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Communication

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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.6b10836 • Publication Date (Web): 23 Nov 2016

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Photocatalytic Asymmetric Epoxidation of Terminal Olefins Using Water as an Oxygen Source in the Presence of a Mononuclear Nonheme Chiral Manganese Complex

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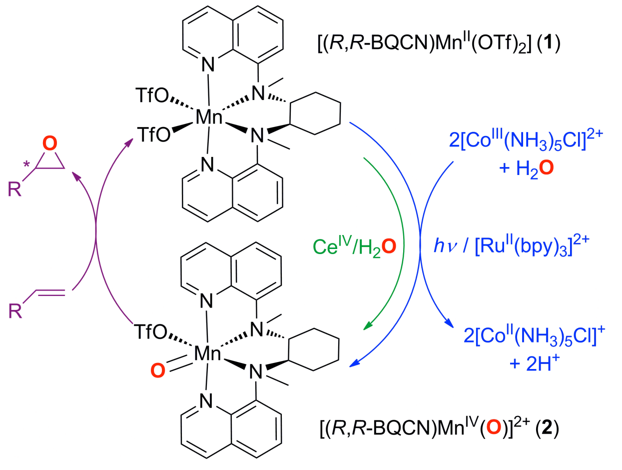
Supporting Information Placeholder

ABSTRACT: Photocatalytic enantioselective epoxidation of terminal olefins using a mononuclear nonheme chiral manganese catalyst, [(*R*,*R*-BQCN)Mn^{II}]$^{2+}$, and water as an oxygen source yields epoxides with relatively high enantioselectivities (e.g., up to 60% enantiomeric excess). A synthetic mononuclear nonheme chiral Mn(IV)-oxo complex, [(*R*,*R*-BQCN)Mn^{IV}(O)]$^{2+}$, affords similar enantioselectivities in the epoxidation of terminal olefins under stoichiometric reaction conditions. Mechanistic details of each individual step of the photoinduced catalysis, including formation of the Mn(IV)-oxo intermediate, are discussed from a combined study of laser flash photolysis and other spectroscopic methods.

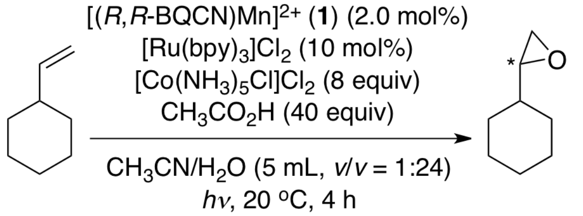
Development of highly efficient and environmentally benign catalytic oxidation reactions using bioinspired metal complexes under mild conditions is of current interest in the communities of synthetic organic, oxidation, and bioinorganic chemistry.[1] Recently, enantioselective epoxidation of olefins using bioinspired metal catalysts has attracted much attention,[2] since the resulting epoxides are important building blocks and intermediates that can be used in fine chemical and pharmaceutical industries and understanding mechanistic details of the biomimetic catalysis may provide clues for the development of biologically relevant and catalytically efficient and selective oxidation systems. Indeed, it has been shown recently that nonheme manganese (and iron) complexes supported by chiral tetradentate aminopyridine ligands are highly promising catalysts in the enantioselective epoxidation of electron-deficient olefins, affording excellent enantioselectivities up to 99% enantiomeric excess (*ee*) values;[2-5] it is notable that an environmentally benign oxidant, hydrogen peroxide (H_2O_2), has been used in those asymmetric olefin epoxidation reactions. However, to the best of our knowledge, no photocatalytic oxidation reactions using water as the environmentally benign oxygen source have been attempted for the asymmetric expoxidation of olefins. Further, although high-valent manganese(V)-oxo species have been proposed as reactive epoxidizing intermediates in the asymmetric epoxidation of olefins invariably,[4,5a] direct evidence for the intermediacy of such Mn(V)-oxo species under catalytic and/or stoichiometric reaction conditions has yet to be obtained. Thus, the nature of the asymmetric epoxidizing intermediate(s) (e.g., Mn(V)-oxo, Mn(IV)-oxo, or Mn-OX (X = OH or OR)) remains to be clarified.[6] In addition, although the formation of a nonheme Mn(IV)-oxo complex (and nonheme Fe(IV)-oxo and Ru(IV)-oxo complexes) under photocatalytic oxidation conditions has been demonstrated recently,[7-10] detailed mechanism(s) of the photoinduced generation of the M(IV)-oxo complex has yet to be addressed.

Scheme 1. Enantioselective Epoxidation of Terminal Olefins by a Mn(IV)-Oxo Complex under Photocatalytic and Stoichiometric Reaction Conditions



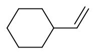
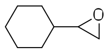
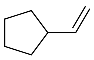
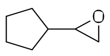
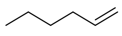
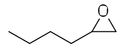
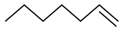
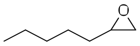
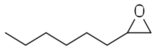
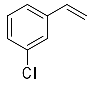
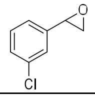
Herein, we report the photocatalytic enantioselective epoxidation of terminal olefins using a chiral manganese catalyst, [(*R*,*R*-BQCN)Mn^{II}(OTf)$_2$] (**1**; BQCN = *N*,*N*'-dimethyl-*N*,*N*'-bis(8-quinolyl)cyclohexanediamine, OTf = $CF_3SO_3^-$),[11] [Ru^{II}(bpy)$_3$]$^{2+}$ (bpy = 2,2'-bipyridine) as a photocatalyst, [Co^{III}(NH$_3$)$_5$Cl]$^{2+}$ as a one-electron oxidant, and water as an oxygen source (Scheme 1); it should be noted that terminal olefins are challenging substrates in (asymmetric) epoxidation reactions.[12] We also report the first direct evidence for the involvement of a high-valent Mn(IV)-oxo complex as an epoxidizing intermediate in the asymmetric epoxidation of olefins; a mononuclear nonheme Mn(IV)-oxo complex, [(*R*,*R*-BQCN)Mn^{IV}(O)]$^{2+}$ (**2**), synthesized using cerium(IV) ammonium nitrate (CAN) as an oxidant,[11] afforded moderately high *ee* values in the asymmetric epoxidation of olefins (Scheme 1). The photocatalytic formation mechanism and kinetics of the Mn(IV)-oxo complex were elucidated using a combination of nanosecond laser flash photolysis and other spectroscopic measurements.

The chiral Mn(II) complex, [(*R*,*R*-BQCN)Mn^{II}(OTf)$_2$] (**1**), was synthesized by reacting Mn(OTf)$_2$ with a chiral *R*,*R*-BQCN ligand (Supporting Information (SI), Experimental Section). Photoirradiation (λ > 420 nm) of a solvent mixture of CH_3CN and H_2O (v/v = 1:24) containing vinylcyclohexane (0.030 mmol), **1** (2.0 mol%), [Ru^{II}(bpy)$_3$]$^{2+}$ (10 mol%), [Co^{III}(NH$_3$)$_5$Cl]$^{2+}$ (8 equiv to substrate), and acetic acid (40 equiv to substrate) yielded the epoxide product, 2-cyclohexyloxirane (59 ± 4% yield, TON = 30 ± 2) with a moderately high enantioselectivity (>50% *ee*) (eq 1) (Table 1, entry 1; SI, Table S1 for the optimization of reaction conditions; see also Table S2). When the photocatalytic epoxidation of vinylcyclohexane was performed using $H_2{}^{18}O$ (97% ^{18}O-enriched) instead of $H_2{}^{16}O$, the epoxide product contained 94 ± 2% ^{18}O (SI, Figure S1) in the absence and presence of air, indicating that the oxygen in the epoxide product was derived from water. Other terminal olefins were also oxidized to the corresponding epoxides with moderate yields and enantioselectivities (Table 1; SI, Table S2); the highest yield (68 ± 5%) was obtained for vinylpentane with 50 ± 2% *ee* (Table 1, entry 2), whereas the highest ee (60 ± 2% *ee*) but with a lower yield (26 ± 3%) was obtained for 1-heptene (Table 1, entry 4). No or negligible amounts of epoxides were formed when the photocatalytic oxidation reactions were performed in the absence of **1**, [Ru^{II}(bpy)$_3$]$^{2+}$, [Co^{III}(NH$_3$)$_5$Cl]$^{2+}$, or acetic acid,[13] indicating that all these components are required for the formation of the epoxide products.



(1)

Table 1. Photocatalytic Enantioselective Epoxidation of Terminal Olefins by **1**[a]

entry	substrate	product	yield (%)[b]	*ee* (%)[b]
1			59 ± 4	53
2			68 ± 5	50
3			24 ± 3	57
4			26 ± 3	60
5			35 ± 4	56
6			65 ± 5	43

[a] A solvent mixture of CH_3CN and H_2O (v/v = 1:24) containing substrate (0.030 mmol), **1** (2.0 mol%), [Ru^{II}(bpy)$_3$]$^{2+}$ (10 mol%), [Co^{III}(NH$_3$)$_5$Cl]$^{2+}$ (8 equiv), and acetic acid (40 equiv) was photoirradiated at 20 °C for 4 h. [b] The *ee* values were determined by GC with chirasil-Dex CB column.

Then, what is the nature of the intermediate responsible for the asymmetric epoxidation of olefins? As proposed in most of the catalytic asymmetric epoxidation reactions,[4,5a] a Mn(V)-oxo species can be considered as a plausible intermediate generated in the photocatalytic oxidation reactions. A Mn(IV)-oxo species is also a viable intermediate; however, such a Mn(IV)-oxo complex has been rarely suggested as an epoxidizing intermediate in the catalytic asymmetric epoxidation reactions. Since it has been shown recently that mononuclear nonheme Mn(IV)-oxo complexes are capable of epoxidizing olefins,[14] we synthesized a Mn(IV)-oxo complex bearing the *R*,*R*-BQCN ligand, [(*R*,*R*-BQCN)Mn^{IV}(O)]$^{2+}$ (**2**), according to the published procedures,[11] and investigated its reactivity in asymmetric epoxidation of terminal olefins (Figure 1; SI, Figure S2). Upon addition of vinylcyclohexane to a solution of **2**, the absorption band at 640 nm due to **2** disappeared and the decay rate obeyed first-order kinetics (Figure 1, inset). The pseudo-first-order rate constant increased linearly with the increase of vinylcyclohexane concentration (SI, Figure S3), giving a second-order rate constant of 1.1(1) M^{-1} s^{-1} at 20 °C. Importantly, analysis of the reaction solution revealed the formation of epoxide product, 2-cyclohexyloxirane (70 ± 4% yield based on the amount of **2** and 62 ± 2% *ee*). Similarly, a second-order rate constant of 2.6(2) × 10^{-1} M^{-1} s^{-1} at 20 °C was obtained in the reaction of **2** with 1-heptene, which yielded 1,2-epoxyheptane as the product (80 ± 4% yield based on the amount of **2**) with an *ee* value of 63 ± 2% (SI, Figure S4; see also Table S3). In these reactions, Mn(II) species was formed as the decay product of **2** (SI, Figure S5). Thus, the present results demonstrate that a chiral Mn(IV)-oxo complex indeed epoxidizes terminal olefins to give the corresponding epoxides with moderately high

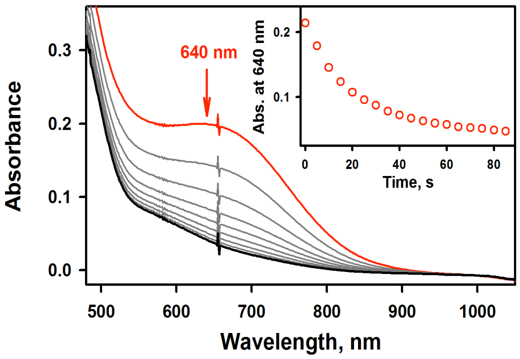


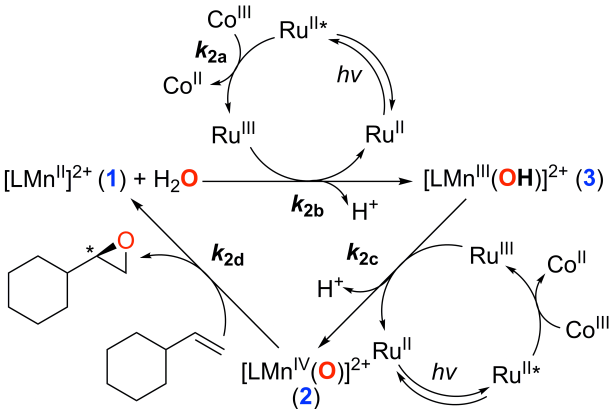
Figure 1. Absorption spectral changes observed in the reaction of **2** with vinylcyclohexane (50 mM) in CH_3CN/H_2O (*v*/*v* = 9:1) at 20 °C. **2** was prepared by reacting **1** (0.50 mM) with CAN (3.0 mM).

enantioselectivities (Scheme 1). Further, based on the present results, we suggest that Mn(IV)-oxo species should be considered as active oxidants responsible for the asymmetric epoxidation of olefins reported in previous studies.[2-5]

We then investigated each individual step of the photocatalytic oxidation of **1** carried out in the presence of $[Ru^{II}(bpy)_3]^{2+}$ and $[Co^{III}(NH_3)_5Cl]^{2+}$. The initial steps of the photocatalytic cycle were too fast to be followed using a photodiode array spectrophotometer. Thus, nanosecond laser flash photolysis was used to examine the kinetics and the reaction mechanism (see Scheme 2). Laser excitation (λ_{ex} = 430 nm) of a CH_3CN/H_2O (*v*/*v* = 1:1) solution of $[Ru^{II}(bpy)_3]^{2+}$ resulted in the formation of the triplet excited state species, $[Ru(bpy)_3]^{2+*}$, which decayed back to the starting $[Ru^{II}(bpy)_3]^{2+}$ complex with the rate constant of $k_T = 1.2(1) \times 10^6$ s^{-1} (lifetime = 830(40) μs)[7a,9a] at 20 °C, as indicated by the full recovery of the bleaching at 450 nm (SI, Figure S6; see also Figure S7, black line). In the presence of $[Co^{III}(NH_3)_5Cl]^{2+}$, the recovery was faster but not complete (SI, Figure S7, red line), indicating that electron transfer (ET) from $[Ru(bpy)_3]^{2+*}$ to $[Co^{III}(NH_3)_5Cl]^{2+}$ occurred to give $[Ru^{III}(bpy)_3]^{3+}$ and $[Co^{II}(NH_3)_5Cl]^{+}$ (Scheme 2, reaction *a*); the latter is known to decompose irreversibly to release NH_3.[9a] The rate of the ET, monitored by the recovery of the bleaching at 450 nm, obeyed first-order kinetics and the pseudo-first-order rate constant increased linearly with increasing the concentration of $[Co^{III}(NH_3)_5Cl]^{2+}$ (SI, Figure S8). The second-order rate constant (k_a in Scheme 2) was determined to be $6.2(5) \times 10^7$ M^{-1} s^{-1}. The intercept was 1.1×10^6 s^{-1}, which agrees well with the decay rate constant of $[Ru(bpy)_3]^{2+*}$ in the absence of $[Co^{III}(NH_3)_5Cl]^{2+}$ ($k_T = 1.2(1) \times 10^6$ s^{-1}) (*vide infra*).

The fast dynamics of the first ET of Mn^{II} to give Mn^{III} was also examined with laser flash-photolysis (Scheme 2, reaction *b*). In contrast to the case without **1**, complete recovery of the bleaching at 450 nm was observed within 180 μs after nanosecond laser excitation of a CH_3CN/H_2O (*v*/*v* = 1:1) solution of $[Ru^{II}(bpy)_3]^{2+}$ and $[Co^{III}(NH_3)_5Cl]^{2+}$ with **1** due to the full regeneration of $[Ru^{II}(bpy)_3]^{2+}$ (Figure 2; SI, Figure S7, blue line). The recovery rate obeyed first-order kinetics and the rate constant of ET from **1** to $[Ru^{III}(bpy)_3]^{3+}$ (k_b in Scheme 2) was determined to be $3.7(3) \times 10^7$ M^{-1} s^{-1} at 20 °C from the slope of the linear plot of the pseudo-first-order rate constant vs concentration of **1** (SI, Figures S9).

Scheme 2. Mechanistic Details for the Photoinduced Generation of 2 and Its Reaction with Olefin



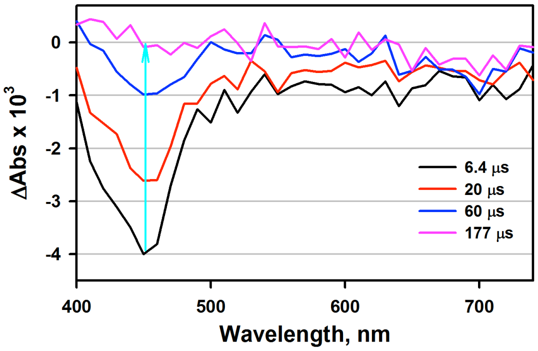


Figure 2. Representative transient absorption spectra observed at 6.4, 20, 60, and 177 μs after nanosecond laser pulse excitation (λ_{ex} = 430 nm) of a CH_3CN/H_2O (*v*/*v* = 1:1) solution of $[Ru^{II}(bpy)_3]^{2+}$ (40 μM), $[Co^{III}(NH_3)_5Cl]^{2+}$ (4.0 mM), and **1** (0.80 mM) at 20 °C.

The second ET from **3** to $[Ru^{III}(bpy)_3]^{3+}$ was slow (Scheme 2, reaction *c*); therefore, the reaction was followed using a photodiode array spectrophotometer. As reported previously,[8] **3** was produced in the one-electron oxidation of **1** with 1.1 equiv of $[Ru^{III}(bpy)_3]^{3+}$ in CH_3CN/H_2O (*v*/*v* = 1:1). Further addition of 1.1 equiv of $[Ru^{III}(bpy)_3]^{3+}$ to the solution of **3** resulted in ET from **3** to $[Ru^{III}(bpy)_3]^{3+}$, yielding **2** and $[Ru^{II}(bpy)_3]^{2+}$ after deprotonation (SI, Figures S10 and S11). The second-order rate constant of the second ET (k_c in Scheme 2) was then determined under second-order kinetics conditions to be $1.6(1) \times 10^3$ M^{-1} s^{-1} in CH_3CN/H_2O (*v*/*v* = 1:1) at 20 °C (SI, Figure S10), where the same k_c value was obtained using different concentrations of **3** and $[Ru^{III}(bpy)_3]^{3+}$ (1:1). In the final step of the reaction cycle (Scheme 2, reaction *d*), $[(R,R\text{-BQCN})Mn^{IV}(O)]^{2+}$ (**2**) oxygenated vinylcyclohexane to give the epoxide product with the rate constant of 1.1(1) M^{-1} s^{-1} at 20 °C (k_d in Scheme 2) (SI, Figure S3).

In conclusion, photocatalytic enantioselective epoxidation of terminal olefins with a chiral manganese complex has been achieved using H_2O as an oxygen source,

$[Ru^{II}(bpy)_3]^{2+}$ as a photocatalyst, and $[Co^{III}(NH_3)_5Cl]^{2+}$ as a weak one-electron oxidant. The present study has paved a new way to use water as the most environmentally benign oxygen source in asymmetric epoxidation reactions. We have also provided the first example of using a synthetic chiral Mn(IV)-oxo complex in the asymmetric epoxidation of olefins. We are currently synthesizing more chiral Mn-oxo complexes with different ligands and will investigate their reactivities in various asymmetric oxidation reactions to understand the detailed mechanisms as well as the ligand effect on the enantioselectivity in the asymmetric epoxidation of olefins.

ASSOCIATED CONTENT

Supporting Information.

Experimental details, Figures S1 – S11, Tables S1 – S4, and GC chromatograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by NRF of Korea through the CRI (NRF-2012R1A3A2048842 to W.N.) and GRL (NRF-2010-00353 to W.N.) programs, JSPS KAKENHI (No. 16H02268 to S.F.), and NSFC (National Natural Science Foundation of China, 21473226 to W.S.).

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(13) Replacement of acetic acid by other acids (e.g., HOTf, $HClO_4$, trifluoroacetic acid, and 2-ethylhexanoic acid) and acetate anions (e.g., CH_3CO_2Na) has failed to yield epoxide in the photocatalytic oxidation of vinylcyclohexane (SI, Table S4). However, using propionic acid instead of acetic acid afforded the same amount of epoxide product (e.g., 59 ± 4%) but with a low enantioselectivity (e.g., 25 ± 2% *ee*; SI, Table S4). Thus, acetic acid plays an important role in the photocatalytic enantioselective epoxidation of terminal olefins. However, the exact role of acetic acid has yet to be clarified.

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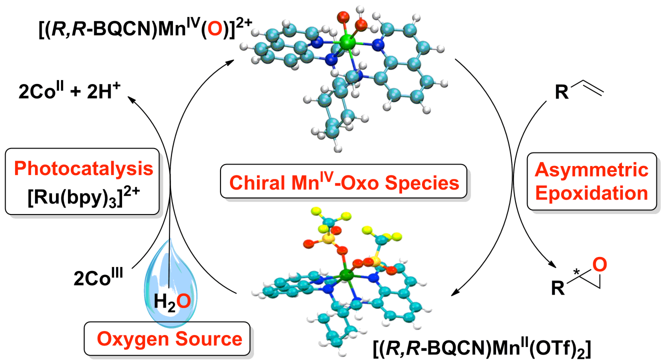
TOC Graphic


[(R,R-BQCN)Mn^{IV}(O)]$^{2+}$
2Co^{II} + 2H^{+}
R
Photocatalysis
[Ru(bpy)$_3$]$^{2+}$
Chiral Mn^{IV}-Oxo Species
Asymmetric
Epoxidation
2Co^{III}
H$_2$O
O
R
*
Oxygen Source
[(R,R-BQCN)Mn^{II}(OTf)$_2$]