/min under nitrogen. UV-Visible spectral measurements were carried out using a Varian Cary 500 spectrometer. ICP was measured by ICP-9000(N+M) (USA Thermo Jarrell-Ash Corp).

S2. Synthesis

The ligand tris(4-pyridyl)triazine (TPT) were prepared following the method as described in the literatures.[1] $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 7H_2O$ was prepared by the previous procedure.[2]

$[Co(H_2O)_6][(TPT)_2Co_2(H_2O)_5]_2[Co_4(H_2O)_2(B\text{-}\alpha\text{-}PW_9O_{34})_2]\cdot 10H_2O$ (1): A mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.29 g, 1mmol), $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 7H_2O$ (0.300 g, 0.10 mmol), TPT (0.100 g, 0.31 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 7-8 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 180 °C for 4 days. After slow cooling to room temperature, rose needle-like crystals were collected by hand and washed with distilled water (38.11 % yield based on W). Elemental analysis calcd (%) for **1** $C_{72}H_{104}Co_9N_{24}O_{96}P_2W_{18}$ (6743.40): C 12.82, H 1.55, N 4.99%; found: C 13.10, H 1.32, N 5.23%. IR (cm^{-1}): 3416(m), 1634(s), 1576(s), 1522(m), 1374(m), 1315(s), 1191(s), 1040(m), 939(m), 877(m), 801(w), 666(w), 650(w), 514(w).

S3. Photocatalytic degradation experiments

The photochemical experiment was performed in a 250mL Pyrex reactor with the corresponding light source. H_2O_2 (1.5 mmol/L) and powder of compound **1** (0.6 g/L)

were added to the RB solution (12 mg/L, pH = 6-7) with continuous shaking at room temperature. The photocatalytic experiments were carried out under visible light (λ>420 nm) irradiation with regular intervals, respectively. 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. Electrochemical characterizations

The Mott-Schottky curves were measured using an advanced electrochemical system (PARSTAT 2273, Ametek, USA) in a three-electrode cell. Pt plate was used as counter electrode and Ag/AgCl electrode (3M KCl) was used as reference electrode. The electrolyte was a 0.5 M Na_2SO_4 solution, which was purged with nitrogen gas for 0.5 h prior to the measurements. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass by dipping the mixed slurry containing the sample and H_2O on it which was prepared by mixing 0.05 g powder sample of **1** and 1 g water, and the covering area of the electrode was 0.25 cm^2. Before measurement, the working electrode was dried on a warm plate.

S5. X-ray crystallography

Single-crystal X-ray diffraction data were recorded on a Bruker Apex CCD diffractometer with graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71069 Å) at 293K. Absorption corrections were applied using multi-scan technique. All the structures were solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program[3] within WINGX.[4] Non-hydrogen atoms were refined with anisotropic temperature parameters. During the refinement, three free water molecules (O12W, O13W), (O14W, O15W),(O16W, O17W) were found to be disordered over two positions with the occupancies being fixed at 0.5 : 0.5. The two disordered parts for one atoms were restrained using "SIMU" instruction. These disordered water molecules were refined as isotropic. In

the whole structure, The H atoms on the coordinated and free water molecules cannot be found from the residual peaks and directly add to the final formula, which leads to some Level-B errors. The detailed crystallographic data and structure refinement parameters for **1** are summarized in Table S1. Crystallographic data for the structure reported in this paper have also been deposited with the CCDC as deposition no. CCDC 1058033 (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**

Compound reference	**1**
Chemical formula	$C_{72}H_{104}Co_9N_{24}O_{96}P_2W_{18}$
Formula Mass	6743.40
Crystal system	Orthorhombic
a/(Å)	29.325(5)
b/(Å)	13.413(5)
c/(Å)	36.016(5)
α/°	90
β/°	90
γ/°	90
Unit cell volume/(Å)^3	14166(6)
Temperature/K	293(2)
Space group	*Pbca*
No. of formula units per unit cell, *Z*	4
Theta range for data collection (degree)	1.13 to 25.06
No. of reflections measured	70383
No. of independent reflections	12490
R_{int}	0.0949
Final R_1 values ($I > 2\sigma(I)$)^a	0.0391
Final $wR(F^2)$ values ($I > 2\sigma(I)$)^b	0.0984
Final R_1 values (all data)	0.0643
Final $wR(F^2)$ values (all data)	0.1185
Goodness of fit on F^2	1.044

$^aR_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bwR_2= |\Sigma w(|F_o|^2-|F_c|^2)|/\Sigma|w(F_o^2)^2|^{1/2}$

Table S2. Selected bond lengths (Å) and bond angles (°)

Bond lengths (Å)			
W(1)-O(29)	1.733(9)	W(9)-O(35)	1.919(10)
W(1)-O(21)	1.861(9)	W(9)-O(14)	2.030(9)
W(1)-O(25)	1.877(8)	W(9)-O(2)	2.416(9)
W(1)-O(26)	1.902(9)	W(10)-O(30)	1.735(8)
W(1)-O(34)	1.975(9)	W(10)-O(34)	1.859(9)
W(1)-O(4)	2.501(8)	W(10)-O(33)	1.886(8)
W(2)-O(23)	1.722(10)	W(10)-O(7)	1.889(9)
W(2)-O(24)	1.829(8)	W(10)-O(27)	1.916(9)
W(2)-O(11)	1.879(9)	W(10)-O(1)	2.526(8)
W(2)-O(20)	1.913(9)	Co(2)-O(2W)	2.064(11)
W(2)-O(25)	1.958(8)	Co(2)-O(4W)	2.073(11)
W(2)-O(4)	2.414(9)	Co(2)-O(3W)	2.083(11)
W(3)-O(8)	1.699(9)	Co(2)-O(31)	2.103(9)
W(3)-O(15)#1	1.833(8)	Co(2)-N(4)#1	2.136(11)
W(3)-O(6)	1.862(10)	Co(2)-O(13)	2.179(10)
W(3)-O(11)	1.947(10)	Co(3)-O(12)	2.051(9)
W(3)-O(33)	1.956(8)	Co(3)-O(17)	2.057(9)
W(3)-O(1)	2.474(8)	Co(3)-O(15)	2.091(9)
W(4)-O(9)	1.731(10)	Co(3)-O(24)#1	2.123(9)
W(4)-O(5)	1.800(8)	Co(3)-O(1W)	2.134(9)
W(4)-O(10)	1.917(9)	Co(3)-O(3)	2.153(8)
W(4)-O(7)	1.977(9)	Co(4)-O(16)	2.002(9)
W(4)-O(6)	1.981(9)	Co(4)-O(15)	2.033(9)
W(4)-O(1)	2.420(9)	Co(4)-O(5)#1	2.036(9)
W(5)-O(32)	1.699(8)	Co(4)-O(24)	2.048(9)
W(5)-O(14)	1.876(10)	Co(4)-O(3)#1	2.225(8)
W(5)-O(28)	1.878(9)	Co(4)-O(3)	2.297(8)
W(5)-O(27)	1.905(9)	Co(5)-O(6W)	2.087(11)
W(5)-O(26)	1.932(10)	Co(5)-O(5W)	2.091(10)
W(6)-O(31)#2	1.747(9)	Co(5)-O(29)	2.095(9)
W(6)-O(17)	1.758(9)	Co(5)-N(3)	2.123(12)
W(6)-O(22)	1.921(10)	Co(5)-N(13)	2.120(12)
W(6)-O(35)	1.952(10)	Co(5)-O(30)#3	2.131(9)
W(6)-O(28)	2.018(8)	Co(6)-O(8W)	2.057(11)
W(6)-O(2)	2.401(8)	Co(6)-O(8W)#4	2.057(11)
W(8)-O(19)	1.719(9)	Co(6)-O(9W)#4	2.101(11)
W(8)-O(16)	1.761(9)	Co(6)-O(9W)	2.101(11)
W(8)-O(22)	1.891(9)	Co(6)-O(7W)	2.150(12)
W(8)-O(20)	1.963(9)	Co(6)-O(7W)#4	2.150(12)
W(8)-O(21)	2.012(9)	P(1)-O(1)	1.529(9)
W(8)-O(4)	2.423(9)	P(1)-O(3)	1.541(8)

W(9)-O(13)	1.754(10)	P(1)-O(4)	1.549(9)
W(9)-O(12)	1.777(9)	P(1)-O(2)	1.548(9)
W(9)-O(10)	1.909(9)		
		Bond angles (°)	
O(29)-W(1)-O(21)	100.8(4)	O(34)-W(10)-O(1)	84.9(3)
O(29)-W(1)-O(25)	99.9(4)	O(33)-W(10)-O(1)	72.2(3)
O(21)-W(1)-O(25)	90.4(4)	O(7)-W(10)-O(1)	70.5(3)
O(29)-W(1)-O(26)	104.5(4)	O(27)-W(10)-O(1)	83.8(3)
O(21)-W(1)-O(26)	88.6(4)	O(2W)-Co(2)-O(4W)	175.2(5)
O(25)-W(1)-O(26)	155.4(4)	O(2W)-Co(2)-O(3W)	88.7(5)
O(29)-W(1)-O(34)	103.8(4)	O(4W)-Co(2)-O(3W)	86.6(5)
O(21)-W(1)-O(34)	155.4(4)	O(2W)-Co(2)-O(31)	87.1(4)
O(25)-W(1)-O(34)	84.8(4)	O(4W)-Co(2)-O(31)	92.3(4)
O(26)-W(1)-O(34)	85.9(4)	O(3W)-Co(2)-O(31)	90.7(4)
O(29)-W(1)-O(4)	168.4(4)	O(2W)-Co(2)-N(4)#1	95.9(5)
O(21)-W(1)-O(4)	72.3(3)	O(4W)-Co(2)-N(4)#1	88.8(5)
O(25)-W(1)-O(4)	71.3(3)	O(3W)-Co(2)-N(4)#1	175.0(5)
O(26)-W(1)-O(4)	85.0(3)	O(31)-Co(2)-N(4)#1	87.5(4)
O(34)-W(1)-O(4)	83.3(3)	O(2W)-Co(2)-O(13)	89.0(4)
O(23)-W(2)-O(24)	101.7(4)	O(4W)-Co(2)-O(13)	91.5(4)
O(23)-W(2)-O(11)	102.3(4)	O(3W)-Co(2)-O(13)	87.9(4)
O(24)-W(2)-O(11)	91.0(4)	O(31)-Co(2)-O(13)	175.9(4)
O(23)-W(2)-O(20)	100.2(4)	N(4)#1-Co(2)-O(13)	94.2(4)
O(24)-W(2)-O(20)	90.7(4)	O(12)-Co(3)-O(17)	91.4(4)
O(11)-W(2)-O(20)	156.6(4)	O(12)-Co(3)-O(15)	172.7(4)
O(23)-W(2)-O(25)	101.2(4)	O(17)-Co(3)-O(15)	94.4(4)
O(24)-W(2)-O(25)	156.9(4)	O(12)-Co(3)-O(24)#1	91.3(4)
O(11)-W(2)-O(25)	86.6(4)	O(17)-Co(3)-O(24)#1	174.5(4)
O(20)-W(2)-O(25)	82.7(4)	O(15)-Co(3)-O(24)#1	82.6(3)
O(23)-W(2)-O(4)	170.7(4)	O(12)-Co(3)-O(1W)	87.5(4)
O(24)-W(2)-O(4)	84.7(3)	O(17)-Co(3)-O(1W)	89.9(4)
O(11)-W(2)-O(4)	84.2(3)	O(15)-Co(3)-O(1W)	96.8(4)
O(20)-W(2)-O(4)	72.7(3)	O(24)#1-Co(3)-O(1W)	95.0(4)
O(25)-W(2)-O(4)	72.2(3)	O(12)-Co(3)-O(3)	91.0(3)
O(8)-W(3)-O(15)#1	103.0(4)	O(17)-Co(3)-O(3)	93.4(3)
O(8)-W(3)-O(6)	104.7(4)	O(15)-Co(3)-O(3)	84.3(3)
O(15)#1-W(3)-O(6)	93.9(4)	O(24)#1-Co(3)-O(3)	81.7(3)
O(8)-W(3)-O(11)	99.4(4)	O(1W)-Co(3)-O(3)	176.4(4)
O(15)#1-W(3)-O(11)	88.1(4)	O(16)-Co(4)-O(15)	91.2(4)
O(6)-W(3)-O(11)	154.7(4)	O(16)-Co(4)-O(5)#1	95.0(4)
O(8)-W(3)-O(33)	101.4(4)	O(15)-Co(4)-O(5)#1	99.2(4)
O(15)#1-W(3)-O(33)	155.1(4)	O(16)-Co(4)-O(24)	97.9(4)
O(6)-W(3)-O(33)	84.8(4)	O(15)-Co(4)-O(24)	164.3(4)

O(11)-W(3)-O(33)	82.9(4)	O(5)#1-Co(4)-O(24)	92.7(4)
O(8)-W(3)-O(1)	173.6(4)	O(16)-Co(4)-O(3)#1	173.5(3)
O(15)#1-W(3)-O(1)	83.3(3)	O(15)-Co(4)-O(3)#1	87.8(3)
O(6)-W(3)-O(1)	73.7(3)	O(5)#1-Co(4)-O(3)#1	91.5(3)
O(11)-W(3)-O(1)	81.5(3)	O(24)-Co(4)-O(3)#1	81.7(3)
O(33)-W(3)-O(1)	72.4(3)	O(16)-Co(4)-O(3)	88.5(3)
O(9)-W(4)-O(5)	104.5(4)	O(15)-Co(4)-O(3)	82.0(3)
O(9)-W(4)-O(10)	101.3(4)	O(5)#1-Co(4)-O(3)	176.2(3)
O(5)-W(4)-O(10)	93.0(4)	O(24)-Co(4)-O(3)	85.4(3)
O(9)-W(4)-O(7)	98.3(4)	O(3)#1-Co(4)-O(3)	85.0(3)
O(5)-W(4)-O(7)	156.3(4)	O(6W)-Co(5)-O(5W)	178.5(4)
O(10)-W(4)-O(7)	88.6(4)	O(6W)-Co(5)-O(29)	89.6(4)
O(9)-W(4)-O(6)	100.6(4)	O(5W)-Co(5)-O(29)	89.7(4)
O(5)-W(4)-O(6)	87.3(4)	O(6W)-Co(5)-N(3)	88.6(5)
O(10)-W(4)-O(6)	157.3(4)	O(5W)-Co(5)-N(3)	90.2(5)
O(7)-W(4)-O(6)	82.4(4)	O(29)-Co(5)-N(3)	92.9(4)
O(9)-W(4)-O(1)	168.6(4)	O(6W)-Co(5)-N(13)	88.9(5)
O(5)-W(4)-O(1)	84.9(4)	O(5W)-Co(5)-N(13)	92.4(5)
O(10)-W(4)-O(1)	84.3(3)	O(29)-Co(5)-N(13)	87.1(4)
O(7)-W(4)-O(1)	71.7(3)	N(3)-Co(5)-N(13)	177.5(5)
O(6)-W(4)-O(1)	73.1(3)	O(6W)-Co(5)-O(30)#3	90.8(4)
O(32)-W(5)-O(14)	102.3(4)	O(5W)-Co(5)-O(30)#3	90.1(4)
O(32)-W(5)-O(28)	102.2(4)	O(29)-Co(5)-O(30)#3	176.6(4)
O(14)-W(5)-O(28)	90.7(4)	N(3)-Co(5)-O(30)#3	90.6(4)
O(32)-W(5)-O(27)	102.2(4)	N(13)-Co(5)-O(30)#3	89.5(4)
O(14)-W(5)-O(27)	87.7(4)	O(8W)-Co(6)-O(8W)#4	180.00(12)
O(28)-W(5)-O(27)	155.4(4)	O(8W)-Co(6)-O(9W)#4	90.3(4)
O(32)-W(5)-O(26)	102.8(4)	O(8W)#4-Co(6)-O(9W)#4	89.7(4)
O(14)-W(5)-O(26)	154.7(4)	O(8W)-Co(6)-O(9W)	89.7(4)
O(28)-W(5)-O(26)	86.6(4)	O(8W)#4-Co(6)-O(9W)	90.3(4)
O(27)-W(5)-O(26)	84.6(4)	O(9W)#4-Co(6)-O(9W)	180.0(6)
O(31)#2-W(6)-O(17)	106.1(4)	O(8W)-Co(6)-O(7W)	91.0(4)
O(31)#2-W(6)-O(22)	101.4(4)	O(8W)#4-Co(6)-O(7W)	89.0(4)
O(17)-W(6)-O(22)	93.8(4)	O(9W)#4-Co(6)-O(7W)	91.2(5)
O(31)#2-W(6)-O(35)	99.6(4)	O(9W)-Co(6)-O(7W)	88.8(5)
O(17)-W(6)-O(35)	90.2(4)	O(8W)-Co(6)-O(7W)#4	89.0(4)
O(22)-W(6)-O(35)	156.6(4)	O(8W)#4-Co(6)-O(7W)#4	91.0(4)
O(31)#2-W(6)-O(28)	97.5(4)	O(9W)#4-Co(6)-O(7W)#4	88.8(5)
O(17)-W(6)-O(28)	155.9(4)	O(9W)-Co(6)-O(7W)#4	91.2(5)
O(22)-W(6)-O(28)	85.8(4)	O(7W)-Co(6)-O(7W)#4	180.0(5)
O(35)-W(6)-O(28)	81.3(4)	P(1)-O(1)-W(4)	126.6(5)
O(31)#2-W(6)-O(2)	168.4(4)	P(1)-O(1)-W(3)	125.7(5)
O(17)-W(6)-O(2)	83.4(3)	W(4)-O(1)-W(3)	88.2(3)

O(22)-W(6)-O(2)	84.2(3)	P(1)-O(1)-W(10)	127.2(4)
O(35)-W(6)-O(2)	73.4(3)	W(4)-O(1)-W(10)	89.3(3)
O(28)-W(6)-O(2)	72.6(3)	W(3)-O(1)-W(10)	87.2(3)
O(19)-W(8)-O(16)	103.1(4)	P(1)-O(2)-W(6)	126.8(5)
O(19)-W(8)-O(22)	103.6(4)	P(1)-O(2)-W(9)	125.3(5)
O(16)-W(8)-O(22)	95.9(4)	W(6)-O(2)-W(9)	89.6(3)
O(19)-W(8)-O(20)	99.3(4)	P(1)-O(3)-Co(3)	122.1(5)
O(16)-W(8)-O(20)	87.7(4)	P(1)-O(3)-Co(4)#1	122.9(5)
O(22)-W(8)-O(20)	155.3(4)	Co(3)-O(3)-Co(4)#1	94.8(3)
O(19)-W(8)-O(21)	99.9(4)	P(1)-O(3)-Co(4)	122.5(5)
O(16)-W(8)-O(21)	156.2(4)	Co(3)-O(3)-Co(4)	91.5(3)
O(22)-W(8)-O(21)	84.8(4)	Co(4)#1-O(3)-Co(4)	95.0(3)
O(20)-W(8)-O(21)	82.4(4)	P(1)-O(4)-W(2)	124.4(5)
O(19)-W(8)-O(4)	168.3(4)	P(1)-O(4)-W(8)	124.4(4)
O(16)-W(8)-O(4)	84.4(4)	W(2)-O(4)-W(8)	90.5(3)
O(22)-W(8)-O(4)	84.3(4)	P(1)-O(4)-W(1)	128.1(5)
O(20)-W(8)-O(4)	71.7(3)	W(2)-O(4)-W(1)	88.8(3)
O(21)-W(8)-O(4)	71.9(3)	W(8)-O(4)-W(1)	89.2(3)
O(13)-W(9)-O(12)	104.4(4)	W(4)-O(5)-Co(4)#1	135.4(5)
O(13)-W(9)-O(10)	103.4(4)	W(3)-O(6)-W(4)	124.7(5)
O(12)-W(9)-O(10)	93.5(4)	W(10)-O(7)-W(4)	128.1(5)
O(13)-W(9)-O(35)	96.9(4)	W(9)-O(10)-W(4)	149.9(5)
O(12)-W(9)-O(35)	91.7(4)	W(2)-O(11)-W(3)	149.6(5)
O(10)-W(9)-O(35)	157.0(4)	W(9)-O(12)-Co(3)	137.3(5)
O(13)-W(9)-O(14)	100.0(4)	W(9)-O(13)-Co(2)	145.4(6)
O(12)-W(9)-O(14)	155.3(4)	W(5)-O(14)-W(9)	127.1(5)
O(10)-W(9)-O(14)	84.1(4)	W(3)#1-O(15)-Co(4)	131.5(5)
O(35)-W(9)-O(14)	81.9(4)	W(3)#1-O(15)-Co(3)	126.0(5)
O(13)-W(9)-O(2)	168.1(4)	Co(4)-O(15)-Co(3)	101.4(4)
O(12)-W(9)-O(2)	83.2(4)	W(8)-O(16)-Co(4)	139.0(5)
O(10)-W(9)-O(2)	84.9(3)	W(6)-O(17)-Co(3)	138.3(5)
O(35)-W(9)-O(2)	73.5(3)	W(2)-O(20)-W(8)	124.7(5)
O(14)-W(9)-O(2)	72.1(3)	W(1)-O(21)-W(8)	126.3(5)
O(30)-W(10)-O(34)	103.6(4)	W(8)-O(22)-W(6)	147.7(5)
O(30)-W(10)-O(33)	102.7(4)	W(2)-O(24)-Co(4)	133.3(5)
O(34)-W(10)-O(33)	86.6(4)	W(2)-O(24)-Co(3)#1	124.0(4)
O(30)-W(10)-O(7)	101.3(4)	Co(4)-O(24)-Co(3)#1	101.2(4)
O(34)-W(10)-O(7)	155.1(4)	W(1)-O(25)-W(2)	127.5(4)
O(33)-W(10)-O(7)	89.5(4)	W(1)-O(26)-W(5)	151.5(6)
O(30)-W(10)-O(27)	101.6(4)	W(5)-O(27)-W(10)	151.4(5)
O(34)-W(10)-O(27)	87.2(4)	W(5)-O(28)-W(6)	126.9(4)
O(33)-W(10)-O(27)	155.6(3)	W(1)-O(29)-Co(5)	167.2(6)
O(7)-W(10)-O(27)	86.3(4)	W(10)-O(30)-Co(5)#5	161.5(6)

W(10)-O(33)-W(3)	127.7(4)	W(10)-O(34)-W(1)	149.5(5)
W(9)-O(35)-W(6)	122.4(5)	W(6)#6-O(31)-Co(2)	163.6(5)
O(30)-W(10)-O(1)	170.0(4)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1 #2 -x+3/2,y+1/2,z #3 -x+1,y+1/2,-z+1/2 #4 -x+1,-y,-z+1 #5 -x+1,y-1/2,-z+1/2 #6 -x+3/2,y-1/2,z

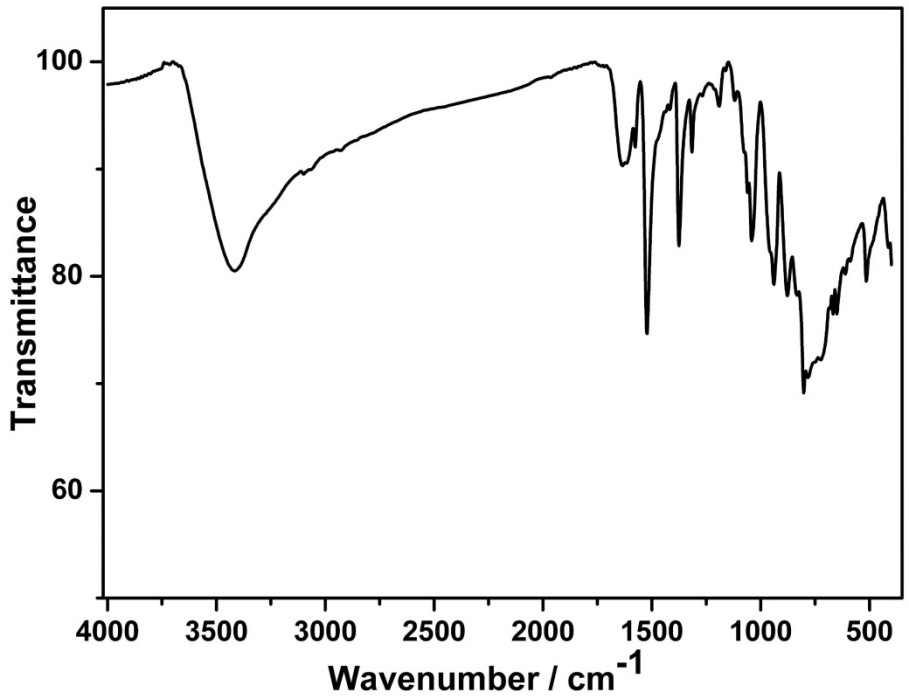

Figure S1. Infrared spectrum of fresh **1.**

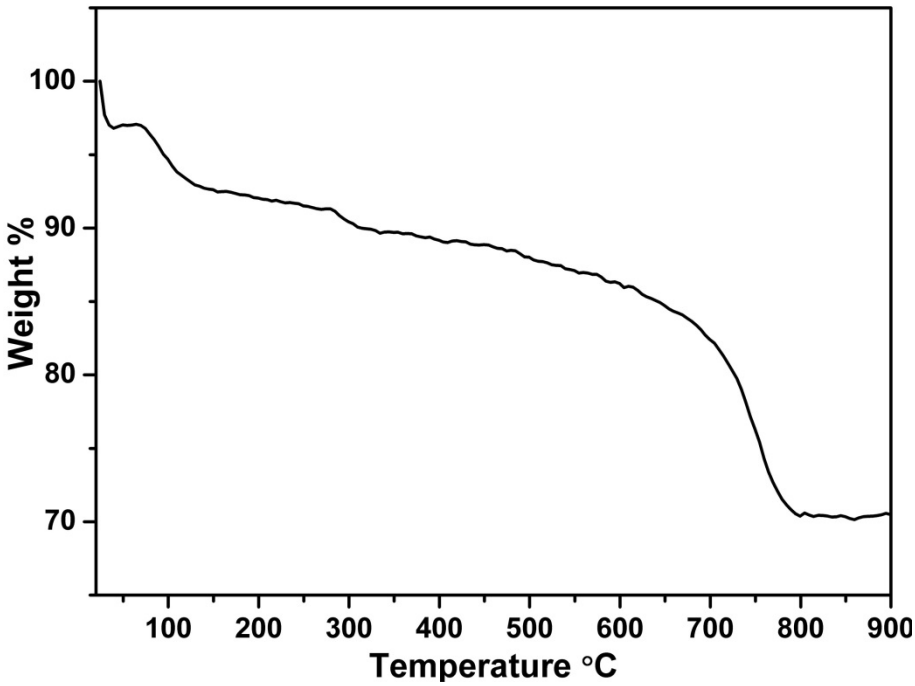

Figure S2. TGA curve of compound **1**.

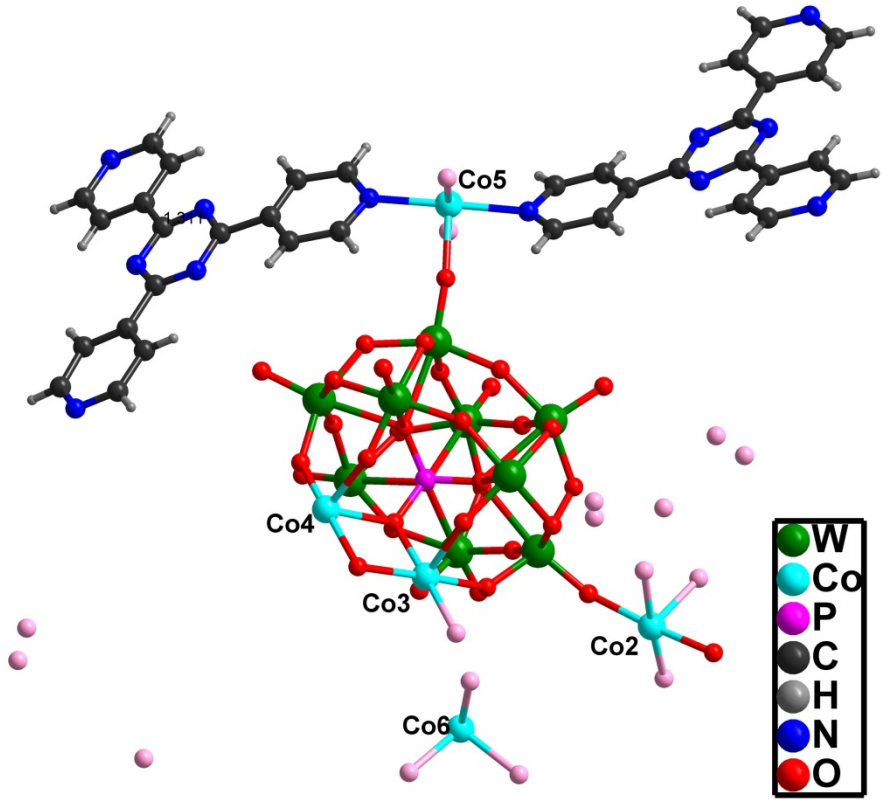

Figure S3. The asymmetric unit for **1** where all the water molecules have been highlighted in rose.

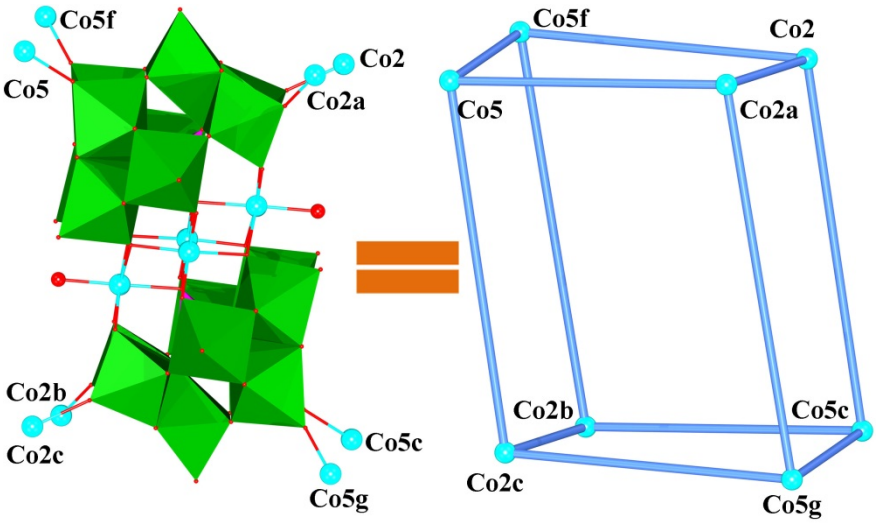

Figure S4. (left) One Co_4POM is bound to eight Co atoms which consists of two different Co^{2+} cations (Co2 and Co5) and can be categorized into two groups with 4 : 4 distribution fashion. Four Co2 (Co5) atoms in which two Co2 (Co5) atoms link to the adjacent terminal oxygen atoms (O_t) of the same Co_4POM subunit arrange in the diagonal direction. (right) Schematic presentation of the special alignment of the eight Co atoms bound to Co_4POM.

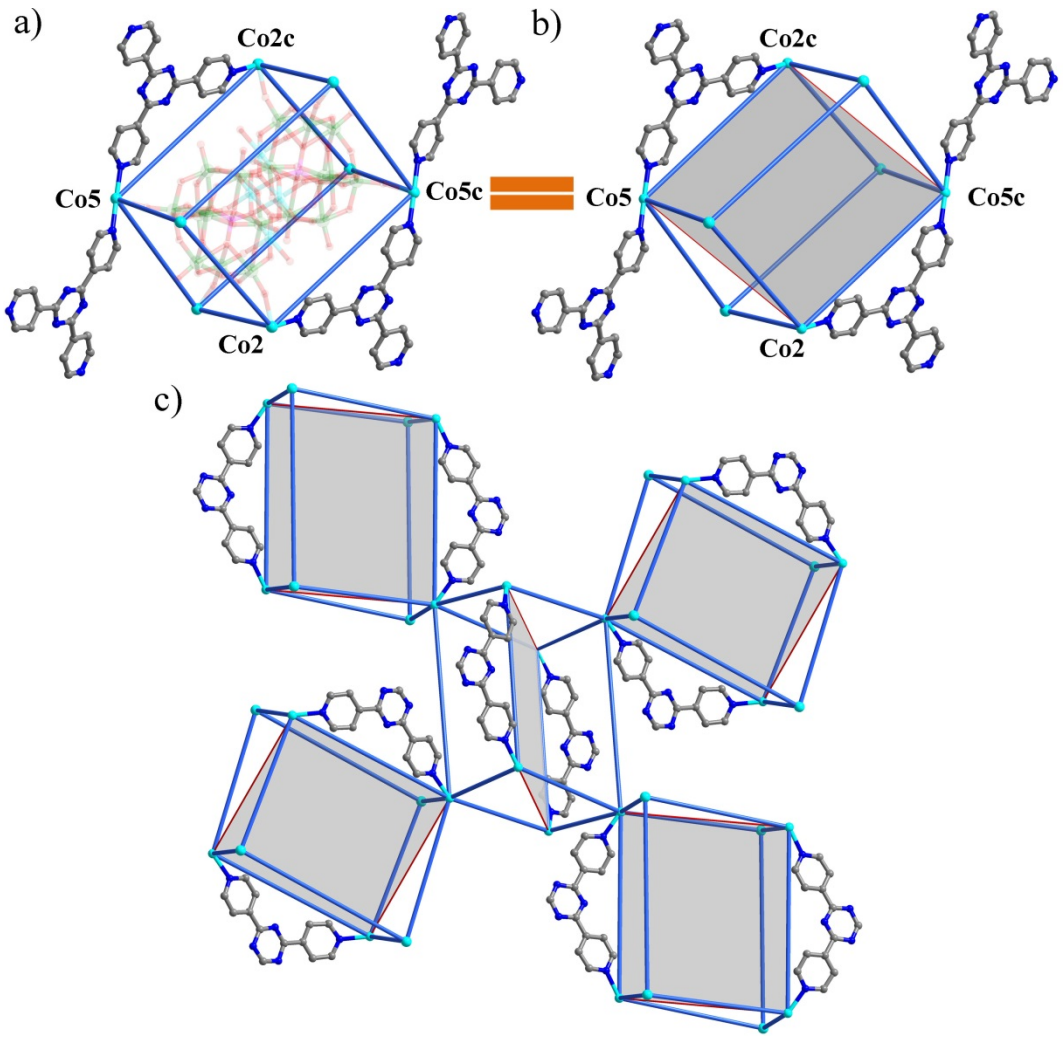

Figure S5. a) Two pairs of Co2 and Co5 atoms in the diagonal plane are clamped by two μ_2-TPT ligands which can stabilize the Co_4POM subunit. The μ_1-TPT ligands grafted on Co5 are also displayed for comparison. b) Schematic presentation of the two pairs of Co2 and Co5 atoms clamped by two μ_2-TPT ligands in the diagonal plane which has been highlighted in light gray. c) The connection between the μ_2-TPT-locked Co_4POM where the uncoordinated pyridine group in μ_2-TPT has been eliminated for clarity.

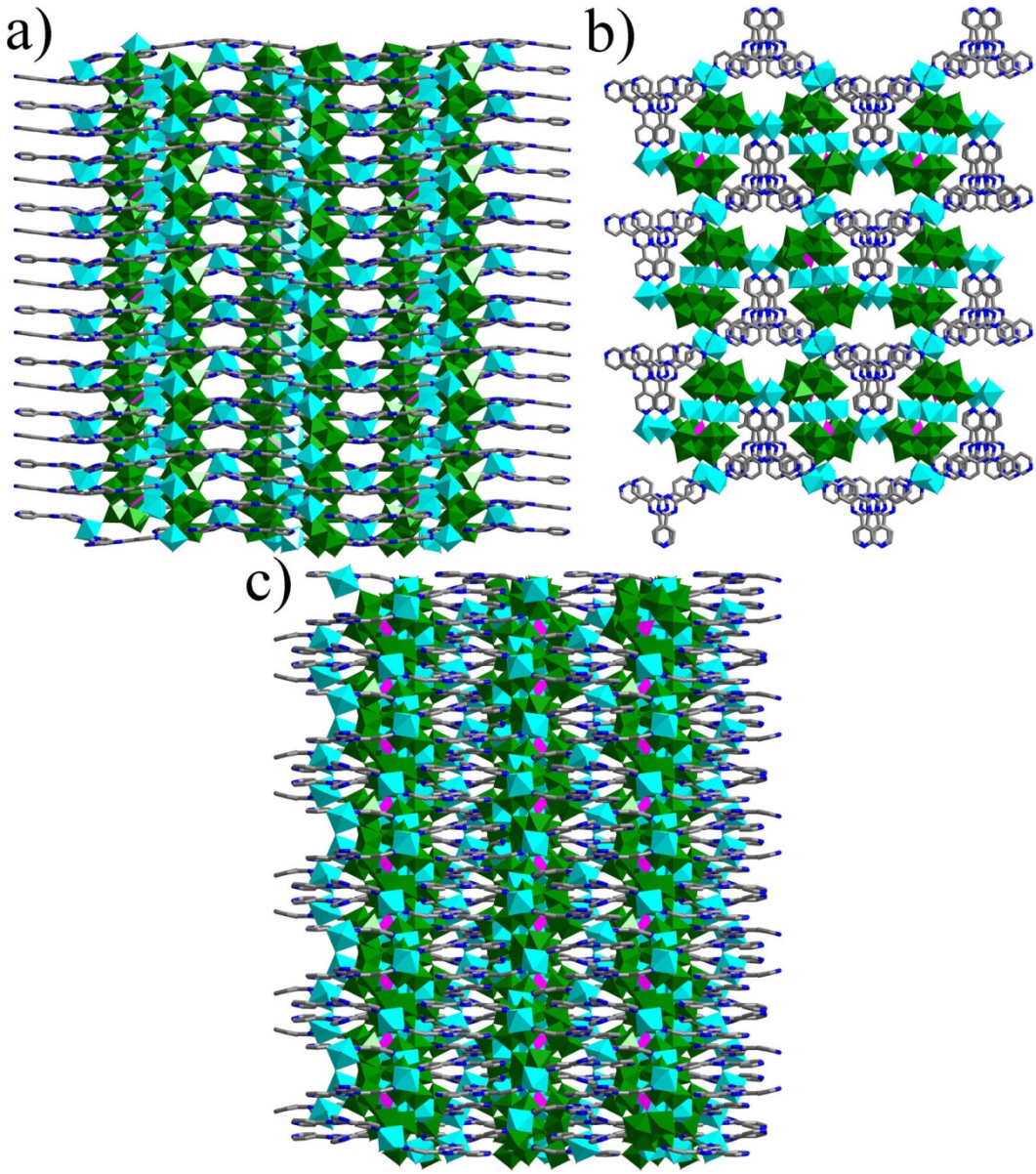

Figure S6. View of the 3D structure of **1** along a, b, c axis; The strong offset π-π stacking interactions between the TPT molecules can be observed.

Table S3. ICP results of metal ions detection in the photocatalytic reaction solution after removing the solid catalyst.

ICP	W	Co
Content	0%	0%

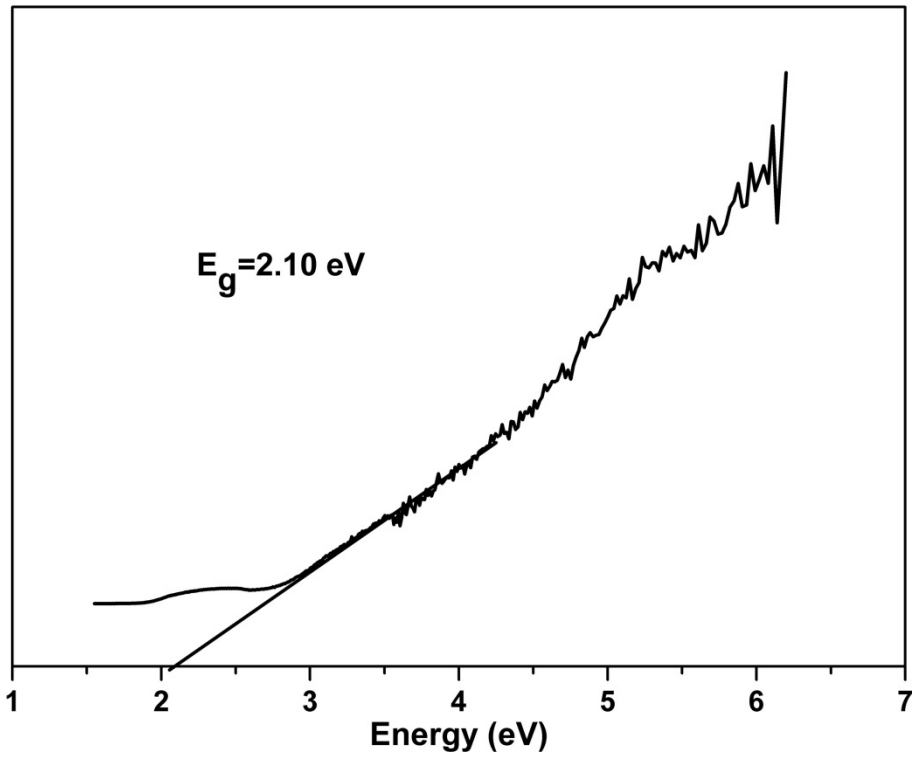

Figure S7. The $(\alpha h\nu)^2$ *vs* hν curve of **1**. The band gap of compound **1** was measured by a solid state ultraviolet−visible (UV−vis) diffuse reflection measurement method at room temperature. According to the equation $(\alpha h\nu)^2 = K(h\nu - E_g)$ (where hν is the discrete photo energy, α is the absorption coefficient, E_g is the band gap energy, and K is a constant), the extrapolated values (the straight lines to the x axis) of hν at $\alpha = 0$ give absorption edge energy corresponding to E_g = 2.10 eV for compound **1.**

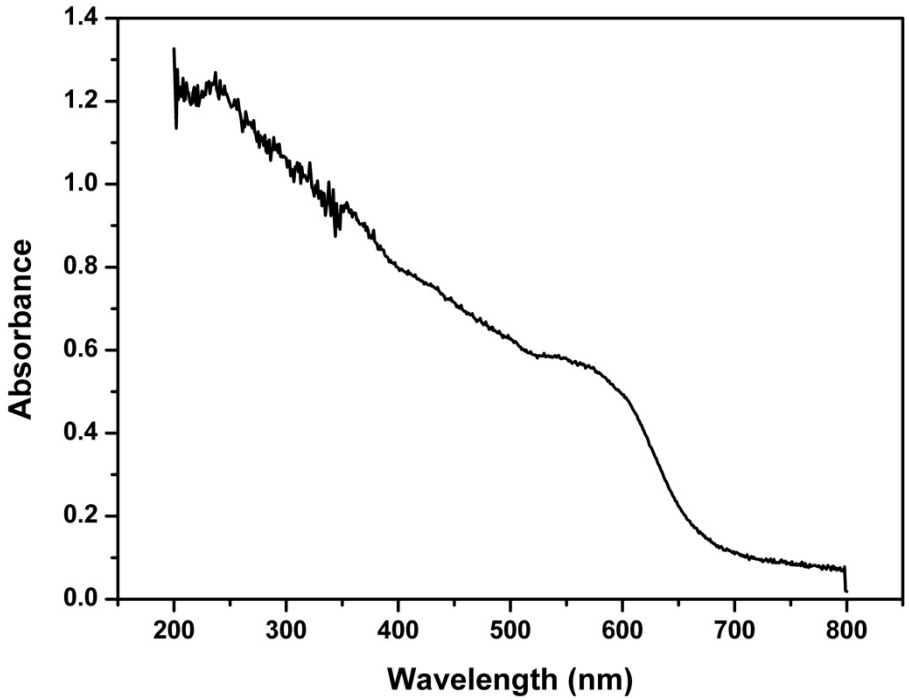

Figure S8. The UV-visible spectra of as-prepared crystalline material **1**.

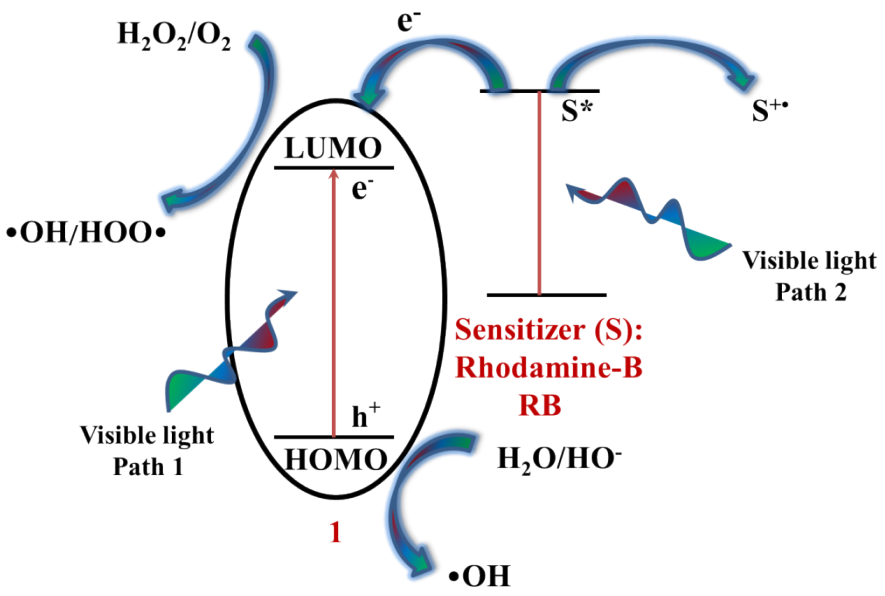

Fig. S9 Proposed catalytic mechanism of **1** under visible light irradiation. Taking the band-gap value and band-edge positions of **1** into account, the photocatalytic mechanism under visible light involving two paths is proposed as following: in path 1, because of the narrow band-gap of **1**, under visible light, electrons (e^-) in the HOMO (VB) of **1** were excited to its LUMO (CB), with same amount of holes (h^+) left in VB. Then each water molecule adsorbed on the surfaces of **1** provides one electron for the holes in the VB to make it return to its stable state, with the water molecule being oxygenated into •OH active species (The holes can also oxidize RB, but the water molecules have better contact with the catalyst surfaces, so finally, the water molecules absorbed on the catalyst surface are oxidized to •OH). Meanwhile, the H_2O_2 and oxygen adsorbed on the surface of catalyst **1** can easily trap an electron in the LUMO to form •OH and $O2^{\bullet-}$, respectively. Notably, the attack of H_2O_2 by the formed •OH radical is one possible way for the formation of superoxide radicals ($O2^{\bullet-}$/HOO•) according to the Haber Weiss mechanism. The formed radicals •OH and $O2^{\bullet-}$/HOO• attack organic substrates and cleave RB effectively to complete the photocatalytic process. As we know, the degradation of RB is finished through oxidation process, so the electrons (e^-) which are excited from the HOMO (VB) of the catalyst to its LUMO (CB) upon light irradiation should be consumed. H_2O_2 is added as sacrificial electron acceptor, which is better than other sacrificial electron acceptors because it can easily trap an electron in the LUMO to form •OH, one active specie in the degradation of RB. And no harmful substances but water will produce at last. In path 2, considering the conduction band (LUMO) of **1** (-0.71 V *vs*. NHE) and the redox potentials of excited RhB*(-1.42 V *vs*. NHE), the electrons from RhB* can also be injected into the LUMO of **1**, which further are captured by H_2O_2 and oxygen. All these injected electrons were further trapped by H_2O_2 to yield the oxidizing species $OH^{\bullet}$, further, radicals attack organic substrates and degrade dye.

References

1. M.-X. Li, Z.-X. Miao, M. Shao, S.-W. Liang and S.-R. Zhu, *Inorg. Chem.*, 2008, **47**, 4481-4489.
2. P. J. Domaille, in *Inorg. Synth.*, John Wiley & Sons, New York, 1990, p. 100.
3. G. M. Sheldrick, *SHELXL-97: Program for X-ray Crystal Structure Refinement;* , University of Göttingen: Göttingen, Germany, 1997.
4. L. J. Farrugia, *WINGX: A Windows Program for Crystal Structure Analysis;* , University of Glasgow: Glasgow, UK, 1988.