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ABSTRACT: Photocatalysis is regarded as one of the most promising technologies to remove organic contaminants. At present, most of the covalent organic frameworks (COFs) used as photocatalysts are connected by imine or borate bonds, which have relatively low stability and relatively poor π-delocalization. Herein, we report, for the first time, vinylene-linked COFs constructed by various diacetylene and triazine moieties for photocatalytic degradation of organic contaminants and disinfection of bacteria. The pioneering introduction of diacetylene moieties not only enhances conjugated π-electrons delocalization but also optimizes the electronic band structures that significantly improve photocatalytic activity. Therefore, the vinylene-bridged COFs have excellent photocatalytic activity with ultrahigh stability and great π-electron delocalization, thus exhibiting ultrafast photocatalytic degradation efficiency for phenol and norfloxacin (>96%, within 15 min). Our work provides a strong basis for the rational regulation of the chemical structure of COFs to enhance their photocatalytic activity, thus broadening the application of COFs in photocatalysis.

KEYWORDS: covalent organic frameworks, photocatalytic degradation, organic contaminants, phenol, norfloxacin

1. INTRODUCTION

The shortage of freshwater resources has become a global problem,1 so water pollution has aroused widespread concern among environmental scientists.2,3 Organic contaminants,4−6 such as antibiotics,7 dyes,8 aromatics,9 and personal care products,10 are the main source of water pollution. They are toxic, carcinogenic, and difficult to degrade, severely threatening the human life and health.11 In view of this, it is imperative to develop a highly efficient technology to remove organic contaminants in wastewater.

Among various strategies used to remove organic contaminants in wastewater, photocatalysis is considered superior due to its energy saving ability and high efficiency.12−15 Up to now, traditional inorganic semiconductors, such as oxides,16,17 sulfides,18 nitrides,19 and TiO2,20,21 have been intensively studied as light-driven photocatalysts. However, the heavy metal toxicity, photocorrosion effect,22 and low photocatalytic efficiency23 limit their practical applications. In recent years,
graphite carbon nitride (g-C$_3$N$_4$)\textsuperscript{24,25} metal–organic frameworks (MOFs),\textsuperscript{26,27} and covalent organic frameworks (COFs)\textsuperscript{28} have attracted research interest as photocatalysts. However, the rapid charge recombination of g-C$_3$N$_4$\textsuperscript{29} and the instability of MOF\textsuperscript{30} seriously hinder their wide application.

COFs constructed by weaving designable organic components via strong covalent bonds are emerging polymers with a regular porous structure and versatile functionalities.\textsuperscript{31,32} Due to their flexible topological connectivity, tunable functionality, large specific surface area, extremely low density,\textsuperscript{33,34} COFs have been widely applied to heterogeneous catalysis,\textsuperscript{35} gas storage and separation,\textsuperscript{36–39} and energy storage.\textsuperscript{40,41} Thanks to their high surface area, abundant accessible catalytic sites, and periodic $\pi$-conjugated aromatic units,\textsuperscript{42,43} COFs are promising in the field of photocatalysis. Over the past few years, several types of COFs have been reported as photocatalysts to remove organic pollutants such as TpMA,\textsuperscript{44} JUC-521-Fe,\textsuperscript{45} and COFA+C.\textsuperscript{46} However, these reported COFs are mainly connected through dynamic covalent bonds such as imine and boronate ester bonds. They have comparatively low stability under harsh chemical conditions\textsuperscript{47,48} and relatively poor $\pi$-delocalization,\textsuperscript{49,50} which greatly limit their practical applications. On the contrary, vinylene-linked COFs displaying ultrahigh stability under extreme chemical conditions\textsuperscript{51–53} and great $\pi$-electron delocalization overcome the limitations of imine-linked COFs. Vinyl-linked COFs have a fully conjugated structure and exhibit interesting semiconductor properties, such as adjustable band position, fast carrier separation capability, and excellent photocatalytic and electrochemical performance.\textsuperscript{51–55} Recently, a series of vinylene-linked COFs (such as Tp-BDDA,\textsuperscript{56} sp$^3$c-COF$_{dpy}$,\textsuperscript{57} LZU-190\textsuperscript{58}) have been reported for reduction of CO$_2$, water decomposition, and organic synthesis via utilization of visible light. However, the photocatalytic degradation of organic pollutants using vinyl-linked COFs has not yet been reported.

Herein, novel vinylene-linked COFs (BDA-TMT, EDA-TMT, TDA-TMT) are prepared by an aldol condensation reaction, mixing various diacetylene linkages and triazine blocks for degrading organic contaminants and disinfecting bacteria through photocatalysis. Experimental results suggest that BDA-TMT constructed by diacetylene and triazine moieties has excellent photocatalytic activity in degrading organic contaminants under visible light (Figure 1), exhibiting ultrafast photocatalytic degradation efficiency for phenol and norfloxacin (>96% in 15 min). The reason for this phenomenon is that the introduction of diacetylene moieties not only enhanced delocalization of conjugated $\pi$-electrons delocalization and optimized the electronic band structures but also significantly improved the photogenerated carrier separation efficiency. Hence, the combined action of diacetylene linkages and triazine blocks in the highly planar $\pi$-conjugated framework clearly enhanced the photocatalytic capability of BDA-TMT. Therefore, the photocatalytic capability of the materials can be enhanced via predesigning the molecular structure, which provides a strong basis for practical application of COFs in photocatalysis.

2. EXPERIMENTAL SECTION

2.1. Materials. Norfloxacin, 1,4-benzoquinone (BQ), methylene blue (MB), KOH, EtONa, and NaOH were obtained from Shanghai Saan Chemical Technology Co., Ltd. 4,4’-(Buta-1,3-diylene-1,4-diyl)-dibenzoaldehyde (BDA), 4,4’-(ethyne-1,2-diyl) dibenzoaldehyde (EDA), [1,1’-4,1’-terphenyl]-4,4’-dicarbalddehyde (TDA), and 2,4,6-trimethyl-1,3,5-triazine (TMT) were obtained from Jilin Chinese Academy of
Sciences—Yanshen Technology Co., Ltd. Analytical grade reagents, such as acetonitrile, methanol, 1,4-dioxane, acetone, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), ethanol, trifluoroacetic acid (TFA), tetrahydrofuran (THF), N,N-dimethylformamide (DMF), 2,2,6,6-tetramethylpiperidine (TEMP), o-dichlorobenzene, ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), phenol, n-butanol, piperidine, isopropyl alcohol (IPA), and mesitylene, were acquired from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of Photocatalysts. TMT was reacted with BDA, EDA, and TDA to produce three vinylene-linked COFs (see the Synthesis of Photocatalysts section in the Supporting Information). The reaction was implemented at 150 °C for 3 days to obtain a red solid. The solid was neutralized with 0.1 mol L\(^{-1}\) NH\(_4\)OH in methanol aqueous solution (50 wt %) and washed three times with acetone, methanol, and THF successively. The product was dried for 12 h at 80 °C under vacuum to obtain BDA-TMT (yield, 65%), EDA-TMT (yield, 66%), and TDA-TMT (yield, 69%). We optimized the reaction conditions by synthesizing BDA-TMT, EDA-TMT, and TDA-TMT COFs under variable conditions (Tables S1–S3) to overcome the low reversibility of the olefin bond produced by the aldol condensation reaction. Based on the PXRD patterns of products obtained in attempts to synthesize BDA-TMT, EDA-TMT, and TDA-TMT COFs under variable conditions (Tables S1–S3) to overcome the low reversibility of the olefin bond produced by the aldol condensation reaction. Based on the PXRD patterns of products obtained in attempts to synthesize BDA-TMT, EDA-TMT, and TDA-TMT under different reaction conditions (Figures S1–S3), we finally chose mesitylene, dioxane, and acetonitrile as reaction solvents, then kept the reaction mixture at 150 °C for 3 days, and obtained BDA-TMT, EDA-TMT, and TDA-TMT with a higher degree of crystallization (Figure 2a).

2.3. Photocatalytic Experiment. Experiments were conducted in a 100 mL photoreactor cooled by circulation water (25 ± 0.2 °C). During each experiment, 20 mg of photocatalysts was suspended in an MB, phenol, and norfloxacin aqueous solution (10 ppm, 50 mL). Then, the mixed solution was fully stirred in the dark for 1 h to make the MB, phenol, and norfloxacin reach the equilibrium of adsorption and desorption on the surface of as-prepared photocatalysts. A 300 W xenon lamp with the wavelength range of 320 nm ≤ \(\lambda\) ≤ 780 nm and a light density of 1 kW m\(^{-2}\) (PLS-SXE300D) was taken as the source of visible light, 2 mL of the blended solution was extracted every 5 min, and then the catalyst powder was removed by filtration with a millipore filter (0.22 μm) for further characterization.

3. RESULTS AND DISCUSSION

3.1. Characterization. The vinylene-linked COFs, BDA-TMT, EDA-TMT, and TDA-TMT, were prepared by reacting 2,4,6-trimethyl-1,3,5-triazine (TMT) with aryl aldehyde monomers (BDA, EDA, and TDA) via aldol condensation under the same conditions (Figure 2a). The chemical composition and structure of the vinylene-linked COFs were confirmed through FT-IR spectra and \(^{13}\)C solid-state CP/MAS NMR spectra. The FT-IR spectrum (Figures S4–S6) exhibited the newly formed C=O group stretching vibration peaks in the trans configuration at \(\sim 1629\) and \(\sim 970\) cm\(^{-1}\), which were found in all COFs. In addition, the C=O characteristic absorbance at \(\sim 1693\) cm\(^{-1}\) was completely eliminated in as-prepared COFs, indicating that BDA-TMT, EDA-TMT, and TDA-TMT were fully condensed. As shown in \(^{13}\)C CP/MAS NMR spectra of all COFs (Figures S7–S9), the peaks at 125
and 138 ppm were assigned to the carbon atoms of the olefin linkages (denoted as 2 and 3, respectively). The peak at about 169 ppm was caused by carbon atoms in the triazine units.

The crystallinity and structure of all COFs were confirmed by PXRD profiles (Figures 2b–d and S10–S12). The crystal structures were elucidated by comparing the structural simulation and the diffraction results. The PXRD pattern of BDA-TMT showed distinguishable peaks at ∼2.6, ∼4.5, ∼5.2, ∼6.9, and ∼25.4° (2θ). Similarly, the PXRD profile of EDA-TMT exhibited five peaks at ∼2.9, ∼5.0, ∼5.9, ∼7.8, and ∼25.6° (2θ). The PXRD pattern of TDA-TMT showed five peaks at ∼2.7, ∼4.6, ∼5.4, ∼7.1, and ∼25.6° (2θ), which were indexed to generate unit cell parameters of \(a = b = 37.9922\text{ Å}\) and \(c = 3.4659\text{ Å}\).

The simulated AA-stacking model of BDA-TMT, EDA-TMT, and TDA-TMT patterns matched their experimental patterns (Tables S4–S6, SI), and the Pawley refined PXRD curves were consistent with the experimental PXRD patterns, resulting in inappreciable differences in the profile.

The inherent porosity of the COFs was tested via N\(_2\) sorption measurements at 77 K. The specific surface areas of BDA-TMT, EDA-TMT, and TDA-TMT were determined as 592.1, 522.6, and 379.5 m\(^2\) g\(^{-1}\), respectively (Figures 3a–c and S13–S15). The pore size distributions of COFs were estimated as 3.47, 3.02, and 3.23 nm with the nonlocal density functional theory (NLDFT) model, which fitted well with the AA-stacking model. The morphologies of BDA-TMT, EDA-TMT, and TDA-TMT were studied by scanning electron microscopy (SEM) (Figures 3d–f and S16) and transmission electron microscopy (TEM) (Figure S17). The synthesized COFs exhibited a homogeneous globular morphology, and their average diameter was 0.8 ± 0.2 μm.

3.2. Stability Test. To verify the high stability, the vinylene-linked COFs were exposed to different chemical conditions for 24 h (Figure 4). After treatment with visible light or being immersed in saturated NaCl, 6.0 M NaOH, and 6.0 M HNO\(_3\), BDA-TMT, EDA-TMT, and TDA-TMT all maintained excellent chemical stability and high crystallinity. Furthermore, our COFs demonstrated predominant thermal stability in N\(_2\) up to 350 °C based on the thermogravimetric analysis (Figure S18). Therefore, BDA-TMT, EDA-TMT, and TDA-TMT had superior stability.

3.3. Studies of Photoelectric Properties. The UV–vis DRS spectra revealed that EDA-TMT and TDA-TMT exhibited high absorption in UV and visible regions up to 800 nm, whereas BDA-TMT exhibited a broad boundary absorption spectrum (Figure 5a). The optical band gap of BDA-TMT was calculated to be 1.97 eV according to the
Kubelka–Munk transformed reflectance spectra, which was smaller than 2.14 eV of EDA-TMT and 2.20 eV of TDA-TMT (Figure 5b). The photogenerated charge separation of the as-prepared samples was studied by photoluminescence (PL) spectra. As shown in Figure 5c, compared with EDA-TMT and TDA-TMT, BDA-TMT showed much smaller fluorescence signal peak intensity, suggesting that the recombination of photogenerated carriers was inhibited by the introduction of acetylene. Furthermore, the carrier lifetimes of the samples were analyzed using photoluminescence (PL) decay spectra. The amplitude-weighted average lifetimes of BDA-TMT, EDA-TMT, and TDA-TMT were 4.73, 3.31, and 3.18 ns, respectively (Figure 5d and Table S7). The longer average PL lifetime of BDA-TMT indicated that the recombination rate of photogenerated carriers was further suppressed with its more highly extended π-conjugated framework; thus, the optical performances of COFs were greatly improved by introducing diacetylene.

The positive slopes of their Mott–Schottky plots (Figures 5e, S19, and S20) suggested that the as-prepared samples were typical n-type semiconductors. Moreover, the conduction band (CB) minimum of n-type semiconductors is more negative by about 0.1–0.2 eV than their flat band potential. The CB positions of BDA-TMT, EDA-TMT, and TDA-TMT were −0.82, −0.77, and −0.75 V vs RHE (pH = 7), respectively. The valence band (VB) positions of the BDA-TMT, EDA-TMT, and TDA-TMT were 1.15, 1.37, and 1.45 V (Figure S21), respectively. The VB position of BDA-TMT was obviously much lower, which meant that the oxidation ability was enhanced after the introduction of diacetylene units. In addition, BDA-TMT had smaller electrochemical impedance (Figure 5f) and higher photocurrent (Figure 5g) than EDA-TMT and TDA-TMT, which might be due to the introduction of diacetylene units.
of the diacetylene structure endowing BDA-TMT with more efficient charge carrier separation and interfacial charge transfer.

To confirm the generation of active oxygen species in the photocatalytic process, electron paramagnetic resonance (EPR) analysis was performed. As shown in Figure 5h, all COFs showed signal peaks of singlet oxygen (\(1^1O_2\)), superoxide radicals (\(-O_2^-\)), and hydroxyl radicals (\(-OH\)) after visible light irradiation. However, as shown in the EPR spectra of ROS generated by BDA-TMT, EDA-TMT, and TDA-TMT in the dark, no signal peak appeared under dark conditions (Figure S22). BDA-TMT exhibited a higher yield of \(1^1O_2\), \(\cdot O_2^-\), and \(\cdot OH\). The result showed the lower recombination rate and higher separation efficiency of photocarriers. The electronic band structures of COFs (Figure S21) suggested that \(\cdot OH\) will not be generated by the oxidation of holes (h\(^+\)). Therefore, a possible mechanism for producing \(\cdot OH\) was considered. The electrons (e\(^-\)) of CB transferred to the surface of photocatalysts and reacted with dissolved oxygen molecules to generate a large amount of \(\cdot O_2^-\), and then, \(\cdot O_2^-\) oxidized H\(_2\)O to form \(\cdot OH\).

3.4. Photocatalytic Performances. The as-prepared COFs might display high antibacterial activity through the destruction of the organic components by the produced ROS. Herein, various bacteria were taken as model microorganisms, such as *Pseudomonas aeruginosa* (P. aeruginosa), *Vibrio alginolyticus* (V. alginolyticus), and *Staphylococcus aureus* (S. aureus). As shown in Figure 6a, BDA-TMT had a better bactericidal effect under visible light irradiation compared with TDA-TMT. After light irradiation, the SEM images of the damaged bacterial cell membrane were observed. As shown in Figure 6b, the *V. alginolyticus* membrane was intact and smooth at the beginning of the experiment. After the photocatalytic experiment, the membrane was broken. The results revealed that BDA-TMT had remarkable antibacterial activity against all tested bacterial strains (Figure 6c).

The photocatalytic degradation of methylene blue (MB), phenol, and norfloxacin was carried out to study the photocatalytic property of the COFs. BDA-TMT showed a more excellent photocatalytic activity than EDA-TMT and TDA-TMT. With BDA-TMT, MB was completely degraded in 15 min (Figure 7a) and the removal efficiency of phenol and norfloxacin reached 100 and 96%, respectively. EDA-TMT and TDA-TMT exhibited much lower photocatalytic activity (Figures 7b–d and S23a,b). As shown in the photographs of MB degradation abilities of all COFs with time (Figures 7e, S24, and S25), BDA-TMT made the MB aqueous solution colorless within 15 min, while EDA-TMT and TDA-TMT required 20 and 30 min, respectively. The reaction rate constants of BDA-TMT to degrade MB, phenol, and norfloxacin were 0.434, 0.1675, and 0.1764 min\(^{-1}\), respectively (Figures 7f and S23c,d). Compared with the photocatalytic degradation performance of various reported materials, BDA-TMT has a faster rate of degradation removal for organic contaminants (Table S8). BDA-TMT could be regenerated by centrifuging at least five times for degrading MB with almost no loss in activity (Figure 7g).

To further explore the mechanisms of MB, phenol, and norfloxacin photocatalytic degradation, ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), 1,4-benzoquinone (BQ), and isopropyl alcohol (IPA) were added into the reaction suspensions to remove h\(^+\), \(\cdot O_2^-\), and \(\cdot OH\), respectively.\(^{13}\) When EDTA-2Na or BQ was added, the photodegradation performance for MB and phenol was significantly inhibited. In contrast, the addition of IPA did not significantly reduce the photocatalytic degradation rate for MB and phenol. The degradation performance of BDA-TMT for MB and phenol with different quenchers showed that h\(^+\) and \(\cdot O_2^-\) played a pivotal role in the photocatalytic degradation of MB and phenol, while \(\cdot OH\) remained insignificant (Figures 7h and S23e). Therefore, the key active species of MB and phenol were the same in the photocatalytic degradation process. As shown in the degradation performance of BDA-TMT toward norfloxacin with different quenchers, the removal efficiency for norfloxacin without scavengers was 100%, while the removal efficiency for norfloxacin with EDTA-2Na, BQ, and IPA was 92.37, 54.70, and 84.21%, respectively (Figure S23f). The above results distinctly showed that \(\cdot O_2^-\) played a pivotal role in the photocatalytic degradation of norfloxacin.

3.5. Possible Photodegradation Intermediates and Pathways. LC-MS was applied to analyze the possible intermediates to further explain the degradation process of phenol and norfloxacin. Usually, these products are produced through a series of oxidation, ring opening, and cracking processes. Ideally, these products would eventually be broken down into CO\(_2\) and H\(_2\)O. According to the part determined intermediates, we proposed possible photodegradation pathways of phenol as shown in Figure 8. Phenol (m/z = 93) was mainly degraded by the hydroxylation of the benzene ring.
Figure 7. UV−vis spectra of MB aqueous solution in the presence of BDA-TMT (a), EDA-TMT (b), and TDA-TMT (c). Comparison of the MB degradation performance of as-prepared samples under light conditions (d). Corresponding photograph of MB degradation abilities of BDA-TMT with time (e). Reaction kinetic curves of as-prepared samples corresponding to the degradation of MB (f). Recyclability study of BDA-TMT (g). MB removal efficiency of BDA-TMT with diverse quenchers in light conditions (h).

Figure 8. Degradation mechanism and degradation pathways of phenol.
When the -OH reacted with phenol, it generated hydroquinone, catechol, and resorcin \((m/z = 109)\). Then, the ring opened to form carboxylic acid compounds. Eventually, these carboxylic acid compounds were oxidatively degraded to produce small molecules of \(\text{H}_2\text{O}, \text{CO}_2\), and inorganic ions.

We also proposed possible photodegradation pathways of norfl oxacin (Figures 9, S26, and S27). The initial substrate norfl oxacin \((m/z = 320)\) was mainly degraded on the quinolone group and piperazinyl group. The first reaction channel was the hydroxylation and further oxidation and decarboxylation of norfl oxacin to obtain the product \((m/z = 292)\). The second reaction channel was decarboxylation and further oxidation to remove the ethyl group, and the product was further degraded with piperazine ring opening and removal and the corresponding product \((m/z = 179)\) was obtained. The third reaction channel was piperazine epoxidation, ring opening, and removal, and the corresponding product \((m/z = 251)\) was obtained. In addition, another possible route was the oxidative removal of norfl oxacin to obtain the product \((m/z = 291)\) and further piperazine ring opening to obtain the corresponding product \((m/z = 251)\). Further degradation of the above products might be mainly manifested as the further opening of the quinolone group and the benzene ring, which degraded to generate small molecules of carboxylic acid compounds and then further degraded to generate small molecules of \(\text{H}_2\text{O}, \text{CO}_2\), as well as inorganic ions.

4. CONCLUSIONS
In summary, we successfully synthesized vinylene-linked COFs for efficiently degrading organic contaminants and disinfecting bacteria. The photocatalytic performances were significantly improved by introducing diacetylene moieties into the triazine-cored COFs, suggesting the significant influence of the diacetylene moieties on enhancing photocatalytic performances. Meanwhile, the C–C linkage with enhanced conjugated \(\pi\)-electron delocalization was used in our COFs, exhibiting superior stability. The unique structure of BDA-TMT was most suitable for the photocatalytic degradation of organic contaminants, with ultrafast photocatalytic degradation efficiency for phenol and norfl oxacin (>96%, within 15 min). We hope this work will provide an innovative pathway to design and synthesize 2D semiconducting COFs via regulating the chemical structure of COFs to enhance their photocatalytic activity, thereby widening the application of vinylene-linked COFs in photocatalysis.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsabm.1c00621.

Additional experimental details and figures including solid-state \(^{13}\text{C}\) CP-MAS NMR spectra; PXRD patterns; \(\text{N}_2\) sorption isotherms; TEM images; TGA results; Mott–Schottky plots; SEM images; EPR spectra; FT-IR spectra; degradation performance of phenol and norfl oxacin under visible light irradiation; photocatalytic degradation performance of various materials toward organic contaminants; and degradation mechanism and degradation pathways of norfl oxacin (PDF)

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Notes
The authors declare no competing financial interest.

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