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### Introduction

Recently, the utilization of metal–organic frameworks (MOFs) as photosensitizers for chemicals transformation has attracted more and more attention because the photocatalytic reaction is carried out under mild conditions and it aligns well with the concepts of green chemistry and sustainable development.<sup>1-3</sup> MOFs can achieve such photochemical reactions where the charge photogeneration of MOFs leads to a pair of redox potentials based on the photoinduced electrons and holes.<sup>4-6</sup> In a typical photocatalytic reaction, either a reductive or an oxidative potential dominates the system where the other oxidation/reduction potential is always balanced by a hole sacrificial agent or electron acceptor to block the fast electron–hole recombination.<sup>7,8</sup> It is hoped that the rational utilization of photoinduced electrons.

During the past few decades, MOFs have been demonstrated to be efficient heterogeneous photocatalysts for  $CO_2$  reduction, water splitting, pollutant degradation and polymerization, as

# A visible-light-responsive metal-organic framework for highly efficient and selective photocatalytic oxidation of amines and reduction of nitroaromatics<sup>†</sup>

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Photocatalysis is a green synthetic method for organics transformation. We present here the synthesis of a novel visible-light-responsive metal-organic framework and its photocatalytic application. The prepared MOF is highly efficient for the self-coupling of primary amines and oxidative dehydrogenation of secondary amines to selectively produce imines assisted by the green and economic oxidant of molecular oxygen. Studies reveal that both energy transfer and electron transfer from the photoexcited MOF to molecular oxygen are important for amine oxidation, where the highly reactive species of superoxide radicals and singlet oxygen together account for the high catalytic performance. The photogenerated electrons of the MOF have also been utilized for the reduction of aromatic nitroarenes. Results show that they are highly selective for the reduction of nitroarenes to produce anilines in the presence of hydrazine hydrate. The work demonstrates the enormous potential of photoactive MOFs for converting organic substrates into valuable chemicals.

well as organic synthesis.7-11 It is notable that the use of MOFs for organics transformation has been far less reported. Imines are an essential class of organic intermediates due to their versatile applications in the production of heterocyclic chemicals, pharmaceutically and biologically active compounds, and fine chemicals.<sup>12-14</sup> For example, the asymmetric reduction of the C=N bond in prochiral imines is of considerable interest for the preparation of chiral amines that feature in many of the world's popular pharmaceuticals.<sup>15,16</sup> Conventionally, imines are prepared by the condensation of amines and aldehydes. The direct synthesis of imines from amines through self-coupling and oxidative dehydrogenation reactions in the presence of molecular oxygen is more appealing, not only because the reaction adopts the environmentally benign oxidant of oxygen but also because the raw materials of amines are inexpensive and versatile.<sup>17-19</sup> As one of the pathways to obtain amines, the reduction of nitro compounds is important in industry and academia. For example, the reduction of nitroarenes is one of the most commonly used methods to prepare anilines which are relevant intermediates in the synthesis of dyes, pigments, pharmaceuticals and agrochemicals.<sup>20-22</sup> In fact, several studies have demonstrated that MOFs are useful photosensitizers for the direct oxidation of amines.8,23-26 However, the use of MOFs for photoinduced reduction of nitroarenes has seldom been reported.27

We report herein the synthesis and photocatalytic application of a novel zinc-based MOF (1) which was constructed from

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#### Paper

organic linker 4,4'-(anthracene-9,10-diylbis(ethyne-2,1-diyl)) dibenzoic acid (ADBEB) under solvothermal conditions. **1** shows a wide-range optical absorption in the visible-light region and good stability in organic solvents. It was then applied for the direct synthesis of imines, where the photocatalytic conversion of primary and secondary amines to imines proceeds efficiently in the presence of oxygen. In addition to amine oxidation, it has also been utilized for the photoreduction of aromatic nitro compounds where various anilines have been selectively produced.

### Results and discussion

Single crystal X-ray diffraction analysis shows that 1 possesses a three-dimensional network and crystallizes in monoclinic space group C2/m with the formula  $[Zn_3(OH)_2(ADBEB)_2] \cdot 3DEF$ (Fig. 1). In the structure, there are two crystallographically unique zinc ions, Zn(1) and Zn(2). The Zn(1) ion in octahedral geometry coordinates with four oxygen atoms from different ligands and two hydroxyl groups. The Zn(2) ion in tetrahedral geometry coordinates with two oxygen atoms from ligands and two hydroxyl groups. Such coordination modes of zinc ions lead to the formation of inorganic Zn–OH–Zn chains along the c axis in the structure (Fig. 1a). The Zn-O bond lengths are in the range of 2.005-2.077 Å, which are among typical values reported for Zn-MOFs.<sup>28-30</sup> These Zn-OH-Zn chains are further connected by highly conjugated ADBEB ligands that have close stacking interactions with a face-to-face distance of ca. 3.5 Å (Fig. 1b).

The purity of the bulk sample was studied by powder X-ray diffraction (PXRD) and the experimental pattern fits well with the one simulated from the crystal structure, indicating that the as-prepared sample has good purity (Fig. 2a). Thermogravimetric measurement of **1** shows a two-step weight loss (Fig. S1†). The first weight loss of *ca.* 20.6 wt% before 450 °C corresponds to the removal of guest *N*,*N*-diethylformamide (DEF) molecules (calcd: 20.8 wt%). The following sharp weight loss of *ca.* 62.1 wt% is attributed to the removal of organic linkers in the structure (calcd: 62.6 wt%). It is notable that the removal of guest DEF would lead to the collapse of the framework, preventing nitrogen adsorption. The bulk sample of **1** was also characterized by Fourier transform infrared spectroscopy (FTIR, Fig. S2†). The characteristic peak of ethynyl groups ( $-C \equiv C$ -) in ADBEB is observed at *ca.* 2190 cm<sup>-1</sup> in the



Fig. 1 (a) The infinite chain of Zn-OH-Zn. (b) View of the face-to-face stacking of ligands. (c) Crystal structure of 1.



Fig. 2 (a) PXRD patterns of 1 under different conditions. (b) UV-vis spectrum of 1. The inset shows the energy gap of 1.

spectrum. The strong peak at *ca*. 1650 cm<sup>-1</sup> should be due to the stretching vibration of the carbonyl group in the DEF molecule.<sup>31,32</sup> The intense absorptions at 1596 and 1407 cm<sup>-1</sup> should be due to vibrations of carboxylate groups in the linker.<sup>33,34</sup> The peak at *ca*. 3400 cm<sup>-1</sup> is attributed to the hydroxyl group (–OH) in the structure. The several weak peaks near 2975 cm<sup>-1</sup> should originate from the methyl asymmetric stretching vibration of the DEF molecule. The intense peaks at *ca*. 761, 780, and 859 cm<sup>-1</sup> should result from the out-of-plane bending vibration of the C–H bonds in the benzene groups of ADBEB.

Solid-state UV-vis spectroscopy measurement (Fig. 2b and S3†) shows that the optical absorption edge of **1** locates at *ca*. 600 nm in the visible-light region. The absorption spectrum is replotted in accordance with the frequency-dependent relationship  $\alpha hv = (hv - E_g)^{1/2}$  to evaluate the band gap of **1**, where  $\alpha$  and  $E_g$  are the absorption coefficient and band gap energy, respectively. The plot of  $(\alpha hv)^2$  *versus* photon energy displays a well-fitted linear dependence near the absorption edge; thus, the band gap energy of **1** is estimated to be *ca*. 2.20 eV (inset in Fig. 2b).

The photocatalytic capability of **1** was first evaluated by the reaction of self-coupling of primary amines to produce imines, which are versatile organic intermediates. The economic and green oxidant of molecular oxygen has been adopted in the reaction and benzylamine was selected as a model substrate. As shown in Table 1 (entry 1), the experiment suggests that **1** is capable of oxidizing benzylamine to generate an imine under visible light irradiation. Control experiments suggest that acetonitrile is the most adaptive reaction medium among various examined solvents (Table S2†). Thus, the subsequent coupling reactions of amines were carried out in acetonitrile.

Series of experiments were then carried out to understand the nature of the visible-light-driven coupling reaction over **1** (Table S3<sup>†</sup>). Without **1** and visible light, no reaction occurred, indicating the photocatalytic nature of the reaction. The use of organic linker ADBEB as a photosensitizer provides a much lower conversion (24%) of the substrate, possibly owing to the fact that it is insoluble and amorphous in acetonitrile. Control experiments suggest that oxygen is important for the reaction. When the reaction was carried out under aerobic conditions, the conversion of benzylamine was *ca.* 50% at 1 hour. However, the substrate could be completely transformed (>99%) if the reaction was carried out under oxygen conditions (entry **1**, Table

Table 1 Photooxidation self-coupling of benzylamines using 1 as a photocatalyst under visible light<sup>a</sup>

$R \xrightarrow{II} NH_2 \xrightarrow{I. Visible light} R \xrightarrow{I. Visible light} R$						
Entry	Substrate	T[min]	Conv. <sup><i>b</i></sup> [%]	Select. <sup>b</sup> [%]		
1	NH <sub>2</sub>	60	99	99		
2	NH <sub>2</sub>	75	99	99		
3		65	99	99		
4	NH <sub>2</sub>	90	99	99		
5	NH <sub>2</sub>	96	99	99		
6	F NH2	50	99	99		
7		90	99	99		
8	Br NH2	120	99	99		
9	F NH2	210	99	99		
10	F NH2	216	99	99		

<sup>*a*</sup> Reaction conditions: 0.2 mmol benzylamines, 5 mg 1, 1 mL solvent, and  $O_2$ . <sup>*b*</sup> Reactions were analysed by GC using *n*-decane as an internal standard.

1). The turnover frequency (TOF) is calculated to be 45.8  $h^{-1}$ . It is notable that this value is higher than that shown by other reported MOFs such as NH<sub>2</sub>-MIL-125(Ti), PCN-222, ZJU-56 and Zn-PDI (Table S4†).<sup>23-26</sup>

Benzylamine derivatives with various substituted groups were examined for the visible-light-driven coupling using 1 as a photocatalyst. As shown in Table 1, it is notable that all substrates exhibit high selectivity (>99%) to produce symmetrical imines, avoiding formation of any by-product, although the time durations for complete conversion of substrates differ from each other (50-215 minutes). Derivatives with electron-donating groups (-CH<sub>3</sub> and -OCH<sub>3</sub>) at the para-position are highly reactive for the self-coupling reaction in the reaction system (Table 1, entries 2 and 3). When the steric effect is considered, the order para- > meta- > ortho-position is observed for methyl-substituted benzylamines (Table 1, entries 1, 4 and 5). It is interesting that the complete transformation of 4-fluorobenzylamine can be implemented in 50 minutes (Table 1, entry 6). However, the transformation of substrates modified by other electronwithdrawing groups such as chlorine (-Cl) and bromine (-Br) at the *para*-position needs longer reaction time (Table 1, entries 7 and 8). The steric effect also plays an important role in the transformation of benzylamine derivatives with electron-withdrawing groups, where the order *para- > meta- > ortho*-position is observed for fluorobenzylamines (Table 1, entries 6, 9 and 10). The reusability of **1** was verified by recycling experiments during which **1** was recollected by centrifugation. As shown in Fig. 3, both the conversion rate and the selectivity were retained in subsequent runs. PXRD, FTIR and SEM measurements suggest the conservation of the photocatalyst (Fig. 2a, S2 and S4†).

Beyond the self-coupling of primary amines, the oxidative dehydrogenation of secondary amines is another direct method to prepare imines. We further explored the photocatalytic performance of 1 towards the oxidation of secondary amines. Dibenzylamine was selected as a model substrate and N.Ndimethylformamide (DMF) was chosen as an optimum reaction medium (Table S5<sup>†</sup>). Dibenzylamine can transform into the corresponding imine with an excellent selectivity of 99% within 2 hours in an O2 atmosphere in DMF (Table 2, entry 1 and Table S6<sup>†</sup>). The TOF value of the reaction is calculated to be 22.9  $h^{-1}$ . indicating that 1 shows better catalytic performance than other typical photocatalysts such as BiVO<sub>4</sub>, BiOCl, porous organic polymer CF-HCP, Rh/carbon nanotubes and polyoxometalates (Table S7<sup>†</sup>).<sup>17,19,35-37</sup> Control experiments indicate that 1 and visible light are essential for the dehydrogenation of dibenzylamine (Table S6,† entries 2 and 3). Experiments suggest that also O<sub>2</sub> is important and the reaction was significantly quenched if it was performed under nitrogen or air conditions (Table S6,† entries 4 and 5).

As shown in Table 2, we further investigated the photooxidation of benzylamine-based secondary amines over **1**. For derivatives with *tert*-butyl and isopropyl groups, the photocatalytic reaction exhibits a highly selective transformation (99%) into the corresponding imine at an excellent conversion rate (Table 2, entries 2 and 3). For the oxidation of *N*-benzylaniline, the reaction is slow but shows a good yield of 99% (Table 2, entry 4). However, for derivatives substituted with methyl, ethyl and butyl groups, the reactions show relatively lower selectivity (38–60%) to produce imines (Table 2, entries 5–7). The recollected **1** was used for recycling reactions where it maintains photocatalytic activity during continuous dehydrogenation of secondary amines (Fig. S5†).

Photocatalytic experiments for self-coupling of primary amines and dehydrogenation of secondary amines show that



**Fig. 3** (a) Consecutive reactions for the photooxidation of benzylamine. (b) Conversion and selectivity in different runs.

	DMF, O <sub>2</sub>					
Entry	Substrate	<i>T</i> [h]	Conv. <sup>b</sup> [%]	Select. <sup>b</sup>		
1		2	99	99		
2		2	99	99		
3		4	99	99		
4		27	99	99		
5		7	99	60		
6		4	99	45		
7		4	99	38		

Table 2Photocatalytic oxidative dehydrogenation of secondaryamines using 1 as a photocatalyst under visible light $^{a}$ 

[%]

<sup>*a*</sup> Reaction conditions: 0.2 mmol secondary amines, 5 mg 1, 1 mL solvent, and  $O_2$ . <sup>*b*</sup> Reactions were analysed by GC using *n*-decane as an internal standard.

oxygen is vital in the system. Then we evaluated the potential reactive oxygen species (ROS) in these photocatalytic reactions via quenching experiments. According to reported studies, 5,5dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) are efficient at capturing the superoxide radical  $(O_2^{\cdot-})$  and singlet oxygen  $({}^{1}O_2)$ , respectively.<sup>38-40</sup> They were added into the reaction system to provide clarity regarding the ROS in the reactions. Upon the addition of DMPO, only 12% benzylamine was converted (Table S3,† entry 9), indicating that O<sub>2</sub><sup>•-</sup> serves as a ROS in the reaction. When TEMP was added into the same system, 37% benzylamine was transformed into an imine (Table S3,† entry 8), suggesting that <sup>1</sup>O<sub>2</sub> also serves as a ROS in benzylamine oxidation. As for the dehydrogenation of secondary amines, experiments also suggest the coexistence of both O2<sup>•-</sup> and <sup>1</sup>O<sub>2</sub> ROS in the reaction, where TEMP and DMPO quenched the reaction obviously (Table S6,† entries 7 and 8).

The occurrence of  ${}^{1}O_{2}$  was also examined using a sensitive indicator, 1,3-diphenylisobenzofuran (DPBF).<sup>7</sup> In oxygensaturated solution, the absorption of DPBF at 410 nm decreased quickly upon the addition of 1 under visible light, indicating the trapping of  ${}^{1}O_{2}$ , which is generated by energy transfer (ET) of excited 1 (Fig. 4a). The absorption of DPBF disappears within 70 s, indicating the high efficiency of 1 in sensitizing oxygen. Beyond  ${}^{1}O_{2}$ , excited 1 can also produce



Fig. 4 (a) Time-dependent absorption and photograph (inset) of DPBF under visible light in the presence of 1. (b) Absorption and photograph (inset) of TMPD under visible light with or without 1 in acetonitrile under a  $N_2$  atmosphere.

another ROS,  $O_2$ ., through charge transfer (CT), leaving oxidative holes on the MOF. This has been evaluated by the oxidation of N, N, N', N'-tetramethylphenylenediamine (TMPD), which has a very low oxidation potential in acetonitrile.<sup>41</sup> As shown in Fig. 4b, the holes on 1 after photoinduced charge separation could effectively oxidize TMPD into its oxidized form (TMPD<sup>++</sup>) with strong absorption at 563 nm and 612 nm, accompanied by a visible colour change from colourless to blue. Then we conducted hole-trapping experiments to study the impact of photoinduced holes on amine oxidation. When sacrificial agent triethanolamine (TEOA) was added into both reaction systems, the photocatalytic transformation of substrates was severely blocked (Table S3,† entry 7 and Table S6,† entry 6), indicating that the photoinduced holes oxidize the substrates, forming cationic species to facilitate the reactions.<sup>42,43</sup> On the basis of these findings, a plausible mechanism is illustrated in Scheme 1a. The excited MOF sensitizes triplet oxygen to singlet oxygen through energy transfer.7 Simultaneously, photoinduced charge transfer occurs from the MOF to



Scheme 1 (a) A plausible reaction mechanism for the photooxidation of primary and secondary amines to generate imines. (b) Photo-catalytic reduction of nitroarenes to produce anilines assisted by hydrazine hydrate.

oxygen, producing another ROS, the superoxide radical.<sup>8</sup> These highly reactive species oxidize the amine cations, generating aldehydes which further condense with amines to produce imines. This is reasonable since a very small amount of aldehyde reaction intermediate can be detected from gas chromatography (Fig. S6<sup>†</sup>).

Inspired by the facile photoinduced electron transfer shown by the above studies, we concluded that this process can be used for reductive reaction. The reduction of nitrobenzene to aniline was chosen as a model reaction, because the selective reduction of aromatic nitro compounds is one of the most commonly used methods to prepare anilines.44-46 Anilines are relevant intermediates in the synthesis of dyes, pigments and pharmaceuticals.47-49 For example, one of the classical methods to prepare important dyes of azo compounds is the Mills reaction where anilines react with nitroso derivatives.50 The photoreduction of nitrobenzene over the MOF photocatalyst has been rarely studied. Only a Ni(II)-porphyrin metal-organic framework has been reported for the reduction of nitrobenzene in the presence of NaBH<sub>4</sub>.<sup>27</sup> In our experiment, the direct interaction between photoexcited 1 and nitrobenzene gave no product. As shown in Scheme 1b, this is probably because of the lack of protons that are essential for the reaction. Hence, hydrazine hydrate  $(N_2H_4 \cdot H_2O)$  was introduced into the reaction system not only

Table 3 Photoreduction of nitroaromatics using 1 as a photocatalyst under visible light<sup> $\alpha$ </sup>

	R	NO <sub>2</sub> 1, Visible light EtOH, O <sub>2</sub>		
Entry	Substrate	<i>T</i> [h]	Conv. <sup><i>b</i></sup> [%]	Select. <sup>b</sup> [%]
1		4	99	99
2	F NO2	4	99	99
3	F NO2	5	99	99
4	F NO2	1	99	99
5		10	99	99
6	Br NO2	10.5	99	99
7	NO <sub>2</sub>	8.5	99	99
8		6	99	99

<sup>*a*</sup> Reaction conditions: 0.1 mmol nitroaromatics, 5 mg **1**, 1 mL solvent, and 0.4 mmol hydrazine hydrate. <sup>*b*</sup> Reactions were analysed by GC using *n*-decane as an internal standard.

because it provides hydrogen species resulting in only clean N<sub>2</sub> as the by-product, but it can also effectively reduce the oxidative holes to boost electron–hole separation.<sup>51,52</sup> As expected, nitrobenzene could be photoreduced to aniline upon the addition of hydrazine hydrate into the photocatalytic reaction system. A control experiment suggests that hydrazine hydrate does not reduce nitrobenzene directly (Table S8†). Besides, it is found that visible light and 1 are essential for the reaction (Table S8†). Ethanol has been demonstrated to be the most optimal reaction solvent with a TOF of *ca.* 5.8 h<sup>-1</sup> (Table S9†). This catalytic performance is comparable to that shown by other visible-light-driven reactions using CdS, eosin Y (EY) and Au(Ag)/LDH/GO composites (Table S10†).<sup>53–55</sup>

We further studied the photocatalytic reduction of a series of nitroaromatics by **1**. As shown in Table 3, it is notable that all substrates exhibit high selectivity (>99%) to produce anilines, avoiding formation of any by-product. The reaction times for complete conversion of these substrates differ from each other. The results reveal that the conversion of nitro compounds with a  $-CH_3/-OCH_3$  group is faster than that with a -Cl/-Br group, but much slower than that of fluoronitrobenzene (Table 3, entries 2–4). It is obvious that the reaction of fluorine substitution at the *meta*-position is the most efficient, with a complete transformation of the substrate to the corresponding aniline being accomplished within 1 hour (Table 3, entry 4). The reusability of **1** has been verified by recycling experiments during which **1** was recollected by centrifugation and reused. **1** retained its photocatalytic activity in subsequent runs (Fig. S7†).

### Conclusions

In summary, we report here a novel three-dimensional Zn-MOF with desirable optical absorption in the visible light region owing to the incorporation of photoactive organic linkers. The photoactive MOF is used for the oxidation of primary and secondary amines in the presence of molecular oxygen. Photocatalytic experiments demonstrate that the reactions are highly selective and efficient for producing useful imines. The results suggest that the energy transfer and charge transfer from the photoexcited MOF to molecular oxygen are important, where the reactive species of both superoxide radicals and singlet oxygen together account for the highly efficient photooxidation of amines to produce imines. Furthermore, the rational utilization of electron transfer from the excited MOF to nitroaromatics enables the selective generation of various anilines. This study not only presents a comprehensive investigation of the redox ability of MOF photocatalysts, but also illustrates the great potential of MOFs for organics transformation to produce valuable chemicals.

### **Experimental section**

#### Synthesis of 1

Orange crystals of  $[Zn_3(OH)_2(ADBEB)_2] \cdot 3DEF$  (1) were synthesized by solvothermal reaction of  $Zn(NO_3)_2 \cdot 6H_2O$  (38 mg, 0.13 mmol) with ADBEB (60 mg, 0.13 mmol) in a mixed solvent of DEF/H<sub>2</sub>O/CH<sub>3</sub>CN (23 mL, 20 : 3 : 2, v/v/v). Then, 0.2 mL HNO<sub>3</sub>

(0.1 M) was added to obtain a clear solution. The mixture was sealed in a 25 mL Teflon-lined stainless-steel autoclave and kept at 85 °C for 72 hours, and then cooled to room temperature. The synthesized strip-shaped crystals were collected and washed with fresh DMF and ethanol several times. Yield: 50% based on the linker.

#### Physical characterization

Single-crystal X-ray diffraction data of a selected crystal were collected on a Bruker SMART APEXII CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature. The crystal structure was solved by a direct method and refined using full-matrix least-squares on  $F^2$  with anisotropic displacement using SHELXTL-2017.<sup>56</sup> The X-ray crystallographic coordinates of **1** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC 1945598.<sup>†</sup> The details of the crystal data collection and refinement are provided in the ESI (see Table S1<sup>†</sup>).

Powder X-ray diffraction patterns were collected on a Rigaku SmartLab X-ray diffractometer operated at 40 kV/30 mA with Cu K $\alpha$  radiation ( $\lambda = 0.15417$  nm) with  $2\theta$  ranging from 3° to 40° at room temperature. UV-vis spectra of the solid-state samples were recorded on a HITACHI U-4100 spectrophotometer. FTIR spectra were measured using KBr pellets in the range of 400-4000 cm<sup>-1</sup> on a Mattson Alpha-Centauri spectrometer. TG measurement was carried out on a PerkinElmer TGA-7 thermogravimetric analyzer from 30 to 800 °C with a heating rate of 10 °C min<sup>-1</sup> in an air atmosphere. A 300 W xenon arc lamp was used as the light source for photocatalytic experiments, and a filter with a cut-off wavelength of 420 nm was used to remove UV light. Gas chromatography (GC) was performed on a GC-2010 Pro under the following conditions: oven temperature 300 °C, injector temperature 240 °C, column temperature program 10 °C min<sup>-1</sup>, from 120 to 240 °C with a holding time of 5 min.

#### **Photocatalytic reactions**

In a typical reaction of the photooxidation of benzylamines, 5.0 mg of photocatalyst 1 and 0.2 mmol substrate were placed in a Pyrex vial containing 1 mL of acetonitrile in the dark. Then, the *n*-decane internal standard was added. The sealed Pyrex vial (3 mL) was then stirred magnetically in an O<sub>2</sub> atmosphere and cooled with circulating water. Then it was irradiated under visible light. The distance between the lamp and the reaction vial was ca. 10 cm, and the optical power at the vial was measured to be ca. 20.0 mW cm<sup>-2</sup>. A small amount of reaction suspension was taken out at fixed time intervals and the suspension was injected into the GC after it was filtered through a porous membrane (22 µm in diameter). The chemical structures of products were confirmed by comparison with standard chemicals. For the reaction of the photooxidation of secondary amines, the conditions were the same as those for primary amines except that the solvent was changed to DMF.

For the photoreduction of nitroaromatics, 5.0 mg of **1** was loaded into a dried Pyrex vial equipped with a stir bar. Then,

0.1 mmol nitroarene, 1 mL of ethanol, 4 mmol hydrazine hydrate and *n*-decane were added. The chemical structures of the products were confirmed by comparison with standard chemicals.

In order to study the contribution of the substrate inside the pores of the MOF, we performed the following experiment. 10 mg MOF was first soaked in benzylamine for 24 hours, with the benzylamine solvent being replaced every 4 hours. After that, the MOF was thoroughly washed with acetonitrile. Then the sample was placed in acetonitrile under visible light irradiation for 2 hours, and the yield of the imine was determined by GC. It is found that only 2–4% product was detected. This result indicates that the photocatalytic reaction primarily occurred on the surface of the MOF.

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 X. Deng, Z. Li and H. Garcia, *Chem.-Eur. J.*, 2017, 23, 11189-11209.
- 2 W. Zhan, L. Sun and X. Han, Nano-Micro Lett., 2019, 11, 2-28.
- 3 S. Wang and X. Wang, Small, 2015, 11, 3097-3112.
- 4 H. Zhao, Q. Xia, H. Xing, D. Chen and H. Wang, ACS Sustainable Chem. Eng., 2017, 5, 4449–4456.
- 5 L. Wang, P. Jin, S. Duan, J. Huang, H. She, Q. Wang and T. An, *Environ. Sci.: Nano*, 2019, **6**, 2652–2661.
- 6 P. Li, J. Li, X. Feng, J. Li, Y. Hao, J. Zhang, H. Wang, A. Yin, J. Zhou, X. Ma and B. Wang, *Nat. Commun.*, 2019, **10**, 2177.
- 7 X. Liang, Z. Guo, H. Wei, X. Liu, H. Lv and H. Xing, *Chem. Commun.*, 2018, **54**, 13002–13005.
- 8 H. Wei, Z. Guo, X. Liang, P. Chen, H. Liu and H. Xing, ACS Appl. Mater. Interfaces, 2019, **11**, 3016–3023.
- 9 L. Jiao, J. Y. R. Seow, W. S. Skinner, Z. U. Wang and H.-L. Jiang, *Mater. Today*, 2019, 27, 43–68.
- 10 D. Chen, H. Xing, C. Wang and Z. Su, J. Mater. Chem. A, 2016, 4, 2657–2662.
- 11 Y. Liu, D. Chen, X. Li, Z. Yu, Q. Xia, D. Liang and H. Xing, *Green Chem.*, 2016, **18**, 1475–1481.
- 12 R. W. Layer, Chem. Rev., 1963, 63(5), 489-510.
- 13 S. Kobayashi, Y. Mori, J. S. Fossey and M. M. Salter, *Chem. Rev.*, 2011, **111**, 2626–2704.
- 14 M. E. Belowich and J. F. Stoddart, *Chem. Soc. Rev.*, 2012, **41**, 2003–2024.
- 15 G. Grogan, Curr. Opin. Chem. Biol., 2018, 43, 15-22.
- 16 G. Grogan and N. J. Tumer, *Chem.-Eur. J.*, 2016, **22**, 1900–1907.

- 17 B. Yuan, R. Chong, B. Zhang, J. Li, Y. Liu and C. Li, *Chem. Commun.*, 2014, **50**, 15593–15596.
- 18 X. Lang, W. Ma, Y. Zhao, C. Chen, H. Ji and J. Zhao, *Chem.-Eur. J.*, 2012, 18, 2624–2631.
- 19 Y. Wu, B. Yuan, M. Li, W. H. Zhang, Y. Liu and C. Li, *Chem. Sci.*, 2015, **6**, 1873–1878.
- 20 D. Formenti, F. Ferretti, F. K. Scharnagl and M. Beller, *Chem. Rev.*, 2019, **119**, 2611–2680.
- 21 P. Lara and K. Philippot, *Catal. Sci. Technol.*, 2014, 4, 2445–2465.
- 22 Y. Shiraishi, Y. Togawa, D. Tsukamoto, S. Tanaka and T. Hirai, *ACS Catal.*, 2012, **2**, 2475–2481.
- 23 D. Sun, L. Ye and Z. Li, Appl. Catal., B, 2015, 164, 428-432.
- 24 C. Xu, H. Liu, D. Li, J. H. Su and H. L. Jiang, *Chem. Sci.*, 2018, 9, 3152–3158.
- 25 H. Li, Y. Yang, C. He, L. Zeng and C. Duan, *ACS Catal.*, 2019, 9, 422–430.
- 26 L. Zeng, T. Liu, C. He, D. Shi, F. Zhang and C. Duan, *J. Am. Chem. Soc.*, 2016, **138**, 3958–3961.
- 27 M. S. Deenadayalan, N. Sharma, P. K. Verma and C. M. Nagaraja, *Inorg. Chem.*, 2016, 55, 5320–5327.
- 28 X.-Y. Guo, F. Zhao, J.-J. Liu, Z.-L. Liu and Y.-Q. Wang, J. Mater. Chem. A, 2017, 5, 20035–20043.
- 29 Y. Zhao, L. Wang, N.-N. Fan, M.-L. Han, G.-P. Yang and L.-F. Ma, *Cryst. Growth Des.*, 2018, **18**, 7114–7121.
- 30 Z.-W. Zhai, S.-H. Yang, M. Cao, L.-K. Li, C.-X. Du and S.-Q. Zang, *Cryst. Growth Des.*, 2018, **18**, 7173–7182.
- 31 H. J. Park, Y. E. Cheon and M. P. Suh, *Chem.–Eur. J.*, 2010, **16**, 11662–11669.
- 32 M. Y. Chao, W. H. Zhang and J. P. Lang, *Molecules*, 2018, 23, 755–768.
- 33 S. A. Boer, P. X. Wang, M. J. MacLaclan and N. G. Whiter, *Cryst. Growth Des.*, 2019, **19**, 4829–4835.
- 34 F. Yu, Y. M. Zhang, Y. H. Guo, A. H. Li, G. X. Yu and B. Li, *CrystEngComm*, 2013, **15**, 8273–8279.
- 35 Y. Zhi, K. Li, H. Xia, M. Xue, Y. Mu and X. Liu, *J. Mater. Chem. A*, 2017, **5**, 8697–8704.
- 36 D. V. Jawale, E. Gravel, N. Shah, V. Dauvois, H. Li, I. N. Namboothiri and E. Doris, *Chem.-Eur. J.*, 2015, 21, 7039–7042.

- 37 H. Yu, Y. Zhai, G. Dai, S. Ru, S. Han and Y. Wei, *Chem.-Eur. J.*, 2017, 23, 13883–13887.
- 38 L. Y. Zang, Z. Y. Zhang and H. P. Misea, *Photochem. Photobiol.*, 1990, 52, 677–683.
- 39 Y. Nosaka and A. Y. Nosaka, Chem. Rev., 2017, 117, 11302– 11336.
- 40 Z. J. Wang, S. Ghasimi, K. Landfester and K. A. Zhang, *Adv. Mater.*, 2015, **27**, 6265–6270.
- 41 J. R. Choi, T. Tachikawa, M. Fujitsuka and T. Majima, *Langmuir*, 2010, **26**, 10437–10443.
- 42 W. Yu, D. Zhang, X. Guo, C. Song and Z. Zhao, *Catal. Sci. Technol.*, 2018, **8**, 5148–5154.
- 43 T. Ghosh, T. Slanina and B. Konig, *Chem. Sci.*, 2015, **6**, 2027–2034.
- 44 M. H. Huang, Y. B. Li, T. Li, X. C. Dai, S. Huo, Y. H. He,
  G. C. Xiao and F. X. Xiao, *Chem. Commun.*, 2019, 55, 10591–15094.
- 45 Z. Y. Liang, M. H. Huang, S. Y. Guo, Y. Yu, W. Chen and F. X. Xiao, *Catal. Sci. Technol.*, 2019, **9**, 672–687.
- 46 Q. C. Xu, J. X. Zeng, H. Q. Wang, X. Y. Li, J. Xun, J. Y. Wu, G. C. Xiao, F. X. Xiao and X. Y. Liu, *Nanoscale*, 2016, 8, 19161–19173.
- 47 K. Sarmah, S. Mukhopadhyay, T. K. Maji and S. Pratihar, *ACS Catal.*, 2019, **9**, 732–745.
- 48 Y. Yamamoto, M. Fukui, A. Tanaka, K. Hashimoto and H. Kominami, *Catal. Sci. Technol.*, 2019, **9**, 966–973.
- 49 T. Song, P. Ren, Y. Duan, Z. Wang, X. Chen and Y. Yang, *Green Chem.*, 2018, **20**, 4629–4637.
- 50 E. Merino, Chem. Soc. Rev., 2011, 40, 3835-3853.
- 51 A. Kumar, P. Kumar, C. Joshi, M. Manchanda, R. Boukherroub and S. L. Jain, *Nanomaterials*, 2016, **6**, 59.
- 52 C. Yao, A. Yuan, Z. Wang, H. Lei, L. Zhang, L. Guo and X. Dong, *J. Mater. Chem. A*, 2019, 7, 13071–13079.
- 53 M. Kaur and C. M. Nagaraja, ACS Sustainable Chem. Eng., 2017, 5, 4293-4303.
- 54 X.-J. Yang, B. Chen, L.-Q. Zheng, L.-Z. Wu and C.-H. Tung, *Green Chem.*, 2014, **16**, 1082–1086.
- 55 M. Sahoo, S. Mansingh and K. M. Parida, *J. Mater. Chem. A*, 2019, 7, 7614–7627.
- 56 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112–122.