Supporting Information

A Copper(II)–ethylenediamine modified polyoxoniobate with photocatalytic H$_2$ evolution activity under visible light irradiation

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Experiment Section

General Information: Unless otherwise stated, all chemicals used were analytical grade, commercially available and used without further purification. K$_8$ [Nb$_6$O$_{19}$] ·16H$_2$O and Co^{III}(dmgH)$_2$ pyCl were prepared according to the literatures 1 and 2 methods, respectively. Elemental analyses (H, C, and N) were performed using a Perkin–Elmer 2400 CHN elemental analyzer; K, Nb, Cu and Co were analyzed on a PLASMA-SPEC(I) ICP atomic emission spectrometer; FT-IR spectra of the samples were recorded in the range of 400–4000 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. The UV-Visible diffuse reflectance spectra were recorded at ambient temperature on a Cary-500 UV-vis Spectrophotometer. The thermal gravimetric analysis (TGA) was carried out performed on a Perkin-Elmer TGA-7 instrument under flowing N$_2$ with a heating rate of 10°C / min at 20-1000°C; Powder X-ray diffraction (PXRD) measurements were characterized using a D/max200PC X-ray powder diffractometer with Cu-Kα radiation (λ= 1.5418 Å) and a Lynx Eye detector at a scanning rate of 10°/min in the 2θ range of 5° to 50°. GC analyses were performed on GC-7890T instrument with a thermal conductivity detector and a 5 Å molecular sieve column (2 mm × 2 m) using N$_2$ as carrying gas.

Synthesis of Compound 1

$Co^{III}(dmgH)_2pyCl$ (structure is shown in Scheme S1)was synthesized according to the literature.[1] Anal. Calcd. for $C_{13}H_{19}N_5O_4ClCo$: C, 38.67; H, 4.74; N, 17.35;Co, 14.60. Found: C, 38.63; H, 4.79; N, 17.40; Co, 14.64. $K_8[Nb_6O_{19}]\cdot16H_2O$ (**1a**) was synthesized according to the literature.[2]Anal. Calcd. for $K_8[Nb_6O_{19}]\cdot16H_2O$ (%): K, 21.39. Nb, 38.12. H, 2.19. Found (%): K, 21.36. Nb, 38.16. H, 2.22.

The synthetic section as shown in the text (yield: 55% based on $K_8[Nb_6O_{19}]\cdot16H_2O$). Anal. Calcd for $[Cu(en)_2]_{11}K_6Na_2[Nb_{24}O_{72}H_9]_2\cdot120H_2O$(**1**) (%): K, 2.09; Na, 0.41; Nb, 39.66; Cu, 6.21; C, 4.70; H, 3.89; N, 5.48. Found (%): K, 2.01; Na, 0.33; Nb, 39.60; Cu, 6.26; C, 4.78; H, 3.96; N, 5.54. IR (KBr pellet): 3222(s, v_{O-H}), 3121(s, v_{N-H}), 1588(s, v_{C-N}), 1458 (m, v_{C-C}), 869(ms, γ_{CH2}) (Fig. S2). The crystal structure of **1** was determined by single crystal X-ray diffraction.

Reference:

1. F. Y. Wen, J. H. Yang, X. Zong, B. J. Ma, D. G. Wang and C. Li, *J Catal*, 2011, **281**, 318-324.

2. M. Nyman, T. M. Alam, F. Bonhomme, M. A. Rodriguez, C. S. Frazer and M. E. Welk, *J Cluster Sci*, 2006, **17**, 197-219.

Crystallography

During the refinement, the command 'omit-3 50' was used to omit the weak reflections above 50 degree. During the refinement, most of the non-H atoms were refined ansiotropically, but some of the C and N atoms on en ligands are just refined isotropically due to their weak reflections. Furthermore, The $[Cu_{15}(en)_2]$ unit is disordered in two positions with 50% for each. All the C and N atoms on this fragment are also refined isotropically.

In the final refinement, four disordered K^+ cations and 40 lattice water moleclues are assigned from the difference Fourier Maps. Parts of the solvent water molecules can just be refined isotropically because of their obvious ADP problems. The rest cations or solvents cannot be exactly assigned from the weak reflections. Thus, the

SQUEEZE program was used to calculate and estimate the possible numbers of the cations and solvents in the accessible void of this crystal structure. The calculation result is shown below. Based on the SQUEEZE calculation results, elemental analysis and the TG analysis, as well as the charge-balance consideration, another two Na^+ cations and 80 water molecules were directly included in the final molecular formula. The *.hkl generated by the SQUEEZE program was used to substitute the original *.hkl to carry out more refinement cycles and obtain the final cif file.

In the final refinement, the highest residual peak $2.40e\text{Å}^{-3}$ was close to the heavy atom K3 with the distance of 1.52Å and featureless. It is noteworthy that there are extensive short connections between O(POM) and O(water) atoms in the range of 2.50-2.90Å, suggesting the extensive H-bonding interactions between solvent water molecules and the polyoxoanions, however, non suitable H atoms on water molecules can be found from the difference fourier maps. It is also worth noting that the restraint command 'isor' was used to restrain some non-H atoms with NPD and/or ADP problems. These atoms are as follows: C31 C32 C33 C34 N31 N32 N33 N34 C2 C9 N40 C42 C36 C28 C35 N39 C39 C27 C12 N41 C26 C24 C205 N210 C42 C33 C26 C23 C25 C24 C6 C5 C1 C41 K3>K6A. Futhermore, the bond distances and angles of most en ligands were fixed with the restrained command 'dfix'. All these restrained refinement led to a relative high restraint value of 262.

Photocatalysis Experiments

The photocatalytic reaction was carried out in a Pyrex inner-irradiation-type reaction vessel with magnetic stirring at room temperature. The photocatalytic reactions were performed in 100 mL 10% TEA solution, containing 1×10^{-4}mol/L compound **1** (0.1g)and 2.5mmol/L Cobalt complex(0.1001g). Before the photocatalytic reaction, nitrogen gas was bubbled through the reaction mixture for 0.5h to remove air. The mixture was then irradiated using a Xe lamp (500W) with a Pyrex-glass filter ($\lambda > 400$ nm). The H_2 produced was analyzed using a GC 7890T instrument.
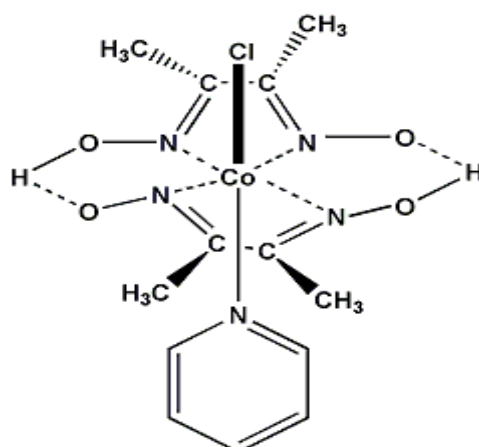
Scheme S1. Structure of Co^{III} (dmgH) $_2$pyCl complex,
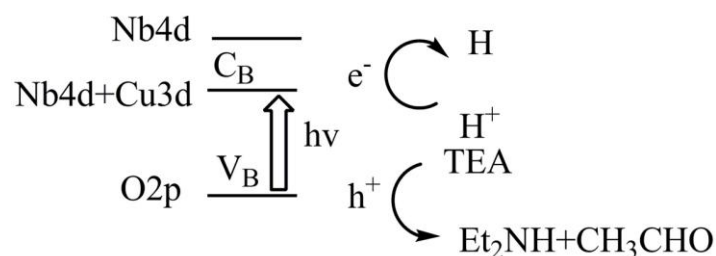
Scheme S2. The proposed mechanism of photocatalytic H_2 production of **1** in the

visible light. (C_B: Conduction Band; V_B: Valence Band; h^+: Photogenerated holes; D:

electron donor; P: photosensitizer; C: electron carrier; Cat: proton reduction catalyst)

The schematic diagram for a homogeneous system for photocatalytic H_2 production is

shown in the following illustration (**Scheme S2**)[3-8]. The conduction band (C_B)

formed with the orbital of Nb4d and Cu3d in compound **1** is below the conduction

band only consisting of Nb4d orbital, which make the energy gap (EG) narrower,

finally the energy gap extends to the visible region, so the catalyst compound **1** is

capable of photocatalytic H_2 production in the visible light (**Scheme S2**) [3-8].

The proposed mechanism of photocatalytic H_2 production in the visible light of

compound **1** is as follows: **Firstly**, the Cu(II) of dimmer polyoxoniobate (**1**,

photosensitizer) yields its excited-state (**1***) after a certain wavelengths of light irradiation; **Secondly**, **1*** obtains electrons from TEA (electron donor), and donates the excited electrons to the Co(III) complexes surface (proton reduction catalyst); **Thirdly**, the H^+ obtains the electron from the Co(III) complexes surface to be reduced to H atom to form H_2[3-8].

Reference:

3. A. Ioannidis, E. Papaconstantinou, *Inorg. Chem.*1985, **24**, 439-441;

4. R. Akid, J. R. Darwent, *J. Chem. Soc. Dalton Trans.*1985, 195-399;

5. T. Yamase, R. Watanabe, J. Chem. Soc. Dalton Trans. 1986, 1669-1675;

6. J. R. Darwent, J. Chem. Soc., Chem. Commun., 1982, 798-799;

7. Y. H. Guo, C. W. Hu, J. Mole. Catal. A: Chem., 2007, 262 ,136-148;

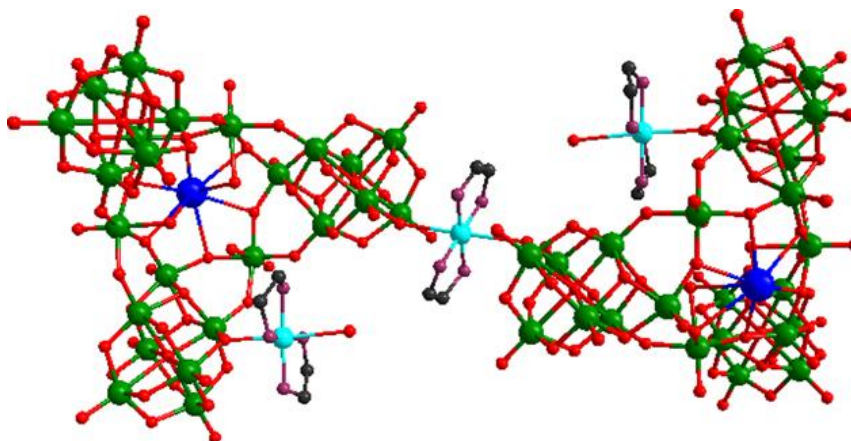8. A. Kudo, Y. Miseki, *Chem. Soc. Rev.,* 2009, 38, 253-278.

Fig. S1. The ball-and-stick representation of the dimer polyanion of **1**. Color codes: {Nb}, green; K (blue), Cu (cyan), C (grey), N (pink) and O (red).
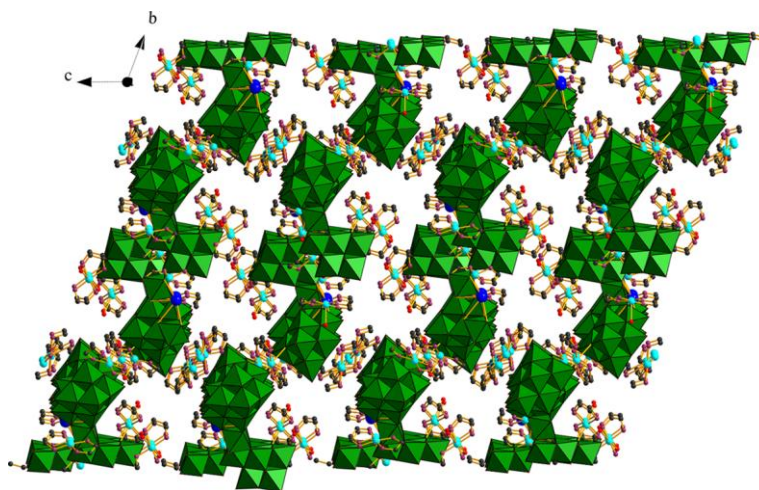
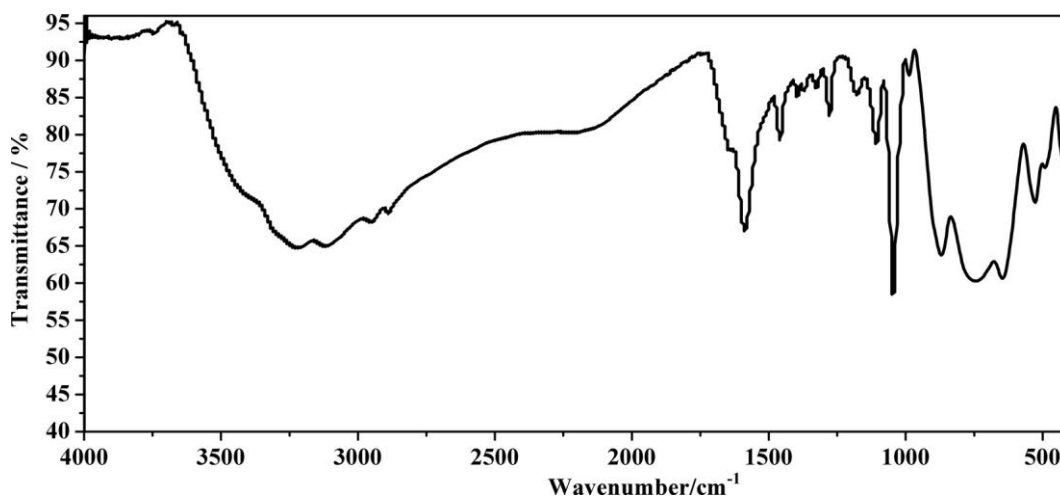**Fig. S2.** The packing arrangement of compound **1** viewed along *a* axis.
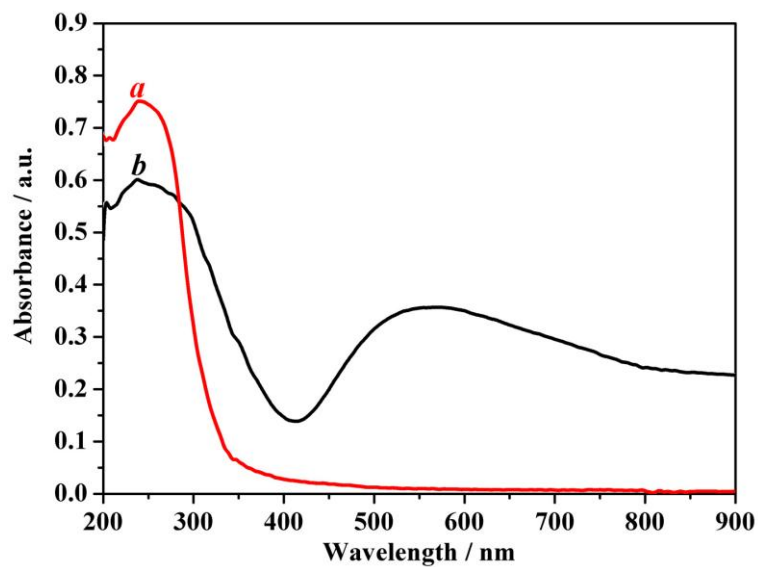

Fig.S3. IR spectrum of **1**

Fig.S4. UV-Vis diffuse reflectance spectra of a) K_8 [Nb_6O_{19}]·$16H_2O$ and b) compound **1**.
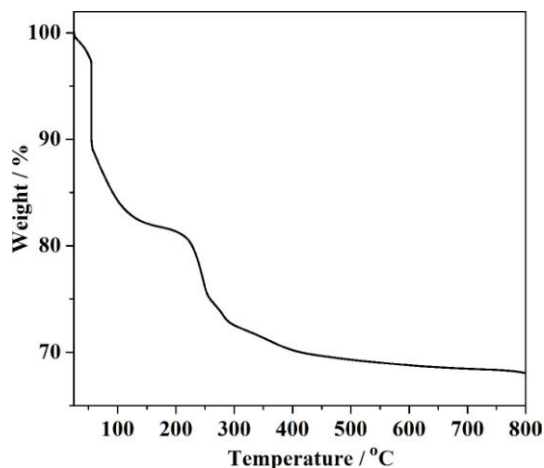
Fig. S5. TG of compound **1**. Compound **1** exhibit two weight loss steps in the temperature range 30-800°C, the first weight loss is 19.4% (theoretical value 19.2%) in the temperature range 30-220°C, corresponding to the loss of noncoordinated and coordinated water molecules. And the second weight loss is 11.9% in the temperature range 220-600°C, corresponding to the loss of ethanediamine molecules, which is consistent with the theoretical value 11.7%.
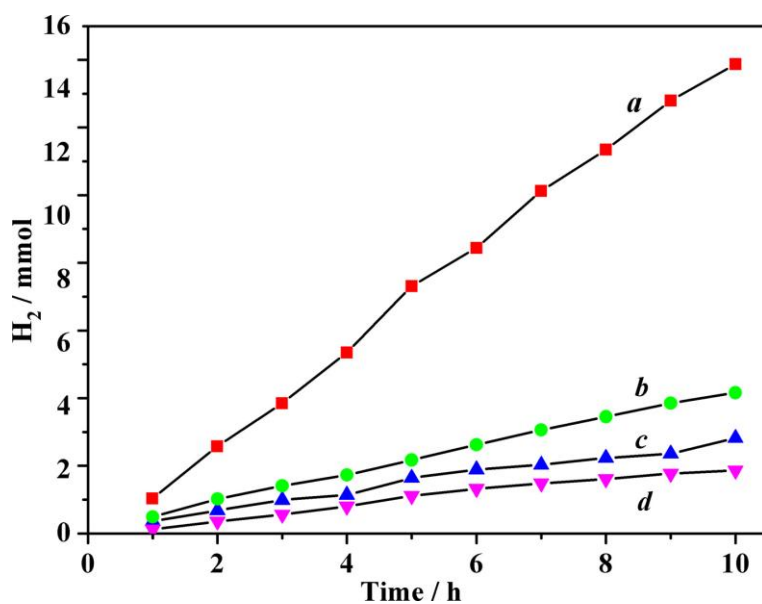

Fig. S6. Time courses of photocatalytic H_2 evolution over $Co(dmgH)_2pyCl$/ **1** hybrid system in 100 mL solution (line a,b,c,d: 0 vol.%, 30 vol. %, 45 vol.% and 60 vol.% acetonitrile)under visible light irradiation ($\lambda > 400$ nm). Compound **1** (0.1g); $Co^{III}(dmgH)_2pyCl$(0.25 mM); 10 vol.% TEA (total solution volume 100 mL, 0.72mM); light source, Xe lamp (500 W).
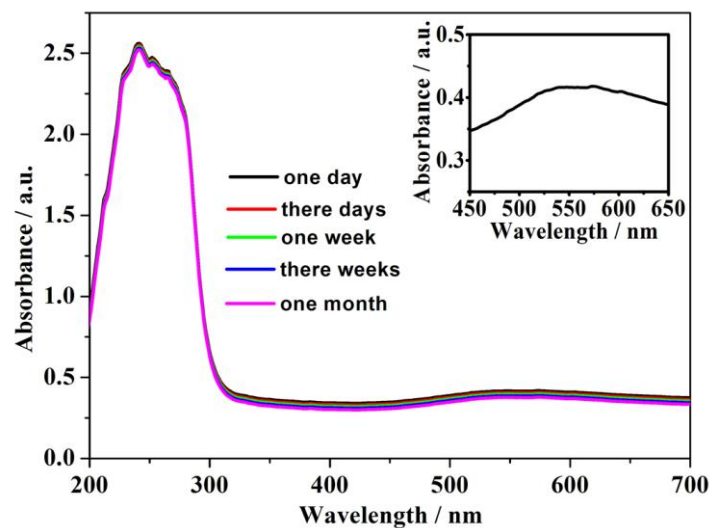
Fig. S7. UV-Vis spectra of compound **1** kept at room temperature. The insert figure is the UV-Vis spectra of compound **1** in the rang of 450~650nm.
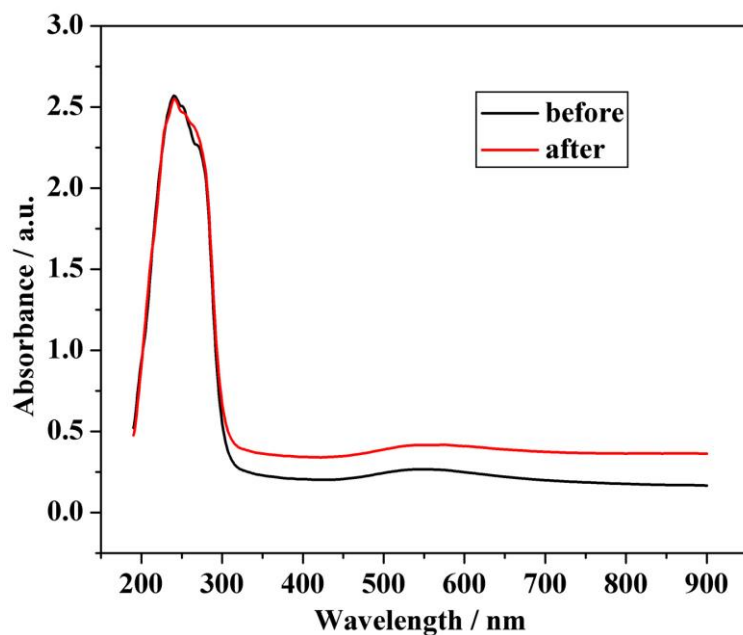

Fig.S8. UV-Vis spectra of compound 1 before(black) and after(red) 5 runs of the photocatalytic reactions with 100mg compound **1** and 0.25mmol cobaloximes in 100mL 10% TEA solution.
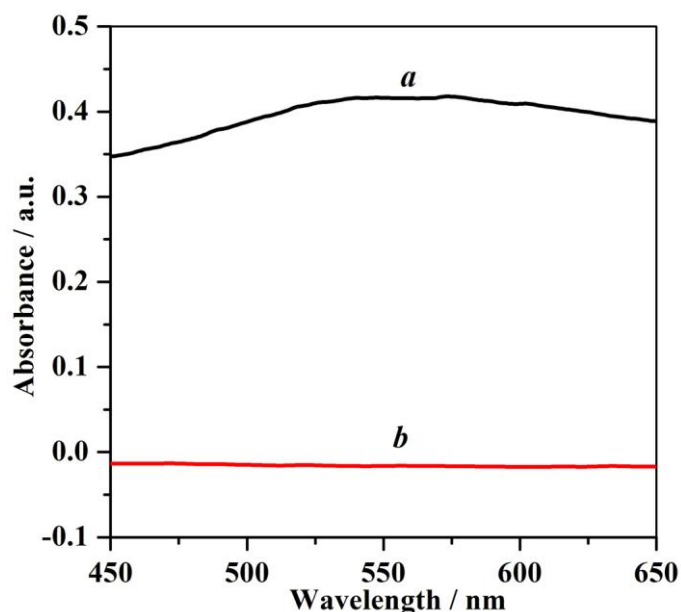
Fig. S9. UV-Vis spectra of a) compound **1** and b) $K_8[Nb_6O_{19}]\cdot16H_2O$. From Fig. S9, there is a wide absorption at 550nm in the visible region in compound **1**, but there is no adsorption of $K_8[Nb_6O_{19}]\cdot16H_2O$, we can conclude that the $[Cu(en)_2]$ cation still remains coordinating to the polyoxoniobate in solution.

Table S1. Crystal data and structure refinement for 1

Empirical formula	$C_{44}H_{434}Cu_{11}K_6N_{44}Na_2Nb_{48}O_{264}$
Formula weight	11245.55
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	$a =24.2748(16)$ Å $\alpha =110.3980(10)^o$ $b = 25.4804(17)$ Å $\beta = 95.0640(10)^o$ $c = 34.443(2)$ Å $\gamma = 96.8080(10)^o$
Volume	19634(2) Å^3
Z, Calculated density	2, 1.902Mg/m^3
Absorption coefficient	2.086 mm^{-1}
F(000)	11082
Crystal size	$0.25 \times 0.23 \times 0.20$ mm

Theta range for data collection	0.99 to 25.00 deg.
Limiting indices	$-24 \leq h \leq 28$, $-30 \leq k \leq 28$, $-40 \leq l \leq 37$
Reflections collected / unique	101071 / 68353 [R_{int}=0.0213]
Completeness to theta = 25.00	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6804 and 0.6236
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	68353 / 262 / 3015
Goodness-of-fit on F^2	1.076
Final R indices [I>2sigma(I)]	$R_1 = 0.0500$, $wR_2 = 0.1272$
R indices (all data)	$R_1 = 0.0768$, $wR_2 = 0.1351$
Largest diff. peak and hole	2.409 and -1.331 e$\mathrm{\AA}^{-3}$

Table S2. The TON values of photocatalysis experiments by soluble compound **1**.

$$TON = n_{H2}/n_{catalyst}$$

Run	Compound 1 concentration (mM)	Co(III) concentration (mM)	TON value of UV	TON value of Vis
1	0.089	0.25	111	1.6
2	0.089	0.25	106	1.6
3	0.089	0.25	114	1.5
4	0.089	0.25	106	1.6
5	0.089	0.25	111	1.5