Visible-Light-Induced Photoredox Catalysis with a Tetracerium-Containing Silicotungstate**

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Abstract: *The development of visible-light-induced photocatalysts for chemoselective functional group transformations has received considerable attention. Polyoxometalates (POMs) are potential materials for efficient photocatalysts because their properties can be precisely tuned by changing their constituent elements and structures and by the introduction of additional metal cations. Furthermore, they are thermally and oxidatively more stable than the frequently utilized organometallic complexes. The visible-light-responsive tetranuclear cerium(III)-containing silicotungstate $TBA_6[\{Ce(H_2O)\}_2\{Ce(CH_3CN)\}_2\text{-}(\mu_4\text{-}O)(\gamma\text{-}SiW_{10}O_{36})_2]$ (CePOM; TBA = tetra-n-butylammonium) has now been synthesized; when CePOM was irradiated with visible light ($\lambda > 400$ nm), a unique intramolecular Ce^{III}-to-POM(W^{VI}) charge transfer was observed. With CePOM, the photocatalytic oxidative dehydrogenation of primary and secondary amines as well as the α-cyanation of tertiary amines smoothly proceeded in the presence of O_2 (1 atm) as the sole oxidant.*

The development of photocatalytic systems that utilize visible light for chemoselective transformations of organic molecules has received much attention.[1] Although organometallic complexes have frequently been utilized as effective chromophores for visible light, there are several concerns, for example, their durability and reusability. Polyoxometalates (POMs) are a large class of structurally well-defined anionic molecular metal–oxygen clusters and thermally and oxidatively more stable than organometallic complexes.[2] Their chemical and physical properties, such as redox potentials, charge-transfer properties, and acidities, can be accurately controlled by their constituent elements, structures, and charges. By utilizing the intramolecular oxygen-to-metal charge transfer of POMs (LMCT) in response to ultraviolet light, they are suitable photocatalysts for various transformations, including functionalization reactions of C–H bonds,[3a,b] H_2 evolution,[3c] and CO_2 reduction.[3d] However, it is difficult to utilize the LMCT by irradiation with visible light ($\lambda >$

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400 nm) because of the large energy gaps, and therefore, the design of visible-light-responsive POM-based catalysts is required.

Lacunary POMs can be utilized as multidentate inorganic macroligands and accommodate various types of metal cations in their vacant sites for the construction of well-defined mono-, di-, tri-, and multinuclear metal–oxygen clusters.[4] We have recently shown that the divacant lacunary silicotungstate $TBA_4H_4[\gamma\text{-}SiW_{10}O_{36}]$ can act as an efficient ligand for the construction of multinuclear metal–oxygen clusters with unique catalytic and magnetic properties.[5]

Herein, we describe the synthesis of a tetranuclear cerium(III)-containing sandwich-type silicotungstate, $TBA_6[\{Ce(H_2O)\}_2\{Ce(CH_3CN)\}_2(\mu_4\text{-}O)(\gamma\text{-}SiW_{10}O_{36})_2]$ (CePOM; TBA = tetra-n-butylammonium; Figure 1), by the reaction of $TBA_4H_4[\gamma\text{-}SiW_{10}O_{36}]$ with $[Ce(acac)_3]$ in acetone
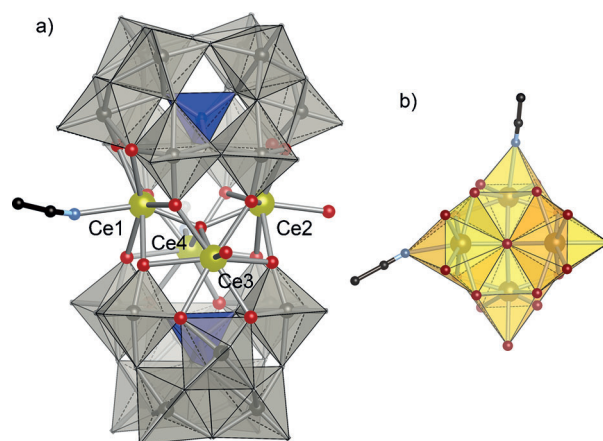

Figure 1. a, b) Polyhedral and ball-and-stick representation of the anionic component of CePOM (side view; a) and the tetranuclear Ce^{III} core in CePOM (top view; b). Carbon black, cerium yellow, nitrogen light blue, oxygen red, silicon blue, tungsten gray.

(acac = acetylacetonate). CePOM displays unique properties: 1) Intramolecular Ce^{III}-to-POM(W^{VI}) charge transfer occurs in response to visible light ($\lambda > 400$ nm), 2) CePOM possesses coordination sites for substrates on the tetranuclear cerium core, and 3) it displays a sufficient oxidation ability, which is derived from the Ce^{IV}/Ce^{III} redox potential. When irradiated with visible light ($\lambda > 400$ nm), CePOM showed remarkable catalytic properties for oxidative transformations of primary, secondary, and tertiary amines (see the Supporting Information for comparisons). Although visible-light-induced metal-to-POM(W^{VI}) charge transfers have very recently been observed upon anchoring Ce^{III} to $[PW_{12}O_{40}]^{3-}$ on the solid

surface of mesoporous silica[6] or by introducing $[Re(CO)_3]^+$ into $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$,[7] selective functional group transformations by using these systems have not been investigated. To the best of our knowledge, CePOM is the first efficient POM-based visible-light-responsive photocatalyst for liquid-phase chemoselective functional group transformations in the absence of any additional sensitizers.

CePOM was synthesized by the reaction of $TBA_4H_4[\gamma\text{-}SiW_{10}O_{36}]$ with two equivalents of $[Ce(acac)_3]$ in the presence of one equivalent of *p*-toluenesulfonic acid (TsOH) in acetone (92 % yield based on $TBA_4H_4[\gamma\text{-}SiW_{10}O_{36}]$). Upon addition of the pale-yellow $[Ce(acac)_3]$ powder to a colorless solution of $TBA_4H_4[\gamma\text{-}SiW_{10}O_{36}]$ in acetone, the solution color dramatically changed to reddish-brown, indicating the formation of a complex with a characteristic charge transfer in response to visible light. The positive-ion cold-spray ionization mass spectrum (CSI-MS) in acetonitrile showed two sets of signals, which may be assigned to $[TBA_7Ce_4O(SiW_{10}O_{36})_2]^+$ (centered at *m/z* 7158) and $[TBA_8Ce_4O(SiW_{10}O_{36})_2]^{2+}$ (*m/z* 3700; Supporting Information, Figure S1), indicating that CePOM is composed of four Ce^{III} and two $[SiW_{10}O_{36}]^{8-}$ units. The ^{29}Si NMR spectrum in CD_3CN showed a single signal at -120 ppm (Figure S2), showing that CePOM is a single species and stable in solution. The ^{183}W NMR spectrum showed three signals at 64.4, -90.3, and -96.8 ppm with an intensity ratio of 2:1:2 (Figure S3). The prominently downfield-shifted signal at 64.4 ppm is assignable to tungsten atoms with neighboring paramagnetic Ce^{III} centers.

Single crystals of CePOM that were suitable for X-ray crystallographic analysis were successfully obtained by recrystallization from a mixture of acetonitrile and diethyl ether. The bond valence sum (BVS) values of the silicon (3.90, 4.09), tungsten (5.76–6.52), and cerium (2.99–3.16) atoms in CePOM indicate corresponding valences of $+4$, $+6$, and $+3$, respectively (Table S1). Six TBA cations per anion of CePOM could be assigned crystallographically, which is in accord with the elemental analysis data. The anionic component of CePOM consists of a tetranuclear cerium(III) core, $[\{Ce(H_2O)\}_2\{Ce(CH_3CN)\}_2(\mu_4\text{-}O)]^{10+}$, which is sandwiched between two $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ units (Figure 1; see also Tables S2, S3); and each cerium atom was eight-coordinated. The anion without outer ligands that are coordinated to the cerium atoms had approximately inherent D_{2d} symmetry, which is in good agreement with the ^{183}W NMR spectrum (Figure S3). To the best of our knowledge, the present CePOM is the first example of a cerium-containing POM with the γ-Keggin framework.[8]

All of the above-mentioned data confirm that the formula of CePOM is $TBA_6[\{Ce(H_2O)\}_2\{Ce(CH_3CN)\}_2(\mu_4\text{-}O)(\gamma\text{-}SiW_{10}O_{36})_2]$. The formation of CePOM can be expressed by Eq. (1).

$$2\,TBA_4H_4[SiW_{10}O_{36}] + 4\,[Ce(acac)_3] + 2\,TsOH + 3\,H_2O + 2\,CH_3CN$$
$$\rightarrow TBA_6[\{Ce(H_2O)\}_2\{Ce(CH_3CN)\}_2(\mu_4\text{-}O)(\gamma\text{-}SiW_{10}O_{36})_2] \quad (1)$$
$$+2\,TBAOTs + 12\,acacH$$
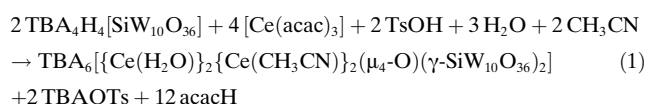
The UV/Vis spectrum of CePOM showed a characteristic absorption band around 460 nm (Figure S4). In contrast, the absorption band in the visible region was not observed for $TBA_4H_4[\gamma\text{-}SiW_{10}O_{36}]$, indicating that the absorption band at 460 nm is likely derived from an intramolecular Ce^{III}-to-$POM(W^{VI})$ charge transfer.[6,9] Upon irradiation of an acetonitrile solution of CePOM with visible light ($\lambda > 400$ nm) under argon atmosphere in the presence of 4-methoxybenzylamine as an electron donor, the color of the solution changed from reddish-brown to purple (Figure 2a). The intensity of
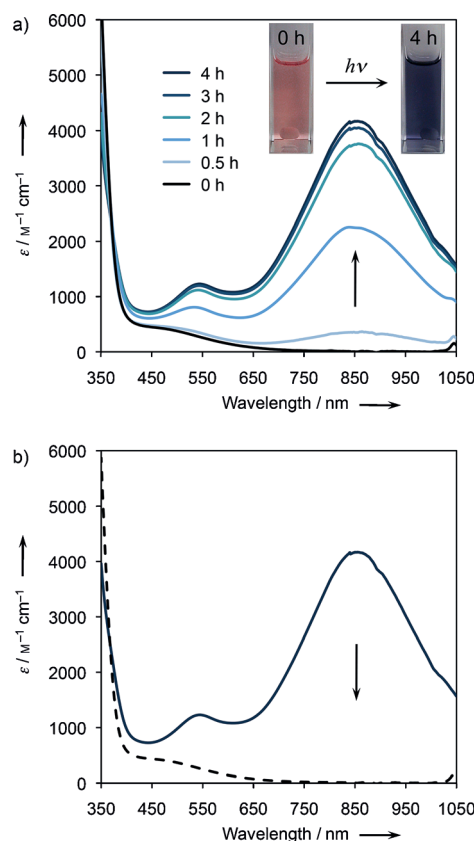

Figure 2. UV/Vis spectra of a) CePOM (0.5 mm) upon irradiation with visible light ($\lambda > 400$ nm) for 0–4 hours in the presence of 4-methoxybenzylamine (2 M) in acetonitrile under Ar (1 atm) and of b) photoreduced CePOM before (——) and after exposure to air for 20 s (– – –).

the band around 830 nm, which is assignable to the W^V-to-W^{VI} intervalence charge transfer, increased upon irradiation with visible light ($\varepsilon = 4200\,M^{-1}\,cm^{-1}$ after 4 hours; Figure 2a), indicating the reduction of CePOM (and the formation of a W^V species; steps 1 and 2 in Scheme 1).[10] The UV/Vis spectrum of photo-reduced CePOM was almost identical to that of a CePOM species that had been subjected to electrochemical one-electron reduction (Figure S5).[11] These results support the hypothesis that the absorption band around 460 nm is derived from Ce^{III}-to-$POM(W^{VI})$ charge transfer, and one-electron transfer from Ce^{III} to the POM framework was possibly induced by visible light.[12] The photo-reduced CePOM was readily reoxidized by exposure to air for 20 seconds, and the UV/Vis spectrum of reoxidized CePOM was almost identical to that of the original CePOM sample (Figure 2b; step 3 in Scheme 1).

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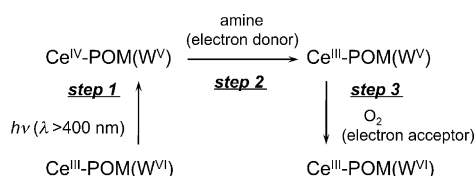
Scheme 1. CePOM-mediated visible-light-induced electron transfer from an amine to O_2.

The CSI-MS spectrum of an acetonitrile solution of a mixture of CePOM and 4-methoxybenzylamine showed two main signal sets, which may be assigned to $[TBA_7Ce_4(CH_3OC_6H_4CH_2NH_2)_4O(SiW_{10}O_{36})_2]^+$ (centered at m/z 7707) and $[TBA_8Ce_4(CH_3OC_6H_4CH_2NH_2)_4O(SiW_{10}O_{36})_2]^{2+}$ (m/z 3905), indicating the interaction of 4-methoxybenzylamine with the Ce^{III} sites (Figure S6).[13] The interaction is likely responsible for the efficient electron transfer from 4-methoxybenzylamine to CePOM and prevents charge recombination (reverse reaction of step 1 in Scheme 1).

Next, we intended to apply the photocatalytic properties of CePOM for aerobic oxidative transformations of amines in the presence of the visible-light-responsive POM. Imines and α-amino nitriles are important classes of compounds that have been utilized as versatile synthetic intermediates for nitrogen-containing pharmaceutical and biologically active compounds.[14] The oxidative dehydrogenation of primary and secondary amines as well as the α-cyanation of tertiary amines provide convenient methods for the preparation of imines and α-amino nitriles, respectively, and the one-electron oxidation of an amine is an essential step of both reactions. Considering that CePOM can readily accept one electron from an amine (step 2 in Scheme 1) and provide the electron to O_2 (step 3), the development of visible-light-induced photocatalytic transformations of amines with CePOM using O_2 as the sole oxidant should be possible.

As expected, various kinds of structurally diverse primary and secondary amines could be oxidized by irradiation with visible light ($\lambda > 400$ nm) in the presence of only catalytic amounts of CePOM. For example, benzylamine was oxidized to N-benzylidenebenzylamine in 96% yield (Table 1, entry 1), and the catalytic performance of CePOM was superior to those of $TBA_4H_4[\gamma\text{-}SiW_{10}O_{36}]$ and $[Ce(acac)_3]$ (entries 2 and 3). The reaction did not proceed at all in the dark (entry 4) and hardly proceeded under argon atmosphere (entry 5). The catalytic performance of a mixture of fully occupied $TBA_4[\alpha\text{-}SiW_{12}O_{40}]$ and $[Ce(acac)_3]$ was almost the same as that of $[Ce(acac)_3]$, probably because the Ce^{III} centers could not interact with the $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ ions in solution, and therefore, no charge transfer occurred in this case (entry 7). Benzylamine and its derivatives with electron-donating groups on the aryl rings were suitable substrates for this transformation and gave the corresponding imines in high yields (Table 2, entries 1, 2, 6, and 7). The reactions of *para*-trifluoromethylbenzylamine and *ortho*-chlorobenzylamine, which are benzylamines with electron-withdrawing groups, also afforded the corresponding imines, but longer reaction times were required to obtain high yields (entries 8 and 9).

Table 1: Oxidation of benzylamine and control experiments.[a]

Entry	Catalyst (mol%)	Yield [%]
1	CePOM (1)	96
2	$TBA_4H_4[\gamma\text{-}SiW_{10}O_{36}]$ (2)	2
3	$[Ce(acac)_3]$ (4)	35
4[b]	CePOM (1)	<1
5[c]	CePOM (1)	4
6	$[Ce(acac)_3]$ (4) and $TBA_4H_4[\gamma\text{-}SiW_{10}O_{36}]$ (2)	56
7	$[Ce(acac)_3]$ (4) and $TBA_4[\alpha\text{-}SiW_{12}O_{40}]$ (2)	37

[a] Reaction conditions: catalyst, benzylamine (0.2 mmol), acetonitrile (2 mL), 30°C, $h\nu$ ($\lambda > 400$ nm), O_2 (1 atm), 24 h. Yields were determined by GC using naphthalene as an internal standard. [b] Without photo-irradiation. [c] Under Ar atmosphere (1 atm).

Table 2: CePOM-catalyzed oxidation of primary and secondary amines.[a]

Entry	Substrate	t [h]	Product	Yield [%]
1		24		96
2[b]		26		85
3[c]		24		93
4[c]		24		90
5[c]		24		93
6		24		95
7		20		95
8		48		94
9		54		90
10		24		94
11		45		76
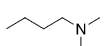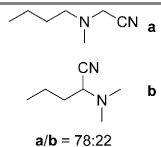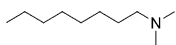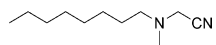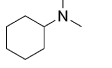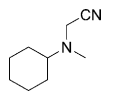
[a] Reaction conditions: CePOM (1 mol%), amine (0.2 mmol), acetonitrile (2 mL), 30°C, $h\nu$ ($\lambda > 400$ nm), O_2 (1 atm). Yields were determined by GC using naphthalene as an intern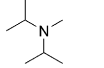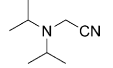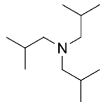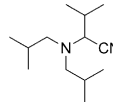al standard. [b] CePOM (0.4 mol%). [c] These experiments used recovered CePOM: first reuse (entry 3), second reuse (entry 4), and third reuse (entry 5).

The present system could also be applied to a heterocyclic compound, 2-thiophenemethylamine, which afforded the corresponding imine in 94% yield (entry 10). Furthermore, the secondary amine dibenzylamine was converted into the corresponding imine (entry 11). After the reaction, the CePOM catalyst could easily be recovered by the addition of diethyl ether (by precipitation). The IR and CSI-MS spectra of the recovered catalyst showed that the structure of CePOM was preserved after the oxidative dehydrogenation of benzylamine (Figure S7 and S8). The recovered CePOM could be reused at least three times without an appreciable loss of its high catalytic activity, and the total turnover number for the repeated-reuse runs reached up to 372 (entries 3–5).[15]

Inspired by the highly efficient CePOM-catalyzed aerobic oxidative dehydrogenation reactions of primary and secondary amines, the oxidative α-cyanation of tertiary amines was

also studied. As summarized in Table 3, various kinds of structurally diverse trialkylamines could react with trimethyl-silyl cyanide (TMSCN)[16] in the presence of CePOM (1 mol%), to afford the corresponding α-amino nitriles.[15]

Table 3: Oxidative α-cyanation of tertiary amines catalyzed by CePOM.[a]

Entry	Substrate	t [h]	Product	Yield [%]
1		26	a/b = 78:22	90
2		14		54
3		24		70
4		14		82
5		40		92

[a] Reaction conditions: CePOM (1 mol%), amine (0.2 mmol), TMSCN (0.4 mmol), acetonitrile (2 mL), 30°C, $h\nu$ ($\lambda > 400$ nm), O_2 (1 atm). Yields were determined by GC using naphthalene as an internal standard.

Monocyanated products were selectively obtained in all cases without formation of the di- and tricyanated products. Cyanation of various *N*-methylalkylamines proceeded regio-selectively at the α-methyl positions to give the corresponding α-amino nitriles in moderate to high yields (Table 3, entries 1–4). Even a sterically hindered trialkylamine was efficiently converted into the corresponding α-amino nitrile in high yield (entry 5).

In summary, we have synthesized the first visible-light-responsive tetranuclear cerium(III)-containing silicotung-state, CePOM. CePOM showed unique intramolecular Ce^{III}-to-POM(W^{VI}) charge transfer, which was induced by irradiation with visible light. In the presence of CePOM, aerobic photocatalytic oxidative transformations of various structur-ally diverse primary, secondary, and tertiary amines smoothly proceeded under irradiation with visible light with O_2 (1 atm) as the sole oxidant.

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[9] DFT calculations showed that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of CePOM were Ce^{III}- and POM(W^{VI})-based orbitals, respectively (Figure S9). Furthermore, the Ce^{III}-based HOMO was observed to lie between the POM(W^{VI})-based LUMO and oxygen-based orbitals (HOMO-1). These results support the hypothesis that the absorption band around 460 nm is due to Ce^{III}-to-POM(W^{VI}) charge transfer.

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[11] The cyclic voltammogram of CePOM in acetonitrile showed one-electron reduction peaks at −0.61, −0.86, −1.18, and −1.35 V (vs. the normal hydrogen electrode (NHE)), which are assignable to successive W^{VI}/W^V redox waves (Figure S10). When CePOM was subjected to electrochemical one-electron reduction at −0.61 V, the UV/Vis spectrum showed the broad band around 830 nm and was almost identical with that of photo-reduced CePOM (Figure S5).

[12] In sharp contrast, upon irradiation of a mixture of 4-methoxy-benzylamine and $TBA_4[SiW_{12}O_{40}]$ in acetonitrile with visible light, the color of the solution did not change.

[13] The CSI-MS spectrum of a mixture of $TBA_4[SiW_{12}O_{40}]$ and 4-methoxybenzylamine in acetonitrile showed only a signal that is assignable to $[TBA_5SiW_{12}O_{40}]^+$ (*m/z* 4087), indicating that 4-methoxybenzylamine is coordinated to the tetranuclear cerium core in CePOM rather than to the $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ frameworks.

[14] a) S.-I. Murahashi, *Angew. Chem.* **1995**, *107*, 2670 – 2693; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2443 – 2465; b) D. Enders, J. P. Shilvock, *Chem. Soc. Rev.* **2000**, *29*, 359 – 373; c) S.-I. Murahashi, D. Zhang, *Chem. Soc. Rev.* **2008**, *37*, 1490 – 1501.

[15] The catalytic performance of the present system was compared with those of the previously reported systems (Tables S4 and S5).

[16] We have recently reported that POMs can effectively activate TMSCN to generate a nucleophile (CN⁻).[5e,f]