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Application of an electron-transfer catalyst in light-induced aerobic oxidation of alcohols†

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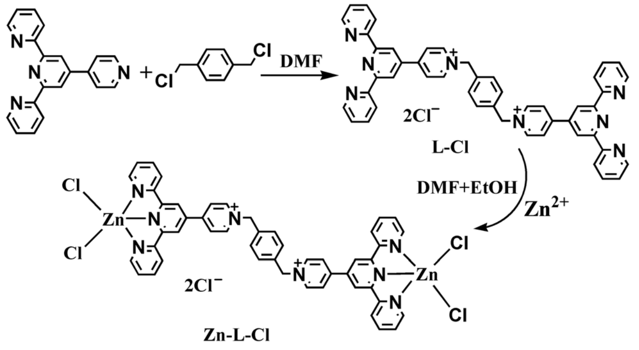
The first heterogeneous photocatalysis system including a bipyridinium-based complex as the electron-transfer catalyst was developed for aerobic oxidation of alcohols without the use of any noble-metal, external N-oxide or peroxide co-oxidant. The current work provides an efficient strategy for alcohol oxidation through a cost-effective, convenient and eco-friendly route.

The selective oxidations of alcohols to aldehydes are of great importance in fine chemical production.[1] The transformation is conventionally achieved by using chromium-based reagents, activated manganese dioxide or dimethyl sulfoxide reagents, as well as hypervalent iodine compounds and peroxides, *etc.*, which show considerable drawbacks due to the use of toxic/explosive reagents or heavy metals, high cost, and discharge of environmentally pernicious wastes.[2] It is urgently necessary to develop new protocols for the selective oxidation of alcohols to corresponding aldehydes through a cost-effective eco-benign route. Of particular significance is the use of molecular oxygen as the oxidant because of its remarkable merits, such as low cost, high safety, abundance, and water as the sole byproduct.[3]

To boost oxygen activation, extensive efforts have been devoted to develop various catalysis systems,[4] including noble metal–ligand complexes,[1a,b] nonprecious transition metal oxides or complexes,[5] metal nanoparticles[6] and metal–organic framework (MOF) compounds,[7] *etc.* as catalysts. Some metal oxides,[8] MOFs[9] and metal nanoparticle/MOF composites[10] have also been studied as photocatalysts for the selective oxidation of alcohols. However, the expense of noble metals, undesired overoxidation, high reaction temperature, use of co-catalyst (TEMPO) and sacrificial co-oxidant (H_2O_2, *t*-BuOOH, or concentrated HNO_3), and cumbersome synthesis still remain large obstacles to the practical applications of these approaches in a cost-effective fashion.

Viologen/bipyridinium derivatives can undergo a one-electron reduction to form a free-radical state upon their exposure to external stimuli such as chemical, photochemical or electrochemical reactions. The reduced forms are easily re-oxidized to the initial state, especially under an oxygen atmosphere.[11] This attribute endows them with great potential to take advantage of O_2 and mediate redox reactions as electron-transfer catalysts (ETCs).[12] Although it has been observed a long time ago that alcohols can serve as sacrificial electron donors to photoreduce viologens to yield viologen free radicals and form corresponding aldehydes or ketones,[13] most research attention has been paid to the formation and characterization of viologen free radicals. The conversion of alcohols into carbonyl compounds has been little explored: these reactions are carried out in homogenous conditions, which increase the difficulty of separation, thus leading to high production costs. Due to the above issues, we have now explored a bipyridinium derivative L-Cl, one substituted with multiple aromatic rings, with this derivative having multidentate coordination sites and low solubility in common solvents (Scheme 1). The incorporation of Zn(II) metal ion not only greatly decreased the solubility of L-Cl but also enhanced the photoreaction efficiency, enabling the compound as a heterogeneous electron-transfer catalyst to be easily separated and reused, and to exhibit excellent selectivity and catalytic activity in the



Scheme 1 Route used to synthesize L-Cl and Zn–L-Cl.

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oxidation of primary alcohols to aldehydes at ambient temperature and pressure without the assistance of any noble metal, peroxide or other co-catalyst.

The synthesis and coordination assembly routes of L-Cl are shown in Scheme 1. Compared with the IR spectrum of L-Cl, that of Zn–L-Cl (Fig. S1, ESI†) showed a new band at 418 cm^{-1}, which has been attributed to the Zn–N bond.[14a] The peaks at 987 cm^{-1} and 1389 cm^{-1}, attributed to the vibrations (ν_{ring} and $\delta_{(CH)}$) of the pyridine ring, underwent shifts to 1009 and 1411 cm^{-1}, demonstrating the occurrence of coordination interactions.[14b] The elemental analysis revealed the presence of six chloride anions and gave the final sum formula of $C_{48}H_{36}N_8Zn_2Cl_6\cdot 8H_2O$. According to the prevalent coordination pattern of the Zn(II) ion in the presence of the terpyridine derivatives and chloride anions, demonstrated by the Cambridge Crystallographic Data Centre, the Zn(II) ion in the compound Zn–L-Cl was considered to be five-coordinated, specifically by two chloride anions and three nitrogen atoms from the terpyridine group (Scheme 1), leaving two chloride ions and eight water molecules in a dissociated form. To confirm the presence of different types of chloride ions, X-ray photoelectron spectroscopy (XPS) analysis was carried out (Fig. S2, ESI†). The Cl 2p core-level region of the spectrum showed one pair of broad peaks that were well-resolved into two pairs of spin–orbit-split doublets Cl $2p_{3/2}$ and Cl $2p_{1/2}$ lying at 196.4 and 198.3 eV for free chloride ions,[15] and 196.9 and 198.5 eV for the coordinated one,[16] respectively. These results supported the coexistence of two kinds of chloride anions in Zn–L-Cl.

Compound L-Cl is slightly soluble in methanol, ethanol, water, dimethylformamide and dimethylsulfoxide, and hardly soluble in acetonitrile, methylene chloride, tetrahydrofuran, and acetone (<0.01 g per 100 g of solvent). After coordination of L-Cl with Zn(II) ions, the formed Zn–L-Cl showed a further decrease in solubility. As shown in the UV-Vis electronic absorption spectra, the intense peaks at 245 and 278 nm and a weak shoulder at about 325 nm for L-Cl (Fig. S3, ESI†), which can be assigned to the π–π* transition of the pyridine rings and the intramolecular charge-transfer transition of the pyridinium molecule,[17] were very weak in the absorption spectrum of Zn–L-Cl in acetonitrile. Therefore, Zn–L-Cl should be a good heterogeneous mediator in the solution-phase oxidation of alcohols.

Light-driven aerobic oxidation of alcohols was investigated at atmospheric pressure and room temperature. It was found that solvents had a great effect on catalytic activity. The conversion was low in methanol, ethanol and water, whereas it was obviously improved in acetonitrile and acetone (Table S1, ESI†). This observation may have been related to the ability of methanol and ethanol to serve as electron donors and hence participate in the electron-transfer reaction, while the aromatic alcohols and aldehydes have very low solubility in water. Furthermore, a dramatic difference in catalytic activity was observed for selective oxidations of L-Cl and Zn–L-Cl. The conversion yield of 4-methoxy benzyl alcohol (BA) to the corresponding aldehyde in the presence of L-Cl was 35% while the conversion yield facilitated by Zn–L-Cl reached 73% with an extremely high selectivity (>99%) in 4 hours in acetonitrile under an LED395 light source (395 nm; 450 mW). These results indicated that the coordination of Zn(II) ions not only effectively decreased the solubility of the catalyst but also sensitized the photochemical reaction. An investigation of the influence of different catalyst loadings revealed that increasing the amount of catalyst (Zn–L-Cl) from 4 μmol to 20 μmol increased the rate of conversion, but led to a decrease in the turnover frequency (TOF) from 29 to 9.8 h^{-1} (Fig. 1a and Fig. S4, ESI†). Therefore, we considered 4 μmol of Zn–L-Cl to be the appropriate amount for ensuring maximal performance of the catalyst. The obtained UV-Vis diffuse reflectance spectrum of Zn–L-Cl showed two strong peaks centered at 288 and 357 nm, with an additional shoulder at about 520 nm (Fig. S5, ESI†). The photocatalytic performance of Zn–L-Cl evaluated under different irradiation sources (Fig. S6, ESI†) revealed that LED365 (365 nm; 420 mW) and LED395 light effectively promoted the conversion of aromatic alcohols to aldehydes, while the light sources with wavelengths longer than 425 nm failed to facilitate the formation of aldehydes. These results demonstrated the close relationship of the photocatalytic performance of the complex to its light-capturing capability. The lower conversion yield under 365 nm-wavelength light irradiation than that under 395 nm-wavelength light irradiation may have been mainly caused by the difference in their output powers. Upon increasing the light irradiation power of the 395 nm-wavelength light source from 30% to 200% (double light source), the conversion yield was improved about 6-fold (from 14% to 86%, and to 91% upon a slight prolongation of irradiation time; Fig. 1b). One noteworthy phenomenon was the appearance of an aromatic acid product under 365 nm-wavelength irradiation, which also led to the decrease of the level of conversion of the alcohols to aldehydes. Therefore, the photoreaction was mainly carried out under 395 nm-wavelength light irradiation. After the reaction, Zn–L-Cl was easily

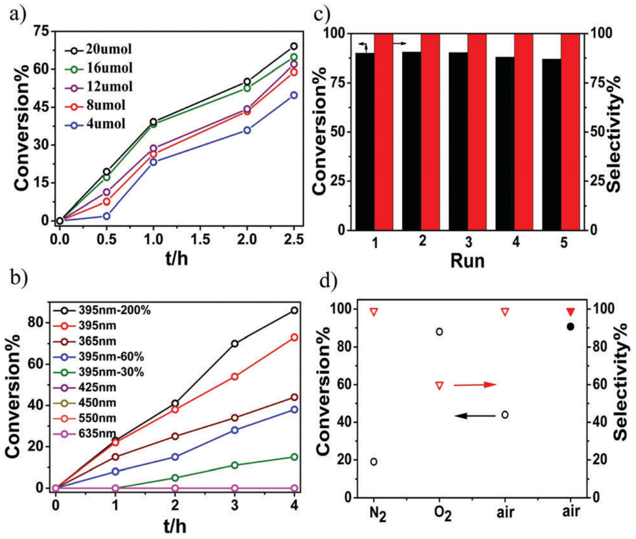


Fig. 1 (a) Conversion yields vs time for the aerobic oxidation of 4-methoxy BA in the presence of various amounts of Zn–L-Cl, specifically from 4 μmol to 20 μmol. (b) Conversion yield–time plots for the aerobic oxidation of 4-methoxy BA using various light sources and output power levels. (c) Conversion yields and selectivities of 4-methoxy BA oxidation during a five-cycle test. (d) Conversion yield (○) and selectivity (▽) values of 4-methoxy BA oxidation carried out for 2.5 h under different atmospheres and 4.2 h in the air (the conversion (●) and selectivity (▼)) after irradiation.

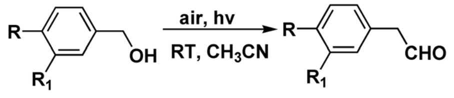
separated by carrying out centrifugation or filtration accompanied by washing with diethyl ether, and was suitable for reuse without significant loss of catalytic activity or selectivity. In the five successive runs of a cycling experiment (Fig. 1c), the conversion yields of 4-methoxy BA and the selectivities for the desired product remained nearly unchanged, as did the FT-IR spectra and XRPD patterns, confirming the stability of Zn–L-Cl (Fig. S7 & S8, ESI†). To further confirm the heterogeneous nature of Zn–L-Cl, the catalyst was removed from the reaction mixture by performing centrifugation after 2 h of reaction and the supernatant was tested for activity under the same conditions. The reaction was completely stopped by the removal of Zn–L-Cl, confirming that the catalytic reaction was truly heterogeneous and occurred over the solid catalyst rather than in solution.

To investigate the scope and limitation of this catalytic process, the substituted benzyl alcohols were chosen for experimental validation (Fig. S9, ESI†). Remarkably, the aromatic alcohols were converted into the corresponding aldehydes with high selectivity (>99%), while the electronic properties of the substituents significantly influenced the conversions. The primary benzyl alcohols containing electron-donating groups (such as $-OCH_3$ and $-CH_3$; Table 1, entries 1 and 4) were found to be more easily oxidized than those bearing electron-withdrawing groups (such as –Cl; Table 1, entry 6). In the latter case, the conversion yield was lower than that for the bare benzyl alcohol. The reactions were also found to be sensitive to the steric environment produced by the substituents. The benzyl alcohols substituted at the 4-position showed a greater conversion yield than did the benzyl alcohol containing substituents at the 3-position (Table 1). The Zn–L-Cl was found to be able to offer comparable catalytic activity and selectivity without the assistance of any noble or rare metal, and to allow the reaction to proceed at very mild conditions (ambient pressure and temperature). In particular, the current system was also shown to overcome the obstacles of non-noble metal catalysts (such as nanoshell carbon,[18a] MOF materials,[7,9,18b] porous polymerized organocatalysts,[18c] *etc.*) that commonly need to use a co-catalyst (TEMPO) and sacrificial co-oxidant (H_2O_2, *t*-BuOOH, or concentrated HNO_3).

To gain a more thorough understanding of the mechanism, we undertook a comparative study of the catalyst systems using 4-methoxy BA as a substrate. A control reaction under an N_2 atmosphere gave a much lower conversion yield (Fig. 1d), and the Zn–L-Cl exhibited a remarkable color change from earth yellow to blue purple. This color development was reminiscent of the generation of bipyridinium radicals, which commonly show intense blue or purple color upon photo-triggered or chemical reduction.[11] As a comparison, only a lighter purple color appeared during the reaction process under an air atmosphere, accompanied by a rapid fading after stopping irradiation and stirring (Fig. 2 and Fig. S10 in ESI†). These phenomena were consistent with the easy quenching of bipyridinium radicals by O_2 to revert the bipyridinium to its original state.[11,19] The low level of conversion under an N_2 atmosphere was attributed to the poor recovery of the bipyridinium radicals in the absence of O_2, and thus the interruption of the progression of the electron transfer. Using pure O_2 instead of air effectively quenched the radicals (Fig. S10, ESI†) and facilitated a rapid conversion of alcohol to aldehyde, but the by-product 4-methoxybenzoic acid was produced under this condition, and thus using pure O_2 led to a decreased selectivity (Fig. 1d and Fig. S11, ESI†). Therefore, operating the reaction under an air atmosphere was concluded to be very convenient and economical for practical applications.

X-band ESR spectroscopy was performed to confirm the generation of radicals during the oxidation of the alcohols. The initial mixture of 4-methoxy BA and Zn–L-Cl in the CH_3CN solution under an air atmosphere at 298 K was ESR-silent. After irradiation for two minutes, a symmetric singlet signal without hyperfine splitting emerged at $g = 2.0030$ (Fig. 2). This signal profile and g value were very close to that of the bipyridinium radical observed commonly in the solid state, indicating that the coloration of reaction system involved the generation of bipyridinium radicals. Remarkably, upon the addition of a spin-trapping agent (DMPO) to the control reaction mixture, a new set of ESR signals with hyperfine splitting appeared besides the strong signal of the bipyridinium radical. Disregarding the background effect from the strong ESR signal, these ESR hyperfine lines were determined to be similar to those of the superoxide anion $O_2^{-\bullet}$.[20] These results were consistent with the quenching of bipyridinium radicals by air oxygen to produce $O_2^{-\bullet}$ radicals. The variance in relative intensity may have been due to the contribution of the subsequently produced $^{\bullet}OOH$ radicals.

Table 1 Aerobic oxidation of benzyl alcohol



Entry[a]	R/R$_1$	Time/h	TOF/h^{-1}	Con./Sel.[b]/%
1	OCH_3/H	4.2	29.0	91/99
2	OCH_3/H	4	29.0	86/99
3	H/CH_3	4	17.1	79/99
4	CH_3/H	6	16.9	80/99
5	H/H	6	13.4	58/99
6	Cl/H	7	16.2	59/99
7	H/Cl	6	15.0	45/99

[a] Standard conditions: alcohols (0.5 mmol), 4 μmol catalyst Zn–L-Cl, 2 ml acetonitrile, irradiation with 395 nm-wavelength light (900 mW). [b] Conversion yield was calculated by carrying out a GC analysis.

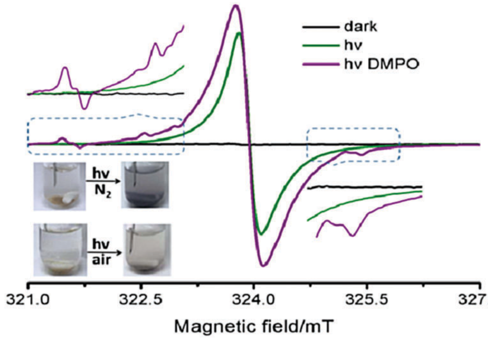
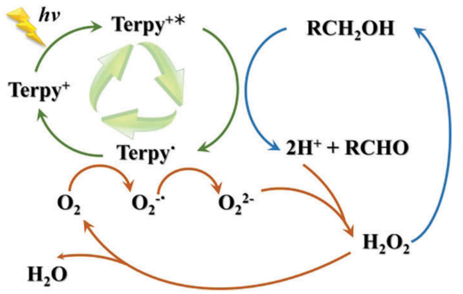


Fig. 2 The ESR spectra of 4-OCH_3-BA at room temperature in the dark, under light irradiation and in the presence of DMPO. The inset shows the color change of the reaction before and after light irradiation in N_2 and air atmospheres, respectively.



Scheme 2 The proposed mechanism for the light-induced aerobic oxidation of an alcohol with bipyridinium complexes used as the electron-transfer catalyst.

Adding benzoquinone, a scavenger for superoxide radicals ($O_2^{-\bullet}$), into the reaction system only resulted in a small change in the conversion of 4-methoxy BA (Fig. S12, ESI†). This result suggested that the photoinduced oxidation of 4-methoxy BA was not driven by photogenerated $O_2^{-\bullet}$ radicals, consistent with the $O_2^{-\bullet}$ radical being the reduced product of the quenching of bipyridinium radicals.

Based on the above results, the photoinduced aerobic oxidation of alcohols over Zn–L-Cl is considered to mainly proceed by the following mechanism (Scheme 2). The excited bipyridinium unit receives an electron from alcohol and causes the dehydrogenation of alcohols to give the corresponding aldehyde, bipyridinium radical and proton. The oxygen molecule captures the electron from the bipyridinium radical to result in the latter being oxidized and reverted to the initial bipyridinium state, while the oxygen itself is reduced to form superoxide and hence peroxide ions. These peroxide ions may combine with the protons dissociated from the alcohols to yield H_2O_2, which can make some additional contribution to the oxidation of alcohols or become photodecomposed into oxygen and water. Since no other product was observed to be produced during the reaction cycles, and since the photooxidation was successful when carried out at room temperature, the current system for oxidizing alcohols may be considered to be quite green, efficient, simple, low-cost and convenient.

In conclusion, we have demonstrated for the first time the superiority of the bipyridinium complex as an electron-transfer catalyst for photo-oxidation of aromatic alcohols to the corresponding aldehydes. Without the use of any noble-metal, external N-oxide or peroxide co-oxidant, the reactions proceeded at ambient pressure and temperature with high chemoselectivity and activity in the presence of various aromatic alcohols. The catalyst was easily separated and reused in the reaction process, and was recycled without a noticeable loss in activity. The current work provides a promising strategy to overcome the obstacles that alcohol oxidation is currently facing, and represents an important step towards the realization of a mild, noble metal-free, recycled catalyst system for industrially important aerobic oxidation of alcohols.

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Conflicts of interest

There are no conflicts to declare.

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