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Pyrenediones as versatile photocatalysts for oxygenation reactions with *in situ* generation of hydrogen peroxide under visible light†

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Pyrenediones (PYDs) are efficient photocatalysts for three oxygenation reactions: epoxidation of electron deficient olefins, oxidative hydroxylation of organoborons, and oxidation of sulfides *via in situ* generation of H_2O_2 under visible light irradiation, using oxygen as a terminal oxidant and IPA as a solvent and a hydrogen donor.

Oxygenation reactions are of crucial importance in the syntheses of fine chemicals, natural products, and pharmaceutically active molecules.[1–3] The preparation of O-containing molecules in a highly selective, environmentally friendly, and sustainable manner is challenging in both laboratory and industrial settings. Light-induced oxygenation (or photooxygenation) using molecular oxygen as a stoichiometric oxidant is appealing compared to the conventional use of strong oxidants, such as hydrogen peroxide (H_2O_2), ozone, hypervalent iodine, and *tert*-butyl hydroperoxide (TBHP), which is usually associated with the risk of explosion and adverse environmental impact. In general, photooxygenation with O_2 could be accomplished through two pathways, namely singlet oxygen ($^1O_2$) generated *via* energy transfer from $3O_2$[4] or a superoxide radical anion ($O_2^{•-}$) and hydrogen peroxide (H_2O_2) produced *via* a single electron transfer (SET) process.[5] Appropriate choice of the photocatalytic system is the key to achieve efficient incorporation of an oxygen atom from molecular oxygen. Thus, a great number of photocatalysts have been developed for this purpose, the majority of which are transition-metal catalysts[6–8] and inorganic semiconductors.[9,10]

In the field of photocatalysis, metal-free organophotocatalysts have recently gained momentum because they are more environmentally benign than metal catalysts.[11–13] In particular, Zhang[14] and Chen[15] groups have reported rose Bengal-mediated oxidative hydroxylation of organoborons with *in situ*

generated H_2O_2. Photocatalytic hydroxylation of alkenes and sulfide oxidation were achieved by using 9-mesityl-10-methyl-acridinium ions (Acr[+]-Mes) or rose Bengal.[16,17] However, most of these approaches require sacrificial electron donors or additives to complete the photocatalytic cycle. Therefore the development of organophotocatalysts for versatile oxygenation reactions with a milder and more economical protocol is still highly desired. Notably, Itoh and co-workers have disclosed elegant studies on H_2O_2 generation using anthracene or anthraquinone as a photocatalyst by aerobic photo-oxidation of IPA, which was further applied for the efficient synthesis of *gem*-dihydroperoxides,[18,19] epoxidation of unsaturated ketones,[20] and oxidation of arylboronic acids.[21]

We were intrigued by conjugated molecules containing the quinone hydroquinone-like redox system that absorbs visible light,[22] which may act as photocatalysts for hydrogen atom transfer.[11] One family of such molecules is pyrenedione (PYD). Two isomers 1,6-PYD and 1,8-PYD were conveniently prepared by directly oxidizing pyrene using potassium dichromate (Fig. 1a).[23] With the extended conjugated structure, both isomers exhibited strong absorption bands in the visible region (λ_{max} = 428 and 461 nm, ε = 8.3 × 10³ M⁻¹ cm⁻¹ and 6.1 × 10³ M⁻¹ cm⁻¹, respectively, Fig. 1b). Cyclic voltammetry (CV) scans revealed two half wave potentials at −0.30 V and −0.52 V for 1,6-PYD and −0.35 V and −0.59 V for 1,8-PYD, indicating their ability to undergo two electron reductions (Fig. 1c). Peaks **Ia/Ic** and **IIa/IIc** correspond, respectively, to the reversible redox couples of pyrenedione/radical anion (1,6-PYD/1,6-PYD$^{•-}$) and radical anion/dianion (1,6-PYD$^{•-}$/1,6-PYD^{2-}). The same phenomenon applies to 1,8-PYD. The excited state reductive potentials ($E_{1/2}$ (P*/P$^{•-}$)) were calculated to be 2.28 V for 1,6-PYD and 2.12 V for 1,8-PYD based on the Rehm–Weller equation (see Tables S1 and S2 for details†). The high oxidizing ability of their excited states enables them potentially efficient hydrogen abstractors. The excited state lifetime of one isomer, 1,8-PYD, has been reported to be 29 μs (benzene), which is sufficient for the following hydrogen atom transfer (HAT) process.[24]

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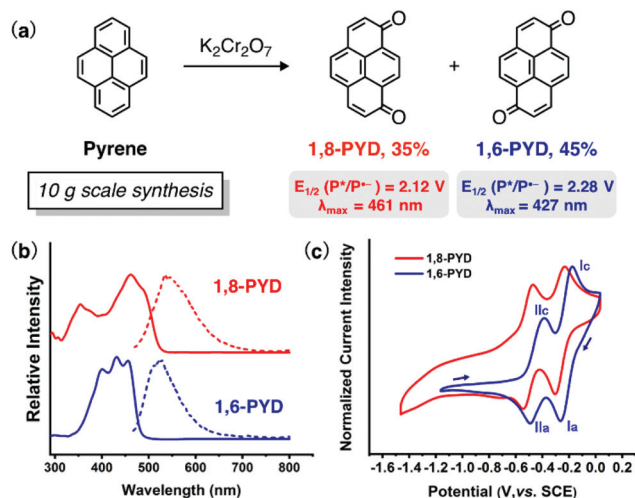
Fig. 1 (a) Preparation reaction of 1,6-PYD and 1,8-PYD. (b) Normalized UV-Vis absorption (solid) and fluorescence emission spectra (dash) of 1,8-PYD and 1,6-PYD in MeCN/THF (1/1). (c) Cyclic voltammetry of 1,8-PYD and 1,6-PYD with a scan rate of 100 mV s^{-1} in MeCN. $E_{1/2}$ (P*/P$^{•-}$) represents the excited state reductive potential.
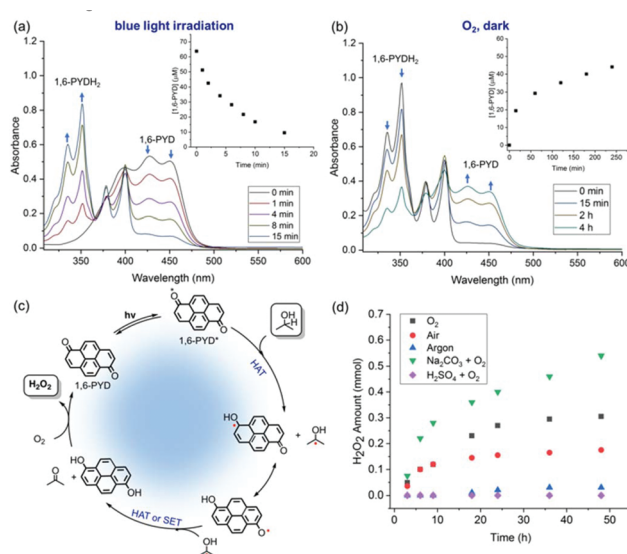

Fig. 2 (a) Changes of the UV-Vis absorbance spectra of 1,6-PYD (64 µM) with IPA (100 mM) in deaerated MeCN under 18 W blue LED light. Concentration of 1,6-PYD over time (Inset). (b) Changes in the UV-Vis absorbance spectra of 1,6-PYDH$_2$ (60 µM) in MeCN under an aerobic atmosphere in the dark. Concentration of 1,6-PYD over time (Inset). (c) Proposed photocatalytic cycle of 1,6-PYD-promoted H$_2$O$_2$ generation in IPA under an aerobic atmosphere. (d) H$_2$O$_2$ generation under different conditions. Reaction conditions: 1,6-PYD (0.01 mmol), IPA (4 mL), irradiated by an 18 W blue LED strip. The H$_2$O$_2$ amount was determined by iodometric assay.

Upon irradiation of a solution of 1,6-PYD in IPA using an 18 W blue LED strip for 10 min, the yellowish solution turned colourless (Fig. S1†). The dynamic photochemical reaction of 1,6-PYD and IPA was monitored by UV-Vis spectra. Irradiation of deaerated acetonitrile (MeCN) solution containing 1,6-PYD and IPA with an 18 W blue LED strip at room temperature resulted in decreased absorbance at 457 nm and 428 nm and in the appearance of new absorption bands at shorter wavelengths (Fig. 2a). ^{1}H-NMR and HRMS-ESI spectra revealed the product to be 1,6-pyrenediol (1,6-PYDH$_2$).

Mechanistically, the process likely started from the photoexcited 1,6-PYD accepting sequentially two hydrogen atoms from IPA, which was converted to acetone (Fig. 2c and Fig. S2†). Molecular oxygen then acted as the hydrogen acceptor and was converted to hydrogen peroxide, confirmed by iodometric experiments and ^{1}H-NMR spectra (Fig. S3†), to complete the catalytic cycle. The oxidation of 1,6-PYDH$_2$ to 1,6-PYD was feasible due to the low oxidative potential of 1,6-PYDH$_2$ ($E_{1/2}$ = +0.50 V vs. SCE, Fig. S4†). An irreversible electrochemical behaviour of 1,6-PYDH$_2$ is shown in Fig. S4,† which corresponded to the two electron oxidation to [1,6-PYDH$_2$]$^{2+}$.[25] The different shapes of 1,6-PYDH$_2$ and 1,6-PYD were due to the influence of the protons in 1,6-PYDH$_2$, because the CV of 1,6-PYD in the presence of excess amounts of acids, shows only one oxidation peak similar to that of 1,6-PYDH$_2$ (Fig. S4†). An analogous situation has been observed with anthraquinone.[26] The changes in the UV-Vis spectra of 1,6-PYDH$_2$ was observed in aerobic MeCN in the dark (Fig. 2b). The peak at 457 nm increased over time, suggesting the formation of 1,6-PYD. Alternative to a second HAT, the possibility of two mono-reduced pyrenedione radicals undergoing disproportionation to give PYD and PYDH$_2$ cannot be ruled out. Several control experiments were performed (Table S3†). Significantly

decreased yield of H$_2$O$_2$ in the presence of 2,2,6,6-tetramethyl-piperidin-1-oxyl (TEMPO) supported a radical process. Addition of a singlet oxygen quencher, NaN$_3$, only gave a slightly decreased yield of H$_2$O$_2$, thus excluding the energy transfer pathway.[27]

It was observed that the H$_2$O$_2$ amount increased over time under an oxygen atmosphere (Fig. 2d). The amount of H$_2$O$_2$ generated increased 52% after 48 hours of irradiation by the addition of aqueous Na$_2$CO$_3$ solution (TON = 54). This could be explained by the deprotonation of 1,6-PYDH$_2$ in alkaline solution and the anion species formed is more prone to be oxidized by oxygen. The H$_2$O$_2$ production rate in the presence of a base was calculated to be 6.75 mM h^{-1} within the first 10 hours. Nearly no H$_2$O$_2$ was detected when H$_2$SO$_4$ was added. The H$_2$O$_2$ generation in an air atmosphere was less efficient than that in an oxygen atmosphere. A negligible amount of H$_2$O$_2$ was detected when the reaction was conducted under argon. The industrial production of H$_2$O$_2$ is currently based on the anthraquinone oxidation (AO) process in which hydrogen gas and oxygen in air are reacted indirectly in the presence of anthraquinone to yield H$_2$O$_2$, which is further extracted with water to obtain 30–37% H$_2$O$_2$ solution.[28,29] Although economical and relatively stable, aqueous solution of H$_2$O$_2$ is not always ideal for organic reactions and the high concentration of H$_2$O$_2$ may cause side-reactions. Our method provides a mild pathway for the slow release of H$_2$O$_2$ with IPA as the solvent.

Making use of the *in situ* generated H_2O_2 by the 1,6-PYD/ IPA photocatalytic system, we achieved several environmentally benign oxidative transformations. Our initial study found that the epoxidation of electron deficient alkene **1a** in IPA with 5 mol% 1,6-PYD under blue LED irradiation in an oxygen atmosphere delivered epoxide **2a** in 68% yield after 24 h (Table 1, entry 1). Prolonging the reaction to 48 h afforded excellent yield (93%, entry 2). The reaction was less effective in air (entry 3). Increasing the temperature to 50 °C resulted in a decreased yield of the product, which was likely attributed to the instability of epoxide **2a** (entry 4). Decreasing the loading of the photocatalyst to 2.5 mol% or 1 mol% afforded much lower product yields (55% and 45%, respectively, Table S6†). The screening of several alcohols as solvent indicated the decreased hydrogen donating ability from secondary alcohols to primary alcohols (entries 6–8, Fig. S5†). A negligible amount of **2a** was observed in *tert*-butanol due to the absence of hydridic proton (entry 9). Control experiments confirmed that oxygen, light and photocatalyst were all essential for an efficient transformation (entries 5, 10, and 11). Several other common photocatalysts were also evaluated (Table S4†). No epoxide product was formed with eosin Y and $[Ru(bpy)_3]^{2+}$, and only moderate yields of the products were obtained with anthraquinone as the photocatalyst. Both 1,6-PYD and 1,8-PYD afforded excellent yields (93% and 90%, respectively). Due to the better isolation yield of 1,6-PYD (Scheme 1a), it was utilized as the photocatalyst in our subsequent studies.

To rule out the possibility of singlet oxygen as the reactive oxygen species (ROS) in this reaction process, $^1O_2$ quenching experiment was conducted (see the ESI†). In the presence of NaN_3, a commonly used singlet oxygen quencher,[14] the epoxi-
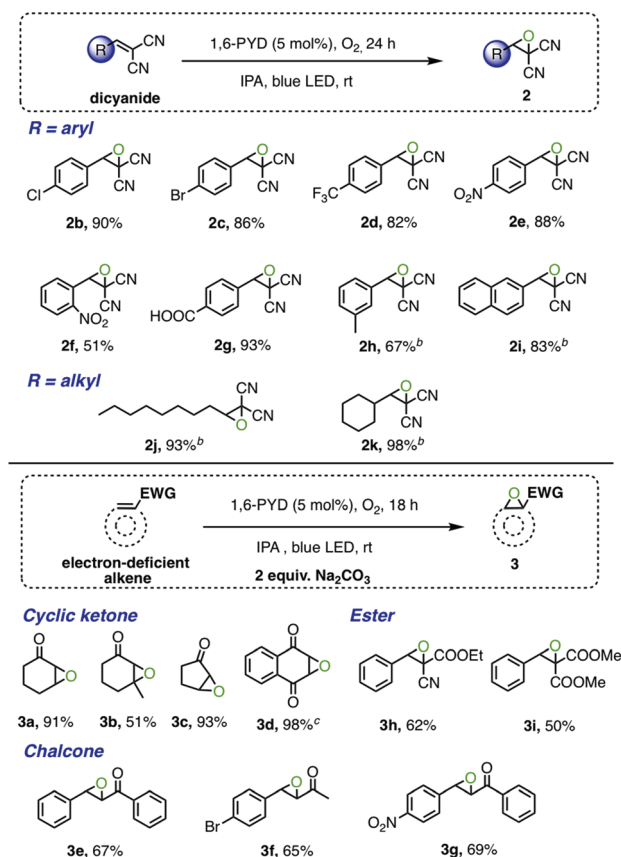
Scheme 1 . Substrate scope of epoxidation with electron-deficient alkenes[a]. Reaction conditions: dicyanide (0.2 mmol), 1,6-PYD (0.01 mol, 5 mol%), IPA (4 mL), irradiated by a blue LED strip under an oxygen atmosphere at room temperature for 24 h. Unsaturated ketone (0.2 mmol), 1,6-PYD (0.01 mmol, 5 mol%), IPA (4 mL), aqueous Na_2CO_3 solution (1 mmol mL^{-1}, 0.4 mL), irradiated by a blue LED strip under an oxygen balloon at room temperature for 18 h. [a]Isolated yields. [b]Reaction time was 40 h instead of 24 h. [c]Na_2CO_3 powder was added.

Table 1 Optimization of alkene epoxidation[a]

Entry	Solvent	Atmosphere	Time (h)	Yield[b] (%)
1	IPA	O_2	24	68
2	IPA	O_2	48	93
3	IPA	Air	48	62
4[c]	IPA	O_2	48	60
5	IPA	Argon	48	13
6	MeOH	O_2	24	0
7	EtOH	O_2	24	21
8	*n*-Butanol	O_2	24	21
9	*tert*-Butanol	O_2	48	Trace
10[d]	IPA	O_2	48	0
11[e]	IPA	O_2	48	0

[a] Reaction conditions: **1a** (0.2 mmol), 1,6-PYD (0.01 mmol, 5 mol%), solvent (4 mL), irradiated under an 18 W blue LED strip at room temperature. [b] Yields were determined by the ^{1}H-NMR spectra of the crude product using 1,3,5-trimethoxybenzene as an internal standard. [c] Reaction performed at 50 °C. [d] Without light. [e] Without photocatalyst.

dation was still efficient (80% yield). This excluded the energy transfer process from excited PYD to $^3O_2$. In contrast, a small amount of epoxide **2a** was obtained in the presence of 1,4-benzoquinone, a superoxide quencher,[30] suggesting that the formation of a superoxide radical was crucial for the reaction to take place.

With the optimized reaction conditions in hand, the scope for epoxidation of various electron-deficient alkenes was evaluated (Scheme 1). As shown in Scheme 1a, 1,6-PYD effectively promoted the epoxidation of methylene-malono-nitriles bearing a phenyl or alkyl group with good to excellent yields (51% to 98%, **2b–2k**). Functionalities including chloride, bromide, trifluoromethyl, and nitro compounds and acids were well-tolerated under the reaction conditions. However, no epoxidation product was observed with weaker Michael acceptors such as 2-cyclohexen-1-one. We envisioned that a base might be required to promote the formation of hydroperoxide anions, which would facilitate the nucleophilic addition to alkenes.[31] Indeed, in the presence

of 2 equivalents of sodium carbonate, the reaction proceeded effectively to afford **3a** in excellent yield (91%) within 18 h. Among the bases screened, Na_2CO_3 was the optimal one (Table S5†) and was employed in the substrate scope study. The photocatalytic protocol was extended to other cyclic ketones, esters and chalcones (**3a–3g**), in each case affording the corresponding epoxides in good yields.

This PYD/IPA photocatalytic system was effective for oxidative hydroxylation of organoborons as well. Phenylboronic acid (**4a**) was converted to the desired phenol **5a** in excellent yield (90%) after 40 h in the presence of 10 mol% PYD and IPA under blue LED irradiation (Table 2, entry 1). Again, light, oxygen and photocatalysts were all essential for this transformation (see the ESI†). Other phenylboronic acids bearing electron-donating or electron-withdrawing substituents (entries 2–6) were all good candidates for this oxidative hydroxylation, affording the corresponding phenols in excellent yields ranging from 90% to 98% (**5b–5f**). Moreover, 1,6-PYD could also effectively promote the hydroxylation of alkylboronic acids and boronic pinacol esters in excellent yields (88–98%, entries 7–10).

Lastly, the ability of 1,6-PYD to catalyse the photo-oxidation of sulfides was investigated. The oxygenation of sulfides through the visible-light-promoted approach has attracted considerable interest in recent years.[32] However, a mixture of sulfoxides and sulfones was normally produced, which caused downstream isolation problems. Notably, oxidation of thioanisole (**6a**) using the 1,6 PYD/IPA photocatalytic system selectively afforded sulfoxide **7a** exclusively in 90% yield after 24 hours (Table 3, entry 1). Oxidation of substrates **6b** and **6c** afforded sulfoxides **7b** and **7c** in good yields, respectively (entries 2–3). An alkyl sulfide such as tetrahydrothiophene (**6d**) was also well-tolerated, and excellent yield of the product was obtained (entry 4).

Table 3 Selective oxidation of sulfides to sulfoxides[a]

6a: R_1 = Ph, R_2 = CH_3
6b: R_1 = 4-BrPh, R_2 = CH_3
6c: R_1 = R_2 = Ph

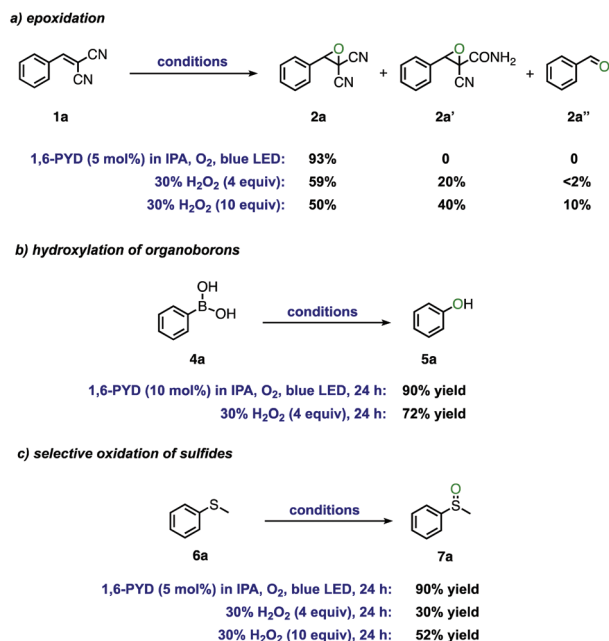| Entry	Substrates	Products	Time (h)	Yield[b] (%)
1	**6a**	**7a**	24	90
2	**6b**	**7b**	24	95
3	**6c**	**7c**	40	75
4	**6d**	**7d**	24	95

[a] Reaction conditions: sulfide (0.2 mmol), 1,6-PYD (0.01 mmol, 5 mol%), IPA (4 mL), irradiated by a blue LED strip under an oxygen atmosphere at room temperature. [b] Isolated yields.

A comparative study of the PYD/IPA photocatalytic system with direct treatment of commercially available 30% H_2O_2 solution as an oxidant was further conducted to demonstrate the merits of our protocol (Scheme 2). Apart from clean epoxidation of alkene **1a** with the photocatalytic method, oxidation of **1a** using 30% of aqueous solution of H_2O_2 gave a complex mixture of products, with hydrolyzed product **2a′** and aldehyde **2a″**being detected, illustrating the side-effect of water content (Scheme 2a). Oxidative hydroxylation of phenylboronic acid **4a** and oxidation of sulfide **6a** with 30% H_2O_2 exhibited lower efficiency compared to the PYD/IPA photocatalytic system (Schemes 2b and c). The superoxide radical anion was formed based on quenching experiments (see the ESI†), which may be another reason for the observed enhanced reactivity associated with the PYD/IPA photocatalytic system (see Scheme S1† for the proposed mechanisms for the three photocatalytic reactions).

Table 2 Substrate scope of the hydroxylation of organoborons[a]

4a: R = H
4b: R = 3-F
4c: R = 4-F
4d: R = 3-OMe
4e: R = 4-OMe
4f: R = 4-F,2-OCH_2CH_3

R = H, 4i
R = 3-F, 4j

Entry	Substrate	Product	Yield[b] (%)	Entry	Substrate	Product	Yield[b] (%)
1	**4a**	**5a**	90	6	**4f**	**5f**	95
2	**4b**	**5b**	90	7	**4g**	**5g**	98
3	**4c**	**5c**	92	8	**4h**	**5h**	88
4	**4d**	**5d**	98	9	**4i**	**5a**	86
5	**4e**	**5e**	98	10	**4j**	**5b**	90

[a] Reaction conditions: boronic acids or boronic acid pinacol esters (0.2 mmol), 1,6-PYD (0.02 mmol, 10 mol%), IPA (4 mL), irradiated by a blue LED strip under an oxygen atmosphere at room temperature for 40 h. [b] Isolated yields.

a) *epoxidation*

1a	**2a** **2a'** **2a''**	
1,6-PYD (5 mol%) in IPA, O₂, blue LED:	93%	0	0
30% H₂O₂ (4 equiv):	59%	20%	<2%
30% H₂O₂ (10 equiv):	50%	40%	10%

b) *hydroxylation of organoborons*

4a	**5a**
1,6-PYD (10 mol%) in IPA, O₂, blue LED, 24 h:	90% yield
30% H₂O₂ (4 equiv), 24 h:	72% yield

c) *selective oxidation of sulfides*

6a	**7a**
1,6-PYD (5 mol%) in IPA, O₂, blue LED, 24 h:	90% yield
30% H₂O₂ (4 equiv), 24 h:	30% yield
30% H₂O₂ (10 equiv), 24 h:	52% yield

Scheme 2 . Comparison studies between the 1,6-PYD/IPA photocatalytic system and commercial 30% H₂O₂ aqueous solution.

Conclusions

In conclusion, we discovered 1,6-PYD as an organophotocatalyst under visible-light irradiation for oxygenation reactions. H₂O₂ was smoothly generated by 1,6-PYD in IPA in the presence of O₂ under visible light, and this catalytic system can be applied to achieve effective epoxidation of electron-deficient alkenes, oxidative hydroxylation of organoborons, and selective oxidation of sulfides to sulfoxides. The results agreed well with those obtained using commercial aqueous H₂O₂. This mild and metal-free protocol, which uses oxygen as a terminal oxidant and IPA as a hydrogen donor and green solvent, is promising for its wide applications in oxidative transformations, especially where the reaction components suffer from poor robustness in the presence of excess H₂O₂ or water.[33]

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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