Polyoxometalate-Supported Aminocatalyst for the Photocatalytic Direct Synthesis of Imines from Alkenes and Amines

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S *Supporting Information*

ABSTRACT: Developing efficient photocatalysts for direct oxidative coupling of alkenes and amines with O_2 under mild conditions is very significant. Herein, **ZnW–PYI** is well-designed by assembling a $[PZnW_{11}O_{39}(H_2O)]^{5-}$ photooxidation catalyst and chiral aminocatalyst pyrrolidine-2-ylimidazole (PYI) via a coordination model. **ZnW–PYI** efficiently catalyzed the synthesis of imines from alkenes and amines using O_2 as the oxidant through nucleophilic catalysis by employing pyrrolidine as an organocatalyst. Combining a polyoxometalate and PYI within one single framework is an effective approach not only for stabilization and heterogenization of the redox-active catalyst and aminocatalyst but also for realization of compatibility between the reaction intermediates and synergy of multiple catalytic cycles.

Imines are essential building blocks of biologically active heterocycles and important electrophilic intermediates in organic synthesis.[1] Recently, many scientists have studied high-performance reaction systems to prepare imines by the oxidative coupling of amines.[2−7] Especially, direct catalytic oxidative coupling of alcohols and amines provide a more promising and green synthesis strategy to synthesize imines.[8] In essence, in the above system, one first generates the aldehyde intermediate and then forms C=N bonds by condensation of C=O and NH_2 groups to complete the reaction. In 2014, the Belen Cid group first applied the concept of nucleophilic catalysis by employing pyrrolidine as an organocatalyst for the synthesis of aldimines from aldehydes and amines.[9] Inspired by the pioneering work, we aimed to develop a tandem process to directly synthesize imines from alkenes (Scheme 1). In this tandem reaction, the key fundamental scientific issues are effectively controlling the reaction rate of each step and ensuring that a multistep reaction occurs in order.[10]

In addition, utilizing a sustainable and clean O_2 alternative to the oxidants H_2O_2 and *t*-BuOOH is also a significant project considering the green and atom economy. However, the lower efficiency and inferior selectivity in the photocatalytic oxidation with O_2 has severely restricted practical application.[11] Superoxide radicals ($O_2^{•-}$), produced by photocatalysts through photogenerated electrons transferring to O_2, display excellent catalytic performance in oxidation reactions.[12] Therefore, it is necessary to develop excellent heterogeneous

Scheme 1. Design Concept for Realizing a Photocatalyst for the Direct Synthesis of Imines from Alkenes and Amines Using Iminium Activation
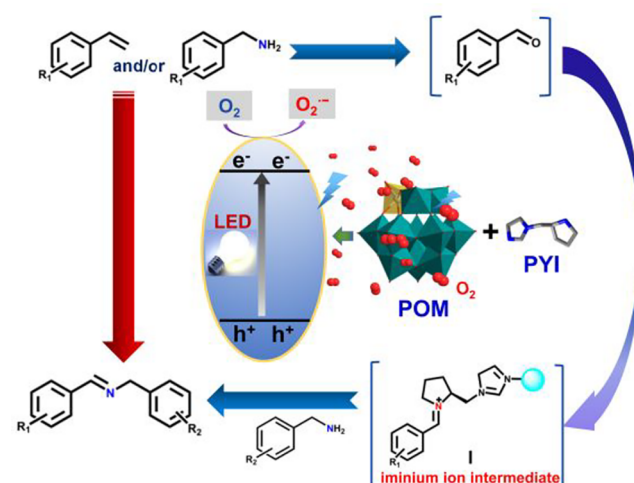

photocatalysts capable of forming long-lived charge-separated states for advances in solar energy conversion and oxygen activation for imine synthesis.[13−17] By assembling a judicious selection of electron donors and acceptors in a coordination mode, one can realize efficient electron transfer, high activity, and good stability.

Polyoxometalates (POMs), with excellent photosensitivity and redox-active properties, have revealed broad prospects in photocatalytic multi-electron-transfer reactivity for the light-driven hydrogen evolution reaction and water-splitting catalysts.[18−22] Especially, POMs can be easily photoreduced via ultraviolet excitation, and the resulting heteropoly blues can transfer electrons to O_2 for $O_2^{•-}$ generation.[23] Transition-metal-substituted POMs, especially $[PZnW_{11}O_{39}(H_2O)]^{5-}$ complexes, showed a better photocatalytic performance for activating O_2 compared to $[PW_{12}O_{40}]^{3-}$ because of tuning of the electronic structure and high stability for the redox states.[24−27] Combining $[PZnW_{11}O_{39}(H_2O)]^{5-}$ and aminocatalyst pyrrolidine-2-ylimidazole (PYI) within one single framework would be an effective approach for achieving compatibility between the reaction intermediates and synergy of the multiple catalytic cycles.[28−31]

In this study, a new hybrid, $\{[Zn(PYI)_3][H_3PW_{11}O_{39}Zn\text{-}(PYI)]\}\cdot 3H_2O$ (**ZnW−PYI**), was assembled by the $[PZnW_{11}O_{39}]^{5-}$ anion, zinc cation, and aminocatalyst PYI via a coordination model. **ZnW−PYI** can efficiently catalyze the synthesis of imines from alkenes with amines with O_2 as the oxidant and can be easily separated from the reaction mixture. In this reaction, $[PZnW_{11}O_{39}]^{5-}$ as a photocatalyst under visible light activates O_2 to form $O_2^{\bullet-}$; then $O_2^{\bullet-}$ reacts with a benzylamine radical ($PhCH_2NH^{\bullet}$) or alkene to produce aldehyde. PYI can not only enhance the stability of heteropoly blue but also activate the intermediate aldehyde into an iminium-ion intermediate, which improves the photocatalytic reaction markedly.

Single-crystal X-ray diffraction analysis indicates that **ZnW−PYI** crystallizes in the space group $P2_12_12_1$. The asymmetric **ZnW−PYI** unit consists of a $[H_3PW_{11}O_{39}Zn(PYI)]^{2-}$ unit, a supported $[Zn(PYI)_3]^{2+}$ cation, and four crystal water molecules (Figure 1a). Each $[H_3PW_{11}O_{39}Zn(PYI)]^{2-}$ unit
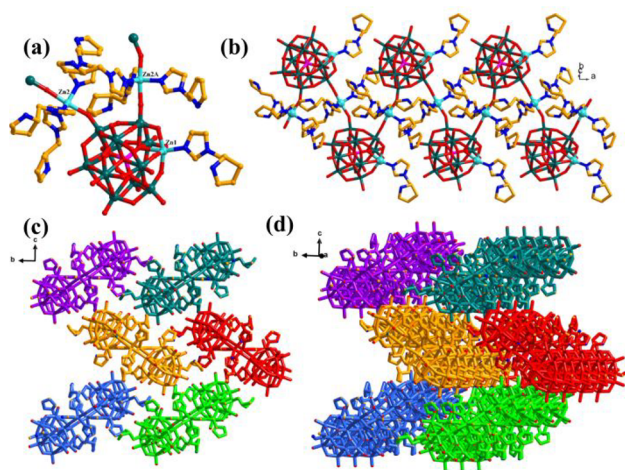

Figure 1. (a) Coordination environment of **ZnW−PYI**. (b) 1D chainlike **ZnW−PYI**. (Symmetry operation code: A, 0.5 + *x*, 3.5 − *y*, 3 − *z*. Color code: Zn, turquoise spheres; W, teal spheres; N, blue spheres; O, red spheres; C, gray. All hydrogen atoms and crystal water molecules are omitted for clarity.) (c and d) Antiparallel packing model between the 1D chain along the *a* axis.

supported two $[Zn(PYI)_3]^{2+}$ cations via adjacent terminal oxygen atoms. Thus, the $[H_3PW_{11}O_{39}Zn(PYI)]^{2-}$ units are connected by a Zn(2) atom as a node to form a one-dimensional (1D) chain structure (Figure 1b). The PYI moieties were generated in situ with the butoxycarbonyl group of the 5-bromo-4-chloro-3-indolyl phosphate removed. Hydrogen bonds between the pyrrolidine nitrogen and terminal oxygen atoms of the $[H_3PW_{11}O_{39}Zn(PYI)]^{2-}$ anion were found with an N···O_{POM} separation of approximately 2.86–3.01 Å (Figures S5 and S6). By intermolecular interactions, the 1D chains are parallelly stacked in one layer, and then the adjacent layers are further antiparallelly stacked, thus furnishing a three-dimensional network structure along the *a* axis with a porosity of 9.7% (682.1 Å^3; Figure 1c,d). In the structure, the $[H_3PW_{11}O_{39}Zn(PYI)]^{2-}$ anion can be photoexcited by UV−vis light to form POM*, and then POM* accepts the electron, forming the reduced POM$^-$, which is applicable to O_2 activation.[32,33] The direct assembly of $[Zn(PYI)_3]^{2+}$ into the skeleton of POM makes electron transfer more efficient. PYIs are beneficial for interacting with the resulting aldehydes for

the generation of iminium-ion intermediates, thus promoting a smooth tandem reaction.[34]

The diffuse-reflectance spectra for fresh **ZnW−PYI** exhibited two intense bands at approximately 301 and 372 nm, which are assigned to the transitions from n−π* and π−π* in PYI and the $O_{b,c} \rightarrow W$ charge-transfer (CT) of $[PW_{11}ZnO_{39}]^{5-}$, respectively (Figure 2a). After irradiation
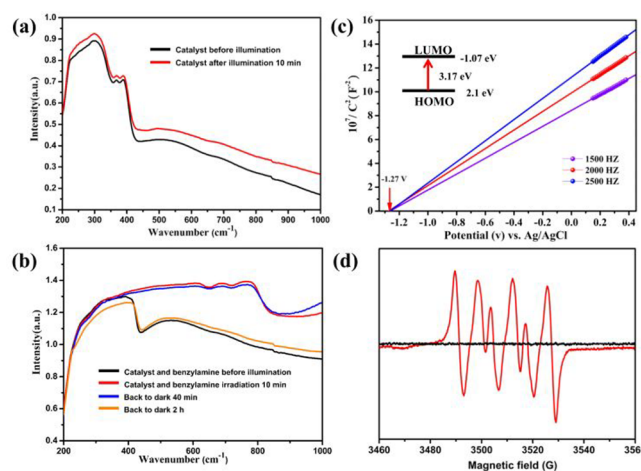
Figure 2. (a) Diffuse-reflectance spectra for **ZnW−PYI**. (b) Diffuse-reflectance spectra for benzylamine/**ZnW−PYI** before and after irradiation. (c) Mott−Schottky plots for **ZnW−PYI** in a 0.1 M Na_2SO_4 aqueous solution. (d) EPR spectra for a solution in air-saturated methanol of **ZnW−PYI** (1.0 mg/mL) with DMPO (0.1 M; black line, in the dark; red line, irradiation).
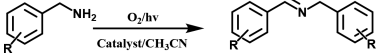
for 10 min, the absorption intensity increased slightly. **ZnW−PYI** immersed in benzylamine exhibited intense absorption at approximately 532 nm, which verified that the substrate has a good auxiliary effect on the electron transfer in catalysis. After irradiation of the catalyst and benzylamine for 10 min, new intense absorption bands appeared at 608, 688, and 768 nm (Figure 2b). The blue-shifted absorption band at approximately 768 nm is assigned to W^V d−d transitions and W^V−W^{VI} intervalence charge-transfer (IVCT) transitions in the reduced anionic ligand.[35] The valence state of tungsten in POM might be changed because benzylamine transfers electrons to $[PW_{11}ZnO_{39}]^{5-}$ and a hydrogen atom is removed, generating the benzylamine radical ($PhCHNH_2^{\bullet+}$). After 40 min in the dark, the absorption intensity of the catalyst declined slightly, and after remaining there for up for 2 h, the absorption peak at 765 nm disappeared and the catalyst was restored to the state observed before irradiation, which verified that electron transfer in the system was reversible. Consequently, **ZnW−PYI** will be a good candidate for photocatalysis of the oxidative coupling of the benzylamine.

The result of Mott−Schottky measurements on **ZnW−PYI** is consistent with that found for typical n-type semiconductors (Figure 2c).[36,37] The more negative potential of the lowest unoccupied molecular orbital (LUMO) level (−1.07 V vs NHE) in **ZnW−PYI** compared to the reduction potential for the conversion of O_2 to $O_2^{\bullet-}$ further proved the possibility of forming $O_2^{\bullet-}$ [ROS; $E(O_2/O_2^{\bullet-})$ = −0.33 V vs normal hydrogen electrode (NHE)].[38] On the basis of a Tauc plot (Figure S8), the valence band (highest occupied molecular orbital, HOMO) was estimated to be 2.13 V versus NHE, which guarantees a high oxidation ability for benzylamine [$E_{1/2}(M^+/M)$ = +1.47 V vs NHE].[39] Compared with the

LUMO level (−0.75 V vs NHE) of (TBA)$_3$[PW$_{12}$O$_{40}$], **ZnW−PYI** has a more negative potential, which further verified the fact that the activated oxygen capacity of **ZnW−PYI** is higher than that of [PW$_{12}$O$_{40}$]$^{3−}$ (Figure S9).

On the basis of the above results, **ZnW−PYI** was initially explored for the catalytic oxidative coupling of primary amines to imines with O$_2$ under 365 nm light. The oxidative coupling of benzylamine as a model reaction afforded N-benzylidene-benzylamine with a conversion of 99% after 36 h (Table 1,

Table 1. Photocatalytic Oxidative Coupling of Various Amines into Imines[a]

Entry	Substrate	Product	Yield (%)[b]
1			92
2			93
3			92
4			95
5			85
6			90
7			0

[a]Reaction conditions: amine (5 mmol), **ZnW−PYI** (10 mg, 14 μmol, 0.03 mol %), 10 W white LED lamp; room temperature, CH$_3$CN 3 mL, in air, 36 h. [b]Yield determined by ^{1}H NMR spectroscopy for the crude products.

entry 1), which revealed the moderate oxidation ability of **ZnW−PYI** in such a heterogeneous system. The oxidation of benzylamine derivatives with electron-donating and electron-withdrawing groups led to successful conversion of the corresponding imines with excellent yields (Table 1). However, the oxidative coupling of aniline without a hydrogen atom at its α-carbon atom did not proceed (Table 1, entry 7), which suggested that the reaction might occur via hydrogen abstraction and formation of the aldehyde intermediate. In addition, the **ZnW−PYI** samples can be easily separated from the reaction mixture by simple centrifugal operation after the reaction. The experimental results indicated that the catalyst can maintain a high activity up to the fifth cycle; the XRD pattern for the recovered catalyst showed that the structure of **ZnW−PYI** remained (Figure S1).

The control experiments indicated that L-**PYI** or K$_5$[PW$_{11}$O$_{39}$Zn(H$_2$O)] can only afford imines with an 8% and 18% yields under similar reaction conditions, respectively. The use of L-**PYI** and K$_5$[PW$_{11}$O$_{39}$Zn(H$_2$O)] as multi-component catalysts provided an imine with a yield of 46%, which proved that assembly of the polyacid and organic aminocatalyst into one framework can greatly improve the catalytic efficiency. The control experiment carried out in N$_2$ proved that molecular O$_2$ is vital for this reaction. In the absence of the catalyst, the yield was negligible, which confirmed that the **ZnW−PYI** catalyst is very important for amine transformation. Furthermore, electron paramagnetic resonance (EPR) employing 5,5-dimethylpyrroline-N-oxide

(DMPO) as a classical O$_2$$^{•−}$ probe and 2,2,6,6-tetramethylpi-peridine as a typical spin-trapping agent for ^{1}O$_2$ revealed that both active oxygen species (O$_2$$^{•−}$ and ^{1}O$_2$) were involved in the photooxidative coupling reaction of benzylamine (Figures 2d and S10).[40] Furthermore, EPR using potassium monop-ersulfate triple salt/DMPO as a hydroxyl radical ($^•$OH) probe also detected the formation of $^•$OH (Figure S11).[41] Thus, we surmised that $^•$OH, which was generated from H$_2$O$_2$ as a side product in the oxidative coupling reaction when the benzyliminium ion further converted into benzylimine, played a certain role in the reaction process.[42]

On the basis of the above results, a possible cooperative catalytic mechanism for oxidative coupling of amines is proposed (Scheme 2). First, upon irradiation,

Scheme 2. Possible Cooperative Catalytic Mechanism of the Oxidative Self-Coupling of Amines
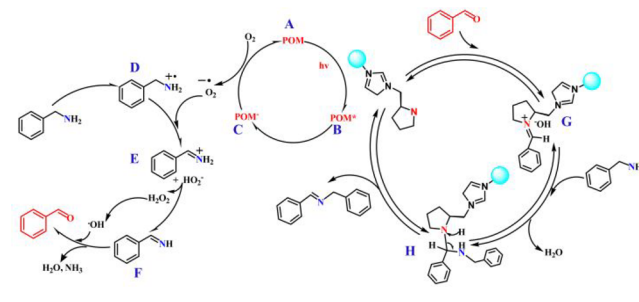
[PZnW$_{11}$O$_{39}$]$^{5−}$ (**A**) was transformed into the CT excited state [PZnW$_{10}$W(VI)O$_{39}$]$^{5−}$* (**B**) and then **B** gained an electron from the benzylamine to form [PZnW$_{10}$W(V)O$_{39}$]$^{6−}$ (**C**), followed by oxidization of benzylamine to the benzyl-amine radical cation PhCH$_2$NH$_2$$^{•+}$ (**D**).[43] Then, along with the reoxidation of **C** by O$_2$, O$_2$$^{•−}$ was generated and **D** was transformed to the PhCHNH$_2$$^+$ (**E**) intermediate.[44] O$_2$$^{•−}$ extracted the hydrogen protons from **E** to produce PhCH=NH (**F**) and H$_2$O$_2$, and H$_2$O$_2$ further dissociated into $^•$OH, which also acts as an oxidant to oxidize **F** to benzaldehyde.[45] Next, the secondary amine of pyrrolidine reacts with the resulting aldehyde to form an iminium ion (**G**). Then, the compounds containing NH$_2$ groups act as nitrogenated nucleophiles to attack the iminium ion, generating an aminal intermediate (**H**). The aminal **H** transforms into the imine through a favored concerted process involving a four-membered transition state, as proposed by Di Stefano et al.[46]

In this work, **ZnW−PYI** could easily oxidize olefin into aldehyde with >99% selectivity within a short time. According to the above experiments, the self-coupling of amines to imines proceeds through the formation of an aldehyde intermediate. The direct synthesis of imines from alkenes and amines is another excellent approach to preparing imines. Moreover, the conversion rate of alkenes into aldehydes is faster than that of amines. Inspired by this, the aerobic oxidative coupling of alkenes and amines was initially examined by using styrene and benzylamine as oxidants in CH$_3$CN along with **ZnW−PYI** (0.3% mole ratio) with white-light irradiation in a heterogeneous manner at room temperature. The result revealed the successful execution of our catalyst design, showing an excellent yield (>95%) for N-benzylidenebenzylamine in 18 h (Table 2). Importantly, aniline and styrene all produced the corresponding imine with a yield of 95%, which further verified

Table 2. Photocatalytic Oxidative Coupling of Various Aldehydes and Amines into Imines[a]

Entry	Substrate a	Substrate b	Product	Yield (%)[b]
1				> 99
2				> 99
3				90
4				67
5				75
6				> 99
7				> 99
8				95

[a]Reaction conditions: amine (5 mmol), **ZnW−PYI** (10 mg, 14 μmol, 0.03 mol %), 10 W white LED lamp; room temperature, CH_3CN 3 mL, in air, 18 h. [b]Yield determined by ^1H NMR spectroscopy of the crude products.

that the formation rate of the intermediate aldehyde determines the overall reaction rate and selectivity.

ASSOCIATED CONTENT

○S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b02056.

Experimental details, tables, and figures (PDF)

Accession Codes

CCDC 1949346 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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