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Visible-light photocatalytic aerobic oxidation of sulfides to sulfoxides with a perylene diimide photocatalyst†

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Photosensitized oxygenation has been recognised as a modern method of incorporating oxygen into a substrate, as it offers environmentally benign alternatives to several conventional synthetic procedures. A metal-free aerobic selective sulfoxidation photosensitized by a perylene diimide photocatalyst has been developed. The reaction utilizes visible light as the driving force and molecular oxygen as the oxidant. The advantages of the developed method include high efficiency and selectivity, extremely simple operation and work-up procedure, mild reaction conditions, and practical application in late-stage functionalization.

Oxidation is one of the most fascinating organic transformations and has been extensively studied in the past few years.[1] Traditionally, toxic or hazardous oxidizing agents, such as toxic metal oxides and peroxides, in stoichiometric amounts were usually used for these chemical transformations.[2] Therefore, a catalytic, environmentally-friendly, and economical oxidation process is always in demand. Photochemistry is a powerful synthetic technique that can promote various functional group transformations through the use of light as a green[3] and traceless reagent.[4] Visible-light photocatalysis has become a prominent sector of synthetic methodology in the last several years[5] as it offers environmentally benign alternatives to several conventional synthetic procedures.[6] Consequently, photocatalysis has been recognised to comply with the concepts of the *Twelve Principles of Green Chemistry*.[7] Photosensitized oxygenation has been recognised as a modern method of incorporating oxygen into a substrate. Photooxygenation is based on the activation of molecular oxygen by the excited state of a sensitizer. It can occur either by the singlet oxygen or by the electron transfer (ET) mechanism.[8] However, the employment of precious and toxic metals significantly limits its practical application. Owing to its lower cost and wide availability, a metal-free photocatalytic system provides an environmentally friendly alternative synthetic route for selective photocatalytic oxidation under mild conditions.

Chemoselective transformation of sulfides to sulfoxides is of great interest, as many sulfoxides are biologically active compounds often used as pharmaceuticals[9,10] (Fig. 1). Sulfoxidation is also attractive in organic synthesis,[11] fossil fuel desulfurization,[12] industrial wastewater treatment,[13] and chemical warfare agent disposal.[14] Therefore, there is a demand for green and mild methods of sulfide oxidation producing sulfoxides chemoselectively, without overoxidation to sulfones. Traditionally, this oxidation has been achieved under metal catalysis using peroxides or peracids as the oxidants. However, the over-oxidation to sulfones and the safety issues associated with handling peracids[10,15] are the main drawbacks associated with its use in industrial processes. Photosensitized oxidation of sulfides is one promising way to sulfide–sulfoxide transformations, as molecular oxygen is the terminal oxidizing agent.[16–18] Several sensitizers were investigated for the photooxidation of sulphides, involving organic molecules (Fig. 2),[16,18,19] inorganic materials[20] or metal complexes.[17,21] However, most of them produce substantial amounts of byproducts, especially sulfones and aldehydes, as a result of overoxidation or competitive carbon oxidation, respectively. Furthermore, some catalysts are unstable, which makes their use in industrial processes difficult. For these reasons, a more

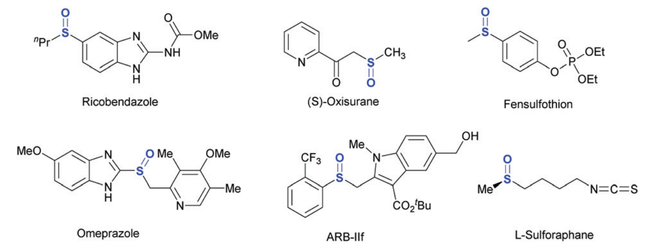

Fig. 1 Biologically active sulfoxide derivatives.

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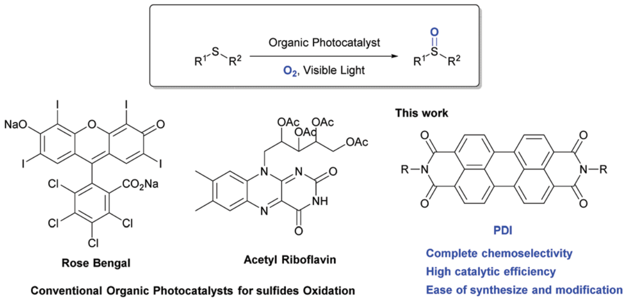
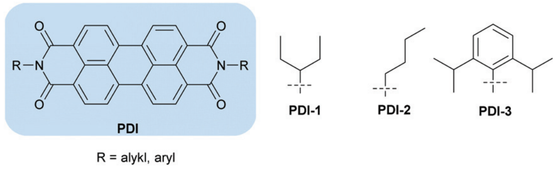


Fig. 2 Visible-light organic photocatalysts for the photooxidation of sulfides.

robust organic photocatalyst which is capable of oxidising a large variety of sulfides is highly desirable.

In the same manner as the π-conjugated polyaromatic molecules, perylene-3,4,9,10-tetracarboxyl disimides (PDIs) have emerged as a class of fluorescent dye molecules because of their tunable absorption and emission features.[22] PDI derivatives find widespread applications in organic photovoltaics,[23] organic field-effect transistors,[24] sensors,[25] bioimaging,[26] and supramolecular assemblies[27] owing to their tunable π-backbone, which is further achieved either by aromatic core extension or expansion. Despite these remarkable properties of PDIs like photosensitization, there is little research on their use as a visible-light-driven photocatalyst for synthetic transformations,[28] in particular, for selective aerobic oxidation. Herein, we report a photooxygenation of sulfides to sulfoxides, mediated by visible light with PDIs as the photocatalyst (Scheme 1).



Scheme 1 PDIs as the photocatalysts for the oxygenation of sulfides to sulfoxides.

Table 1 Optimization of the oxidative reaction conditions[a]

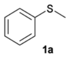
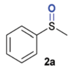
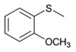
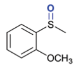
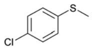
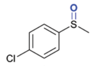
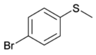
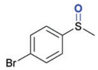
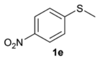
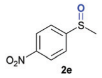
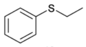
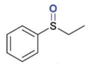
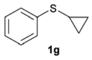
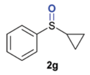
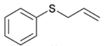
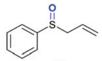
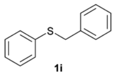
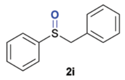
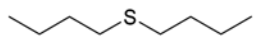
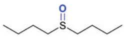
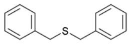
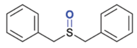
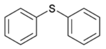
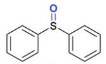
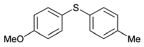
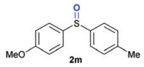
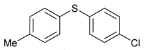
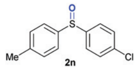
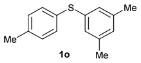
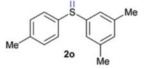
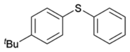
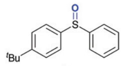
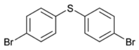
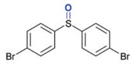
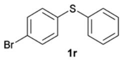
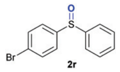
Entry	Catalyst	Solvent	Yield[b] (%)
1	**PDI-1**	DMSO	5
2	**PDI-1**	DMF	18
3	**PDI-1**	CH_3CN	32
4	**PDI-1**	EtOH	20
5	**PDI-1**	CH_3OH	40
6	**PDI-2**	CH_3OH	Trace
7	**PDI-3**	CH_3OH	91
8[c]	**PDI-3**	CH_3OH	82
9[d]	**PDI-3**	CH_3OH	71
10[e]	**PDI-3**	CH_3OH	66
11[f]	**PDI-3**	CH_3OH	78
12[g]	**PDI-3**	CH_3OH	68
13[h]	**PDI-3**	CH_3OH	72
14	**PDI-3**	CH_3OH	20
15[i]	**PDI-3**	CH_3OH	Trace
16[j]	**PDI-3**	CH_3OH	Trace

[a] All reactions were carried out on a scale of 0.5 mmol of **1a** in 2 mL of solvent under visible light at room temperature equipped with an oxygen balloon. [b] Yields of the isolated product. [c] 1 mol% of **PDI-3** as a catalyst. [d] 0.5 mol% of **PDI-3** as a catalyst. [e] 5 W green LED as the light source. [f] 15 W CFL as the light source. [g] Air as an oxidant. [h] DTBP as an oxidant. [i] Without light. [j] Under a nitrogen atmosphere.

We commenced our study by exploring the oxidation of thioanisole (**1a**) with 2 mol% of **PDI-1** under visible light (5 W blue LED) for 10 h under an oxygen atmosphere at room temperature (Table 1). The reaction was first conducted in DMSO, but the desired product was formed only in a negligible amount (entry 1). Solvent optimization was performed and the results indicated that solvents play an important role in the oxidation reactions (entries 2–5). The use of solvents such as DMF, CH_3CN and EtOH afforded products in low yields (entries 2–4), but CH_3OH delivered the highest conversion (40%) after 10 h at room temperature (entry 5). Next, screening experiments were conducted to determine the effect of photosensitizer PDIs with different substituents on amides (entries 6 and 7). **PDI-3** with diisopropyl on the benzyl ring, which has better solubility in CH_3OH than **PDI-1**, gave the highest conversion (91%) and selectivity (100%) (entry 7). No over-oxidation was observed. Another PDI derivative **PDI-2** was also examined as the photocatalyst in this reaction and a trace amount of product was obtained (entry 6) because of its extremely weak solubility and UV–Vis absorption in MeOH (see the ESI†). A decrease in the amount of catalyst leads to a decrease in yield (entries 8 and 9). The effect of the light source was also optimized and a blue LED performed as the most excellent light source compared with green LED light and a CFL (compact fluorescent lamp) (entries 10 and 11). Although **PDI-1** and **PDI-3** exhibit the maximum absorption at 520 nm, three absorption peaks (450, 470, and 520 nm) exist in the spectra. The higher yield obtained with a blue LED may be attributed to the wide absorption range of **PDI-3**. Air and DTBP were also tested as the oxidants and lower yields were obtained compared with O_2 (entries 12 and 13). The control experiments showed that no reaction proceeded in the absence of either **PDI-3** (entry 14), light (entry 15) or even O_2 (entry 16).

Having established optimal reaction conditions, we investigated the substrate scope of this procedure using 2 mol% of **PDI-3** as the catalyst under an oxygen atmosphere at room temperature and by photoirradiation with a 5 W blue LED (Table 2). The results demonstrate that alkyl aryl thioethers (**1a–1i**), dialkyl thioethers (**1j–1k**) and diphenyl thioethers (**1l–1r**) almost uniformly afforded good yields and selectivity. Substituted thioanisoles containing electron-donating or electron-withdrawing groups at the aryl moiety (**1a–1e**) were all oxidized, but for the electron-deficient aryl groups, longer reaction times were needed to obtain high conversions (**1c–1e**).

Table 2 PDI-catalyzed selective photooxidation of sulfides[a]

Entry	Substrate	Product	Time (h)	Yield[b] (%)
1	 **1a**	 **2a**	16	91
2	 **1b**	 **2b**	14	68
3	 **1c**	 **2c**	14	82
4	 **1d**	 **2d**	14	85
5	 **1e**	 **2e**	16	79
6	 **1f**	 **2f**	12	89
7	 **1g**	 **2g**	11	75
8	 **1h**	 **2h**	12	79
9	 **1i**	 **2i**	10	92
10	 **1j**	 **2j**	8	95
11	 **1k**	 **2k**	8	90
12	 **1l**	 **2l**	12	78
13	 **1m**	 **2m**	12	81
14	 **1n**	 **2n**	12	77
15	 **1o**	 **2o**	12	87
16	 **1p**	 **2p**	12	83
17	 **1q**	 **2q**	12	72
18	 **1r**	 **2r**	12	70

[a] All reactions were carried out using **1** (0.5 mmol) and 2 mol% of catalyst **PDI-3** in 2 mL of CH_3OH under blue LED irradiation. [b] Isolated yields.

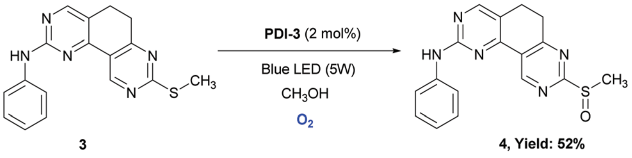
Additionally, the Cl and Br groups were well tolerated in this reaction (**1c** and **1d**), providing the possibility for further functionalization. Moreover, sterically hindered *ortho*-substituted thioanisole **1b** was oxidised to sulfoxide **2b**, albeit with longer times and lower yield. The oxidation of sulfides containing other alkyl groups, instead of a methyl group, was also possible (**1f–1i**). Ethyl, cyclopropyl, allyl or benzyl sulfides were also oxidized in good yields, without the detection of benzaldehydes, sulfones or unidentified by-products, as was found with other catalytic systems. Compared to aryl alkyl thioethers, the rate of dialkyl thioether sulfoxidation was generally faster (**1j–1k**). Dialkyl sulphides were oxidized to sulfoxides in high yields under these reaction conditions. Diphenyl thioethers (**1l–1r**) showed a slow reaction, possibly due to the low electron density on the sulfur atom.

The photostability of **PDI-3** under these reaction conditions was also investigated.[29] UV-Visible spectra of the reaction mixture at the beginning and during the course of the reaction were collected to confirm the stability of the photocatalytic system (see the ESI†). To demonstrate that the photocatalytic selective oxidation of sulfides is practical and scalable, the gram-scale reactions were carried out (Scheme 2). Comparable yields were obtained, thus providing a possibility for the large-scale synthesis of sulfoxides in a sustainable and environmentally friendly manner.

Lastly, to demonstrate the synthetic utility of this photocatalytic methodology, late-stage functionalization of sulfide compounds was performed (Scheme 3). Treatment of sulfide **3** with O_2 under the standard reaction conditions afforded the corresponding sulfoxide derivative, which shows important bioactivities as a potent CDK2 inhibitor.[30]

Since the above experiments indicated that oxygen (O_2), photoirradiation, and PDI as the oxidation catalyst are all essential for the photocatalytic oxidative reactions with high activity and selectivity, it motivated us to gain insight into the mechanistic details of the reactions. The time profiles of the photooxidation (Fig. S1, see the ESI†) revealed that the reactions were totally inhibited in the absence of light. These

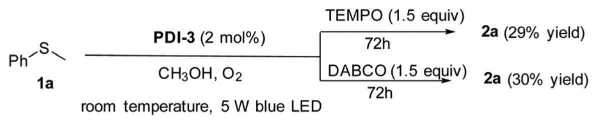
Scheme 2 Gram-scale reactions for the PDI-catalyzed selective oxidation.



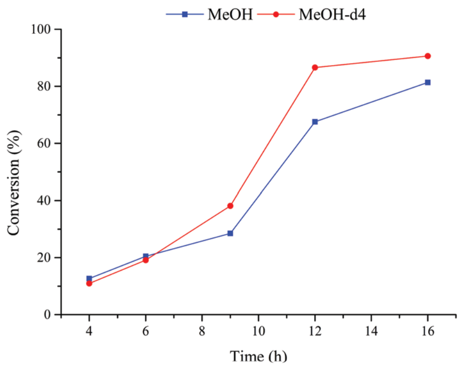
Scheme 3 Late-stage functionalization of sulfides for the synthesis of bioactive sulfoxide **4**.

results indicated that continuous irradiation with visible light is essential for the photocatalytic transformations. Two main mechanisms for the visible-light photocatalytic oxidation of sulfides have been proposed in the literature:[18,31] singlet oxygen oxidation through an energy transfer and a radical pathway through electron transfer. In order to gain further insight into the mechanism, additional experiments were carried out (Fig. 3). The addition of the radical inhibitors TEMPO or 1,4-benzoquinone significantly inhibited the transformation. Furthermore, the effect of DABCO (1,4-diazabicyclo[2.2.2]-octane, a singlet oxygen scavenger) on the photocatalytic oxidative reactions was also studied. We found that the photooxidative reaction of sulfides can also be significantly suppressed (Fig. 3a). It is well known that oxidations *via* $^1O_2$ can be accelerated using deuterated solvents.[16–18] We observed the obvious change in the oxidation rate when MeOH or deuterated MeOH was used (Fig. 3b). We employed the ESR spin-trapping technique (with DMPO) to probe the nature of the reactive oxygen species generated during the reaction under visible irradiation and characteristic peaks of DMPO-$O_2^{\bullet-}$ and DMPO-$^1O_2$ were obviously observed (Fig. 3c).[32] Therefore, we propose that the presence of both $O_2^{\bullet-}$ and $^1O_2$ is responsible for the photooxidation reaction of sulfides.

(a) Effect of TEMPO and DABCO on the PDI-catalyzed selective oxidation



(b) Kinetic experiments using MeOH or deuterated MeOH



(c) ESR spin-trap of PDI-catalyzed selective oxidation with DMPO

(g constant = 2.00609)

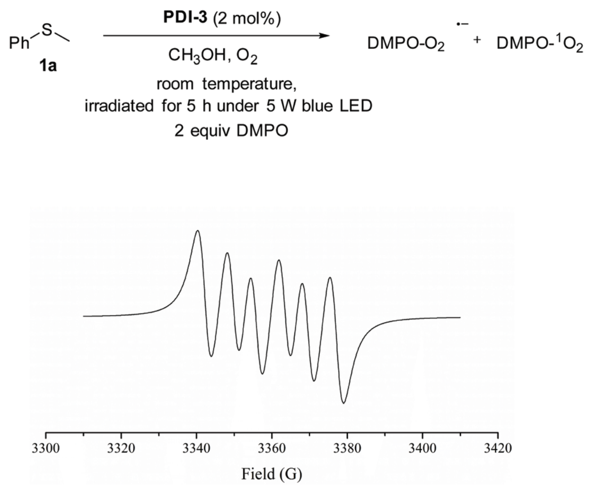
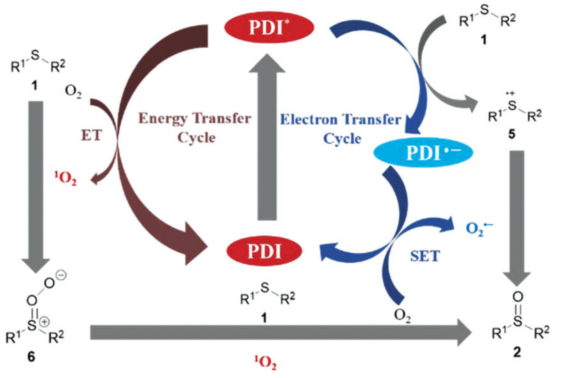


Fig. 3 Control experiments.



Scheme 4 Proposed mechanism.

The reaction mechanism of the PDI-catalyzed selective oxidative reactions is summarized in Scheme 4. Both electron transfer (ET) and energy transfer (EnT) may exist in the photocatalytic oxidation of sulfides to sulfoxides. By employing the EnT process, sulfide radical cation **5** was generated, which can be oxidized to sulfoxide **2**. Upon employing the energy transfer pathway, $^1O_2$ was produced using PDI. Then, singlet oxygen could grab one electron from the lone pair of electrons of sulfide **1**, forming radical cation **6**, which could react with another molecule of **1** to afford **2** as the product.

Conclusions

In summary, we have documented PDI as a cost-effective and environmentally friendly photocatalyst by activating molecular oxygen (O_2) for the selective oxidation of sulfides to sulfoxides with high efficiency under mild conditions. The catalyst is able to oxidize sulfides containing different functional groups with excellent yields, and without over-oxidation to sulfones or the formation of other by-products. The method meets the criteria for environmentally friendly procedures and agrees with the important concepts of green chemistry with the use of inexpensive household light. Meanwhile, this new class of photoredox catalyst may be used for other chemical reactions, awaiting further investigation.

Conflicts of interest

There are no conflicts to declare.

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