Electronic Supplementary Information

Chemical and photochemical oxidation of organic substrates by ruthenium aqua complexes with water as an oxygen source

Fei Li,*a Miao Yu,a Yi Jiang,a Fang Huang,a Yanqing Li,a Biaobiao Zhang,a and Licheng Sun*ab

aState Key Laboratory of Fine Chemicals, Dalian University of Technology (DUT), DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian 116024, China. E-mail: lifei@dlut.edu.cn; Fax: +46 84986245; Tel: +46 84986247
bDepartment of Chemistry, School of Chemical Science and Engineering, Royal Institute of Technology (KTH), 100 44 Stockholm, Sweden. E-mail: lichengs@kth.se.

Materials

All synthetic reactions were carried out under N₂ atmosphere with standard Schlenk techniques. Solvents were dried and distilled prior to use according to the standard methods. Compounds [Ru(dmp)₂(H₂O)₂](PF₆)₂ (1), [Ru(bpy)₃]Cl₂ [2], Ru(tpy)Cl₃ [3] and [Ru(tpy)(bpy)Cl]Cl [4] were prepared according to known procedures and stored in fridge under N₂ atmosphere. All other chemicals are commercially available. [Co(NH₃)₅Cl]Cl₂ and Ce(NH₄)₂(NO₃)₆ (Ce⁴⁺) were purchased from Aldrich and Tianjin chemical company, respectively. H₂¹⁸O (97 atom%) was purchased from Aladdin chemical company.

Instruments

¹H 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). EI-MS analyses were carried out on a gas chromatograph fitted with a mass spectrometer (GC–MS 6890/5973, Agilent, USA). UV-Vis absorption measurements were carried out on a HP 8450 spectrophotometer.

Synthesis of [Ru(tpy)(bpy)(H₂O)](ClO₄)₂ (2)
[Ru(tpy)(bpy)(H₂O)](ClO₄)₂ was synthesized by a modified procedure reported by Berlinguette. To a 5 mL MeOH/H₂O (1:1 v:v) solution of [Ru(tpy)(bpy)Cl]Cl (168 mg, 0.3 mmol), was added AgNO₃ (102 mg, 0.6 mmol), the resulting mixture was heated at reflux for 3h and filtrated through Celite. Excess of NaClO₄ was added to the filtrate, slow evaporation of MeOH resulted in the formation of red crystals, which was collected and dried under vacuum (159 mg, 75%). The structure of this complex was characterized by ¹H NMR, which is identical to that reported in literature.[⁴]

**General procedure for catalytic oxidation with Ce⁴⁺ as oxidant**

To a N₂-degassed D₂O solution (1 mL) of alkene (0.1 mmol) and catalyst (0.001 mmol) was added Ce⁴⁺ (0.4 mmol), the mixture was stirred at room temperature for 3 h. The final solution was directly analyzed by ¹H NMR spectroscopy by adding fixed amount of DMF as an internal standard. Control experiment was carried out in a similar manner described above but without catalyst.

**General procedure for photocatalytic oxidation**

A N₂-degassed aqueous phosphate buffer solution (5 mL, pH 6.8) containing catalyst (2 × 10⁻⁵ M), [Ru(bpy)₃]Cl₂ (2 × 10⁻⁴ M), organic substrate (alcohol or sulfide 2 × 10⁻² M) and [Co(NH₃)₅Cl]Cl₂ (2 × 10⁻² M) was exposed to irradiation of an Xe lamp light source (500 W) with a cut-off filter (λ > 400 nm) and stirred for 5 h at room temperature. The resulted solution was extracted with CH₂Cl₂ for three times and dried with anhydrous Na₂SO₄. After removal of solvent, the products were characterized and quantified by ¹H NMR spectroscopy. Control experiment was carried out in a similar manner described above but without catalyst.

**¹⁸O labeling experiment with cyclohexene as substrate**

To a N₂-degassed H₂¹⁸O solution (0.5 mL) of cyclohexene (0.1 mmol) and catalyst (0.001 mmol) was added Ce⁴⁺ (0.4 mmol), the mixture was stirred at room temperature for 3 h. The final solution was extracted by diethyl ether and analyzed by GC-MS.
\(^{18}\text{O}\) labeling experiment with thioanisole as substrate

A \(\text{N}_2\)-degassed \(\text{H}_2^{18}\text{O}\) phosphate buffer solution (1 mL, pH 6.8) containing catalyst (2 \(\times\) 10\(^{-5}\) M), \([\text{Ru(bpy)}_3]\text{Cl}_2\) (2 \(\times\) 10\(^{-4}\) M), organic substrate (alcohol or sulfide 2 \(\times\) 10\(^{-2}\) M) and \([\text{Co(NH}_3)_5\text{Cl}]\text{Cl}_2\) (2 \(\times\) 10\(^{-2}\) M) was exposed to irradiation of an \(\text{Xe}\) lamp light source (500 W) with a cut-off filter (\(\lambda > 400\) nm) and stirred for 5 h at room temperature. The resulted solution was extracted with \(\text{CH}_2\text{Cl}_2\) and purified by a short column. The product was finally analyzed by ESI-MS.

Electrochemistry

The electrochemical measurements were recorded on a BAS-100W electrochemical potentiostat in a three-electrode cell under argon atmosphere. The working electrode was a glassy carbon disk (diameter, 3 mm) successively polished with 3 and 1 \(\mu\)m diamond pastes and sonicated in ion-free water before use. The counter electrode was a platinum wire. The reference electrode was an aqueous Ag/AgCl electrode. Potential versus NHE was calibrated by using Ru(bpy)_3Cl_2 as a reference with \(E(\text{Ru}^{II/III}) = 1.26\) V.
Figure S1 a) EI-MS spectrum of adipic acid generated with H$_2^{18}$O as solvent. The spectrum is identical to that of $^{18}$O labeled adipic acid reported by Kojima and Funkuzumi et al.$^{[5]}$ b) ESI-MS spectra of methyl phenyl sulfoxide generated with H$_2^{16}$O (left) and H$_2^{18}$O (right) as solvents. Left: PhS(16O)CH$_3$, m/z = 141 [M + H$^+$], m/z = 143 [M + Na$^+$] and m/z = 303 [2M + Na$^+$]. Right: PhS($^{18}$O)CH$_3$, m/z = 143 [M + H$^+$], m/z = 165 [M + Na$^+$], m/z = 285 [2M + H$^+$] and m/z = 307 [2M + Na$^+$].
Figure S2 The adsorption of phosphate buffer solution consisting of complex 2 (6 × 10^{-5} M), [Ru(bpy)$_3$]$^{2+}$ (3 × 10^{-5} M) and [Co(NH$_3$)$_5$Cl]$^{2+}$ (3 × 10^{-4} M) before and after visible light illumination. The band with maximum at 460 nm arising from MLCT transitions of 2 disappears as Ru$^{II}$=O oxidized to Ru$^{IV}$=O upon illumination,$^6$ while the adsorption of photosenzitizer at 420 and 450 nm remains.

Fig. S3 UV/Vis spectral changes upon addition of 1 to 5 equiv. of Ce$^{IV}$ into a deaerated aqueous solution of complex 1 (5 × 10^{-5} M), which reflects the species variation from Ru$^{II}$ to Ru$^{VI}$. 
Fig. S4 Cyclic voltammograms of complex 1 (1 mM, black curve) and [Ru(bpy)3]2+ (1 mM, red curve) in phosphate buffer (pH 6.8, 50 mM) solutions, which indicates the oxidation of 1 by photogenerated [Ru(bpy)3]3+ is thermodynamically favorable. Electrode: GC, scan rate: 100 mV/s.

Control experiments in the absence of catalysts

Fig. S5 1H NMR spectrum of the resulted solution from chemical oxidation of cyclohexene (internal standard DMF (■)). Reaction conditions: cyclohexene (0.1 mmol) and CeIV (0.4 mmol) in D2O solution (1 mL) stirred for 3 h.
Fig. S6 $^1$H NMR spectrum of the resulted solution from chemical oxidation of sodium $p$-styrene sulfate (sodium $p$-styrene sulfate (●), sodium 4-formylbenzenesulfonate (▲), sodium 4-(1,2-dihydroxyethyl)benzenesulfonate (◆), internal standard DMF (■)). Reaction conditions: sodium $p$-styrene sulfate (0.1 mmol) and Ce$^{IV}$ (0.4 mmol) in D$_2$O solution (1 mL) stirred for 3 h.

Fig. S7 $^1$H NMR spectrum of the residue extracted by DCM from resulted solution of photocatalytic oxidation of thioanisole (solvent CDCl$_3$, thioanisole (●), methyl phenyl sulfoxide (▲)). Reaction conditions: [Ru(bpy)$_3$]Cl$_2$ (2 × 10$^{-4}$ M), sulfide (2 × 10$^{-2}$ M),
and [Co(NH₃)₅Cl]Cl₂ (2 × 10⁻² M) in 5 mL neutral phosphate buffer solution stirred for 5h under visible light illumination.

**Catalytic oxidation**

Fig. S8 ¹H NMR spectrum of the resulted solution from chemical oxidation of cyclohexene (adipic acid (▲), internal standard DMF (■)). Reaction conditions: complex 1 (0.001 mmol), cyclohexene (0.1 mmol) and Ce⁴⁺ (0.4 mmol) in D₂O solution (1 mL) stirred for 3 h.

Fig. S9 ¹H NMR spectrum of the resulted solution from chemical oxidation of sodium p-styrene sulfate (sodium 4-formylbenzenesulfonate (▲)). Reaction conditions:
complex 1(0.001 mmol), sodium \( p \)-styrene sulfate (0.1 mmol) and Ce\(^{IV} \) (0.4 mmol) in D\(_2\)O solution (1 mL) stirred for 3 h.

Fig. S10 \(^1\)H NMR spectrum of the residue extracted by DCM from resulted solution of photocatalytic dehydrogenation of benzyl alcohol (solvent CDCl\(_3\), benzyl alcohol (●), benzaldehyde (▲)). Reaction conditions: complex 1 (4 × 10\(^{-5}\) M), [Ru(bpy)\(_3\)]Cl\(_2\) (4 × 10\(^{-4}\) M), alcohol (2 × 10\(^{-2}\) M), and [Co(NH\(_3\))\(_5\)Cl]Cl\(_2\) (2 × 10\(^{-2}\) M) in 5 mL neutral phosphate buffer solution stirred for 5 h under visible light illumination.

Fig. S11 \(^1\)H NMR spectrum of the residue extracted by DCM from resulted solution
of photocatalytic oxidation of thioanisole (solvent CDCl₃, thioanisole (●), methyl phenyl sulfoxide (▲)). Reaction conditions: complex 1 (4 × 10⁻⁵ M), [Ru(bpy)₃]Cl₂ (4 × 10⁻⁴ M), sulfide (2 × 10⁻² M), and [Co(NH₃)₅Cl]Cl₂ (2 × 10⁻² M) in 5 mL neutral phosphate buffer solution stirred for 5h under visible light illumination.

References