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Selective photooxidation of sulfides mediated by singlet oxygen using visible-light-responsive coordination polymers†

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A novel coordination polymer has been synthesized using an anthracene-based linker, and the photocatalytic properties of this visible-light-responsive compound are evaluated where it shows highly selective photooxidation of sulfides to produce sulfoxides relying on reactive species of singlet oxygen.

Sulfoxides are important complexes in organic synthesis or as biologically active compounds in the pharmaceutical industry.¹ One of the desirable methods to chemoselectively synthesize sulfoxides is through photooxidation of sulfides by molecular oxygen, which is a secure, inexpensive and environmentally friendly oxidant.² Hence, there is a practical demand for effective photocatalysts to achieve the aerobic oxidation of sulfides producing sulfoxides.

Recently, coordination polymers (CPs) have opened up remarkable performance in the growing field of photocatalysis, which is primarily benefited from the apt incorporation of various chromophores and/or functional groups in organic linkers.^{3–5} Emerging studies have shown that CPs incorporated with typical molecular catalysts of metal complexes are efficient for the aerobic oxidation of sulfides.⁶ Nevertheless, the oxygenation of sulfides over CP photocatalysts is still rarely reported and some of the reactions using CPs suffer from a low conversion rate or selectivity. Further development needs the synthesis of new kinds of CP photocatalysts and the mechanism study of the aerobic reaction.

We describe herein a novel visible-light-photoactive coordination polymer for triggering selective aerobic transformation of sulfides to generate sulfoxides. Orange strip-shaped crystals of **1** were prepared by a solvothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$ and 4,4'-(anthracene-9,10-diylbis(ethyne-2,1-diyl))dibenzoic acid (ADBEB) in a mixed solvent of $H_2O/CH_3CN/DMA$ (DMA = N,N-dimethylacetamide). 1 can also be synthesized in the mixed solvent of H_2O/DMA with a lower quality and yield, but cannot be synthesized using DMA solely.

Single-crystal X-ray diffraction shows that 1 crystallizes in the triclinic space group $P\overline{1}$ with the formula of Zn(ADBEB)(DMA) (Table S1, ESI†). The asymmetric unit contains two divalent Zn(II) ions, two deprotonated ligands and two DMA molecules (Fig. S1, ESI†). The Zn(II) ions in the structure are in distorted tetrahedral geometries coordinated with three ADBEB linkers and one DMA molecule by oxygen atoms (Fig. 1a). The bond lengths of Zn–O bonds are in the range of 1.942(2)-2.016(3) Å and are among typical values reported for Zn-CPs.⁷ The two unique ADBEB molecules are both deflected from planner configuration, showing different torsion angles of *ca.* 44.58 and 48.27 degrees from one benzoic acid group to the other one measured along the longitudinal direction of the molecule (Fig. S2, ESI†).



Fig. 1 (a) The coordination environment of Zn(II) ions. (b) The crystal structure of **1** showing ABCD stacking. (c) A view of a single layer showing stacking interactions between ADBEB linkers. (Hydrogen atoms and DMA molecules are omitted for clarity.)

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The inorganic–organic layers in **1** are closely stacked in an ABCD fashion (Fig. 1b). In each layer, the adjacent zinc-carboxylate chains are connected by highly conjugated backbones of linkers, exhibiting long-range stacking interactions with face-to-face distances of *ca.* 3.60 Å between adjacent anthracene groups (Fig. 1c).

The synthesized bulk sample was characterized by powder X-ray diffraction (PXRD) where it shows an identical pattern with that simulated from the crystal structure (Fig. 2a), indicating a good phase purity. Thermogravimetric (TG) measurements suggest a two-step thermal weight loss of 1 from room temperature to 600 °C (Fig. S3, ESI⁺). The first weight loss of *ca.* 13.6 wt% occurs at 300-350 °C due to the removal of coordinated DMA molecules (calcd: 14.1 wt%), while the second weight loss of ca. 71.6 wt% at 400-500 °C corresponds to the removal of ADBEB linkers (calcd: 72.6 wt%). The peak at *ca.* 2194 cm^{-1} on the FTIR spectrum is attributed to the characteristic stretching vibration of ethynyl ($C \equiv C$) groups in the ADBEB ligand (Fig. S4, ESI^{\dagger}). The peaks at *ca.* 1404 and 1387 cm⁻¹ are due to vibrations of carboxylate groups in the ligand. The peaks at *ca.* 860, 779 and 759 cm^{-1} can be ascribed to the out-of-plane bending vibration of the C-H bonds in benzene groups of ADBEB. The intense peak at *ca.* 1541 and 1600 cm⁻¹ ($\nu_{C=0}$) suggests the presence of DMA molecules. In addition, weak peaks around 3057 and 2934 cm⁻¹ are associated with vibrations of C-H bonds in the DMA molecule. The FTIR spectrum confirms the existence of components shown in crystal structure determination.

UV-Vis measurements show that the absorption edge of **1** locates at *ca.* 550 nm in the visible light region (Fig. 2b). Compared with the ADBEB linker (Fig. S5, ESI†), **1** exhibits a broaden absorption band in the visible light region, probably due to the close stacking interactions between conjugated ADBEB molecules in the network. The absorption spectrum of **1** is replotted in accordance with the frequency-dependent relationship $\alpha h\nu = (h\nu - E_g)^{1/2}$ to evaluate the band gap of **1**, where α and E_g are the absorption coefficient and the band gap energy. The plot of $(\alpha h\nu)^2$ *versus* photon energy displays a well-fitted linear dependence near the absorption edge, and the band gap energy of **1** is thus estimated to be *ca.* 2.26 eV (insert in Fig. 2b).

The capability of **1** serving as a visible-light photocatalyst to carry out aerobic oxidation of sulfides was then investigated, where a typical sulfide of thioanisole (PhSMe) was used as a model substrate and the conversion of thioanisole was monitored *via* gas chromatography-mass spectrometry (GC-MS). Previous reports have demonstrated that the photooxidation of sulfides might be sensitive to the solvent.⁸ Hence the influence of the solvent on the reaction was first investigated. As shown in Table S2 (ESI†), the results suggest that a mixed solvent of CHCl₃/MeOH (4:1, v/v) is the optimum reaction medium, as it shows a much superior conversion rate than other solvents of MeOH, CHCl₃, CH₂Cl₂/MeOH, CH₂Br₂/MeOH and BrCH₂CH₂Br/MeOH. Therefore, the following photocatalytic reactions were carried out in CHCl₃/MeOH where the transformation of PhSMe into PhS(O)Me completes within 4 h.

To further clarify the nature of the reaction, various control experiments were performed (Table S3, ESI[†]). The reaction did not proceed in the absence of either visible light irradiation or **1**. These results clearly demonstrate the photocatalytic nature of the reaction. Control experiments under an N_2 atmosphere gave no conversion of substrate, suggesting that molecular oxygen is essential for the reaction. The use of zinc nitrate, *i.e.* the metal salt for the synthesis of **1**, as the catalyst cannot initiate the reaction, which indicates that the photocatalytic activity of **1** results from the organic linker. The reaction using ADBEB powder as a photocatalyst afforded a 68% conversion of PhSMe within 4 h. This conversion rate is much lower than that shown by **1**, indicating the advantage of the coordination polymer over the organic linker.

The photooxidation progression of PhSMe over 1 has been tracked at different time intervals (see the ESI⁺). The reaction trace suggests that the photooxidation completes within 4 h but needs an induction period of about 2 h during which the reaction proceeds gradually, followed by a fast conversion of the substrate (Fig. 3a). It is found that the photocatalytic reaction is highly chemoselective to produce the sulfoxide of PhS(O)Me, without overoxidation to generate the sulfone (Fig. 3b). The high selectivity of the photocatalytic reaction has also been proved by ¹H NMR spectra (see the ESI[†]). However, it is noted that the reaction in deuterated solvents was shortened by about half an hour compared to that in nondeuterated solvents (Table 1, entry 1). The total turnover number (TON) is estimated to be ca. 20 with a turnover frequency (TOF) equal to 5 h^{-1} . The conversion rate and selectivity shown by 1 are comparable with that shown by metalloporphyrin-based CPs and other reported photocatalysts including coenzyme NAD⁺ models



Fig. 2 (a) XRD patterns of ${\bf 1}$ under different conditions. (b) UV-Vis spectrum of ${\bf 1}.$



Fig. 3 (a) Consecutive reaction traces of the photooxidation of PhSMe over **1**. (b) GC signals. Asterisks designate an internal standard of *n*-decane.

Table 1 Photooxidation of sulfides using 1 as a photocatalyst under visible light^a

	R ₁ ^S R ₂ ⁺	O ₂ 1 (5 mol%) CHCl ₃ /MeOH, R.T.		$\rightarrow \qquad \begin{array}{c} 0 \\ 11 \\ S \\ R_1 \\ S \\ R_2 \end{array}$	
Entry	R ₁	R_2	<i>T</i> (h)	Conv. (%)	Selec. (%
1		—CH3	3.5	>99	>99
2	CI	—CH3	3	>99	>99
3	Br	—CH3	5	>99	>99
4	Br	—CH₃	10	>99	>99
5		-CH ₂ CH ₃	4	>99	91
6	H ₃ C	—СН ₃	8	98	90
7			12	6	>99
8 ^b		—СН ₃	4	2	>99

 a Reaction conditions: 0.16 mmol sulfide, 5 mg 1, 1.25 mL solvent, and O₂. Reactions were analysed *via* ¹H NMR spectroscopy. b DABCO was added.

and Cd₁₀S₁₆ molecular clusters (Table S4, ESI⁺).^{6a,9} It is worth noting that almost all reported CPs used for aerobic photooxidation of sulfides are constructed by integration of molecular catalysts of metal complexes into their networks,⁶ while 1 differs from these ones as it does not contain a metal complex in the structure. To further testify the photocatalytic performance shown by 1, typical photocatalysts of Ru(bpy)₃Cl₂ and the organic dye Rose Bengal were tested for comparison.^{2b} The results suggest that 1 shows a comparable photocatalytic efficiency with them, but exhibits a higher selectivity for sulfide photooxidation (Table S3, entries 8 and 9, ESI[†]). Cycling experiments were performed using 1 recollected via centrifugation, where it showed a good reusability in the consecutive photooxidation reactions (Fig. S6, ESI[†]). PXRD, FTIR and SEM studies suggest that 1 maintained its pristine structure and morphology during the reactions (Fig. 2a and Fig. S4 and S7, ESI[†]).

To test the validity of **1** for aerobic oxidation of sulfides, several substrates have been examined (Table 1). It is notable that all these substrates could be transformed into sulfoxides with high selectivities larger than 90% (see also ¹H NMR spectra in the ESI†). The calculated TOFs are in the range of 2–6.7 h⁻¹. If PhSMe was substituted with electron-withdrawing halogen elements of –Cl and –Br, the photooxidation reaction is highly chemoselective to produce sulfoxides, without over-oxidation to generate sulfones (entries 2–4). In contrast, the reaction selectivity would decrease to *ca.* 90% if an electron-donating methyl group was substituted on PhSMe (entries 5 and 6).

These results illustrate that the electron effect of substrates is important for the reaction selectivity. Besides, the substituted position is also important for the reaction. The *p*-substituted sulfide is more reactive than the *o*-substituted one (entries 3 and 4). The lower conversion rate of the latter is considered owing to the steric effect.

Presently, two main mechanisms relying on different reactive oxygen species (ROS) are interpreted for the photocatalytic oxidation of sulfides.^{8b,10} One is photooxidation promoted by singlet oxygen $({}^{1}O_{2})$ through energy transfer sensitization, and the other is photooxidation with a superoxide radical $(O_2^{\bullet-})$ via electron transfer sensitization. In our case, the observation of extremely low conversion of diphenylsulfides (Table 1, entry 7) and a faster conversion rate in deuterated solvents suggests that the oxidation may follow the ¹O₂ mechanism.^{2,11} We further explored this by recognizing the ROS in the reaction. First, the photooxidation reaction was carried out in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO), a well-known ¹O₂ quencher, to ascertain the potential formation of such species.^{10a,11} As shown in Table 1 (entry 8), only a trace amount (ca. 2%) of thioanisole was transformed into sulfoxide after 4 h when DABCO (equimolar with thioanisoles) was added. It's significant that the sulfoxidation was substantially inhibited, indicating that ¹O₂ might be an important active substance involved in the photocatalytic system.

Then a sensitive indicator DPBF (1,3-diphenylisobenzofuran) was used to capture reactive ${}^{1}O_{2}$. The absorption of DPBF centred at 410 nm decreased quickly, indicating the trapping of photoinduced ${}^{1}O_{2}$ on DPBF to generate colourless products (Fig. 4a).¹² The absorption of DPBF disappears within 30 s, indicating a high efficiency of photoactive coordination polymers to sensitize dissolved molecular oxygen generating ${}^{1}O_{2}$. This result also suggests that the photooxidation of sulfides over **1** might go through the ${}^{1}O_{2}$ mechanism as shown in Scheme **1**.



Fig. 4 (a) Time-dependent absorption of DPBF under visible light. (b) EPR spectra for ${}^{1}O_{2}$ detection by TEMP. (c) ${}^{1}O_{2}$ signal attenuation after adding PhSMe. (d) EPR detection of $O_{2}^{\bullet-}$ by DMPO.



It has been widely corroborated that 2,2,6,6-tetramethylpiperidine (TEMP) reacts with ¹O₂ producing a stable nitroxide radical (TEMPO) that can be detected via electron paramagnetic resonance (EPR) spectroscopy.¹³ Hence we further performed in situ EPR measurements to detect photoinduced ${}^{1}O_{2}$ in the reaction. The characteristic EPR signals of TEMPO radicals at g = 2.005 were observed when TEMP was added (Fig. 4b). Significantly, the intensity of the EPR response increased with exposure time, which is powerful evidence for the photosensitized generation of ¹O₂ in the system. The very weak ¹O₂ signal before lighting may be due to the TEMP oxidation during the preparation of the test.¹⁴ To further access the reactivity of sulfides with 1O2, PhSMe was added after the EPR signal of TEMPO has been saturated. The addition of PhSMe obviously decreased the EPR signal intensity of TEMPO with elongated reaction time, which suggests the strong interaction between PhSMe and ¹O₂ (Fig. 4c). As mentioned before, O₂^{•-} generated by electron transfer from photoexcited 1 to ${}^{3}O_{2}$ can also be effective for the oxidation of sulfides. This potential ROS was also investigated using the EPR technique with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) employed as a specific trapping agent.15 There is no detectable EPR signal for O₂^{•-} captured by DMPO under visible light irradiation (Fig. 4d). These observations collectively prove that ${}^{1}O_{2}$ generated from the energy-transfer process serves as the main reactive species for the oxidation reaction.

In summary, a new visible-light-responsive coordination polymer is constructed using an anthracene-based organic linker. The synthesized CP is capable of aerobic photooxidation of sulfides. The results demonstrate that the photocatalytic reaction is highly efficient and selective to produce sulfoxides, avoiding overoxidation to generate sulfones. Both spectroscopy studies and trapping experiments indicate that ${}^{1}O_{2}$ generated by energy transfer from photoexcited coordination polymers to triplet oxygen molecules works as the active species for the photooxygenation reaction. The study illustrates the great potential of light-harvesting coordination polymers driving desirable photocatalytic reactions to produce valuable chemicals.

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Conflicts of interest

There are no conflicts to declare.

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