

Benzoxazole-Linked Ultrastable Covalent Organic Frameworks for Photocatalysis

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S Supporting Information

ABSTRACT: The structural uniqueness of covalent organic frameworks (COFs) has brought these new materials great potential for advanced applications. One of the key aspects yet to be developed is how to improve the robustness of covalently linked reticular frameworks. In order to make the best use of π -conjugated structures, we develop herein a "killing two birds with one stone" strategy and construct a series of ultrastable benzoxazole-based COFs (denoted as LZU-190, LZU-191, and LZU-192) as metal-free photocatalysts. Benefiting from the formation of benzoxazole rings through reversible/irreversible cascade reactions, the synthesized COFs exhibit permanent stability in the presence of strong acid (9 M HCl), strong base (9 M NaOH), and sunlight. Meanwhile,



reticulation of the benzoxazole moiety into the π -conjugated COF frameworks decreases the optical band gap and therefore increases the capability for visible-light absorption. As a result, the excellent photoactivity and unprecedented recyclability of LZU-190 (for at least 20 catalytic runs, each with a product yield of 99%) have been illustrated in the visible-light-driven oxidative hydroxylation of arylboronic acids to phenols. This contribution represents the first report on the photocatalytic application of benzoxazole-based structures, which not only sheds new light on the exploration of robust organophotocatalysts from small molecules to extended frameworks but also offers in-depth understanding of the structure–activity relationship toward practical applications of COF materials.

INTRODUCTION

The past decade has witnessed rapid development in the research field of covalent organic frameworks (COFs).¹ Featuring periodicity, porosity, and covalent bonding in structure, crystalline COFs have shown great potential for diverse applications.² In this regard, further improvement of their structural robustness turns out to be crucial³⁻¹¹ for practical applications. Following the basic principles of reticular chemistry¹² and dynamic covalent chemistry,¹³ the rational construction of COF structures mostly relies on the reversible formation of covalent bonds between the rigid building blocks. The Achilles' heel of COF structures is therefore the mortiseand-tenon joints¹⁴ where dynamic covalent chemistry operates. Elegant efforts have thus been devoted to strengthening the covalent linkages via different strategies.^{3,6,7,9} However, applications have rarely been conducted to further demonstrate the extra advantages offered by the strengthened frameworks. We report herein a "killing two birds with one stone" approach through which the construction of an ultrastable structure and functionalization for metal-free photocatalysis have been simultaneously achieved.

Photocatalysis¹⁵ is one of the most promising applications tailored for COFs.^{2d,16–22} The extended π -conjugated frame-

work, regular pore structure, and high surface area of COFs are all advantageous for enhancing their photocatalytic activity.^{2d,17–19,21,22} For example, pioneering work by the Lotsch group^{2d} has illustrated the superior photoactivity of hydrazonebased COFs when incorporated with metal cocatalysts. We¹⁸ and the Wu group¹⁹ realized the metal-free photocatalysis of cross-dehydrogenative coupling reactions with hydrazone-based COFs. In this aspect, the key bottleneck for utilizing COFs in photocatalysis is still the stability of the reticular frameworks. Although they are relatively stable, the hydrazone linkages in photocatalytic COFs could not remain unchanged after four catalytic cycles.^{18,19} As a result, significant loss in crystallinity and severe decrease in photocatalytic activity were exclusively observed. We therefore targeted the construction of more robust COFs for practical photocatalysis.

The rational design of COFs for applications requires one to consider both the stability and the functionality.^{14,23} These two criteria are governed, in most cases, by different sites in the COF structure: the stability comes from the covalent joints, while the functionality comes from the building blocks. This

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Scheme 1. (a) Classical Formation of the Benzoxazole Structure, such as 2-Phenylbenzoxazole (PBO-1), from Benzaldehyde and *o*-Aminophenol via Cascade Imine Formation/Cyclization/Oxidation; (b) One-Pot Construction of Benzoxazole-Linked COFs (LZU-190, LZU-191, and LZU-192) via the Cascade Reactions Shown in $(a)^a$

a) Classical formation of benzoxazole structure via cascade reactions



^aAs depicted in the mortise-and-tenon model, the structural robustness has been strengthened through the ubiquitous formation of benzoxazole cyclic joints. The best solvothermal conditions for synthesizing highly crystalline benzoxazole-linked COFs are to use N-methyl-2-pyrrolidone (NMP) and mesitylene (1:1 v/v) as the mixed solvent, benzimidazole (4.5 equiv) as the additive, and 185 °C as the reaction temperature.

brings much complexity in each step from the designed synthesis of building blocks to the concise construction of reticular frameworks. We envisioned offering a straightforward solution by making the covalent joints both ultrastable and functional. The benzoxazole linkage (Scheme 1) was therefore selected for the following reasons. The classical synthesis²⁴ of the benzoxazole structure (Scheme 1a) applies cascade reactions²⁵ involving reversible imine bond formation followed by irreversible oxazole ring formation. This reversible/

irreversible sequence could be ideal³ for the construction of robust COF structures (Scheme 1b). On the other hand, benzoxazole-related small molecules have shown advantageous photophysical properties and can undergo photoinduced electron transfer in the solid state.²⁶ Although, like many π -conjugated analogues, they have not found photocatalytic applications because of a narrow absorption region and short-lived photoexcited state,²⁷ reticulation into COF frameworks should make a difference.

We accordingly developed a facile approach to construct a series of benzoxazole-linked ultrastable COFs via the cascade reactions shown in Scheme 1. After extensive screening, we found that the best conditions involved the use of benzimidazole as the additive and N-methyl-2-pyrrolidone (NMP)/mesitylene as the mixed solvent, through which the benzoxazole-linked COFs LZU-190,7 LZU-191, and LZU-192 were obtained with high crystallinity. As a result of the irreversible formation of aromatic benzoxazole joints throughout the frameworks, the synthesized COFs exhibit superior stability in structure compared with imine-linked COFs, such as COF-LZU1.^{2c} Moreover, LZU-190 showed excellent activity in visible-light-driven aerobic oxidation,²⁸ which is a new and benign process in photocatalysis. Control experiments identified that the photocatalytic activity of LZU-190 indeed originates from the benzoxazole-linked π -conjugated crystalline framework. Meanwhile, benefiting from the strengthened covalent linkages in its structure. LZU-190 showed unprecedented recyclability among all the COF catalysts: its activity and crystallinity were retained well after at least 20 runs. This contribution may not only boost the designed synthesis of COFs as robust photocatalysts but also shed light on the exploration of unique advantages originating from the COF structures.

RESULTS AND DISCUSSION

Designed Synthesis and Structural Characterization. The benzoxazole-linked COFs LZU-190, LZU-191, and LZU-192 were synthesized under solvothermal conditions in sealed ampules via the condensation of 2,5-diamino-1,4-benzenediol dihydrochloride (1) with different aldehyde building blocks, such as 1,3,5-triformylbenzene (2), 2,4,6-tris(4-formylphenyl)-1,3,5-triazine (3), and 1,3,6,8-tetrakis(4-formylphenyl)pyrene (4). The solvothermal conditions were thoroughly screened, and the detailed results are shown in the Supporting Information (SI). The best crystallinity was obtained using NMP mixed with mesitylene (1:1 v/v) as the solvent, an excess of benzimidazole (4.5 equiv) as the additive, and 185 °C as the reaction temperature (Figures S6 and S7). These conditions have never been applied in COF synthesis and are much different from those for synthesizing benzoxazole-related small molecules²⁴ or polymeric materials.^{7,29} The formation of benzoxazole rings^{24e-g} under these condition includes three steps: (1) formation of imine-linked intermediates, (2) ring closure to form benzoxazoline intermediates, and (3) acceptorless dehydrogenation of benzoxazoline intermediates. The determining step is the first one, through which the crystalline structure can possibly be formed via the reversible formation of imine linkages. It should be noted that the addition of a base such as benzimidazole can indeed facilitate the aromatization in the third step.^{24g} In addition, as evidenced in Figure S7, in comparison with other bases, benzimidazole can improve the crystallinity of the COFs to a larger extent. Therefore, benzimidazole was employed herein not only as the dehydrogenation agent^{24g¹} to form the benzoxazole rings but also as the templating agent²ⁿ to obtain COF crystals with high quality.

The key issue in the structural characterization was to verify the formation of benzoxazole rings in the reticular frameworks. The FT-IR spectra showed typical *N*-heterocyclic bands at 1624, 1421, and 1120 cm⁻¹, respectively (Figures S12, S23, and S37), which are similar to those of the molecular counterpart, 2-phenylbenzoxazole (PBO-1) (Figure S3). The ¹³C crosspolarization/magic-angle spinning (CP/MAS) NMR spectra of LZU-190 (Figure 1a), LZU-191 (Figure S24a), and LZU-192



Figure 1. (a) 13 C CP/MAS and (b) NQS/MAS spectra of LZU-190. Asterisks denote spinning sidebands. The assignments of the 13 C chemical shifts of LZU-190 are indicated in the chemical structure. The presence of the signal at 163 ppm in the 13 C NQS/MAS NMR spectrum (b) indicates the successful formation of the benzoxazole rings.

(Figure S38a) exhibited signals at 163, 148, and 140 ppm, which originate from the carbon atoms of the *N*-heterocyclic rings (the assignments are shown in Figure 1). The signal at 163 ppm is indicative of the formation of benzoxazole rings. The ¹³C nonquaternary suppression (NQS)/MAS NMR experiment on LZU-190 (Figure 1b) further confirmed that the signal at 163 ppm corresponds to the quaternary carbon atoms of the benzoxazole rings.³⁰ Similar information was also obtained from ¹³C NQS/MAS NMR measurements on LZU-191 (Figure S24b), LZU-192 (Figure S38b), and PBO-1 (Figures S1 and S2). All of these data provided overwhelming evidence for the successful formation of benzoxazole rings.

The crystalline structures of LZU-190, LZU-191, and LZU-192 were verified by powder X-ray diffraction (PXRD) measurements. As shown in Figure 2, the observed PXRD pattern of LZU-190 exhibited an intense peak at 4.99° and four other peaks at 8.55°, 9.83°, 12.98°, and 26.03°, which correspond to the 100, 110, 200, 210, and 001 reflections, respectively. Similarly, the experimental PXRD pattern of LZU-191 showed five peaks at 2.97°, 5.24°, 6.01°, 7.83°, and 26.27°, and the experimental PXRD pattern of LZU-192 showed three peaks at 3.95°, 5.67°, and 7.93°. Simulation of their PXRD patterns (Figures S17, S28, and S42) suggested that all of these COFs should be preferably assigned as the eclipsed structures, as shown in the Figure 2 inset. Scherrer analysis revealed that the domain sizes of LZU-190, LZU-191, and LZU-192 are approximately 43, 43, and 33 nm, respectively.

Nitrogen adsorption-desorption experiments at 77 K were used to assess the porosities of the benzoxazole-linked COFs. LZU-190 (Figure S9) and LZU-192 (Figure S34) showed type-I isotherms for microporous structures, while LZU-191 (Figure S20) displayed a type-IV isotherm for mesoporous structures. Furthermore, nonlocal density functional theory gave rise to narrow pore size distributions centered at 1.2, 2.3, and 1.3 nm for LZU-190 (Figure S10), LZU-191 (Figure S21), and LZU-192 (Figure S35), respectively, the data of which agree well with the calculated pore sizes based on the eclipsed stacking models (Figure 2, top inset). The Brunauer-Emmett-Teller (BET) surface areas of LZU-190 (Figure S11), LZU-191 (Figure S22), and LZU-192 (Figure S36) were calculated to be 1035, 1305, and 706 m² g⁻¹, respectively. The total pore volumes $(P/P_0 = 0.99)$ were estimated as 1.59, 1.13, and 0.45 cm³ g⁻¹ for LZU-190, LZU-191, and LZU-192, respectively.



Figure 2. Indexed experimental (black), Pawley-refined (red), and predicted (blue) PXRD patterns of LZU-190, LZU-191, and LZU-192. The difference plots are presented in green. Top inset: eclipsed structures proposed for LZU-190, LZU-191, and LZU-192. C, gray; O, red; N, blue. H atoms have been omitted for clarity.

All of the data acquired from the structural characterization confirmed that the benzoxazole-linked COFs were successfully constructed with high crystallinity.

Ultrastability of Benzoxazole-Linked COFs. As a result of the formation of robust benzoxazole linkages throughout the frameworks, the synthesized COFs exhibited extraordinary stability. Thermogravimetric analysis (TGA) indicated that they are thermally stable up to 400 °C (Figures S13, S25, and S39), which is superior to most 2D COFs, whose decomposition temperatures are normally below 350 °C. Most importantly, these COFs showed excellent chemical stability under harsh conditions, such as upon 3 day treatment in boiling water, pure trifluoroacetic acid (TFA), aqueous HCl (9 M), or aqueous NaOH (9 M). For example, after the treatment, the PXRD patterns (Figure 3a and Table S4) and ¹³C CP/MAS NMR spectra (Figure S48) of LZU-190 remained unchanged. The N₂ adsorption and desorption isotherms (Figure 3b) displayed only very small changes (Figures S49, S51, S53, and S55). The residual weight percentages were 91, 89, 86, and 93% after 3 day treatments in boiling water, TFA, 9 M HCl, and 9 M NaOH, respectively (Figure S46), which further verified the chemical stability of LZU-190. The scanning electron microscopy (SEM) images revealed that the morphology was also retained after the treatment (Figure S47). On the contrary, the structure of imine-linked COF-LZU1 decomposed under these conditions. All of these benzoxazole-linked COFs also possess excellent photostability: the crystalline structures remained intact upon continuous exposure (for at least 3 days) to visible light (irradiation with 20 W white light-emitting diodes (LEDs)). Again, the structure of imine-linked COF-LZU1 decomposed upon visible-light irradiation (Figure S60). With the data from the stability tests in hand, we further explored the photocatalytic performance of these robust COFs.



Figure 3. (a) PXRD patterns measured after 3 day treatment of LZU-190 in boiling water (red), TFA (blue), 9 M HCl (magenta), 9 M NaOH (purple), and visible light (green). (b) N_2 adsorption (solid symbols) and desorption (open symbols) isotherms measured after 3 day treatment of LZU-190 in boiling water (red), TFA (blue), 9 M HCl (magenta), 9 M NaOH (purple), and visible light (green). For the purpose of comparison, the isotherms have been shifted vertically in the figure; the original data are shown in the SI.

Photocatalytic Application. As a start for the photocatalytic test, we assessed the optical properties of the benzoxazole-linked COFs. Figure 4 shows their UV/vis spectra, which indicate that all of them can absorb light in the UV and visible regions. The optical band gaps of LZU-190 (Figure S66), LZU-191 (Figure S68), and LZU-192 (Figure S70) were



Figure 4. UV/vis absorption spectra of LZU-190 (black), LZU-191 (red), LZU-192 (blue), the model compound PBO-2 (green), and the building blocks (1, magenta; 2, navy; 3, violet; 4, purple).

calculated to be 2.02, 2.38, and 2.10 eV, respectively. In comparison with benzoxazole-based small molecules,²⁶ such as PBO-1 (3.06 eV; Figure S72) and PBO-2 (2.96 eV; Figure S73), these π -conjugated COFs exhibit a shift of their lowest-energy absorption to longer wavelength and enhanced intensity of visible-light absorption.³¹ These ultrastable benzoxazole-linked COFs may therefore act as new candidates³² for metal-free photocatalysts in visible-light-driven reactions.

We chose visible-light-driven aerobic oxidation²⁸ to examine the photocatalytic activity of benzoxazole-linked metal-free COFs, as photocatalytic aerobic oxidation is a new, versatile, and environmentally benign strategy for oxidation processes.² Through this strategy, molecular oxygen can be readily excited to produce superoxide radical anion, which is subjected to further transformations. For example, the oxidative hydroxvlation of arylboronic acids via photocatalysis³³ in homogeneous media has recently been elucidated by the Xiao^{33a} and Scaiano^{33b} groups. $[Ru(bpy)_3Cl_2] \cdot 6H_2O^{33a}$ and methylene blue^{33b} were applied therein as small-molecule photosensitizers to initiate the activation of oxygen. Here we found that LZU-190 exhibited high stability, excellent activity, broad universality, and unprecedented recyclability as a heterogeneous metalfree photocatalyst in the oxidative hydroxylation of arylboronic acids to phenols. Specifically, this transformation can still be efficiently catalyzed by LZU-190 in the absence of a sacrificial agent such as *i*Pr₂NEt.

The transformation of 4-carboxyphenylboronic acid to 4hydroxybenzoic acid was initially selected as the model reaction for the systematic assessment. The factors that influence this transformation were thoroughly evaluated via control experiments, and the key results are listed in Table 1. The reaction yield can reach 99% with LZU-190 as the photocatalyst and iPr_2NEt as the sacrificial agent under an air or oxygen atmosphere (entry 1). In the absence of either light (entry 2), photocatalyst (entry 3), or oxygen source (entry 4), this transformation can hardly occur. For comparison with

Table	1.	Control	Experiments ^a
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H000-		visible light hotocatalysts, <i>i</i> Pr ₂ NEt (5 eq.)	H000-	
11000		CH ₃ CN/H ₂ O (4/1), air		
entry	visible light	photocatalyst	air	yield (%) ^b
1	on	LZU-190	+	99
2	off	LZU-190	+	N.D. ^{<i>c</i>}
3	on	none	+	trace
4	on	LZU-190	-	trace
5	on	AMP-190 ^d	+	78
6	on	PBO-1 ^e	+	trace
7	on	PBO-2 ^f	+	10
8	on	COF-LZU1	+	decomp. ^g
9	on	COF-TpPa(OH) ₂ ^h	+	trace
10	on	LZU-191 ^{<i>i</i>}	+	99
11	on	LZU-192 ^j	+	99

^{*a*}Conditions: 4-Carboxyphenylboronic acid (0.2 mmol), LZU-190 (21.2 mg, 0.015 mmol), CH₃CN (1.6 mL), H_2O (0.4 mL), iPr_2NEt (5.0 equiv), irradiation with 20 W white LEDs, 48 h. ^{*b*}Yields of the isolated products. ^{*c*}N.D. = not detected. ^{*d*}AMP-190 (21.2 mg, 0.015 mmol) is amorphous LZU-190. ^{*e*}PBO-1 (19.5 mg, 0.1 mmol) as a molecular photocatalyst. ^{*f*}PBO-2 (31.2 mg, 0.1 mmol) as a molecular photocatalyst. ^{*g*}COF-LZU1 showed decomposition. ^{*h*}COF-TpPa-(OH)₂ (21.2 mg, 0.012 mmol). ^{*i*}LZU-191 (25.3 mg, 0.01 mmol). ^{*j*}LZU-192 (25.0 mg, 0.01 mmol).

crystalline LZU-190, amorphous LZU-190 (denoted as AMP-190) and the molecular counterparts (PBO-1 and PBO-2) were also tested. AMP-190 was less efficient (entry 5, 78% yield), and the molecular catalysts PBO-1 and PBO-2 showed negligible activity only (entries 6 and 7). In addition, the imine-linked COF-LZU1^{2c} decomposed under these reaction conditions (entry 8 and Figure S88). Another robust COF, COF-TpPa-(OH)₂,³⁴ showed no catalytic activity either (entry 9). In addition, LZU-191 and LZU-192 exhibited excellent photoactivity in this reaction (entries 10 and 11). All of these data demonstrated that the excellent photocatalytic activity originates from the benzoxazole-linked π -conjugated crystalline framework.

The superiority of crystalline LZU-190 as the photocatalyst was further demonstrated by recycling experiments. LZU-190 could be easily separated from the reaction solution and serve as a recyclable photocatalyst in the next run (see the SI for details). Being free of any special treatment or reactivation procedure, crystalline LZU-190 presented excellent and unchanged activity even after 20 runs in the visible-light-driven oxidative hydroxylation of 4-carboxyphenylboronic acid (Figure 5). The crystallinity, porosity, covalent bonding, and morphol-



Figure 5. Assessment of the reusability of LZU-190 in photocatalyzing the oxidative hydroxylation of 4-carboxyphenylboronic acid to 4-hydroxybenzoic acid. The reusability tests were carried out under identical conditions as shown in Table 1, entry 1.

ogy of the recycled LZU-190 catalysts are fully comparable to those of pristine LZU-190, as evidenced by the data acquired from PXRD, nitrogen adsorption–desorption isotherm, ¹³C CP/MAS NMR, and SEM measurements (Figures S80–S87). These data show that the reusability of LZU-190 is unprecedented among all of the COF catalysts reported to date.

We then evaluated the substrate scope of arylboronic acids to validate the generality of LZU-190 as a privileged photocatalyst. As shown in Table 2, in the presence of LZU-190, a series of arylboronic acids bearing electron-withdrawing substituents could be effectively converted to the desired phenols in excellent yields (>98%; entries 1–5). Other substrates with electron-neutral or electron-rich substituents also experienced satisfactory conversion with a slightly prolonged reaction time (entries 6–8).³⁵ Furthermore, a heteroarylboronic acid was well-tolerated under these conditions and afforded the corresponding product in 80% isolated yield (entry 9). Meanwhile, the size-dependence effect was observed with polycyclic substrates: the reaction yields decreased with increasing size of the substrate (entries 7, 10, and 11). For example, the large-sized 1-pyrenylboronic acid (11.5 Å \times 9.1 Å)

 Table 2. Photocatalytic Activity Test of LZU-190 in

 Oxidative Hydroxylation of Arylboronic Acids to Phenols⁴

	visil LZU-190, <i>i</i> l	ble light Pr ₂ NEt (5 eq.)	Ar-OH	
	CH ₃ CN/H ₂	₂ O (4/1), air		
entry	Ar	<i>t</i> (h)	yield (%) ^b	
1	4-HO ₂ CC ₆ H ₄	48	99	
2	4-CHOC ₆ H ₄	48	99	
3	$4-NO_2C_6H_4$	30	99	
4	4-MeO ₂ CC ₆ H ₄	48	99	
5	4-CNC ₆ H ₄	48	98	
6	$4-BrC_6H_4$	48	86	
7	C_6H_5	72	88	
8	4-MeOC ₆ H ₄	96	58	
9	3-quinolinyl	72	80	
10	2-naphthyl	96	81	
11	1-pyrenyl	96	55	

^{*a*}Conditions: Arylboronic acid (0.2 mmol), LZU-190 (21.2 mg, 0.015 mmol), CH₃CN (1.6 mL), H₂O (0.4 mL), *i*Pr₂NEt (5.0 equiv), irradiation with 20 W white LEDs. ^{*b*}Yields of the isolated products.

cannot be smoothly accommodated within the pores (~1.2 nm) of LZU-190, resulting in a lower yield even with doubled reaction time (entry 11). This size-selective phenomenon could not exist in homogeneous systems,^{33a} which highlights again the unique advantage of COF photocatalysts.

Moreover, we found that LZU-190 could still work as an efficient photocatalyst in the absence of the sacrificial agent iPr_2NEt (Table S7). It should be noted that the sacrificial agent is considered necessary in homogeneous systems because it works as the electron donor to complete the catalytic cycle.^{33a} Indeed, molecular photocatalysts, such as methylene blue, Ru(bpy)₃Cl₂, PBO-1, PBO-2, and benzimidazole, showed only negligible activity in the absence of iPr_2NEt (Table S7). On the contrary, without the sacrificial agent, 4-carboxyphenylboronic acid could still be photocatalyzed by LZU-190 alone, affording the desired phenol product in 86% yield (Table S7). However, in a slight difference from the data previously obtained in the presence of iPr_2NEt (Figure 5), the photocatalytic activity LZU-190 was gradually reduced in the recycling experiments (Table S9).

In order to understand the photocatalytic role of LZU-190 in the visible-light-driven aerobic oxidation, we performed spintrapping experiments³⁶ and examined the trapped adduct by electron spin resonance (ESR) spectroscopy. When 5,5dimethyl-1-pyrroline *N*-oxide (DMPO) was added to the airsaturated methanol solution containing LZU-190, the adduct of superoxide radical anion with DMPO was detected after visiblelight irradiation (Figure S98). To confirm the source of oxygen, we further carried out two ¹⁸O-labeling experiments with ¹⁸O₂ and H₂¹⁸O (eqs 1 and 2, respectively). High-resolution mass



spectrometry (HRMS) analysis (Figures S89 and S90) showed that the oxygen atom in the product originated from the molecular oxygen instead of water. Accordingly, as shown in

Figure 6, the key mechanistic steps should include generation of excited LZU-190 via irradiation, formation of superoxide



Figure 6. Proposed mechanism for the photocatalytic transformation of arylboronic acids to phenols in the presence of LZU-190. SET stands for single-electron transfer.

radical anion $(O_2^{\bullet-})^{36,37}$ via single electron transfer (SET) from excited LZU-190 to oxygen, rearrangement, and hydrolysis. The photoredox cycle is completed by the regeneration of LZU-190 in the presence of electron donors, such as *i*Pr₂NEt. In the absence of the sacrificial agent, the terminal amino groups of LZU-190 might work as the electron donor, ^{33a} although the detailed pathway is not yet well-understood.

Discussion of the Structure–Activity Relationship. Although COF materials possess many structural advantages,³⁸ the linkages connecting the building blocks are generally weak because of the intrinsic nature of dynamic covalent bonds.¹ Therefore, one of the bottlenecks for the practical applications of COFs is how to further improve their structural robustness. In particular, as new candidates for use as visible-light sensitizers, the π -conjugated COFs must be stable enough to survive repeated photoredox cycles. Although the most developed, imine-linked COFs can act as robust catalysts in many thermal reactions, they tend to decompose upon visible-light irradiation.^{2c} This contribution focuses on the construction of ultrastable COFs as robust photocatalysts.

Only a handful of ingenious approaches³⁻¹¹ have been reported to strengthen the covalent linkages of COF structures. For example, in 2012 the Banerjee group developed a tautomerization strategy to further tautomerize the enol– imine linkages to stable keto–enamine linkages.³ In 2016, the Yaghi group oxidized the imine-linked COFs to afford more stable amide-linked COFs via postmodification.⁶ Closely relevant to this contribution, the McGrier group very recently applied a two-step strategy to construct benzobisoxazole-linked COFs.⁷ Although the applications of these robust COFs have not been further explored, these pioneering works did shed new light on the stability issue.

As shown in Scheme 1, we envisioned further making the covalent linkages both ultrastable and functional. For the first time, benzimidazole was applied as the dehydrogenation agent, which converts the dihydrobenzoxazole intermediates to ultrastable benzoxazole rings in a one-pot fashion. This is the crucial step to make COF structures robust enough for persistent photocatalysis. In addition, using the mixed solvent of NMP and mesitylene resulted in the best crystallinity for benzoxazole-linked COFs. The ubiquitous formation of benzoxazole linkages not only brings structural robustness but also renders the COF frameworks with superior photocatalytic activity. Although benzoxazole-based structures have been widely utilized for optoelectricity and sensing, to the best of our knowledge they have never been applied in photocatalysis.

This contribution has identified that reticulation of benzoxazole moieties into the COF framework decreases the optical band gap and increases the capability for visible-light absorption. The most important findings from the photocatalytic assessment that revealed the structure-activity relationship are summarized in the following: (i) In contrasts to benzoxazole-linked COFs, another robust COF, COF-TpPa-(OH)₂, showed no activity. This indicates that the photocatalytic activity indeed originates from the benzoxazole moieties. (ii) In comparison with LZU-190, the amorphous catalyst AMP-190 was less active, which highlights the contribution from structural regularity. (iii) The fact that molecular counterparts PBO-1 and PBO-2 showed negligible activity verifies the importance of extended π conjugated frameworks. (iv) Often-used small-molecule photosensitizers such as methylene blue and Ru(bpy)₃Cl₂ did not work in the absence of the sacrificial agent. This implies that the COF structure itself may act as the electron donor to complete the photoredox cycle. (v) The reusability of LZU-190 is superior among all of the COF catalysts reported to date, which provides overwhelming evidence for the unique advantage of the ultrastable structure.

Last but not least, this research highlights the difference in the design of COF catalysts for thermal and photoinduced catalysis. The catalyst design for thermal reactions relies on the established knowledge of molecular catalysts; the key consideration is how to concisely reticulate them into the COF framework. In contrast, this reference is absent for the rational design of COF photocatalysts: the molecular counterparts may have no photoactivity at all. For example, the benzoxazole-based small molecules showed negligible photoactivity only, while reticulation of benzoxazole moieties into π conjugated crystalline frameworks made a significant difference. Accordingly, this contribution not only realizes for the first time the photocatalytic application of benzoxazole-based structures but also provides further insight for the exploration of organophotocatalysts from small molecules to extended frameworks.

CONCLUSION

We have developed herein a "killing two birds with one stone" strategy to construct metal-free COFs for robust photocatalysis. The key design is to strengthen the covalent linkages via the one-pot construction of ultrastable benzoxazole rings (Scheme 1). The ultrastability of benzoxazole-linked COFs has been demonstrated upon severe treatments in strong acid/base and under visible-light irradiation. The superior photoactivity of metal-free LZU-190 has been evidenced by its excellent activity, broad universality, and unprecedented recyclability in the oxidative hydroxylation of arylboronic acids. We therefore expect that our contribution will benefit the designed synthesis of robust COFs for practical applications. Specifically, since benzoxazole-linked COFs can be facilely obtained in large quantities from easily available building blocks, they may find a broad variety of applications in the near future. In addition, benzoxazole-related structures have never been able to be applied in photocatalysis before. This research therefore shows a new possibility for expanding the region of organophotocatalysts from small molecules to reticulated frameworks.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b00571.

Detailed synthetic procedures, general procedure for the oxidative hydroxylation reaction, ¹³C CP/MAS NMR spectra, FT-IR spectra, PXRD patterns, modeling details and atomic coordinates, gas adsorption data, TGA traces, SEM images, TEM images, UV/vis spectra, CV data, and liquid NMR data (PDF)

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Notes

The authors declare no competing financial interest.

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(35) The electron density of the aryl precursors bearing an electrondonating substituent is relatively high, hindering the attack by a

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nucleophilic reagent such as the superoxide anion. As a result, the electron-donating precursors showed relatively lower conversion.

(37) When 2,2,6,6-tetramethylpiperidine (TEMP) was added under the same conditions, the adduct of singlet oxygen with TEMP was observed (Figure S97). However, the singlet-oxygen pathway should not be dominant because the photoreaction was accelerated when a singlet-oxygen quencher, 1,4-diazabicyclo[2.2.2]octane, was added to the photocatalytic system (Table S6).

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