

Covalent Organic Frameworks toward Diverse Photocatalytic Aerobic Oxidations

Shuyang Liu^{+,[a]} Miao Tian^{+,[a]} Xiubin Bu,^[a] Hua Tian,^{*[c]} and Xiaobo Yang^{*[a, b]}

Abstract: Photoactive two-dimensional covalent organic frameworks (2D-COFs) have become promising heterogenous photocatalysts in visible-light-driven organic transformations. Herein, a visible-light-driven selective aerobic oxidation of various small organic molecules by using 2D-COFs as the photocatalyst was developed. In this protocol, due to the remarkable photocatalytic capability of hydrazone-based 2D-COF-1 on molecular oxygen activation, a wide range of amides, quinolones, heterocyclic compounds, and sulfoxides were obtained with high efficiency and excellent functional

Introduction

Selective oxidation reactions of small organic molecules are highly important in the chemical industry.^[1] Products of oxidation exist widely in natural molecules, agrochemicals and pharmaceuticals.^[2] Therefore, various oxidants and approaches have been developed to realize selective oxidation in the past decades.^[3] Visible-light-induced oxidation using molecular oxygen as the clean oxidant ranks among the most attractive strategies for their environmentally friendly and sustainable features. For this purpose, numerous homogenous photosensitizers such as Ru^[4] or Ir^[5] complexes and organic dyes,^[6] have been reported to realize these photocatalytic oxidations

[a]	S. Liu, ⁺ M. Tian, ⁺ Dr. X. Bu, Prof. X. Yang	
	Institute of Catalysis for Energy and Environment, College of Chemistry and	
	Chemical Engineering	
	Shenyang Normal University	
	110034 Shenyang (P. R. China)	
	E-mail: bxy1223@gmail.com	
	yangxb@synu.edu.cn	
[b]	Prof. X. Yang	
	Key Laboratory of Bioorganic Phosphorus Chemistry and Chemical Biology (Ministry of Education)	
	Department of Chemistry, Tsinghua University	
	100084 Beijing (P. R. China)	
[c]	Dr. H. Tian	
	State Key Laboratory of Bioactive Substance and Function of Natural Medicines	
	and Beijing Key Laboratory of Active Substances Discovery and Druggability Evaluation	
	Institute of Materia Medica, Chinese Academy of Medical Sciences and	
	Peking Union Medical College	
	100050 Beijing (P. R. China)	
	E-mail: tianh@imm.ac.cn	
[+]	These authors contributed equally to this work.	
	Supporting information for this article is available on the WWW under	S

Chem. Eur. J. 2021, 27, 1-8 Wiley Online Library 1 These are not the final page numbers!

https://doi.org/10.1002/chem.202100398

group tolerance under very mild reaction conditions. Furthermore, benefiting from the inherent advantage of heterogenous photocatalysis, prominent sustainability and easy photocatalyst recyclability, a drug molecule (modafinil) and an oxidized mustard gas simulant (2-chloroethyl ethyl sulfoxide) were selectively and easily obtained in scale-up reactions. Mechanistic investigations were conducted using radical quenching experiments and in situ ESR spectroscopy, all corroborating the proposed role of 2D-COF-1 in photocatalytic cycle.

elegantly (Scheme 1a). However, these photosensitizers may match only limited reactions, and homogenous photosensitizers are generally hard to be separated and reused, which might be a restriction for photocatalyst sustainability and streamlining industrial applications.

Photoactive 2D-COFs, as crystalline porous organic materials with high thermal and chemical stability, large surface areas and excellent optical properties,^[7] have emerged as a new type of heterogeneous photocatalysts for visible-light-driven chemical transformations^[8] *e.g.* water splitting^[9] and CO₂ reduction.^[10] As for visible-light-driven organic transformations, distinguished from frequently-used photocatalysts, they offer an enticing alternative because of easy recyclability and expediently adjustable photoelectric properties. In the past few years, a series of approaches applying well-designed 2D-COFs as photocatalysts



Scheme 1. Strategies of the visible-light-driven selective oxidation of small organic molecules.

into organic transformations have been reported, such as visible-light-induced cross-dehydrogenative coupling (CDC) reactions,^[11] oxidation,^[12] reductive dehalogenation,^[13] *E-Z* isomerization,^[14] showing a great potential in heterogeneous visible-light-irradiated organic processes. In our previous works,^[15] the hydrazone-based two-dimensional covalent organic frameworks 2D-COF-1 had been successfully used as a heterogeneous photosensitizer in visible-light-induced radical addition-cyclization, arylation and alkylation.

According to the measurement of the redox potential and mechanism investigations for 2D-COF-1, we found that it possessed considerable low reductive potential and always served as a reductive agent in the photocatalytic initialization phase. In the light of these observations, we envisioned that there was a great probability for it to be used as an appropriate photosensitizer to activate molecular oxygen under visible-light-irradiation.^[16] Herein, as part of our continuing exploration on using photoactive 2D-COFs as photosensitizers in visible-light-driven organic reactions, we wish to report a highly efficient and sustainable visible-light-driven selective aerobic oxidation of various small organic molecules that utilizes 2D-COF-1 as the heterogeneous photocatalyst (Scheme 1b).

Results and Discussion

To evaluate our hypothesis on the possible photocatalytic activity of 2D-COF-1 on oxygen activation, firstly, three iminelinked 2D-COFs (Figure 1a) were prepared and characterized according reported protocols after to proper adjustments.^[11a,12b,17] Then several key factors for heterogeneous photocatalysts such as BET surface area, band gap, redox potential and UV/Vis absorption were measured and compared. The BET surface area of them resulted to be 1501 m²/g^[11a,15a] (2D-COF-1), $409 \text{ m}^2/g^{[12b]}$ (crystalline laminar COF 1b) and 2349 m²/g^[17] (Py-2,2'-BPyPh COF), presenting that Py-2,2'-BPyPh COF had the largest BET surface area (Figure 1e). However, the band gap and reductive potential of the 2D-COF-1 (2.88 eV, -2.29 V vs. SCE)^[11a,15a] were much wider and more negative than crystalline laminar COF 1b (2.66 eV, -1.65 V vs. SCE)^[12b] and Py-2,2'-BPyPh COF (2.20 eV, -1.52 V vs. SCE), indicating 2D-COF-1 might be more suitable for some photocatalytic aerobic oxidation reactions than the latter two (Figure 1b). The UV/Vis absorption of all three 2D-COFs matched reported homogeneous photosensitizers in photoinduced aerobic oxidations (Figure 1c and 1d), further clarifying that they might have the similar photocatalytic performance in the corresponding transformations. In this context, the three 2D-COFs were employed as the heterogeneous photosensitizers in the visible-light-driven selective aerobic oxidation of 2-methyl-3,4-dihydroisoquinolin-1(2H)-one (1a). After extensive optimizations of the reaction conditions (see details in the Supporting Information, Table S1), unsurprisingly, the desired amide 2a was obtained in 93% yield by employing 2D-COF-1 as the heterogeneous photosensitizer. However, the other two 2D-COFs performed barely satisfactorily, giving 2a in 31% and 72% respectively. The results were

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perfectly consistent with our earlier hypothesis, suggesting that the 2D-COF-1 was the most ideal one among them.

With the optimized reaction conditions in hand, the substrate scope of N-substituted tetrahydroisoguinolines was surveyed. As shown in the Scheme 2, all N-alkyl tetrahydroisoquinolines participated the reactions well, giving the corresponding amides (2a-2i) in good yields. Various N-phenyl tetrahydroisoquinolines were also compatible, affording the desired amides successfully regardless of electron-donating (2k, 21, 2m, 2r), electron-withdrawing (2n, 2o) substituents and halogen (2p, 2q) substituents on the aromatic ring. N-naphthyl tetrahydro-isoquinoline was also a good substrate for this oxidation, providing the corresponding amide 2s in 79% yield. Apart from cyclic amines, two cyclic ethers were also tested with proper changes of the reaction conditions (see details in the Supporting Information, Table S2), and the corresponding esters 2t and 2u were produced in excellent yields. It is worthy noting that there was almost no obvious diminishing reaction efficiency compared with previous works^[18] using homogeneous photosensitizers.

After successfully oxidizing cyclic amines and ethers, attention was turned to explore other categories of 2D-COF-1 catalyzed visible-light-driven selective aerobic oxidation. As is



Scheme 2. Visible-light-driven selective oxidation of cyclic amines and ether by using 2D-COF-1 as the photosensitizer. [a] Reaction conditions: 1 (0.2 mmol), 2D-COF-1 (8 mg), DBN (1.5 equiv.), MeCN (2 mL), air, rt, 40 W blue LED (456 nm), 12 h. [b] Isolated yield. [c] Crystalline laminar COF 1b (6 mg) was used as the heterogeneous photosensitizer. [d] Py-2, 2'-BPyPh COF (4 mg) was used as the heterogeneous photosensitizer. [e] 1 (0.2 mmol), 2D-COF-1 (8 mg), H₂O (2 mL), 40 W blue LED, under O₂ for 12 h at room temperature. Full Paper doi.org/10.1002/chem.202100398





Figure 1. a) Structures of 2D-COF-1, Crystalline laminar COF 1b, and Py-2, 2'-BPyPh COF. b) Redox potentials (in V vs. SCE) of the 2D-COFs and some reported homogeneous photosensitizers. c) Normalized UV/Vis absorption spectra of $[Acr^+-Mes]CIO_4^-$, Ru(bpy)₃Cl₂-6H₂O, Eosin Y, Rose Bengal and 9-fluorenone. d) Normalized UV/Vis absorption spectra of 2D-COF-1, crystalline laminar COF 1b and Py-2, 2'-BPyPh COF. e) BET surface area of 2D-COF-1, crystalline laminar COF 1b, and Py-2, 2'-BPyPh COF. e) BET surface area of 2D-COF-1, crystalline laminar COF 1b, and Py-2, 2'-BPyPh COF.

known that *N*-heterocycles with a pyridine nucleus like quinolones and isoquinolones, widely occur in potential drugs^[19] and diverse biologically active molecules,^[20] they could be obtained from *N*-alkylpyridinium salts' oxidation. Thus, 1-methy quinolinium iodide **3a** was chosen to take the first step under modified reaction conditions (see details in the Supporting Information, Tables S3). To our delight, it performed well and delivered the corresponding quinolone efficiently. In sharp contrast, while using the other two 2D-COFs as heterogeneous photosensitizers, desired product was obtained in lower yield under the same reaction conditions. Subsequently, the sub-

strate scope was investigated. As shown in Scheme 3, various *N*-methylisoquinolinium salts (3a-3d), *N*-methylquinolinium salts (3e-3m) and *N*-alkylisoquinonium salts (3n-3r) salts were compatible and they all gave the corresponding quinolones and isoquinolones in moderate to excellent yields.

Then, catalytic dehydrogenation (CDH) reaction, extensively investigated in aerobic oxidation reactions,^[21] was also tested by employing 2D-COF-1 as the photocatalyst under the visible-light-irradiation. As shown in Scheme 4, under our optimized conditions (see details in the Supporting Information, Table S4), alkyl, halogen and aryl substituted quinolines (**6a–6f, 6z**),

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Scheme 3. Visible-light-driven selective oxidation of *N*-alkylpyridinium salts into quinolones by using 2D-COF-1 as the photosensitizer. [a] Reaction conditions: 3 (0.2 mmol), 2D-COF-1 (8 mg), $C_5_2CO_3$ (1.5 equiv.), THF (2 mL), 40 W blue LED (456 nm), under air at room temperature for 12 h. [b] X = I. [c] X = Br. [d] Isolated yield. [e] Crystalline laminar COF 1b (6 mg) was used as the heterogeneous photosensitizer.

isoquinolines (**6h**) and indoles (**6m–6y**) were all obtained efficiently *via* our 2D-COF-1 catalyzed visible-light-driven CDH reactions with air. Benzylamine, as a very popular molecule in related previous reports, ^[4a,22] was also a good substrate, giving the corresponding imine **6aa** in a competitive yield.

Furthermore, visible-light-driven selective aerobic oxidations were performed with 2D-COF-1 on sulfides. Many different substituted thioethers were investigated (Scheme 5). With proper adjustments of the reaction conditions (see details in the Supporting Information, Table S6), most sulfoxides were selectively obtained in excellent yields, exhibiting a good functional group tolerance and selectivity (8c-8f). The substrate containing electron-withdrawing group was also compatible, but resulting in lower yield (8 g). Notably, modafinil (8 j), a real drug for excessive sleepiness, was successfully produced with the present method in 75% yield; 2-chloroethyl ethyl sulfide (CEES), a highly toxic mustard gas simulant, [23,24] was also selectively oxidized to nontoxic 2-chloroethyl ethyl sulfoxide (CEESO, 8k) in excellent yield (92%). Importantly, because of the excellent porosity and photoactivity of 2D-COF-1, the reactivity and efficiency of the above heterogeneous photocatalytic oxidations were all comparable to the reported homogeneous photocatalysis.

As a heterogeneous photosensitizer, the recyclability and reusability are prominent features in industrial and practical





Scheme 4. Visible-light-driven dehydrogenation by using 2D-COF-1 as the photosensitizer. [a] Reaction conditions: 5 (0.2 mmol), 2D-COF-1 (8 mg), DMA (2 mL), 40 W blue LED (456 nm), under O_2 at room temperature for 20 h. [b] Isolated yield. [c] 11 a (0.4 mmol), 2D-COF-1 (8 mg), MeCN 2 mL, 40 W blue LED, under air at room temperature for 24 h, ¹H NMR yield, 1, 3, 5-trimethoxybenzene as the internal standard. [d] Crystalline laminar COF 1b (6 mg) was used as the heterogeneous photosensitizer.



Scheme 5. Visible-light-driven oxidation of thioethers by using 2D-COF-1 as the photosensitizer. [a] Reaction conditions: 7 (0.25 mmol), 2D-COF-1 (10 mg), EtOH (2.5 mL), 40 W blue LED (456 nm), air, rt, 12 h. [b] Isolated yield. [c] Crystalline laminar COF 1b (6 mg) was used as the heterogeneous photosensitizer. [d] Py-2, 2'-BPyPh COF (4 mg) was used as the heterogeneous photosensitizer.



processes. With this regard, two photocatalyst recycling experiments were carried out for the selective oxidation of 2-methylisoquinolin-2-ium iodide (**3 a**) and (4-methoxyphenyl)(methyl)sulfane (**7 b**) under the standard reaction conditions. As illustrated in Scheme 6a (see details in the Supporting Information, part VII), photocatalyst 2D-COF-1 maintained its high photocatalytic activity even after five runs in these two systems. Moreover, two scale-up experiments were performed, **8 j** and **8 k** was obtained in 69% yield and 89% respectively just by a few simple isolation steps, demonstrating a natural advantage over homogenous catalysis (Scheme 6b).

Finally, to explore the real role of 2D-COF-1 in this visiblelight-driven selective oxidation, several radical quenching experiments were carried out under the standard reaction conditions (Table 1). When stoichiometric 2,2,6,6-tetrameth-



Scheme 6. a) Recycling experiments. b) Scale-up experiments.

BQ=Benzoquinone.

Table 1. Radical quenching experiments and the apparent quantum efficiency (A.Q.E.) values. $^{\left[a\right] }$							
Substrates/products	1 a/2 a	3e/4e	5 a/6 a	7 a/8 a			
TEMPO (2 equiv.) BHT (2 equiv.) DABCO (2 equiv.) CuCl ₂ (1 equiv.) FeSO ₄ (2 equiv.) BQ (2 equiv.)	trace trace 30 % N.R. trace trace	55 % trace 72 % N.R. 35 % N.D.	33% trace 67% trace trace trace	trace trace 32% trace trace trace trace			
A.Q.E.	15.0%	17.6%	11.3%	19.6%			
[a] Standard conditions, ¹ H NMR yield, CH ₂ Br ₂ as the internal standard,							

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ylpiperidinooxy (TEMPO) or 2,6-di-tert-butyl-4-methylphenol (BHT) was added into the four reaction systems (**1 a**, **3 e**, **5 a** and **7 a**), the yields of the corresponding products slashed dramatically, which suggested that a radical process should be involved. The experiments with 1,4-diazabicyclo [2.2.2] octane (DABCO) and benzoquinone (BQ) indicated the formation of ${}^{1}O_{2}^{(25)}$ and $O_{2}^{\bullet-}$.

Besides, when 2,2,6,6- tetramethylpiperidine (TEMP) and 5,5dimethyl-1-pyrroline N- oxide (DMPO) were employed as the radical trapping agents, under the visible-light-irradiation, in the presence of 2D-COF-1 and air, characteristic signals of single oxygen $({}^{1}O_{2})$ and super-oxide radical anion $(O_{2}^{\bullet-})$ was observed by in situ ESR spectra^[26] (Figure 2), reflecting that the 2D-COF-1 could serve as a superior photocatalyst to active molecule oxygen via energy transfer (ET) or single electron transfer (SET). Moreover, four model reaction processes were all obviously suppressed with the addition of CuCl₂ or FeSO₄, and lower yields of the desired products were observed, clearly showing the involvement of SET processes^[27] and the presence of hydroperoxyl radical^[6d,28] in the reactions. Furthermore, the apparent quantum efficiency (A.Q.E) values for the four model reactions were calculated to be 15.0%, 17.6%, 11.3% and 19.6%, revealing that the present aerobic oxidation excluded a radical chain process.

Combining all the results of the mechanistic experiments and reported literatures,^[6c-e,h,29] a plausible reaction mechanism for the present heterogenous visible-light-driven selective aerobic oxidation was proposed (Scheme 7). Initially, 2D-COF-1 was excited by the visible light. As an effective activator of oxygen, the resulted excited state of the photocatalyst reduced the oxygen to generate superoxide radical anion or activate oxygen into the singlet oxygen through energy transfer (ET). Then, for path a, the substrate underwent a single electron transfer (SET) with 2D-COF-1⁺, producing the radical cation intermediate I and the photocatalyst 2D-COF-1. Finally, the singlet oxygen and superoxide radical anion reacted with the intermediate I, delivering the corresponding selective oxidation product in a few steps. For path b, the substrate reacted with the singlet oxygen directly to accomplish the full oxidation.



Figure 2. a) ESR spectra of 2D-COF-1 in the presence of DMPO in MeCN, in air atmosphere under dark and under visible-light irradiation for 5 s, 20 s, 60 s and 120 s. b) ESR spectra of 2D-COF-1 in the presence of TEMP in MeCN, in air atmosphere under dark and under visible-light irradiation.

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Scheme 7. Plausible mechanism for 2D-COF-1 catalyzed the visible-lightdriven selective aerobic oxidation.

Conclusion

In summary, we have developed a sustainable and practical protocol for applying 2D-COF-1 into the visible-light-driven selective aerobic oxidations of many valuable small organic molecules under very mild reaction conditions. The reaction shows high efficiency and good functional group tolerance for the excellent photocatalytic ability of 2D-COF-1 on molecular oxygen activation. Importantly, as demonstrated in scale-up and recycle experiments, the photoactive 2D-COF-1 presents outstanding reusability and promising industrial potential. We expect that this photoactive 2D-COFs could be applied into other visible-light-driven organic transformations and accelerate the further application of covalent organic frameworks.

Experimental Section

Typical procedures for visible-light-driven oxidation of cyclic amines and ethers by using 2D-COF-1 as the photosensitizer: 2D-COF-1 (8 mg), MeCN (2 mL), 1 (0.2 mmol) and DBN (1.5 equiv., 0.3 mmol) were added in a Schlenk tube with a magnetic stir bar in sequence. The mixture was allowed to stir under air with irradiation of a blue LED (40 W, 456 nm) at room temperature for 15 hours. Upon completion, the photocatalyst 2D-COF-1 was removed by centrifugation, washed with ethyl acetate (4 mL), EtOH (4 mL), H₂O (4 mL) and EtOH (4 mL) in sequence, dried at 80 °C under 10⁻² mTorr for 10 h. The reaction solution was concentrated under reduced pressure and the residue was purified by silica gel flash column chromatography (PE/EtOAc=5/1-1/2).

Typical procedures for visible-light-driven oxidation of *N*-alkylpyridinium salts by using 2D-COF-1 as the photosensitizer: 3 (0.2 mmol), 2D-COF-1 (8 mg), Cs_2CO_3 (1.5 equiv., 98 mg) and THF (2 mL) were added in a Schlenk tube with a magnetic stir bar. The mixture was allowed to stir under air with irradiation of a blue LED (40 W, 456 nm) at room temperature for 12 hours. Upon comple-

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tion, the photocatalyst 2D-COF-1 and insoluble inorganic salts were removed by centrifugation, washed with ethyl acetate (4 mL), EtOH (4 mL), H₂O (4 mL) and EtOH (4 mL) in sequence, dried at 80 °C under 10⁻² mTorr for 10 h. The reaction solution was concentrated under reduced pressure and the residue was purified by silica gel flash column chromatography (PE/EtOAc = 5/1 - 1/2).

Typical procedures for visible-light-driven dehydrogenation by using 2D-COF-1 as the photosensitizer: 2D-COF-1 (8 mg), DMA (2 mL) and 5 (0.2 mmol) were added in a Schlenk tube with a magnetic stir bar in sequence. The mixture was allowed to stir under O₂ with irradiation of a blue LED (40 W, 456 nm) at room temperature for 15 hours. Upon completion, the photocatalyst 2D-COF-1 was removed by centrifugation, washed with ethyl acetate (4 mL), EtOH (4 mL), H₂O (4 mL) and EtOH (4 mL) in sequence, dried at 80 °C under 10⁻² mTorr for 10 h. Distilled water (10 mL) was added into the reaction solution, the resulting mixture was extracted with ethyl acetate (5 mL×3). The combined organic layers were washed with brine and dried with MgSO₄ and removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc = 20/1-3/1).

Typical procedures for visible-light-driven selective oxidation of thioether by using 2D-COF-1 as the photosensitizer: 2D-COF-1 (8 mg), EtOH (2 mL) and 7 (0.2 mmol) were added in a Schlenk tube with a magnetic stir bar in sequence. The mixture was allowed to stir under air with irradiation of a blue LED (40 W, 456 nm) at room temperature for 12 hours. Upon completion, the photocatalyst 2D-COF-1 was removed by centrifugation, washed with ethyl acetate (4 mL), EtOH (4 mL), H₂O (4 mL) and EtOH (4 mL) in sequence, dried at 80 °C under 10⁻² mTorr for 10 h. The reaction solution was concentrated under reduced pressure and the residue was purified by silica gel flash column chromatography (PE/EtOAc = 5/1-1/1).

Acknowledgements

Financial support from Natural Science Foundation of Liaoning Province (20180550882), the Program for Creative Talents in University of Liaoning Province and Shenyang Normal University Talents Program is acknowledged. We thank Dr. Jipan Yu, Dr. Yunhe Jin and Dr. Wenbo Liu for valuable suggestions and experimental assistance.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: aerobic oxidation • covalent organic frameworks • visible-light-driven • small organic molecules

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Manuscript received: February 1, 2021 Accepted manuscript online: March 31, 2021 Version of record online:

Chem. Eur. J. 2021, 27, 1-8 www.chemeurj.org 7 These are not the final page numbers! 77

FULL PAPER

COFs in photocatalytic oxidation of organics: Hydrazone-based 2D-COF-1 offers a fascinating alternative photocatalyst for visible-light-driven selective aerobic oxidation of valuable small organics such as amines, ethers, thioethers and pyridinium salts. By means of its superior photocatalytic ability in molecular oxygen activation and inherent heterogenous nature, the present protocol exhibits impressive efficiency, selectivity and sustainability.



S. Liu, M. Tian, Dr. X. Bu, Dr. H. Tian*, Prof. X. Yang*

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Covalent Organic Frameworks toward Diverse Photocatalytic Aerobic Oxidations