

*Electronic Supplementary Information*

**Photocatalytic Oxidation of Organic Compounds in a Hybrid System Composed of Molecular Catalyst and Visible Light-Absorbing Semiconductor**

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## Materials

Solvents were dried and distilled prior to use according to the standard methods.  $\text{WO}_3$  (50 nm in diameter),  $\alpha\text{-Fe}_2\text{O}_3$  (30 nm in diameter),  $\text{H}_2^{18}\text{O}$  (97 atom%) were purchased from Aladdin and  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  was purchased from Alfa Aesar. The ruthenium compounds  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ ,<sup>1</sup>  $[\text{Ru}(\text{tpa})(\text{H}_2\text{O})_2](\text{PF}_6)_2$ ,<sup>2</sup>  $[\text{Ru}(\text{tpy})(\text{bpy})(\text{H}_2\text{O})](\text{ClO}_4)_2$ ,<sup>3</sup> and  $\text{BiVO}_4$  powder (< 200 nm in diameter)<sup>4</sup> were prepared according to literature methods. Phosphate buffer used in this study is a 0.1 M sodium dihydrogen phosphate aqueous solution (pH 4.7). This buffer was adjusted by 6 M HCl or NaOH aqueous solution to other required pH values. All other chemicals are commercially available.

## General methods

$^1\text{H}$  NMR Spectra were collected at 298 K using a Bruker DRX-400 instrument. Electrospray ionization mass spectra were recorded on a Q-ToF Micromass spectrometer (Manchester, England). UV-Vis absorption measurements were carried out on an Agilent 8453 spectrophotometer. Electrochemical measurements were carried out on a CHI660D electrochemical potentiostat.

## General procedure for photocatalytic oxidation

A degassed 0.1 M phosphate buffer solution (10 mL, pH 4.7) containing semiconductor powder (15 mg), organic substrate (10 mM), catalyst (0.04 mM),  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  (25 mM) was stirred at  $\text{N}_2$  atmosphere under irradiation of a 300 W Xe lamp equipped with a cutoff filter ( $\lambda > 400$  nm) for 5 h at 25°C. The resulting solution was extracted with  $\text{CH}_2\text{Cl}_2$  for three times and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of solvent by vacuum, the products were characterized and quantified by  $^1\text{H}$  NMR spectroscopy (two representative  $^1\text{H}$  NMR spectra used for product quantification in the oxidation of benzyl alcohol or sulfide were shown in Figure S2 and S3) or GC.

Method for recovery of BiVO<sub>4</sub>: After photocatalysis, BiVO<sub>4</sub> powder together with the deposition of Co<sup>II</sup> complex were separated from reaction solution by centrifugation. The obtained solid was dispersed in HOAc aqueous solution (pH 2~2.5) and sonicated for 3 hours, then washed with water for several times and dried in oven at 100°C for 3 h. BiVO<sub>4</sub> was found to be quantitatively recovered and was identified by XRD to be unchanged.

### **Oxygen evolution experiment**

BiVO<sub>4</sub> powder (15 mg) and [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> (25 mM) in 0.1 M phosphate buffer solution (10 mL, pH 4.7) were added to a reactor with a space volume of 40 mL. The solution was degassed by argon for 30 min. Photocatalysis was started by light irradiation at 25°C with the same light source as used for hydrocarbon oxidation. The gas sample was taken by syringe from the headspace of the vial and was analyzed on a Techcomp GC 7890T instrument equipped with a 5 Å molecular sieve column and a thermal conductivity detector with argon a carrier gas.

### **<sup>18</sup>O labeling experiment with thioanisole as the substrate**

An Ar-degassed H<sub>2</sub><sup>18</sup>O phosphate buffer solution (1 mL) containing BiVO<sub>4</sub> (2 mg), thioanisole (10 mM), complex **2** (0.04 mM) and [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> (25 mM) was stirred for 4 h under the irradiation of a 300 W Xe lamp light with a cutoff filter ( $\lambda > 400$  nm) and stirred for 4 h at 25°C. The resulted solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the products were analyzed by ESI-MS.

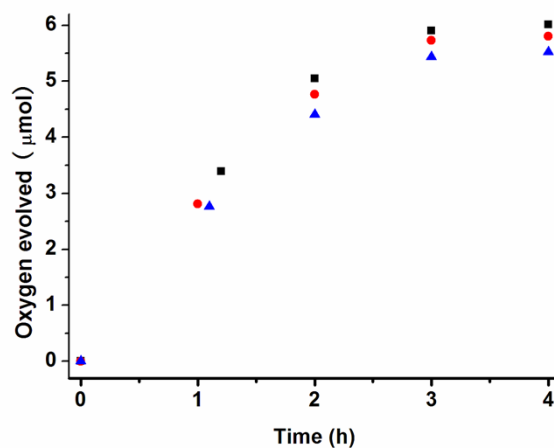
### **Photo-generation of Ru(IV)=O complexes**

A phosphate buffer solution (10 mL) containing ruthenium catalyst (0.04 mM), BiVO<sub>4</sub> (15 mg), and [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> (5 mM) was irradiated for 15 min at 25°C. A 5 mL aliquote was taken from the reaction mixture and was centrifugalized to remove

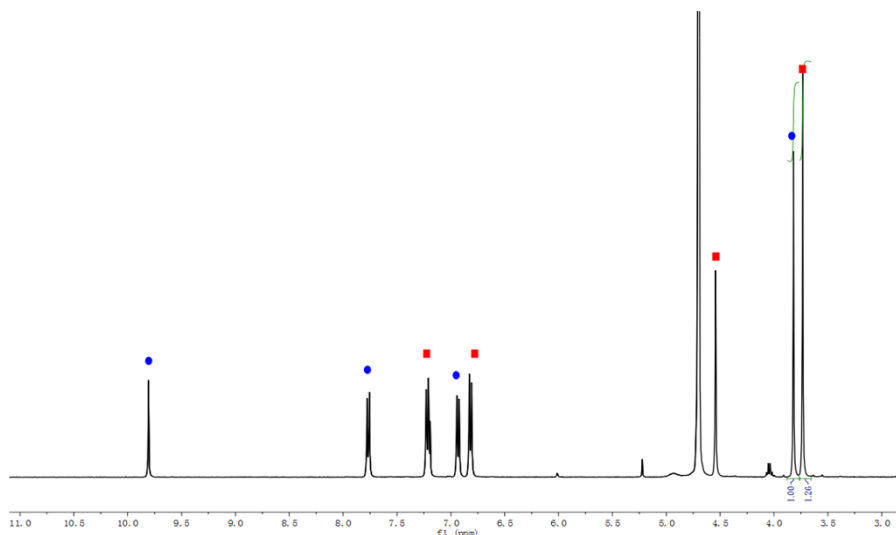
BiVO<sub>4</sub> powder. The resulted transparent solution was used as a sample for spectroscopic analysis by UV-Vis.

### Electrochemical generation of Ru(IV)=O complexes

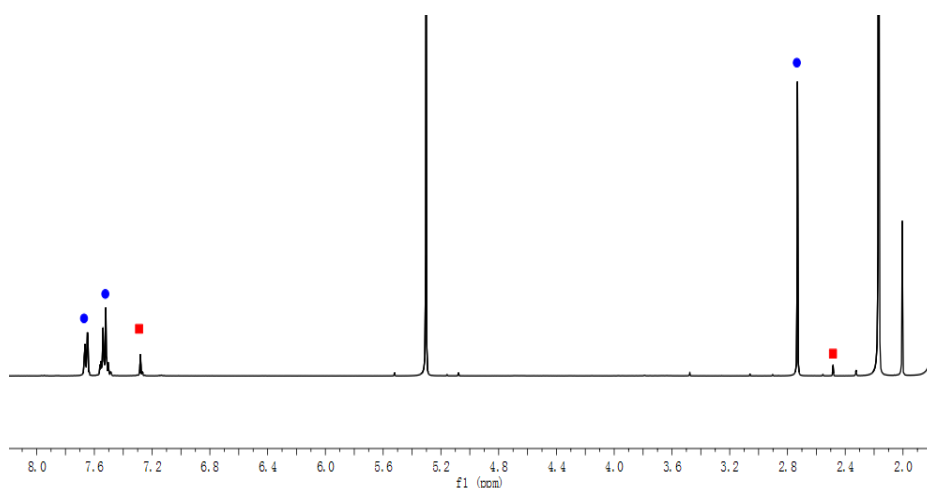
Constant potential electrolyses were carried out in a three-electrode cell equipped with a clean 2 × 2 cm<sup>2</sup> FTO glass as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl (3.5 M KCl) reference electrode at ambient pressure and room temperature. The electrolyte were phosphate buffer solutions (pH 4.7, 20 mL) containing ruthenium 0.04 mM ruthenium complexes. The electrochemical generation of Ru(IV)=O complexes were monitored by UV-Vis absorption. Potentials versus NHE were calibrated by using Ru(bpy)<sub>3</sub>Cl<sub>2</sub> as a reference with  $E(\text{Ru}^{\text{II/III}}) = 1.26 \text{ V vs. NHE}$ .



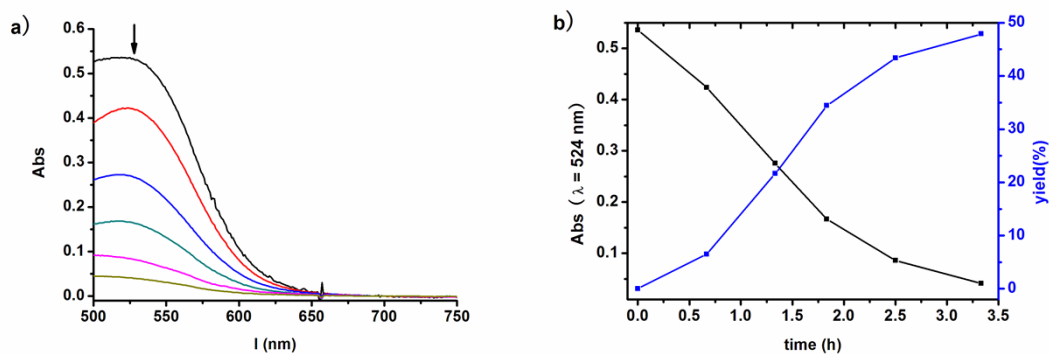
**Figure S1.** Time courses of oxygen evolution from 0.1 M phosphate buffer solutions (10 mL, pH 4.7) containing (■) BiVO<sub>4</sub> (15 mg) and [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> (25 mM), (●) [Ru(tpa)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> (0.04 mM), BiVO<sub>4</sub> (15 mg) and [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> (25 mM), and (▲) BiVO<sub>4</sub> (15 mg), [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> (25 mM) and benzyl alcohol (10 mM) under visible light ( $\lambda > 400 \text{ nm}$ ) irradiation.



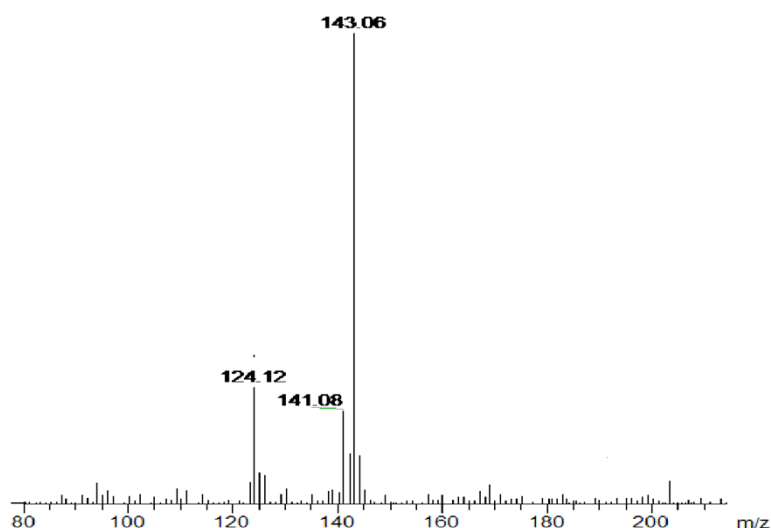
**Figure S2.**  $^1\text{H}$  NMR spectrum of the residue extracted by DCM from the resulted solution of photocatalytic dehydrogenation of 4-methoxybenzyl alcohol (solvent  $\text{CDCl}_3$ ), 4-methoxybenzyl alcohol (●), 4-methoxybenzaldehyde (■)). Reaction conditions: catalyst (0.04 mM),  $\text{BiVO}_4$  (15 mg), 4-methoxybenzyl alcohol (10 mM), and  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  (25 mM) in a 0.1 M (pH 4.7) phosphate buffer solution irradiated for 5 h.



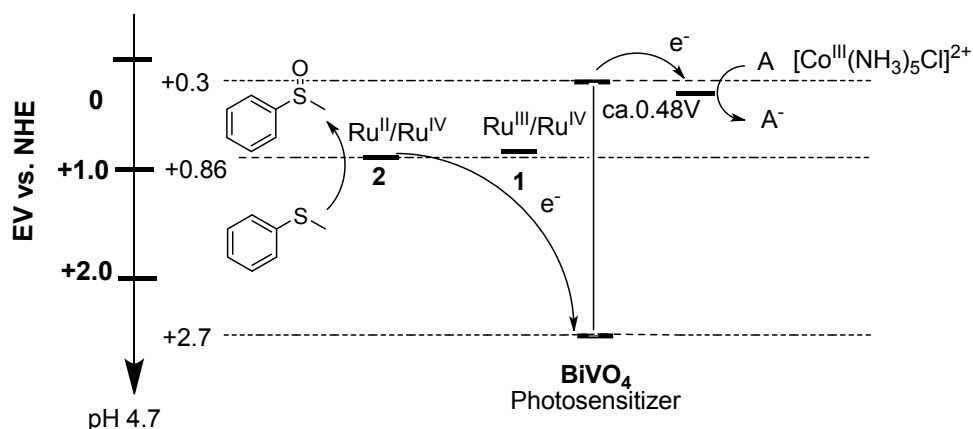
**Figure S3.**  $^1\text{H}$  NMR spectrum of the residue extracted by DCM from resulted solution of photocatalytic oxidation of thioanisole (solvent  $\text{CDCl}_3$ ), thioanisole (■), methyl phenyl sulfoxide (●)). Reaction conditions:  $\text{BiVO}_4$  (15 mg), thioanisole (10 mM),  $[\text{Ru}(\text{tpy})(\text{bpy})(\text{H}_2\text{O})]^{2+}$  (0.04 mM),  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  (10 mM) in 0.1 M sodium dihydrogen phosphate buffer irradiated for 5 h.



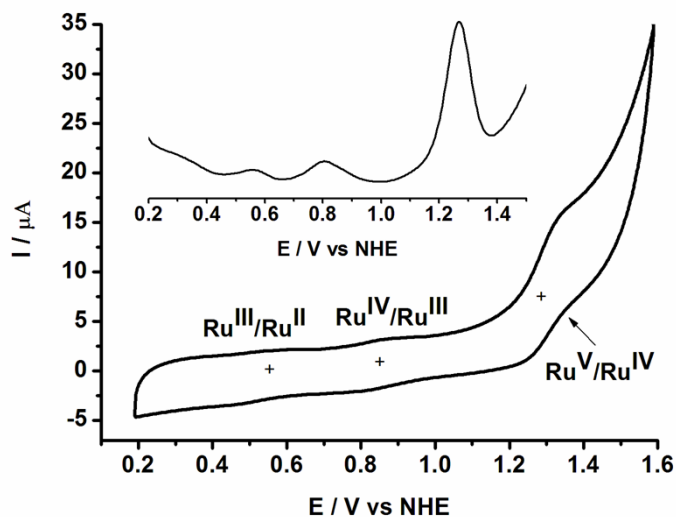
**Figure S4.** (a) Visible absorption spectral changes of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  (10 mM) during photocatalytic procedure in 0.1 M phosphate buffer solution (10 mL, pH = 4.7) containing  $\text{BiVO}_4$  (15 mg),  $[\text{Ru}(\text{tpy})(\text{bpy})(\text{H}_2\text{O})]^{2+}$  (0.04 mM) and thioanisole (10 mM) upon irradiation (UV-Vis absorption analyses were carried out after removing  $\text{BiVO}_4$  from each aliquot of the reaction solution). (b) Time courses of the generation of methyl phenyl sulfoxide (blue) and the consumption of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  decided by the absorption changes at 524 nm in (a). Note that the maximum yield for the conversion of sulfide to sulfoxide is 50% under the present conditions.



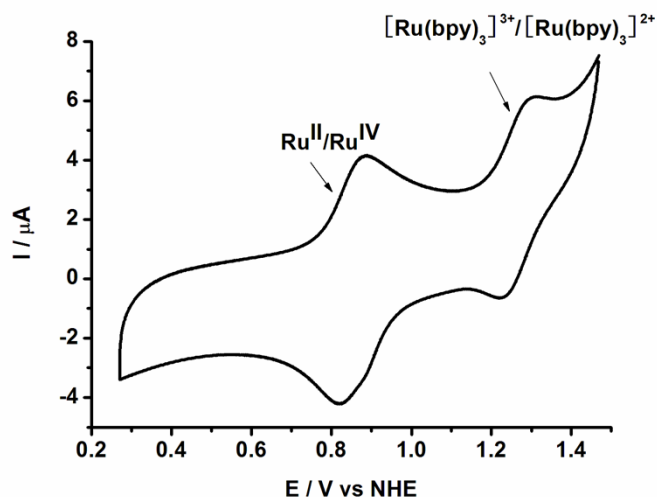
**Figure S5.** ESI-MS spectrum of methyl phenyl sulfoxide generated by photocatalytic oxygenation of thioanisole with  $\text{H}_2^{18}\text{O}$  as solvent.  $\text{PhSCH}_3$   $m/z = 124$ ,  $\text{PhS} (^{16}\text{O}) \text{CH}_3$   $m/z = 141$   $[\text{M} + \text{H}]^+$ ,  $\text{PhS} (^{18}\text{O}) \text{CH}_3$   $m/z = 143$   $[\text{M} + \text{H}]^+$ .



**Figure S6.** Energy levels of  $\text{BiVO}_4$ , catalysts and  $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$  in pH 4.7 aqueous solution<sup>[5]</sup>.



**Figure S7.** Cyclic and different pulse voltammogram of 0.04 mM complexes **1** in 0.1 M phosphate buffer solutions (20 mL, pH 4.7). Complex **1** exhibits three redox couples at 0.51, 0.83 and 1.27 V derived from  $\text{Ru}^{\text{II}}\text{-OH}_2/\text{Ru}^{\text{III}}\text{-OH}$ ,  $\text{Ru}^{\text{III}}\text{-OH}/\text{Ru}^{\text{IV}}\text{=O}$  and  $\text{Ru}^{\text{IV}}\text{=O}/\text{Ru}^{\text{V}}\text{=O}$ .



**Figure S8.** Cyclic voltammogram of 0.04 mM complexes **2** in 0.1 M phosphate buffer solution (20 mL, pH 4.7). Complex **2** shows a small potential separation between  $\text{Ru}^{\text{II}}\text{-OH}_2/\text{Ru}^{\text{III}}\text{-OH}$  and  $\text{Ru}^{\text{III}}\text{-OH}/\text{Ru}^{\text{IV}}\text{=O}$ . The two-electron waves were further confirmed by comparison of integrated area with a known one electron/one proton couple  $[\text{Ru}(\text{bpy})_3]^{2+}/[\text{Ru}(\text{bpy})_3]^{3+}$  under the same conditions.

**Table S1.** Photocatalytic oxidation of benzyl alcohol with  $\text{BiVO}_4$  as light absorber at different pH values.<sup>a</sup>

Entry	pH	Yield (%)	TON
1	2.5	1	-
2	3.0	26	65
3	4.7	29	73
4	6.0	19	47

<sup>a</sup> Reaction conditions: catalyst **1** (0.04 mM),  $\text{BiVO}_4$  powder (15 mg), benzyl alcohol (10 mM), and  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  (25 mM) in 0.1 M phosphate buffer were irradiation with 300 W Xe lamp with a 400 nm cutoff filter for 5 h.



**Table S2.** Photocatalytic oxygenation of thioanisole.<sup>a</sup>

Entry	catalyst	substrate	product	Yield(%)
1	1	Thioanisole	Methyl phenyl sulfoxide	78
2	-	Thioanisole	Methyl phenyl sulfoxide	80
3	2	Thioanisole	Methyl phenyl sulfoxide	79
4 <sup>b</sup>	-	Thioanisole	Methyl phenyl sulfoxide	72

<sup>a</sup> Reaction conditions: catalyst (0.04 mM), [Ru(bpy)<sub>3</sub>]<sup>2+</sup> ( $8 \times 10^{-5}$  M), thioanisole (10 mM) and [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> (25 mM) in 0.1 M phosphate buffers irradiated under 300 W Xe lamp equipped with a 400 nm cutoff filter for 5 h. <sup>b</sup> AM 1.5G solar simulator was used as light source.

## References

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