Electronic Supplementary Information

Photocatalytic Oxidation of Alkenes and Alcohols in Water by a Manganese(V) Nitrido Complex

Gui Chen,^{‡ab} Lingjing Chen,^{‡a} Li Ma,^a Hoi-Ki Kwong^a and Tai-Chu Lau*^a

^a Institute of Molecular Functional Materials and Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Hong Kong, China.

^b Key Laboratory of Coal to Ethylene Glycol and Its Related Technology, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China.

E-mail: <u>bhtclau@cityu.edu.hk</u> . Fax: +852 3442 0522.

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Materials

[PPh₄][Mn(N)(CN)₄], [Ru(bpy)₃]Cl₂·6H₂O and [Ru(bpy)₃](ClO₄)₃ were prepared according to literature methods.¹⁻³ The purity of these complexes was determined by CHN analysis. [Co(NH₃)₅Cl]Cl₂ (98%, Aldrich) was used as received. All organic substrates were obtained from Sigma-Aldrich Chemical Co.. Alkenes were purified by passing through a short column of neutral alumina prior to use. Alcohols were used as received. d_{12} -cyclohexanol (98+ atom %D) was ordered from Medical Isotopes and used as received.

Instrumentation

Gas chromatographic analyses were performed on a Hewlett-packard 5890 gas chromatograph with a DB-5MS ($30 \text{ m} \times 0.25 \text{ mm i.d.}$) column or a DB-FFAP ($30 \text{ m} \times 0.25 \text{ mm i.d.}$) column equipped with a FID detector. GC-MS (Agilent 6890-5975) measurements were carried out with a DB-5MS ($30 \text{ m} \times 0.25 \text{ mm i.d.}$) column. Elemental analyses were done on an Elemental Micro Carbon-Hydrogen-Nitrogen Analyzer (Elementar VARIO Micro Cube). Electrospray ionization mass spectra (ESI/MS) were obtained on a PE-SCIEX API 2000 mass spectrometer.

Procedure for chemical oxidation

In a typical experiment, to an aqueous phosphate buffer solution (5 mL, 0.1 M, pH 6.8)

containing $(PPh_4)_2[Mn^V(N)(CN)_4]$ (20 µM) and substrate (20 mM) was added $[Ru(bpy)_3](ClO_4)_3$ (0.05 mmol, 43.4 mg) and the mixture was stirred for 30 min at 23 °C. The resulted solution was extracted with ethyl acetate (4 mL) and quantified by GC with chlorobenzene as internal standard. Control experiment was carried out in a similar manner but without catalyst.

Procedure for photocatalytic oxidation

In a typical experiment, an aqueous phosphate buffer solution (5 mL, 0.1 M, pH 6.8) containing $(PPh_4)_2[Mn^V(N)(CN)_4]$ (20 μ M), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (0.2 mM), substrate (20 mM) and $[Co(NH_3)_5Cl]Cl_2$ (20 mM) was stirred under argon and irradiated by a LED lamp (10 W) for 30 min at 23 °C. The resulted solution was extracted with ethyl acetate (4 mL) and quantified by GC with chlorobenzene as internal standard.

¹⁸O-labelled experiments with styrene as substrate

An argon-degassed 1:1 mixture of $H_2^{18}O$ and $H_2^{16}O$ buffer solution (1 mL, 0.1 M, pH 6.8) containing (PPh₄)₂[Mn^V(N)(CN)₄] (20 μ M), [Ru(bpy)₃]Cl₂·6H₂O (0.2 mM), styrene (20 mM) and [Co(NH₃)₅Cl]Cl₂ (20 mM) was irradiated by LED lamp (10 W) for 30 min. The resulted solution was extracted with ethyl acetate (1 mL) and analyzed by GC-MS.

Kinetic isotope effect experiments

The kinetic isotope effect (KIE) was determined by competition experiments using an equimolar mixture of cyclohexanol (c-C₆H₁₁OH) and d^{12} -cyclohexanol (c-C₆D₁₁OD) as substrates. An aqueous phosphate buffer solution (5 mL, 0.1 M, pH 6.8) containing (PPh₄)₂[Mn^V(N)(CN)₄] (20 μ M), [Ru(bpy)₃]Cl₂·6H₂O (0.2 mM), substrate (10 mM cyclohexanol and 10 mM d₁₂-cyclohexanol) and [Co(NH₃)₅Cl]Cl₂ (20 mM) was stirred under argon and irradiated by a LED lamp (10 W) for 30 min at 23 °C. The resulted solution was extracted with ethyl acetate (4 mL) and quantified by GC. The kinetic isotope effect (KIE) was found to be 3.5 ± 0.3 from the ratio of corresponding areas of cyclohexanone (c-C₆H₁₀O) and d₁₂-cyclohexanone (c-C₆D₁₀O).

Quantum yield determination

Quantum yield for the photocatalytic epoxidation of styrene was determined using the standard actinometer (potassium ferrioxalate). Since styrene has a very low solubility in the aqueous phosphate buffer solution, one-neck round-bottom flask (10 mL) used in typical photoreaction was also used for this experiment to achieve vigorous stirring condition (the quartz cell limits the size of stir bar and the speed of stirring). Monochromic light of 458 nm obtained using a 500 W Xe lamp with a monochromator was used for evaluating the number of photons. The average light intensity taken before and after photochemical reaction was 6.37×10^{-9} einstein s⁻¹. The one-neck round-bottom flask (10 mL) that contained a vigorously stirred mixture of 1 (20 μ M), styrene (20 mM), [Ru(bpy)₃]Cl₂ (0.2 mM) and [Co(NH₃)₅Cl]Cl₂ (20 mM) in aqueous phosphate buffer at pH 6.8 was irradiated with the monochromic light at 458 nm. The product was analysed by GC and GC-MS revealed the formation of styrene oxide. The quantum yield of the overall catalytic photoredox cycle for styrene epoxidation to styrenen oxide was calculated after irradiation for 4 h at 458 nm using the following equation:

 $\Phi = \frac{\text{number of styrene oxide molecules } \times 2}{\text{number of incident photons}} \times 100\%$

(PPh,						-
	1	2		3	4	
Entry	Catalyst	[Catalyst]	[Ru ²⁺]	[Co ³⁺]	Light	TONh
		(µM)	(mM)	(mM)	Light	IUN
1	1	20	0.2	20	On	91
2	-	-	0.2	20	On	0
3	1	20	-	20	On	0
4	1	20	0.2	-	On	0
5	1	20	0.2	20	Off	0
6	1	10	0.2	20	On	88
7	1	20	0.4	20	On	94
8	1	20	0.2	10	On	66
9	1	20	0.2	40	On	53
10	2	20	0.2	20	On	2
11	3	20	0.2	20	On	2
12	4	20	0.2	20	On	2
13	MnSO ₄	20	0.2	20	On	1

Table S1 Photocatalytic epoxidation of styrene by Mn compounds.^a

^a Catalyst, $[Ru(bpy)_3]Cl_2$, substrate (20 mM) and $[Co(NH_3)_5Cl]Cl_2$ in 5 mL phosphate buffer solution (pH 6.8) under visible light irradiation (10 W LED Lamp) for 30 min. ^b TON = (mol of product)/(mol of catalyst).

	$(PPh_4)_2Mn(N)(CN)_4$ $[Ru(bpy)_3]Cl_2$ $[Co(NH_3)_5Cl]Cl_2$		
	pH 6.8 phospate buffer Ar, RT, 10 W LED		
Entry	Solvent	TON ^b	
1	MeCN	0	
2	H ₂ O	0	
3	Aqueous phosphate buffer	91	
4	Aqueous buffer/MeCN	02	
	(50/1)	92	
5	Aqueous buffer/MeCN	20	
	(16/1)	09	
6	Aqueous buffer/MeCN	70	
	(8/1)	70	
7	Aqueous buffer/MeCN	55	
	(4/1)	33	

Table S2 Effects of solvent on photocatalytic epoxidation of styrene.^a

^a (PPh₄)₂[Mn^V(N)(CN)₄] (20 μ M), [Ru(bpy)₃]Cl₂ (0.2 mM), substrate (20 mM) and [Co(NH₃)₅Cl]Cl₂ (20 mM) in 5 mL phosphate buffer solution (pH 6.8) under visible light irradiation (10 W LED Lamp) for 30 min.

^b TON = (mol of product)/(mol of catalyst).

	(PPh ₄) ₂ Mn(N)(CN) ₄ [Ru(bpy) ₃]Cl ₂ [Co(NH ₃) ₅ Cl]Cl ₂	
	pH 6.8 phospate buffer Ar, RT, 10 W LED	
Entry	pН	TON ^b
1	8.0	45
2	7.4	59
3	7.0	76
4	6.8	91
5	6.0	89
6	5.0	77

Table S3 Effects of pH on photocatalytic epoxidation of styrene.^a

^a (PPh₄)₂[Mn^V(N)(CN)₄] (20 μ M), [Ru(bpy)₃]Cl₂ (0.2 mM), styrene (20 mM) and [Co(NH₃)₅Cl]Cl₂ (20 mM) in 5 mL phosphate buffer solution under visible light irradiation (10 W LED Lamp) for 30 min.

^b TON = (mol of product) / (mol of catalyst).



Figure S1 Plot of yield and turnover number as a function of time for the photocatalytic epoxidation of styrene. Condition: $(PPh_4)_2[Mn^V(N)(CN)_4]$ (20 µM), $[Ru(bpy)_3]Cl_2$ (0.2 mM), styrene (20 mM) and $[Co(NH_3)_5Cl]Cl_2$ (20 mM) in 5 mL phosphate buffer solution (pH 6.8) under visible light irradiation (10 W LED Lamp).



Figure S2 Mass spectra of styrene oxide obtained using standard procedure in phosphate buffer solution at pH 6.8, full spectrum (top) and expanded spectrum (down).



Figure S3 Mass spectra of styrene oxide obtained using standard procedure in $H_2^{16}O-H_2^{18}O$ 1:1mixture phosphate buffer solution at pH 6.8, full spectrum (top) and expanded spectrum (down).



Figure S4 ESI/MS/MS spectra of $(PPh_4)[Mn(N)(O)(CN)_4]^{-}CF_3CH_2OH (m/z 628.1).$ Collision energy = 5 eV.

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