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Polyoxometalate LUMO engineering: strategy for visible-light-responsive aerobic oxygenation photocatalysts

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We report the efficient visible-light-responsive photocatalysis of polyoxometalates (POMs) by engineering the lowest unoccupied molecular orbitals (LUMOs). By introduction of vanadium atoms into the γ-Keggin-type phosphotungstate, a new V3d/W5d mixed LUMO appeared to afford a visible-light-responsive catalyst (I) which showed high photocatalytic activity for aerobic oxygenation of sulfides to sulfoxides.

The development of highly efficient photocatalytic systems that can utilize visible light for selective transformations of organic molecules has received considerable attention.[1] In particular, photocatalytic oxidation utilizing molecular oxygen (O_2) as the sole oxidant is of particular importance because O_2 serves as ubiquitous and the greenest oxidant that produces only water as a byproduct.[2] Although visible-light-responsive photocatalysts based on organometallic complexes and organic dyes have been developed, these catalysts frequently suffer from the poor stability under the oxidative conditions.

Polyoxometalates (POMs) are a class of anionic metal oxide clusters that have been widely studied as efficient oxidation catalysts and photocatalysts.[3] POMs are thermally and oxidatively more stable than commonly utilized organometallic complexes or organic dyes. Furthermore, their chemical and physical properties, such as redox potentials, acidities/basicities, and electronic structures, can be finely controlled at the molecular level by changing their structures, charges, and constituent elements,[4] which makes them promising materials as photocatalysts. Several POM-based photocatalytic systems for oxidative functional group transformations have been developed by utilizing the photo-responsive intramolecular oxygen-to-tungsten charge transfers.[5] However, most of these systems required ultra violet (UV) light because of the large energy gaps between the O2p-based highest occupied molecular orbitals (HOMOs) and the W5d-based lowest unoccupied molecular orbitals (LUMOs).

We focused on that the electronic structures of POMs can be tailored by choosing appropriate constituent elements, metal substitution, and/or post-functionalization.[6] Thus, we have recently developed the strategy to utilize visible light by engineering the HOMOs of POMs (Fig. 1a); for example, a lacunary silicotungstate ($TBA_4H_4[\gamma\text{-}SiW_{10}O_{36}]$, TBA = tetra-*n*-butylammonium) showed the efficient visible-light-responsive photocatalysis by introduction of metal cations (e.g., Ce^{3+})[7] or ligands (e.g., alcohols)[8] at the vacant sites, where new HOMOs were formed on the introduced metal cations or ligands. Afterward, Newton, Oshio, and co-workers reported visible-light-responsive photocatalysts by introducing phosphonate ligands into lacunary POMs.[9] This strategy, however, lowered the oxidation potentials of the photocatalysts, which is undesirable for the oxidation catalysis.

The alternative strategy to utilize visible light would be lowering the energy levels of LUMOs (Fig. 1b); theoretical studies indicated that introduction of vanadium atoms into α-Keggin-type silicotungstate $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ could lower the energy level of the LUMO.[6a] Recently, aerobic photooxiadation catalysis of vanadium-containing POMs has been developed by Streb and co-workers.[10] Herein, we investigated the visible-light-responsive photocatalysis of vanadium-containing POMs for the sulfoxidation by using O_2 as the sole oxidant; γ-Keggin-type divanadium-containing phosphotungstate

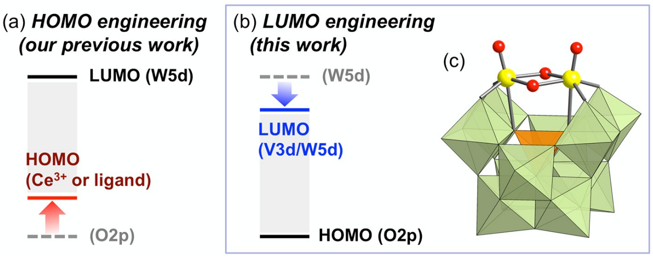

Fig. 1 Schematics of strategies for developing visible-light-responsive POMs by a) HOMO engineering by introduction of cerium or ligand and b) LUMO engineering by introduction of vanadium ions. c) Anion structure of **I**. Light green and orange polyhedra represent $[WO_6]^{6-}$ and $[PO_4]^{3-}$, respectively. Yellow and red spheres represent V and O, respectively.

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† Electronic Supplementary Information (ESI) available: Experimental details, Tables S1, S2, and Fig. S1–S4. See DOI: 10.1039/x0xx00000x

$TBA_4H[\gamma\text{-}PV_2W_{10}O_{40}]$ (**I**, Fig. 1c)[11] revealed to exhibit high performance for the transformation. In the presence of catalytic amounts of **I**, various aryl and alkyl sulfides could be selectively converted into the corresponding desired sulfoxides by irradiation with visible light ($\lambda > 400$ nm) in 1 atm of O_2.

Selective oxygenation of sulfides to sulfoxides is a desirable process due to the importance of sulfoxides as intermediates for natural products, oxygen transfer reagents, bioactive molecules, and functional materials.[12] Although various metal-, peracid-, and oxoacid-based oxidants have been frequently utilized for this transformation, (super)stoichiometric amounts of hazardous or toxic oxidants should be required, which resulted in overoxidation of sulfides to sulfones and/or undesired side-reactions of other functional groups.[13] Therefore, the photocatalytic selective oxygenation of sulfides to sulfoxides using O_2 as the sole oxidant is one of the most desirable processes.

Firstly, we investigated the photocatalysis of vanadium-free and vanadium-containing POMs for the oxygenation of thioanisole (**1a**) by irradiation with visible light ($\lambda > 400$ nm) in 1 atm of O_2 (Table 1). The photocatalytic oxygenation of **1a** hardly proceeded in the presence of vanadium-free phosphotungstates, namely fully occupied $TBA_3[\alpha\text{-}PW_{12}O_{40}]$ and lacunary $TBA_3H_4[\gamma\text{-}PW_{10}O_{36}]$ (Table 1, entries 9 and 10). Notably, introducing vanadium atom(s) into phosphotungstates significantly improved the photocatalytic activities, and the oxygenation of **1a** to methyl phenyl sulfoxide (**2a**) efficiently proceeded; the yields of **2a** using $TBA_4[\alpha\text{-}PVW_{11}O_{40}]$, $TBA_4H[\gamma\text{-}PV_2W_{10}O_{40}]$ (**I**), and $TBA_6[\alpha\text{-}PV_3W_9O_{40}]$ were much higher than those using vanadium-free phosphotungstates (Table 1, entries 1, 11, and 12). In particular, POM **I** possessing a divanadium core on the γ-Keggin-type structure showed the highest photocatalytic activity among the vanadium-containing phosphotungstates examined, giving **2a** in 92% yield (Table 1, entry 1). The photocatalytic activity of **I** was much higher than that of $TBA_4H_2[\gamma\text{-}SiV_2W_{10}O_{40}]$ which possessed the same anion structure as **I** just except for the heteroatoms (Table 1, entry 1 vs entry 13). Notably, **I** showed much higher photocatalytic activity in comparison with decatungstate $TBA_4[W_{10}O_{32}]$ (Table 1, entry 1 vs entry 14), which has been widely utilized for various photocatalytic functional group transformations by irradiation with UV light.[5] Furthermore, the catalytic activity of **I** was superior to that of a cerium-containing silicotungstate $TBA_6[Ce_4L_4(\mu_4\text{-}O)(\gamma\text{-}SiW_{10}O_{36})_2]$ (prepared according to our previous HOMO engineering strategy) under the present conditions (Table 1, entry 1 vs entry 16).[7] Several control experiments revealed that the oxygenation of **1a** did not proceed when lacking **I**, visible light irradiation, and O_2 (Table 1, entries 2–4). When acid ($HClO_4$) or base (TBAOH) was added, the catalytic activity of **I** significantly decreased (Table 1, entry 1 vs entries 5 and 6), indicating that the protonation state of **I** was important. The reaction also proceeded efficiently even under an air atmosphere (Table 1, entry 7) or using blue LED light (Table 1, entry 8). The solvent effect for the **I**-catalyzed photocatalytic oxygenation of **1a** was also studied, and acetonitrile was found to be the best solvent (Table S1, ESI†).

Table 1 Photocatalytic oxygenation of **1a** using various catalysts[a]

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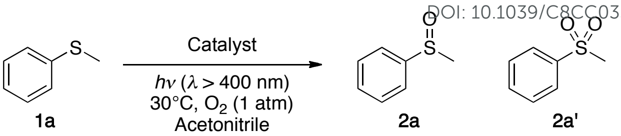

1a **2a** **2a'**

Entry	Catalyst	Yield (%)	
		2a	**2a'**
1	**I** ($TBA_4H[\gamma\text{-}PV_2W_{10}O_{40}]$)	92	6
2	w/o	<1	<1
3[b]	**I**	1	<1
4[c]	**I**	<1	<1
5[d]	**I**	9	<1
6[e]	**I**	37	3
7[f]	**I**	89	7
8[g]	**I**	91	8
9	$TBA_3[\alpha\text{-}PW_{12}O_{40}]$	<1	<1
10	$TBA_3H_4[\gamma\text{-}PW_{10}O_{36}]$	9	<1
11	$TBA_4[\alpha\text{-}PVW_{11}O_{40}]$	10	1
12	$TBA_6[\alpha\text{-}PV_3W_9O_{40}]$	33	8
13	$TBA_4H_2[\gamma\text{-}SiV_2W_{10}O_{40}]$	54	1
14	$TBA_4[W_{10}O_{32}]$	43	2
15	$TBA_3H_3[V_{10}O_{28}]$	17	1
16[h]	$TBA_6[Ce_4L_4(\mu_4\text{-}O)(\gamma\text{-}SiW_{10}O_{36})_2]$	10	1
17[i]	$VO(acac)_2$	10	1
18[i]	V_2O_5	<1	<1
19[i]	$NaVO_3$	<1	<1
20[i]	Na_3VO_4	<1	<1
21[j]	$TBA_3[\alpha\text{-}PW_{12}O_{40}] + VO(acac)_2$	24	2
22[j]	$TBA_3[\alpha\text{-}PW_{12}O_{40}] + V_2O_5$	<1	<1
23[j]	$TBA_3[\alpha\text{-}PW_{12}O_{40}] + NaVO_3$	<1	<1
24[j]	$TBA_3[\alpha\text{-}PW_{12}O_{40}] + Na_3VO_4$	<1	<1

[a] Reaction conditions: **1a** (0.2 mmol), catalyst (2 mol%), acetonitrile (2 mL), 30°C, xenon lamp ($\lambda > 400$ nm), O_2 (1 atm), 24 h. Yields were determined by GC using biphenyl as an internal standard. [b] Dark. [c] Ar (1 atm). [d] $HClO_4$ (2 mol%). [e] TBAOH (2 mol%). [f] Air (1 atm). [g] Blue LED ($\lambda_{max} = 425$ nm). [h] $TBA_6[Ce_4L_4(\mu_4\text{-}O)(\gamma\text{-}SiW_{10}O_{36})_2]$ (1 mol%). [i] Vanadium (4 mol%). [j] POM (2 mol%) + vanadium (4 mol%).

It should be noted that POM **I** showed much higher activity than simple vanadium compounds, such as vanadyl acetylacetonate ($VO(acac)_2$), vanadium oxide (V_2O_5), metavanadate ($NaVO_3$), orthovanadate (Na_3VO_4), or decavanadate ($TBA_3H_3[V_{10}O_{28}]$) (Table 1, entry 1 vs entries 15, 17–20). In addition, the simple physical mixtures of phosphotungstate $TBA_3[\alpha\text{-}PW_{12}O_{40}]$ and vanadium compounds were not effective (Table 1, entries 21–24). All these results indicated that both the introduction of vanadium atoms into the phosphotungstate skeleton and the structure of the divanadium-containing γ-Keggin-type POM are crucial for the high photocatalytic performance. When the oxygenation of **1a** was performed in $^{18}O_2$ (1 atm), the ^{18}O content in the product was 80% (Scheme 1), indicating that O_2 served as the major oxygen source for this reaction.

The UV-Vis spectra showed that the vanadium-free precursor $TBA_3H_4[\gamma\text{-}PW_{10}O_{36}]$ and $VO(acac)_2$ did not exhibit visible light absorption (Fig. 2a). In contrast, by introduction of vanadium atoms into the phosphotungstate skelton, **I** came to possess the apparent absorption bands in visible light region ($\lambda > 400$ nm, Fig. 2a). The density functional theory (DFT)

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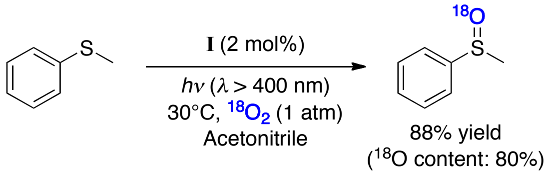


Scheme 1 Photocatalytic oxygenation of **1a** using **I** in $^{18}O_2$ (1 atm).

calculations revealed that the HOMO and LUMO of $TBA_3H_4[\gamma\text{-}PW_{10}O_{36}]$ were mainly observed on O2p and W5d, respectively (Fig. 2b, Fig. S1, ESI†). Notably, by introducing vanadium atoms into the POM skeleton, a new V3d/W5d mixed LUMOs appeared, and the energy gap between HOMO and LUMO became small (Fig. 2c, Fig. S1, ESI†).[14] In addition, the time-dependent (TD) DFT calculations with CAM-B3LYP exchange–correlation energy functional[15] showed that the excitations of the lowest energies were mainly attributed to the charge transfers of HOMO–4 (O2p) to LUMO (W5d/V3d) (3.45 eV) and HOMO–3 (O2p) to LUMO+1 (W5d/V3d) (3.63 eV; Table S2, ESI†).[14] These results supported that the new W5d/V3d-based LUMOs were possibly involved in the photo-excitation in the proposed photocatalytic system.

The UV-Vis spectra showed that **I** can absorb visible light more efficiently than $TBA_4H_2[\gamma\text{-}SiV_2W_{10}O_{40}]$ possessing silicon as the heteroatom (Fig. S2, ESI†). In addition, it is known that the oxidation potentials of POMs increase by changing the heteroatoms from silicon to phosphorous.[4e] Indeed, the cyclic voltammetry of the vanadium-containing POMs clearly revealed that the introduction of vanadium into POMs increased their oxidation potentials (Fig. S3, ESI†). These results supported the higher photocatalytic activity of **I** than that of $TBA_4H_2[\gamma\text{-}SiV_2W_{10}O_{40}]$.

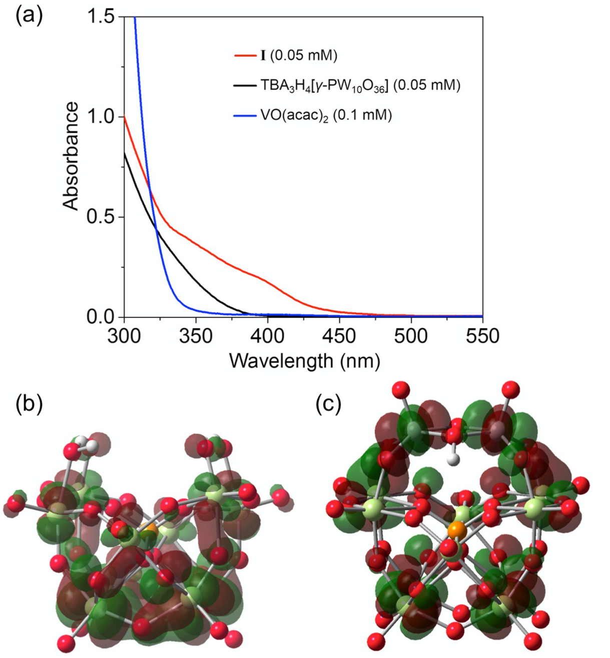
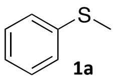
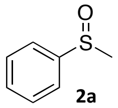
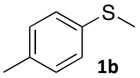
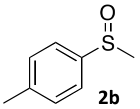
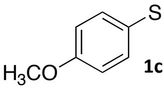
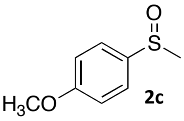
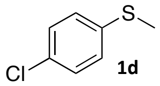
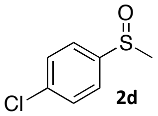
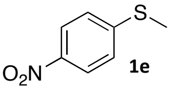
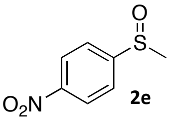
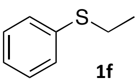
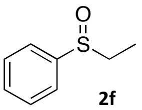
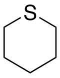
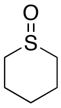
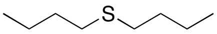
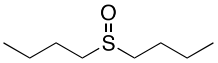


Fig. 2 (a) UV-Vis spectra of **I** (0.05 mM), $TBA_3H_4[\gamma\text{-}PW_{10}O_{36}]$ (0.05 mM), and $VO(acac)_2$ (0.1 mM) in acetonitrile (1 cm cell). Representations of LUMOs for (b) $TBA_3H_4[\gamma\text{-}PW_{10}O_{36}]$ and (c) **I**. The orbitals are represented by dark red and green lobes. The atoms are represented by spheres: W, light green; V, gray; P, orange; O, red; H, light gray.

Table 2 Scope of **I**-catalyzed oxygenation of sulfides by irradiation with visible light[a]

Entry	Substrate	Product	Time	Yield
1	 **1a**	 **2a**	24	92 (6)
2	 **1b**	 **2b**	24	83 (6)
3	 **1c**	 **2c**	24	80 (5)
4	 **1d**	 **2d**	28	93 (5)
5[b]	 **1e**	 **2e**	28	88 (<1)
6	 **1f**	 **2f**	28	88 (5)
7	 **1g**	 **2g**	24	67 (9)
8	 **1h**	 **2h**	24	78 (8)

[a] Reaction conditions: substrate (0.2 mmol), **I** (2 mol%), acetonitrile (2 mL), 30°C, xenon lamp (λ > 400 nm), O_2 (1 atm), 24 h. Yields were determined by GC using biphenyl as an internal standard, and the values in the parentheses are the yields of the corresponding sulfones. [b] Acetonitrile/water (99/1, v/v).

Next, we turned our attention to the substrate scope for the proposed photocatalytic oxygenation of sulfides to sulfoxides with **I** (Table 2). In the presence of catalytic amounts of **I**, thioanisole and its derivatives possessing electron-donating as well as electron-withdrawing functional groups on the aromatic rings (**1a**–**1e**) were all efficiently converted into the desired sulfoxides (**2a**–**2e**) in high yields with high selectivities (Table 2, entries 1–5). In the case of 4-chlorothioanisole (**1d**), the reaction proceeded without any dechlorination (Table 2, entry 4). The oxygenation of 4-nitrothioanisole (**1e**) also gave the corresponding sulfoxide (**2e**) in 88% yield (Table 2, entry 5), which was not successful in some previously reported photocatalytic systems.[16] Ethyl phenyl sulfide (**1f**) could also be converted into ethyl phenyl sulfoxide (**2f**) in 88% yield (Table 2 entry 6). Notably, less reactive alkyl and cyclic sulfides (**1g**, **1h**) could be efficiently oxygenated into the desired sulfoxides (**2g**, **2h**) by using the present photocatalytic system (Table 2, entries 7 and 8). A possible reaction mechanism for the present photocatalytic oxygenation of sulfides is tentatively proposed (see ESI† for

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details). By irradiation with visible light to **I**, the intramolecular oxygen-to-POM(V3d/W5d) charge transfer efficiently occurs, followed by the single electron transfer from a sulfide to the excited POM to afford a sulfide cation radical species. The reduced **I** is reoxidized by O_2, and a superoxide anion radical species is likely formed.[17] Then, the reaction of the cation radical species and the superoxide species gives the corresponding sulfoxide.

In conclusion, we have successfully developed an efficient and selective visible-light-responsive photocatalytic system based on γ-Keggin-type divanadium-containing phosphotungstate $TBA_4H[\gamma\text{-}PV_2W_{10}O_{40}]$ (**I**) for the selective oxygenation of sulfides to sulfoxides utilizing O_2 as the sole oxidant. The introduction of vanadium atoms into the phosphotungstate skeleton and the structure of the divanadium-containing γ-Keggin-type POM were both crucial for its high activity. Various aromatic sulfides with both electron-donating and electron-withdrawing functional groups, and alkyl sulfides could be efficiently oxygenated into the desired sulfoxides using the proposed photocatalytic system.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

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