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Boosting activity of molecular oxygen by pyridinium-based photocatalysts for metal-free alcohol oxidation†

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An eco-friendly and economical approach for the photocatalytic oxidation of organic intermediates by air under mild conditions is highly desirable in green and sustainable chemistry, where the photogeneration of active oxygen species plays a key role in improving conversion efficiency and selectivity. By using pyridinium derivatives as molecular mediators for electron transfer and energy transfer, the simultaneous activation of O₂ from air into superoxide radicals and singlet oxygen species can be achieved, and a photoinduced electron transfer catalytic system for the oxidation of alcohols has been developed. Thus, we have successfully simplified the complicated catalytic system into a single molecular catalyst without any additional noble metals and co-catalysts/additives. The current photocatalytic system shows high catalytic efficiency not only for aromatic alcohols but also for aliphatic alcohols that are generally difficult to undergo aerobic oxidation at room temperature under air atmosphere, representing an ideal photocatalytic platform for green and economical organic syntheses.

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Introduction

The selective oxidation of alcohols to carbonyl compounds is highly significant in the fine chemical and pharmaceutical industry.¹ There are urgent needs to replace traditional oxidation methods, which commonly require stoichiometric amounts of hazardous oxidants with high consumption and pollution, with green and economic reaction systems.² Essential considerations in developing economically and environmentally sustainable oxidation technologies include (a) the selection of stoichiometric oxidants. Herein, molecular oxygen, particularly air that can reduce potential risk along with volatile and flammable organic solvents, should be an ideal oxidant because of its natural, inexpensive, and eco-friendly advantages.³ (b) The usage of light energy instead of the conventional thermal-based chemical process, which not only activates oxygen and allows reactions to occur under mild conditions but also offers a promising solution for energy sus-

tainable alternatives through the transformation of solar energy.⁴ (c) Search for effective catalysts that can activate the molecular oxygen at ambient conditions without the consumption of expensive/rare metals, and co-catalysts.

Significant efforts have been made to develop the photocatalytic oxidation of alcohols using O₂ as an oxidant. Typical examples include some metal-based photocatalysts involving Au–Cu, Au–Pd, CdSe, TiO₂, In₂S₃, bismuth-derived materials, and Pt-functionalized MOFs.⁵ However, the requirement of precious/heavy metals, additives/co-catalysts or intricate syntheses in most of these systems still lead to the exhaustion of raw materials or expensive costs for practical applications. Metal-free photocatalytic systems possess great advantages in design diversity as well as in avoiding heavy metal contamination and the depletion of noble/rare metal resources. Impressive advancements have been made based on carbon nitride derivatives,⁶ fluorenone,⁷ covalent triazine frameworks,⁸ 10-methylacridinium derivatives,⁹ thioxanthenon¹⁰ and trifluoromethanesulfinate,¹¹ but some disadvantages such as limited reactivity, large catalyst loading, high reaction temperature or pressure, and long irradiation time, need to be overcome. The development of a new protocol for achieving facile, highly efficient photocatalytic alcohol oxidation using metal-free catalysts and atmospheric oxygen as the sole oxidant is still highly desirable in green and sustainable chemistry.

Pyridinium derivatives, typically viologens (1,1'-dialkyl-4,4'-bipyridinium salts), have long been known for their light-

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induced electron transfer and electronic-deficient characteristics.¹² They can undergo one-electron reduction to produce pyridinium radicals that are easily reoxidized to the initial state in the presence of atmospheric oxygen. Such an attribute endows them with an excellent ability to serve as an electron transfer catalyst for the activation of oxygen molecules. However, the interest is popularly placed on hydrogen production by the photoreduction of protons with the pyridinium radicals as reducing reagents in the presence of sacrificial electron donors and Pt catalysts.¹³ The profit from the electron transfer process between the sacrificial electron donor and the oxygen quenching of radicals is greatly undervalued and neglected.¹⁴ In fact, the electron-deficient pyridinium receives an electron from the reductive alcohol to form a radical,¹⁴ and then this radical is recovered to the initial state by air oxygen with the generation of active superoxide radical species (O_2^-),¹² representing a good cycle for the regeneration of the electron transfer catalyst and activation of molecular oxygen. Along this line, we have developed a metal-free photocatalytic alcohol oxidation system using this unique property of pyridinium derivatives. The hierarchical incorporation of pyridinium units (Fig. 1) from monopyridinium (EPY·Br: *N*-ethylpyridinium bromide), bipyridinium (DEBPY·2Br: 1,1'-diethyl-4,4'-bipyridinium bromide) to polypyridinium (TTEPY·3Br: 1,1',1''-triethyl-4,4',4''-(1,3,5-triazine-2,4,6-triyl)tripyrindinium bromide) reveals structural insights into the redox activity and photocatalytic performance and renders excellent conversion and selectivity towards the transformation of alcohols to ketones or aldehydes at room temperature under air atmosphere without any noble metals and additional co-catalysts/additives. The current system is effective not only for aromatic alcohols but even for aliphatic alcohols that are generally much more difficult to be oxidized under such mild conditions. Remarkably, the simultaneous activation of O_2 into reactive $^1\text{O}_2$ (singlet oxygen) has also been achieved through the pyridinium-mediated energy transfer to synergize

with O_2^- to facilitate this high-performance photocatalytic conversion.

Results and discussion

The pyridinium-based photocatalysts were synthesized by a direct Menshutkin reaction of pyridine derivatives and bromoethane (Scheme S1 and Fig. S1–S2†). With the increase in the number of the electron-deficient pyridinium rings and conjugation degree, the electron-accepting ability of the compounds was enhanced, as evidenced clearly by a gradually deepening of color from white to yellow to golden yellow and the tendency to display enhanced charge transfer (CT) band in the presence of the same Br^- anions of the electron donor nature. The CT absorption of the monopyridinium EPY·Br in UV-Vis diffuse reflectance spectra was indiscernible, while that of TTEPY·3Br was most intense and broad with a maximum near 365 nm and the threshold at about 800 nm (Fig. 1). The X-ray single-crystal diffraction analysis of TTEPY·3Br revealed that the three pyridinium rings were almost coplanar with the central triazine ring, with an interplanar angle of 8.7° . The bromide anion lies almost perpendicularly below the nitrogen atom of each pyridinium ring with the $\text{Br}\cdots\text{N}1\cdots\text{C}5$ angle of 79.2° and the $\text{Br}\cdots\text{N}1$ distance of 3.83 \AA (Fig. S3†). Such configuration and orientation are typical for the charge transfer bonding of the $\sigma-\pi$ type in bipyridinium salts, supporting the existence of CT interactions in TTEPY·3Br.¹⁵ The cyclic voltammograms of TTEPY·3Br and DEBPY·2Br showed the first-step reduction at -0.51 V and -0.65 V vs. Ag/AgCl , respectively, corresponding to the addition of one electron to each pyridinium derivative, while the reduction of EPY·Br was invisible in the region from -1.2 V to 0.2 V (Fig. S4†). These results also demonstrated a gradually stronger tendency to accept an electron and be reduced from monopyridinium EPY to bipyridinium DEBPY to tripyridinium TTEPY.

Three solid-state compounds do not undergo a significant color change in air atmosphere under light irradiation but present remarkably different photoresponsivities under nitrogen atmosphere. The gold-yellow TTEPY·3Br powder turns green upon the irradiation of 365 nm or 395 nm light, accompanied with the emergence of ESR (electron spin resonance) signal with a g value close to that of a free electron ($g_e = 2.0023$) (Fig. S5a†), which indicates that its photo coloration behavior is related to the generation of free radicals. Such an O_2 -sensitive photo coloration accompanied by the generation of radicals is a typical characteristic of pyridinium derivatives, which involves a photoinduced electron transfer reaction from a donor molecule to a pyridinium acceptor unit.¹⁶ The TTEPY· free radicals are not stable and can be quickly quenched to return to the original gold yellow pyridinium state upon exposure to air for a few seconds, demonstrating the excellent reversibility of the O_2 -dependent redox process. This attribute should be beneficial to the high-performance recovery of the electron transfer catalyst and utilization of oxygen. Under the same O_2 -free conditions, the compounds DEBPY·2Br and EPY·Br do not show perceptible color evolution and ESR

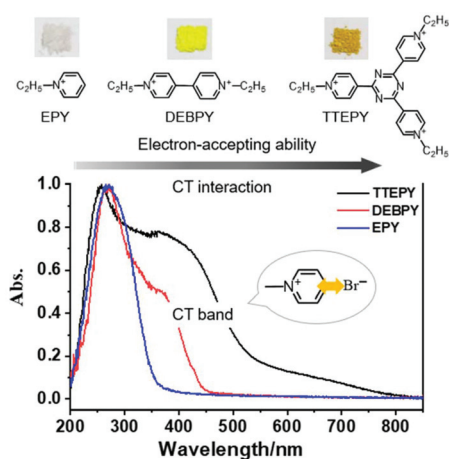


Fig. 1 The structural adjustment and color change of the pyridinium-based photocatalysts with different electron-accepting abilities (top), and their UV-Vis diffuse reflectance spectra (bottom).

signals (Fig. S5b and S5c†), revealing that large-conjugated polypyridinium TTEPY is more efficient in light utilization and photoinduced electron transfer than mono- and bi-pyridinium derivatives.

The ability of pyridinium molecules to mediate electron transfer and activate oxygen was evaluated by the selective oxidation of alcohols. Among three compounds (Fig. 2), TTEPY·3Br showed excellent catalytic performance, achieving high reactivity and selectivity in the aerobic oxidation of 1-phenylethanol under mild reaction conditions. The conversion yield of 1-phenylethanol into acetophenone in acetonitrile reached 87% after 2 h irradiation from a LED 395 nm light source (450 mW) with greater than 99% selectivity towards the desired product. This yield was much higher than that of DEBPY·2Br (40%), EPY·Br (trace amount) and unsubstituted 2,4,6-tris-(4-pyridyl)-1,3,5-triazine (trace amount), demonstrating a close relationship between the photocatalytic performance and electron-accepting ability. It should be specially stated that the reaction was carried out without any external oxidant and heating device, except ambient air and light irradiation at room temperature. If the irradiation time or light intensity was doubled, the yield could easily reach 99% with equally high selectivity for TTEPY·3Br.

The TTEPY-mediated photocatalytic aerobic oxidations of alcohols are broad-spectrum efficient. The selectivity of the primary benzylic alcohols was less than satisfactory under the irradiation of 395 nm light (Fig. S6†), but when white light was used, the oxidation of primary benzylic alcohols to acid could be depressed clearly (Fig. S7†) to give both the conversion and selectivity of above 90% for the transformation of alcohols into aldehydes (Table 1). However, the conversion and selectivity of primary aliphatic alcohols, such as 1-octanol, are low, whether a 395 nm light or a white light is used (Table S1†). For the secondary alcohols, the irradiation of 395 nm light can increase the conversion considerably but does not diminish the selectivity towards the desired product. Most of the substituted secondary benzylic alcohols can be completely oxidized to the corresponding ketones under the same mild conditions with excellent selectivity (>99%) within 4 h, and secondary hetero-aromatic or polycyclic aromatic alcohols are also converted in

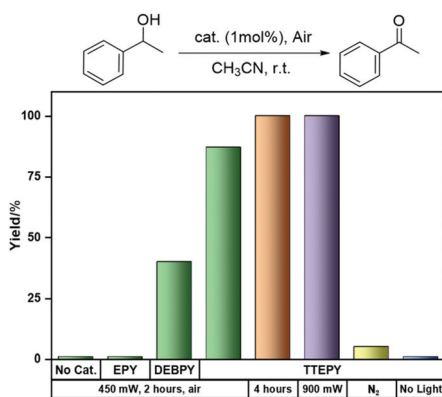


Fig. 2 Control experiments for the oxidation of 1-phenylethanol.

Table 1 General substrate scope for the oxidations of alcohols

| Entry | Substrate | Product | Time/h | Conv. ^d /% | Sel. ^d /% |
|------------------|-----------|---------|--------|-----------------------|----------------------|
| 1 ^{a,e} | | | 4 | >99 | >99 |
| 2 ^{a,e} | | | 4 | >99 | >99 |
| 3 ^{a,e} | | | 6 | >99 | >99 |
| 4 ^{a,e} | | | 4 | >99 | >99 |
| 5 ^{a,e} | | | 8 | 93 | >99 |
| 6 ^b | | | 12 | 63 | >99 |
| 7 ^b | | | 12 | 71 | >99 |
| 8 ^b | | | 12 | 70 | >99 |
| 9 ^b | | | 12 | 54 | >99 |
| 10 ^c | | | 4 | 93 | 93 |
| 11 ^c | | | 3 | >99 | 98 |
| 12 ^c | | | 3 | 94 | 94 |
| 13 ^c | | | 3 | 94 | 92 |
| 14 ^c | | | 3 | 91 | 99 |
| 15 ^c | | | 5 | 90 | 94 |
| 16 ^c | | | 6 | 92 | 91 |
| 17 ^c | | | 8 | 94 | 94 |

^a Irradiation with the 395 nm light source (450 mW). Substrate: 0.2 mmol, 1 mol% TTEPY·3Br, 2 mL acetonitrile, in the air. ^b The same reaction condition as footnote (a) except the irradiation with double 395 nm light sources (900 mW). ^c Irradiation with a white light source (180 mW). Reaction conditions: substrate 0.1 mmol; catalyst: 2 mol%, 2 mL acetonitrile, in the air. ^d Determined by GC analysis. ^e Confirmed by ¹H NMR and ¹³C NMR after isolation.

high yields (Table 1). However, strong electron-withdrawing substituents have a demonstrable effect. A longer irradiation time is needed for 1-(4'-fluorophenyl)-ethanol (6 h) and 1-(2-pyridyl)-ethanol (8 h) than 1-(4'-chlorophenyl)-ethanol. Attractively, TTEPY·3Br also has good catalytic performance for secondary aliphatic alcohols. The straight-chain alcohols, 5-nonanol and 2-octanol, showed yields of 63% and 71% in the conversion into corresponding ketones under the irradiation of double light intensity (900 mW). The secondary aliphatic alcohol was relatively difficult to be oxidized by common catalysts, such as noble metal nanoparticles, g-C₃N₄ materials, transition metal complexes, *etc.*, which often cannot afford the acetophenone derivative or show very low yield under routine experimental conditions.¹⁷ Additional oxidants such as H₂O₂,¹⁸ TBHP,¹⁹ NaIO₄,²⁰ H₅IO₆,²¹ and Ce(IV) complex²² are generally needed, and thus increase several disadvantages, such as expensive consumption of energy and

resources, experimental or environmental hazards. Compared with TEMPO that is a typical and corrosive organocatalyst for the selective oxidations of aromatic alcohols,²³ and fluorenone derivatives that involve the additional consumption of DMSO and the formation of byproduct DMSO₂ during the oxidation reaction,⁷ the current catalytic system is more simple, mild, low cost, highly efficient and environmentally friendly. Owing to the excellent ability of pyridinium derivatives in accepting electrons and activating oxygen molecules, the conversion of amines and thioethers can also be promoted, and further work is in progress.

Light and electron transfer catalyst are indispensable for the oxidation reactions, as evidenced by the scarcely detectable acetophenone in the absence of these conditions. When the photocatalytic reaction was carried out in the N₂ atmosphere, the dramatically lowered conversion of 1-phenylethanol to acetophenone confirmed the essential role of molecular oxygen (Fig. 2). To clarify whether the active oxygen species were actually generated in our system, a series of quenchers including *tert*-butanol, benzoquinone, AgNO₃, catalase and NaN₃ were used (Fig. 3) to specifically inhibit the generation of [•]OH, [•]O₂⁻, electron, H₂O₂ and ¹O₂, respectively.⁷ The experimental results showed that the addition of *tert*-butanol almost has no effect on the reaction, which eliminates the role of hydroxyl radicals in the reaction. However, the addition of benzoquinone and AgNO₃ has a strong inhibitory effect, suggesting that the superoxide radicals are responsible for the oxidation of alcohols and the electron transfer process should be dominantly involved during the photocatalytic reaction. A slight decrease in conversion detected in the reaction containing catalase indicates that H₂O₂ may be generated and contributed to the alcohol oxidation as an oxidant,²⁴ but it was not dominant. Remarkably, the application of NaN₃ also causes obvious suppressed oxidation, demonstrating that singlet oxygen may be generated, and play a significant role in the reaction.

No color development and UV-Vis spectral change could be observed for the MeCN solution of TTEPY·3Br upon light irradiation (Fig. S8[†]), except a tiny light-induced ESR signal that appeared under the N₂ atmosphere, but vanished quickly after stopping the irradiation and exposing it to air (Fig. S9a[†]).

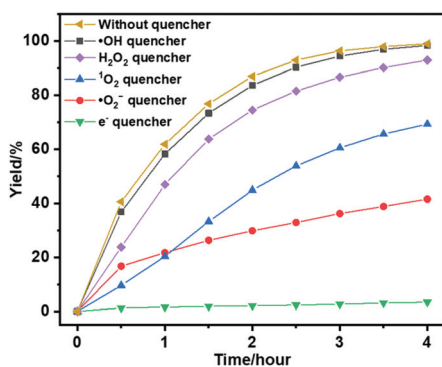


Fig. 3 Oxidation of 1-phenylethanol in the presence of different quenchers.

This observation indicates that the photoinduced electron transfer between TTEPY and the Br⁻ anion was severely weakened in the solution. In the presence of 1-phenylethanol and light irradiation, the N₂-saturated colorless TTEPY·3Br solution quickly turned to yellow and finally to green within 5 min, giving rise to broad absorption bands centered at 405, 598 and 730 nm (Fig. 4a). When placed in dark, the green color of this solution could be kept for a long time but rapidly faded upon exposure to air. A strong symmetric singlet ESR signal with a *g* value of 2.0029 was detected in the green solution (Fig. S9b[†]) but disappeared with the bleaching of the green solution. Such oxygen-sensitive coloration behavior and ESR response are characteristic of pyridinium derivatives, which typically accept electrons to be reduced to colored pyridinium radicals and reversibly revert to their initial state by reacting with O₂. These facts demonstrate that the alcohols dominantly participated in the photoinduced electron transfer reaction as electron donors and contributed to the formation of TTEPY[•] radicals. It was noted that the photoinduced color change in the air-saturated solution of TTEPY·3Br and 1-phenylethanol was not obvious (the inset in Fig. 4b), but a similar ESR signal could be detected (Fig. S9c[†]), and this signal was much weaker than the observation for the N₂-saturated solution of TTEPY·3Br and 1-phenylethanol. Such a result indicates that the TTEPY[•] radical still can be photogenerated in an air-saturated solution, but a rapid electron transfer from TTEPY[•] to O₂ occurred concomitantly to decrease its concentration. This process enables TTEPY as an electron transfer catalyst to mediate the photocatalytic reaction in a highly efficient way. A shoulder peak corresponding to the R absorption band of the acetophenone grows remarkably in the UV-vis spectra of the

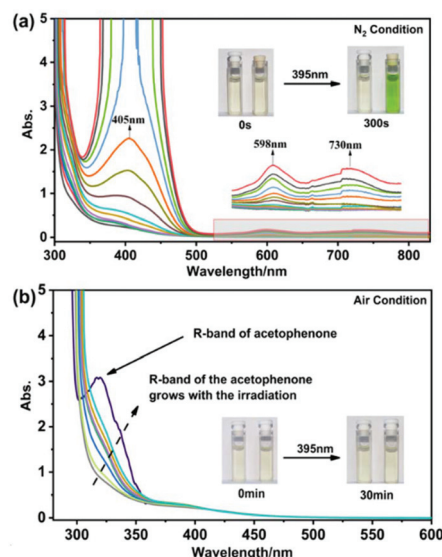


Fig. 4 (a) UV-Vis spectra of TTEPY·3Br and 1-phenylethanol in the MeCN solution and N₂ atmosphere under 395 nm light irradiation. (b) UV-vis spectra of TTEPY·3Br and 1-phenylethanol in the MeCN solution and air atmosphere under 395 nm light irradiation. The sample cell on the left in each photo is a reference sample without irradiation.

air-saturated solution of TTEPY·3Br and 1-phenylethanol (Fig. 4b), confirming the continuous and efficient running of photocatalytic reactions. Under the N₂ atmosphere, the regeneration of TTEPY was blocked and thus resulted in a low catalytic performance (5%, Fig. 2), indicative of the crucial role of oxygen molecules. In the same reaction conditions, the detected ESR signal intensities from TTEPY·3Br to DEBPY·2Br to EPY·Br were gradually diminishing, corresponding with their electron-accepting abilities and photocatalytic activities (Fig. S10†). The pyridinium molecule with larger π -conjugation and a more positively skeleton can significantly improve the photoinduced electron transfer performance and thus facilitate the photocatalytic conversion.

To further validate the generation of active oxygen species, ESR spin trapping experiments have also been carried out (Fig. 5). A complicated superposition signal of the alkoxy radical, superoxide radical, and TTEPY' radical appeared in the air-saturated solution of TTEPY·3Br and 1-phenylethanol by adding 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a trapping agent, and the signal could disappear in the presence of a SOD quencher. Such a situation revealed the occurrence of multiple reactions involving the excited TTEPY* receiving an electron from the alcohol to leave the alkoxy and TTEPY' radicals, while O₂ captures an electron from the TTEPY' radical to yield $\cdot\text{O}_2^-$. Remarkably, for the irradiation of this catalytic system in the presence of 2,2,6,6-tetramethyl piperidine, TEMP, (a specific probe for singlet oxygen), only a weak ESR signal resembling that of TTEPY' radical could be detected (Fig. S11†). However, in an alcohol-free system, the quartet signals appeared, and these signals significantly faded into singlet signals when additional NaN₃ was added, accompanied by a disappearance of a 1 : 1 : 1 triplet characteristic of TEMPO, a reaction product of $^1\text{O}_2$ and TEMP. This observation together with the scavenging experiment showed that an active $^1\text{O}_2$ was indeed formed in the reaction system, and the energy transfer between the excited state of TTEPY* and $^3\text{O}_2$ should be responsible for the generation of $^1\text{O}_2$. The remaining singlet signals

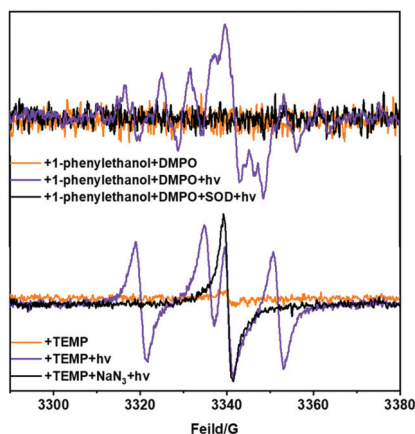


Fig. 5 ESR spectra of the samples after mixing DMPO or TEMP with TTEPY·3Br and in the absence or presence of 1-phenylethanol, SOD and NaN₃ before and after 395 nm irradiation.

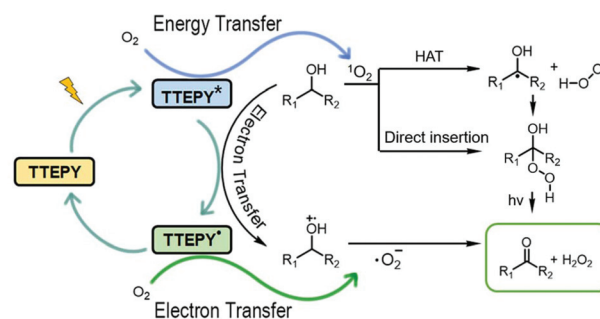


Fig. 6 Proposed mechanism of the photocatalytic aerobic oxidation of alcohols mediated by the pyridinium derivatives.

may have originated from the contribution of the TTEPY' radicals. $^1\text{O}_2$, as a mild and efficient oxidant, has proven to be a versatile reactive oxygen species with applications in multiple organic transformations, including the oxidation of alcohols. Numerous photosensitizers, such as metal nanoparticles, porphyrins and their derivatives, have been explored to generate $^1\text{O}_2$.²⁵ However, the direct observation and application of $^1\text{O}_2$ generated by pyridinium derivatives are rarely reported. Such an O₂ activation reaction provides a synergistic enhancing effect to facilitate the photocatalytic aerobic oxidation of alcohols with high-performance at mild conditions.

From the above-mentioned photophysical and photochemical studies, the aerobic oxidation of alcohols mediated by the pyridinium derivatives was considered to have mainly proceeded by the following mechanism (Fig. 6): under light irradiation, the initial TTEPY transits to the excited-state of TTEPY*, which can capture the electrons of alcohol to convert themselves into a free radical state (TTEPY') via electron transfer,^{14d} and simultaneously transform some $^3\text{O}_2$ to active oxygen $^1\text{O}_2$ by energy transfer. The free radical state of TTEPY' was oxidized back to the initial state by air O₂, completing the electron transport and producing $\cdot\text{O}_2^-$.¹² The single oxygen could interact with an alcohol to form a peroxy hemiacetal intermediate through direct insertion on the carbon atom bearing the hydroxyl group, or a two-step process involving hydrogen atom transfer (HAT) and quick radical recombination, and then collapses to give the product.^{7,10} The combined action of $^1\text{O}_2$ and $\cdot\text{O}_2^-$ facilitate alcohols to be oxidized to the carbonyl compounds, leaving H₂O₂ as a side product that may make some additional contribution in alcohol oxidation, as evidenced by a control experiment with catalase as the H₂O₂ scavenger (Fig. 3). The formation of H₂O₂ can be determined by the titration experiment with the NaI aqueous solution, which causes the reaction solution to turn yellow and exhibit a broad absorption band at $\lambda_{\text{max}} = 360$ nm, typical for triiodide in the solution (Fig. S12†).

Conclusions

In summary, the metal-free photocatalytic oxidation of alcohols to carbonyl compounds under an air atmosphere at room temperature without any noble metals and additional co-cata-

lysts/additives has been developed by using pyridinium-based photocatalysts. Both superoxide radical and singlet oxygen active species were generated and collaboratively contributed to the photocatalytic reactions with excellent efficiency and good substrate application range from aromatic alcohols to aliphatic analogs that are generally difficult to undergo aerobic oxidation under mild conditions. The current metal-free photocatalytic system has the advantages of low cost, easy availability and high efficiency, representing an ideal photocatalytic platform for green and economical organic syntheses.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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