Covalent Organic Frameworks for Photocatalysis: Design, Strategy, and Structure-to-Performance Relationship

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ENGLISH SUMMARY

Covalent organic frameworks (COFs) are a class of crystalline porous materials with promising applications, particularly in the field of photocatalysis. Their well-defined topological structures and highly ordered pores enable precise structural modulation to meet specific application requirements. In this dissertation, we systematically explore various design strategies and investigate the impact of COF structures on photocatalytic performance, aiming to elucidate the structure– property relationships and provide insights for future material optimization.

Chapter 1 gives a comprehensive overview of the design strategies and structureperformance relationships of COFs for photocatalysis, as well as their wide-ranging applications in photocatalysis. The first part introduces the fundamental principles of photocatalysis and highlights the advantages of COF-based materials as photocatalysts. Then, various structural modification strategies to optimize the photocatalytic performance of COFs are discussed, including linkage design, donoracceptor configuration, linker functionalization, π -conjugation enhancement, and defect engineering. This chapter also discusses key photocatalytic applications, such as hydrogen peroxide production, organic transformations, and pollutant degradation, emphasizing how COF design influences reaction efficiency and selectivity.

In **Chapter 2**, two benzothiadiazole-based COFs, containing phenyl and triazine nodes, respectively, were synthesized and their photophysical and electrochemical properties were thoroughly studied. The materials were investigated for sacrificial agent-free photocatalytic H₂O₂ production from water. The triazine-containing COF exhibits superior photo-induced charge separation and many-fold diminished recombination due to their enhanced conjugation. The results showed that the triazine-based COF significantly outperformed the phenyl analogue, which is attributed to the better photophysical properties of the former.

In **Chapter 3**, the pyrene (electron-donating) and porphyrin (electron-accepting) moieties are incorporated into the COF backbone to form Py-Por-COF. For comparison, two other pyrene-based D-D type COFs were also synthesized. The three COFs were utilized for the aerobic coupling of amines under air atmosphere with blue-LED irradiation. Among the three COFs, the Py-Por-COF with D-A structure exhibits the highest photocatalytic performance (99% yield) and demonstrates a remarkable apparent quantum efficiency of 11.3 % at 420 nm. Moreover, the catalyst exhibited a good recyclability, with no significant decrease in catalytic activity after four cycles.

In **Chapter 4**, three vinylene-based COFs were prepared to perform the photocatalytic reduction of Cr (VI) with simultaneous degradation of organic pollutants. The very coplanar TEB-COF, based on triazine (acceptor) and acetylene (donor) linkers shows the best performance, due to the fact that the acetylene groups is a strong donor and to the fact that this COFs showed the highest planarity in the z-axis (dihedral angle only 2°), allowing good charge separation and good charge transfer mobility in all 3 dimensions. The high coplanar TEB-COF is able to completely remove the model dye Rhodamine B and Cr (VI) (10 mg/L) in less than 30 minutes.

Chapter 5 provides a general conclusion of this dissertation and perspectives from a personal standpoint.

NEDERLANDSE SAMENVATTING

Covalente organische raamwerken (COFs) vormen een klasse van kristallijne poreuze materialen met veelbelovende toepassingen, met name op het gebied van fotokatalyse. Hun goed gedefinieerde topologische structuren en sterk geordende poriën maken nauwkeurige structurele aanpassingen mogelijk om te voldoen aan specifieke toepassingsvereisten. In dit proefschrift verkennen we systematisch verschillende ontwerpstrategieën en onderzoeken we de impact van COFstructuren op de fotokatalytische prestaties, met als doel de structuur-eigenschap relaties te verduidelijken en inzichten te bieden voor toekomstige materiaaloptimalisatie.

Hoofdstuk 1 biedt een uitgebreid overzicht van de ontwerpstrategieën en structuurprestatie relaties van covalente organische raamwerken (COFs) voor fotokatalyse, evenals hun brede toepassingen op dit gebied. Het eerste deel introduceert de fundamentele principes van fotokatalyse en benadrukt de voordelen van COFgebaseerde materialen als fotokatalysatoren. Vervolgens worden verschillende structurele modificatiestrategieën besproken om de fotokatalytische prestaties van COFs te optimaliseren, waaronder koppeling ontwerp, donor-acceptor configuratie, functionalisering van de linkers, π -conjugatieversterking en defectengineering. Dit hoofdstuk bespreekt ook belangrijke fotokatalytische toepassingen, zoals de productie van waterstofperoxide, organische transformaties en de afbraak van verontreinigende stoffen, waarbij wordt benadrukt hoe COF-ontwerp de reactiesnelheid en selectiviteit beïnvloedt.

In **Hoofdstuk 2** worden twee benzothiadiazool-gebaseerde COFs, respectievelijk met fenyl- en triazine-knooppunten, gesynthetiseerd en worden hun fotofysische en elektrochemische eigenschappen grondig bestudeerd. De materialen werden onderzocht voor opofferingsreagens-vrije fotokatalytische productie van H₂O₂ uit water. De triazine-bevattende COF vertoont superieure foto-geïnduceerde ladingscheiding en sterk verminderde recombinatie dankzij de verbeterde conjugatie. De resultaten toonden aan dat de triazine-gebaseerde COF aanzienlijk beter presteerde dan de fenyl-tegenhanger, wat wordt toegeschreven aan de betere fotofysische eigenschappen van de eerste.

In Hoofdstuk (elektronendonerend) 3 zijn pyreen en porfyrine (elektronenaccepterend) structuren geïntegreerd in het COF-raamwerk om Py-Por-COF te vormen. Ter vergelijking werden ook twee andere pyreen-gebaseerde D-D type COFs gesynthetiseerd. De drie COFs werden toegepast voor de aerobe koppeling van aminen onder een luchtatmosfeer met blauw-LED-bestraling. Van de drie COFs vertoonde de Py-Por-COF met D-A-structuur de hoogste fotokatalytische prestaties (99% opbrengst) en een opmerkelijke schijnbare kwantumefficiëntie van 11,3% bij 420 nm. Bovendien toonde de katalysator een goede herbruikbaarheid, zonder significante afname van de katalytische activiteit na vier cycli.

In **Hoofdstuk 4** werden drie vinylene-gebaseerde COFs bereid voor de fotokatalytische reductie van Cr (VI), gecombineerd met de gelijktijdige afbraak van organische verontreinigingen. De sterk coplanaire TEB-COF, gebaseerd op triazine (acceptor) en acethyleen (donor) linkers, vertoont de beste prestaties. Dit wordt toegeschreven aan de sterke donoreigenschappen van de acethyleengroepen en aan het feit dat deze COF de hoogste planariteit langs de z-as vertoont (dihedrale hoek slechts 2°), wat een efficiënte ladingscheiding en een goede ladingsmobiliteit in alle drie dimensies mogelijk maakt. De hoog-coplanaire TEB-COF is in staat om de modelkleurstof Rhodamine B en Cr (VI) (10 mg/L) volledig te verwijderen in minder dan 30 minuten.

Hoofdstuk 5 geeft een algemene conclusie van dit proefschrift en biedt perspectieven vanuit een persoonlijk standpunt.

LIST OF ABBREVIATIONS AND ACRONYMS

Α	
AQY	Apparent Quantum Yield
В	
ВА	Benzyl Alcohol
BET	Brunauer-Emmett-Teller
Вру	Bipyridine
ВТ	Benzothiadiazole
С	
СВ	Conduction Band
COFs	Covalent Organic Frameworks
CTFs	Covalent Triazine Frameworks
D	
DCB	1,2-Dichlorobenzene
DETA	Diethylenetriamine
DFT	Density Functional Theory
DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide
DMPO	5,5-Dimethyl-1-Pyrroline N-Oxide
E	
EIS	Electrochemical Impedance Spectroscopy
EDX	Energy Dispersive X-ray
EPR	Electron Paramagnetic Resonance
F	
FT-IR	Fourier Transform Infrared
G	
GC	Gas Chromatography
н	
HR-TEM	High-resolution Transmission Electron Microscopy

I	
ICP	Inductively Coupled Plasma
IPA	Isopropanol
Μ	
MOFs	Metal-Organic Frameworks
Ν	
NMR	Nuclear Magnetic Resonance
0	
ODS	Oxidative Desulfurization
ORR	Oxygen Reduction Reaction
Р	
PSD	Pore Size Distribution
Ру	Pyrene
Por	Porphyrin
Q	
QSDFT	Quenched Solid-state Density Functional Theory
S	
SEM	Scanning Electron Microscopy
т	
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
TOF	Turnover Frequency
TON	Turnover Number
U	
UV-Vis	Ultraviolet – visible
V	
VB	Valence Band
W	
WOR	Water Oxidation Reaction

WHO	World Health Organization
x	
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

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Chapter 1.

Covalent Organic Frameworks for Photocatalysis



1.1 Introduction

Since industrialization, the rapid development of modern society and the heavy reliance on non-renewable energy sources (e.g. coal, oil, and gas) have exacerbated problems such as energy shortages and environmental pollution.^{1, 2} This underlines the urgent need to develop sustainable energy alternatives to replace fossil fuels. One of the best alternatives to fossil fuels is solar energy, an abundant and inexhaustible natural resource. Photocatalytic technology, which converts solar energy into chemical energy, has been in the spotlight since 1972, when Fujishima and Honda first reported the use of titanium dioxide to achieve water splitting under ultraviolet radiation.³ Since then, countless scientists have dedicated their efforts to the research and development of efficient photocatalysts. The photocatalytic process typically involves three main steps: (i) Light harvesting, where the photocatalyst absorbs photons of light with sufficient energy. (ii) Charge separation, where the generated electron-hole pairs separate and migrate to the surface of the photocatalyst. (iii) Surface redox reactions occur: The separated electrons and holes interact with the adsorbed molecules on the catalyst surface. Despite the availability of thousands of photocatalysts, including inorganic metal oxides (e.g., TiO₂ and ZnO),⁴ sulfides (e.g., ZnS, CdS),⁵ graphitic carbon nitrides,⁶ small organic compounds (e.g., aromatics compounds and dyes),⁷ and porous organic materials,⁸ the design and construction of photocatalysts that effectively integrate activity, selectivity, and reusability remains a significant challenge. Achieving precise control of these properties at the molecular level continues to be difficult.

Covalent organic frameworks (COFs), first developed by Omar Yaghi group in 2005,⁹ are crystalline, porous polymers typically constructed from two multitopic precursors through strong covalent bonds (**Figure 1.1 right**). These materials can be considered as light-weight, metal-free semiconductors, with a typical band gap in the visible range. The isoreticular synthesis approach—where frameworks with the same overall topology are constructed using building blocks of similar geometry but varying size or

functionality (as previously applied in Metal-Organic Frameworks, MOFs; Figure 1.1 left)—enables precise control over the structural, chemical, and physical properties of the network by carefully incorporating functional building blocks into COFs. Herein, we aim to provide a concise overview of the major advances in COF photocatalysts in different application areas. In addition, we explore various tunable strategies that could enhance photocatalytic activity, focusing on how donor-acceptor construction, conjugation, coplanarity, linker engineering, linkage engineering, and defect engineering influence and relate to the photocatalytic processes of typical reactions. By addressing these fundamental concepts and recent advances, we predict future directions in the field and identify critical issues that need to be addressed.



Figure 1.1 Schematic structures of typical MOFs and COFs.

1.2 Design Principles and Advantages of COFs for Photocatalysis

Compared to traditional amorphous polymers, COFs are unique in that their structural units can be pre-designed, providing molecular-level designability. Theoretically, COFs possess ordered crystalline frameworks, with tunable topological structures and pore sizes, which are particularly beneficial for gaining deeper insights into the structure-photocatalytic performance relationship. COFs exhibit several following key advantages as photocatalysts:

- (i) Highly Ordered Structure: Their crystalline nature ensures a uniform pore size distribution and predictable topology.
- (ii) Large Surface Area: COFs possess ultra-high specific surface areas, which make them ideal for applications requiring high adsorption or catalytic activity.
- (iii) Chemical and Thermal Stability: Due to their covalent bonding, COFs are stable under harsh conditions, including high temperatures and various chemical environments.
- (iv) **Design Flexibility**: By carefully selecting monomers, COFs' pore size, functionality, and properties can be tailored for specific applications.
- (v) Light absorption: Functional units with π -conjugated systems or photoactive groups can be integrated into the COF framework to extend light absorption across a wider spectral range, from UV to visible or even near-infrared regions.
- (vi) Charge transfer: By incorporating photosensitizers, protonation, or synthesizing COFs with alternating donor and acceptor units to adjust their charge transfer characteristics, the photocatalytic performance can be significantly enhanced.

1.2.1 Linkage Engineering in COFs

COFs are fundamentally composed of two essential components: linkers (building blocks) and linkages (bonds formed between these building blocks during the framework assembly process). This modular design enables precise control over the topology, porosity, and functionality of the resulting material, offering a high degree of tunability for various applications. A key feature that distinguishes COFs from other porous materials is the diversity of their linkage types, which determines their chemical stability, structural rigidity, and functional properties. The choice of linkage not only governs the topology and dimensionality of the resulting framework but also influences its application potential. Over the years, various linkage types such as boronate ester, imine, hydrazone, C=C, and others have been developed, each offering unique structural and functional advantages (**Figure 1.2**). ¹⁰⁻¹³

Boronate ester-linked COFs

Azine-linked COFs



Hydrazone-linked COFs

β-Ketoamine-linked COFs



Quinoline-linked COFs



Thiazole-linked COFs



Vinylene-linked COFs



Figure 1.2 Typical covalent linkage formation reactions.

1.2.1.1 Boronate ester linkage

The boronate ester linkage is one of the earliest and most extensively studied linkages in COFs. First introduced by Yaghi and co-workers, this linkage involves the condensation of boronic acids with catechol to form boronate ester bonds,⁹ which drive the formation of highly crystalline and porous frameworks. The exceptional crystallinity and well-defined porosity of these COFs can be attributed to the dynamic reversibility of the boronate ester bond formation, enabling self-correction of structural defects during the solvothermal synthesis process. Despite these advantages, boronate ester linkages are non-conjugated and exhibit limited electronic interaction between the boron and oxygen atoms. Furthermore, their sensitivity to hydrolysis under humid or aqueous conditions poses a significant challenge, as the framework can degrade over time in such environments. This limitation has spurred efforts to enhance water stability by exploring alternative linkages.

1.2.1.2 Hydrazone linkage

The hydrazone linkage (C=N-N) is a dynamic and versatile bond formed through the condensation reaction between hydrazides and aldehydes or ketones. Compared to the boronate ester linkage, the hydrazone linkage demonstrates superior stability in aqueous environments. This is primarily due to the delocalization of lone pair electrons from the adjacent nitrogen atoms into the C=N bond, which reduces the electrophilicity of the carbon atom and enhances the structural robustness of the hydrazone bond. As a result, hydrazone-linked COFs retain their integrity even under harsh conditions involving strong acids or bases in water, expanding their potential applications in challenging environments. Additionally, the incorporation of heteroatom sites, such as nitrogen and oxygen, into the COF structure through hydrazone linkages provides abundant coordination points and functionalization opportunities. These heteroatom sites enable the formation of supramolecular interactions, such as intra- or interlayer hydrogen bonds, further stabilizing the framework and enhancing its functionality. The rich coordination sites, excellent chemical stability, and diverse functional groups of hydrazone-linked COFs make them highly promising candidates for photocatalysis.¹⁴ Furthermore, these properties allow for post-synthetic modifications, offering a flexible approach to tailor COFs for specific

6

applications.

1.2.1.3 Azine linkage

Azine-linkage is formed through the condensation of hydrazine or its derivatives with aromatic aldehydes. This type of linkage combines the conjugated structure of imines with the enhanced chemical robustness brought by the additional nitrogen atom, making azine-linked COFs a promising alternative to traditional imine-linked frameworks. Compared to hydrazone linkages, azine linkages typically result in more rigid frameworks with smaller pore sizes due to the use of the minimally substituted and highly symmetric hydrazine monomer. However, the absence of reactive functional groups in azine linkages limits their capacity for post-synthetic modifications, thereby reducing the tunability of framework functionalities.

1.2.1.4 Imine linkage

Imine-linked COFs, due to their wide selection of building blocks, have become one of the most extensively applied COFs in the field of photocatalysis. The versatility of building block choices, including a variety of aromatic aldehydes and amines, allows precise tuning of the COF's electronic, optical, and structural properties. This modularity facilitates the integration of diverse photoactive units, such as conjugated chromophores (e.g., porphyrins or phthalocyanines), enabling efficient light absorption and charge transfer. In 2009, Yaghi and co-workers synthesized a threedimensional imine-linked COF with a diamond-like structure, named COF-300, via the condensation reaction of terephthalaldehyde and tetra-(4-anilyl)methane under acetic acid catalysis. While this groundbreaking work originated with a threedimensional structure, subsequent research on two-dimensional imine-linked COFs is more extensive due to their simpler topologies.

Imine-linked COFs exhibit moderate chemical stability, offering higher stability in acidic and basic media compared to boronate ester-linked COFs. However, their integrity can be compromised due to the accumulation of charged groups, which induces electrostatic repulsion and destabilizes the theoretically layered structures—

an undesirable phenomenon in practical applications. To address this limitation, considerable efforts have been made to enhance the stability of imine-linked COFs. Accordingly, Banerjee et al. adopted a new strategy by introducing -OH functional groups adjacent to the Schiff base [-C=N] centers in COFs (**Figure 1.3a**), thereby forming intramolecular O–H····N=C hydrogen bonds. ¹⁰ This helps protect the basic imine nitrogen from hydrolysis in the presence of water and acid. The newly synthesized DhaTph COF maintained its crystallinity for over a week in 3 N HCl and deionized water. Hong Xu and co-workers incorporated methoxy groups into the pore walls to strengthen interlayer interactions (**Figure 1.3b**). The resonance effect of oxygen lone-pair electrons effectively reduced interlayer charge repulsion, resulting in the synthesis of a COF with remarkable stability.¹¹



Figure 1.3 (a) Syntheses of DmaTph and DhaTph by the condensation of square planar Tph building unit and linear Dma/Dha building unit. ¹⁰ (b) Synthesis of TPB-DMTP-COF through the condensation of DMTA and TAPB. ¹¹

Another interesting and widely applicable strategy is to convert imine linkages into more stable functional groups, such as thiazoles, oxazoles, or quinolines. These derivatizations not only significantly enhance the chemical stability of the frameworks but also introduce new functional properties to COFs. In the following, we will discuss several representative examples of imine-derived linkages to illustrate their advantages in improving stability and expanding functionality.

1.2.1.5 β-ketoenamine linkage

The β -ketoenamine linkage represents a significant advancement in the design of chemically robust COFs. In 2012, Banerjee and co-workers pioneered the synthesis of β-ketoenamine-linked COFs by utilizing the reversible Schiff base condensation between aromatic diamines and 1,3,5-triformylphloroglucinol (Tp) to generate a crystalline enol-imine COF intermediate. This intermediate subsequently undergoes an irreversible enol-to-keto tautomerization, forming a β -ketoenamine linkage. Importantly, this tautomerization does not compromise the crystallinity of the framework but significantly enhances its chemical stability. The resulting COFs, such as TpPa-1 and TpPa-2, exhibit exceptional resistance to harsh conditions, including strong acids (9 M HCl) and boiling water.¹² To explore the effects of reduced rigidity on β ketoenamine frameworks, Loh and colleagues introduced 2,4,6-triformylphenol, a building block with only one hydroxyl group, into COFs. This modification led to the formation of a more flexible β -ketoenamine intermediate, allowing reversible proton tautomerization between cis-keto and trans-keto forms within the COF structure. This dynamic structural transformation also enables the framework to exhibit adaptive ionresponsive and chemically dynamic properties on the pore surface, offering new possibilities for tunable functionality in COF applications.¹³

The resonance stabilization between the keto and enamine groups in the β ketoenamine linkage delocalizes electron density, reducing the electrophilicity of the carbonyl group and enhancing the COF's robustness. This combination of structural stability and extended π -conjugation imparts β -ketoenamine-linked COFs with

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remarkable chemical resistance and optical properties, making them ideal for applications such as photocatalysis, energy storage, and gas separation

1.2.1.6 Quinoline linkage

The quinoline linkage is an emerging connection strategy in COFs that offers enhanced chemical stability and electronic functionality. Quinoline-linked COFs can be formed through various approaches, including post-synthetic transformation of iminelinked COFs and direct one-pot methods. In the post-treatment strategy, imine linkages are "locked" into quinoline linkages through organic reactions, significantly enhancing the framework's chemical stability and resistance to hydrolysis. In 2018, Yi Liu and coworkers employed this post-treatment strategy by utilizing the aza-Diels–Alder cycloaddition reaction to kinetically lock reversible imine linkages,¹⁵ converting them into quinoline linkages to form the quinoline-linked COF (**Figure 1.4a**). This approach not only improved the stability of the framework but also leveraged the tunable structure of the starting imine-linked COFs and the diversity of reaction substrates. This allowed for the selective introduction of various functional groups, enabling tailored modifications to the pore surfaces and wettability of the resulting COFs. Such functional versatility, combined with the rigid and π -conjugated quinoline backbone, makes these materials particularly promising for applications in photocatalysis.

Alternatively, quinoline-linked COFs can be directly constructed through facile multicomponent reactions (one-pot methods). Yu-Bin Dong and co-workers reported the synthesis of 12 quinoline-linked COFs using a three-component one-pot reaction via in situ Strecker or Povarov reactions (**Figure 1.4b**). This method achieved high yields (exceeding 80%) and demonstrated excellent efficiency and scalability in producing these frameworks. ¹⁶ The one-pot strategy simplifies the synthesis process and enables the direct formation of quinoline-linked COFs with minimal intermediate steps.

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Figure 1.4 (a) The reaction scheme of COF-1 into MF-1 via a post-synthetic modification. ¹⁵ (b) Synthesis of S-TmTaDm-COF (1) and P-StTaDm-COF (2) via one-pot *in situ* approach and PSM. ¹⁶

1.2.1.7 Thiazole linkage

Another imine-derived linkage that can both enhance the chemical stability and extend the conjugation effect in COFs is the thiazole linkage, which can also be formed through post-modification and direct synthesis. In 2018, Lotsch and co-workers explored a post-synthetic locking strategy by converting triphenyltriazine imine COFs (TTI-COFs) into thiazole-linked COFs (TTT-COFs) through reaction with elemental sulfur (**Figure 1.5a**), ¹⁷ thereby establishing a class of thiazole-based COFs. These COFs exhibit remarkable thermal and chemical stability, maintaining their integrity even under

harsh conditions such as strong acidic, basic, or oxidative environments. In recent developments, Cooper and co-workers introduced a new strategy for synthesizing thiazole-linked COFs through a one-pot multicomponent reaction. ¹⁸ This process involves the reversible formation of Schiff bases, followed by effective irreversible C-H functionalization and oxidative cyclization to yield the final thiazole linkage. Mechanistic studies revealed that imine-linked COFs serve as intermediates in this cascade reaction before forming the final crystalline framework (Figure 1.5b). Interestingly, the one-pot approach demonstrated superior crystallinity compared to the method of first forming imine-linked COFs and then treating them with sulfur. The resulting thiazole-linked COFs exhibited enhanced performance as catalysts for hydrogen evolution. Due to their excellent light absorption properties and optimized band gaps, these thiazole-linked COFs proved to be promising candidates for photocatalytic hydrogen evolution. As shown in Figure 1.5c, among the synthesized COFs, one of the thiazole-linked COF demonstrated a hydrogen evolution rate of 4,296 μ mol g⁻¹ h⁻¹, significantly higher than its amorphous analogues (676 μ mol g⁻¹ h⁻¹) and imine-linked counterpart (1,644 μ mol g⁻¹ h⁻¹).

These findings highlight the potential of thiazole-linked COFs not only improve chemical stability but also enhance their functionality for applications in photocatalysis. Besides, the sulfur and nitrogen atoms in the thiazole rings can act as active coordination sites, enabling interactions with metal ions or guest molecules, which is highly advantageous for applications such as heterogeneous catalysis.

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Figure 1.5 (a) Schematic of the imine to thiazole transformation in the TTI-COF. (b) Synthesis of thiazole-linked COFs by a multicomponent reaction. ¹⁷ (c) Hydrogen evolution rates of crystalline TZ-COF-4, IL-COF-2, and amorphous TZ-COF-4. ¹⁸

1.2.1.8 C=C linkage

C=C linked-COF are commonly referred to as vinylene-based COFs, sp²-COF, or olefin-based COFs. As one of the most irreversible and stable bond types in organic chemistry, double carbon bonds (C=C) serve as ideal candidates for constructing robust

porous materials with significant potential for diverse applications. However, the low reversibility of C=C bond formation poses a significant challenge in achieving highly crystalline structures. The first strategy for synthesizing vinylene-based COFs involves the Knoevenagel condensation of aromatic aldehydes with p-phenylene-diacetonitrile under basic conditions. However, achieving highly crystalline cyano-vinylene-linked COFs using this approach requires meticulous optimization of solvents and bases, which can be challenging. In 2017, Dong-lin Jiang and co-works reported the first fully conjugated C=C-linked sp² COF, synthesized via the condensation reaction of tetra(4-formylphenyl)pyrene and 1,4-phenylenediacetonitrile (**Figure 1.6a**). ¹⁹ The obtained sp²c-COF is a semiconductor with a discrete band gap of 1.9 V and can be chemically oxidized to enhance conductivity by 12 orders of magnitude. However, a potential drawback of cyano-vinylene-linked COFs is their lack of exceptional stability, primarily due to the presence of reactive electron-withdrawing cyano substituents near the newly formed C=C bonds. Additionally, the toxicity of cyano groups poses a significant concern.

To address these issues, a second strategy emerged by utilizing the highly activated methyl groups of 1,3,5-trimethyltriazine.²⁰ Their high reactivity allows these building blocks to undergo catalyzed aldol condensation with aromatic aldehydes under solvothermal acidic conditions, yielding the corresponding olefin-linked COFs (**Figure 1.6b**). These materials represent some of the most chemically stable members of the COF family to date, capable of withstanding harsh alkaline, acidic, or strongly nucleophilic environments. Building on this precedent, other research groups have developed various methods to synthesize olefin-linked COFs.^{21, 22} For example, aldol condensation reactions can also be conducted under different alkaline conditions. Furthermore, other activated mesitylene derivatives have been successfully employed in these syntheses.²³

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Figure 1.6 (a) Schematic representation of the synthesis of the crystalline porous sp²hybridized carbon covalent organic framework (sp²c-COF) with pyrene knots and phenylenevinylene linkers connected by C=C bonds. ¹⁹ (b) Synthesis of COF-701 by aldol condensation between TMT and BPDA. ²⁰

1.2.2 Linker Engineering in COFs

As another key component of COFs, linkers also provide a unique opportunity to fine-tune the electronic and structural properties of the framework. By modifying the chemical functionalities, spatial configurations, or conjugation lengths of the linkers, we can control the light absorption, charge transport, and catalytic activity of COFs. As a result, linker modification has become a powerful and systematic tool for enhancing photocatalytic performance, solidifying its role as a focal point in the development of high-performance COF-based photocatalysts. The main strategies for linker modification include: (1) Linker Functionalization: Introducing functional groups such as halogens to fine-tune the electronic properties and reactivity of the COF. (2) Metal Coordination Modification: Linkers coordinated with single metal atoms (e.g., Fe, Co, Ni) create highly active catalytic sites. (3) Multifunctional Linker Design: Combining photo-responsive groups with catalytically active sites to synergistically enhance photocatalytic efficiency.

1.2.2.1 Linker Functionalization

Functionalizing linkers by introducing specific chemical groups is a widely adopted strategy to enhance COF photocatalytic performance. Functional groups, such as halogens, nitro, or amino groups, can significantly influence the electronic properties of the framework.

Halogens are highly electronegative, enabling π -electrons to delocalize from the conjugated backbone. This strengthens local charge polarization and enhances the dissociation of photogenerated excitons. For instance, Han's research group designed a partially fluorinated 2D triazine covalent organic framework (TF₅₀-COF) through ligand modulation (Figure 1.6a).²⁴ The F substitution introduced abundant Lewis acid sites, which modulated the electronic distribution of adjacent carbon atoms, provided high-activity sites for O₂ adsorption, and broadened the visible light response of the catalyst while improving charge separation. Adjusting the F proportion maximized the interlayer interactions of TF₅₀-COF, resulting in enhanced crystallinity, accelerated charge carrier transport, and improved photostability. The TF₅₀-COF catalyst demonstrated high selectivity and stability in the photocatalytic reduction of O₂ to H_2O_2 , achieving an impressive H_2O_2 production rate of 1739 µmol h⁻¹ g⁻¹ and a notable apparent quantum efficiency of 5.1% under 400 nm illumination. Chen and Xu et al. designed halogen-substituted BT structural units and synthesized imine-linked COFs with tunable photocatalytic activity (Figure 1.7b).²⁵ Compared to the unmodified Py-HTP-BT-COF, the halogen-substituted Py-CITP-BT-COF and Py-FTP-BT-COF exhibited higher photocurrent densities and lower resistance. These enhancements demonstrate the critical role of halogen functionalization in improving the electronic properties and photocatalytic performance of COFs. In addition to halogens, cyano groups are typical electron-withdrawing groups that can alter the electronic structure of building blocks. Sp²-carbon COFs are synthesized through the Knoevenagel reaction between cyano groups and aldehydes, forming cyano-substituted C=C bonds. The cyano side groups polarize the conjugated framework, thereby enhancing the generation and transfer of photoinduced electrons. This modification effectively



boosts photocatalytic efficiency and broadens the scope for designing highperformance COFs.

Figure 1.7 (a) Synthesis design of H-COF, TF-COF and TF₅₀-COF. ²⁴ (b) Synthetic routes of Py-*X*TP-BT-COFs under solvothermal conditions and the top view, side view and partial enlarged detail of AA stacking mode of Py-CITP-BT-COF. ²⁵

Yang et al. investigated the effects of different substituents (-CF₃, -OH) on the performance of COF materials (Figure 1.8).²⁶ Among the synthesized COFs, OH–TFP– TTA exhibited an exceptionally high specific surface area, a remarkably low bandgap, excellent charge separation efficiency, and a strong photocurrent response. Notably, it demonstrated superior photocatalytic performance and broad substrate applicability in photoinduced dehalogenation reactions. This outstanding performance was attributed to the hydroxyl group, which activated nearby amino groups, significantly enhancing the photocatalytic efficiency of the COF. Additionally, the combination of a narrow bandgap, high charge separation efficiency, and superior conductivity contributed to its exceptional performance. The Yaghi research group incorporated electron-withdrawing functional groups (-OMe, -F) into the COF-366-Co structure.²⁷ The integration of OMe and F atoms at the linker positions remotely regulated the electron density of the active sites, while avoiding the challenges associated with direct functionalization of porphyrin and minimizing negative effects such as spatial resistance or non-covalent interactions between functional groups at the active site. The introduction of electron-withdrawing units significantly enhanced the activity of the Co centers, leading to improved catalytic performance due to the strengthened electron-withdrawing effect.



Figure 1.8 Schematic Illustration for the Synthesis of imine COFs with Different Compositions (-H, -CF₃, -OH). ²⁶

1.2.2.2 Metal Coordination Modification

Since COFs are inherently metal-free, they cannot fulfill applications requiring the presence of metal species. However, COFs with potential coordination sites can coordinate with stable metal ions or metallic nanoparticles, thereby further enhancing the functionality of COF-based materials. As metal species are not involved in the construction of the COF framework, metallization generally does not compromise their crystallinity or structural integrity. This provides unmatched flexibility to combine the advantages of COFs with metal species, significantly broadening the application potential of COFs in catalysis area.²⁸

The exciton effect, caused by Coulomb interactions between electrons and holes, plays a subtle yet crucial role in photocatalysis. The Jiang group utilized imine-linked porphyrin-based DhaTph-M (M = H, Zn, or Ni) COFs as regulators of exciton effects during various oxidation processes (**Figure 1.9**).²⁹ Interestingly, by incorporating different metal ions, they selectively generated distinct types of reactive oxygen
species (ROS). Under visible light irradiation, the DhaTph-Zn produced singlet oxygen, while the DhaTph- Ni generated superoxide radicals. Consequently, under identical visible light conditions, the oxidation of α -pinene on DhaTph-Zn and DhaTph-Ni selectively yielded different products. Based on this understanding and modulation of the exciton effect, DhaTph-Zn and DhaTph-Ni could be deliberately used to promote selective oxidation of organic sulfides and hydroxylation of boronic acids, respectively.



Figure 1.9 Synthesis of DHA-Tph-M COFs and modulation of their photoactive behavior depending on the metal identity.²⁹

Additionally, metalized COF materials have demonstrated promising potential in photocatalytic carbon dioxide (CO₂) reduction applications. The roles of metalation include, but are not limited to, providing active centers for CO₂ capture and activation, altering the CO₂ reduction products (*e.g.*, CO, HCOOH, and CH₃OH), and inhibiting the unintended HER. Cobalt porphyrin-based COFs are attractive catalysts for photocatalytic CO₂RR due to their broad absorption extending into the near-infrared region, the efficient adsorption of CO₂ by Co(II), and the activation of CO₂ by CoN₄.³⁰ For instance, in the presence of Ru(2,2'-bipyridine)₃Cl₂ as the photosensitizer, the imine-linked COF-367-Co nanosheets with a thickness of 1.15 nm reduced CO₂ to CO in water at a high rate of 10 162 µmol g⁻¹ h⁻¹ under the irradiation of a xenon lamp equipped with a 420 nm high-pass filter.³¹ The ultrathin COF nanosheets are favourable for mass transfer and exposure of the active sites, resulting in 82-fold and 6-fold enhancements in activity and CO selectivity, respectively, over those of their

bulk counterparts.

Visible-light photoredox catalysis is an invaluable tool in modern organic synthesis, in which light active metal-based catalysts (*e.g.*, Ru-, Ir-, and Au-based complexes) with long excited-state lifetimes and high redox potentials allow the formation of radical intermediates, enabling substrate activation and driving the reaction.³² In 2021, our group reported a new photosensitive triazine-based COF (**Figure 1.10**), decorated with single nickel sites as a dual catalyst denoted as Ace-COF-Ni.³³ The obtained Ace-COF-Ni is an active photoredox catalyst for catalyzing the cross-coupling reaction between aryl iodides and thiols under visible light. It not only showed efficient photocatalytic activity with a yield of up to 96% but also exhibited a broad substrate scope and recyclability.





1.2.2.3 Multifunctional Linker Design

Most COF materials are typically synthesized through a two-component condensation system, which limits the tunability of the framework structure and functionality. In contrast, the multicomponent strategy is a well-established and widely used approach that enables the incorporation of multiple functional building blocks into the lattice structure, facilitating precise regulation of COF functionalities. This

approach not only broadens the light absorption range but also introduces intrinsic catalytic sites into the COF framework, enhancing its overall photocatalytic efficiency. Such designs are particularly promising for applications requiring both light harvesting and direct catalytic activity. In 2023, Liu's research group employed a multicomponent synthesis strategy to introduce electron-deficient triazine and electron-rich benzotrithiophene units into the framework via sp²-carbon and imine linkages,³⁴ constructing two types of photoactive three-component donor- π -acceptor materials (Figure 1.11). The three-component COF (COF-JLU36) demonstrated outstanding photocatalytic activity for hydrogen production from water, achieving an impressive hydrogen evolution rate of 70.8 \pm 1.9 mmol g⁻¹ h⁻¹ in the presence of 1 wt% Pt. This performance significantly surpasses that of the corresponding two-component donoracceptor COF, which contains a single node and linker. Guo et al. employed a similar strategy to synthesize a series of β -ketoenamine-linked multivariate COFs. Using 1,3,5triformylphloroglucinol (Tp) as a fixed node and varying the feed ratio of two amines,³⁵ they obtained β -ketoenamine-linked Tp(BT_xTP_{1-x})-COFs with different contents of BT and TP units. This approach enabled the fine-tuning of the optical bandgap and band positions. Of multivariate species, the Tp(BT_{0.05}TP_{0.95})-COFs exhibit maximum and sustained HER (9839 μ mol g⁻¹ h⁻¹) performance under visible light irradiation, much better than those of the parent TpTP-COF and TpBT-COF. The low quantity of the immobilized BT-component is beneficial for the spatially isolated arrangement of chromophores, which suppresses the formation of excimer traps and in turn, boosts the exciton diffusion towards the catalytic sites for hydrogen production.

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Figure 1.11 Synthesis of three component COF-JLU35 and COF-JLU36 through Knoevenagel and Schiff-base condensation reactions, respectively. ³⁴

1.2.3 Designing Donor–Acceptor Configuration

Since the application of COF materials in photocatalysis, the design of donoracceptor (D-A) structures has been widely acknowledged as an effective strategy to enhance photocatalytic performance. In general, the photocatalytic performance of COFs mainly depends on their light response capability and the migration and separation efficiency of photogenerated electron-hole pairs. Both aspects can be addressed through the rational design of D-A structures. (i) As illustrated in **Figure 1.12a**, donor-acceptor (D-A) type COFs are composed of alternating D and A units. Within the plane, the alternating arrangement of D and A units forms numerous superheterojunctions, which enhance the separation of electrons and holes. Furthermore, the ordered stacking of D-over-D and A-over-A structures between layers establishes independent pathways for electron-hole transport, effectively suppressing electronhole recombination. (ii) Another significant advantage of D-A type COFs is their ability to modulate the band structure. As illustrated in **Figure 1.12b**, the D-A alternation enables the redistribution of the HOMO and LUMO orbitals from the individual electron donor and acceptor units to form new HOMO and LUMO orbitals, thereby reducing the energy band gap and extending the range of light absorption. Furthermore, the bandgap of synthesized D-A type COFs varies with the electrondonating and electron-accepting abilities of the individual units. Therefore, in principle, we can select different donor and acceptor units to tailor and predict the bandgap of D-A type COFs at the molecular level, based on the redox potential requirements of specific photocatalytic reactions.



Figure 1.12 (a) 2D layered structure of Donor-Acceptor COF. (b) Schematic illustration of optical band gap (Eg) in D-A system.

In the design of covalent organic frameworks (COFs), the selection of donor (D) and acceptor (A) building blocks plays a pivotal role in determining the framework's electronic and optical properties. Donor building blocks are molecular units rich in electron density, capable of donating electrons during charge transfer processes. These molecules often contain conjugated systems with electron-rich functional groups, which facilitate their role as electron donors. Conversely, acceptor building blocks are electron-deficient units designed to attract and accept electrons. Their structures typically include electron-withdrawing groups or heteroatoms that stabilize the negative charge formed upon electron transfer.

Donor units are typically constructed from electron-rich aromatic or heteroaromatic systems. Common examples include pyrene, triphenylamine, carbazole, thiophene, and phenothiazine, which provide excellent electron-donating capabilities. Acceptor units, on the other hand, are characterized by their electron-deficient nature. These units often incorporate aromatic or heteroaromatic systems with electron-withdrawing groups. Prominent examples include benzothiadiazole, triazine, thiazolo[5,4-d] thiazole, and so on. In this section, we provide an overview of the common types of units and linkage bonds in D–A type COFs in **Figure 1.13**, by judiciously selecting and engineering donor and acceptor units, researchers can design COFs with tailored properties for specific applications.



Figure 1.13 List of building blocks utilized in the construction of D-A COFs

1.2.3.1 D-A Type COFs with BT Units

The strong electronegativity of the nitrogen atom and the formation of low-energy π -orbitals in the C=N bond give the BT unit a pronounced electron-deficient property, which is widely regarded as an excellent electron acceptor. Liu et al. reported a typical D-A COF, COF-JLU22, which incorporates pyrene as the donor and 4,7-diphenylbenzo[c][1,2,5]thiadiazole as the acceptor in its linker.³⁶ COF-JLU22 exhibited efficient photocatalytic activity in reductive dehalogenation reactions and α -alkylation of aldehydes. In addition, Chen et al. designed a BT-based COF, TPB-BT-COF, and utilized it as a photocatalyst for the reduction of toxic Cr (VI).³⁷ The incorporation of BT units

to construct an ordered D-A heterojunction structure established independent electron and hole transport channels, enabling efficient charge separation. As a result, its photocatalytic performance significantly surpassed that of TPB-TP-COF, which does not contain BT units. Building on this, Zhao et al. employed benzothiadiazole and its derivatives as electron acceptors to construct a series of isostructural, highly crystalline two-dimensional COFs (NK COF-108, -109, and -110).³⁸ By introducing various functional groups (e.g., fluorine) to modify the electron acceptors, they effectively tuned the redox potentials of the NKCOFs. This adjustment of the HOMO and LUMO energy levels expanded their light absorption range. The optimized NKCOF-108 exhibited superior photocatalytic hydrogen production performance, achieving an apparent quantum efficiency (AQE) of 2.96% at 520 nm. Along this direction, SP² benzothiadiazolyl D-A type COFs, Py-BSZ-COFs, (Figure 1.14) have been designed with fully conjugated properties that give them high stability and enhanced charge separation.³⁹ High yields can be obtained in photocatalytic oxidative amine coupling and thioamide cyclisation reactions, and this study demonstrates the great potential of fully conjugated COFs with D-A structures for light-driven organic synthesis.



Figure 1.14 (a) Synthetic scheme of the Py-BSZ-COF. (b) Top and side views of the structural model of the Py-BSZ-COF.³⁹

1.2.3.2 D-A Type COFs with Tz Units

Typically, thiazolo[5,4-d]thiazole (Tz) will exhibit a stronger electron-withdrawal capacity than BT. Its coplanar geometry, rigid structure, and high oxidative stability make Tz an interesting candidate for the construction of stable D-A type COFs.⁴⁰ Wen

et al. reported a COF containing Tz as the acceptor and pyrene (Py) as the donor, named PyTz-COF (Figure 1.15a).⁴¹ Due to the excellent planarity of the Tz and Py units, which facilitates strong interlayer interactions, PyTz-COF exhibited remarkable tolerance to harsh chemical environments. It remained stable for at least three days in highly alkaline (3.0 M KOH) and acidic (3.0 M HCl) aqueous solutions. Additionally, the coplanar geometry of Tz promotes strong π - π stacking and orbital overlap, enabling efficient charge separation and transport. PyTz-COF demonstrated outstanding photocatalytic activity with a hydrogen evolution rate of 2072.4 μ mol g⁻¹ h⁻¹. Furthermore, it exhibited visible-light-driven photocatalytic activity in oxygen reduction to superoxide radicals and subsequent (aryl methyl) amine coupling reactions. Yang and his colleagues reported another D-A example,⁴² PETZ-COF, which incorporates tetraphenylethylene as the donor and Tz as the acceptor (Figure 1.15b). For comparison, a non-D-A structure, PEBP-COF, was also synthesized. Compared to PEBP-COF, PETZ-COF exhibited a significantly reduced HOMO-LUMO gap, an expanded visible light response range, and finely tuned electronic structures. These adjustments enhanced exciton separation efficiency and accelerated electron transport. PETZ-COF demonstrated an impressive hydrogen evolution rate of 7324.3 μ mol g⁻¹ h⁻¹, which is an order of magnitude higher than that of PEBP-COF lacking the D-A structure.



Figure 1.15 (a) Synthetic scheme of PyTz-COF under solvothermal conditions. ⁴¹ (b) Synthetic of the D-A type COF with TZTZ-2BA and 4PE-4NH₂. ⁴²

1.2.3.3 D-A Type COFs with Triazine Units

Similar to BT and Tz, triazine is one of the most significant acceptor units in D-A COF design. Triazine features high planarity, full conjugation, and strong electron affinity, which enhances electron conjugation. Furthermore, the triazine unit can be widely incorporated into various types of COFs, including those connected by imine linkage, vinylene linkage, and covalent triazine frameworks (CTFs). This versatility endows triazine-based COFs with promising potential for diverse applications. Recently, our group investigated triazine-based D-A COFs (TMT-TT-COF and TMT-N-COF) for photocatalytic H₂O₂ production and tandem bisphenol-A degradation.⁴³ The TMT-TT-COF, which features the most strongest donor-acceptor (D-A) structure assembled with sulfur-containing thiophene units, exhibits a narrower bandgap, enhanced intramolecular charge carrier transport, and suppressed charge recombination. These contribute to significantly improved photocatalytic performance. Additionally, the triazine-containing monomer tris-(4-aminophenyl)triazine (TAPT) has been widely utilized in the design of D-A COFs (Figure 1.16).^{44, 45} The extended linker structure of the TAPT monomer facilitates the formation of larger pores, which can enhance the interaction between reactant substrates and active sites, thereby improving the overall photocatalytic efficiency.



Figure 1.16 (a) Schematic representation of the synthesis of BDF-TAPT-COF and the comparison of the experimental PXRD patterns of BDF-TAPT-COF with its AA (black) and AB (red) stacking models. ³² (b) Synthetic of the TpMA followed by irreversible enol-to-keto tautomerization. ³³

1.2.3.4 Other D-A-derived COFs

For typical D-A structures, a single donor (D) unit paired with a single acceptor (A) unit is commonly employed. However, designing novel D-A COFs with structures such as D_1-A-D_2 , $D-A_1-A_2$, D1-D2-A, or A_1-D-A_2 can introduce new optoelectronic properties and unlock potential applications.⁴⁶ Recently, Chen's group synthesized two D-A type COFs and one D-A-A configured COF based on the receptor molecular engineering strategy (**Figure 1.17**).⁴⁷ Among them, TAPPy-DBTDP-COF, which integrates a pyrene-based donor with two types of benzothiadiazole acceptors, achieved an impressive average H₂ production rate of 12.7 mmol h⁻¹ g⁻¹ under visible light. This work highlights the potential of the dual-acceptor engineering strategy as a promising approach to discover efficient semiconductor candidates for photocatalytic

applications. Another derivative structure, the D- π -A type, achieves effective charge transfer between donors and acceptors by introducing highly conjugated linkers.⁴⁸ For instance, in the TP-BDDA-COF structure, acetylene groups are incorporated as bridges connecting the donor and acceptor units (**Figure 1.18**). These groups enhance π -delocalization along the backbone, thereby facilitating carrier transport and the generation of photocurrents. Lan et al. employed a similar D- π -A strategy to synthesize A-CTF-2 COF.⁴⁹ Under visible light irradiation, A-CTF-2 COFs exhibited high photocatalytic activity in the non-metal photocatalytic oxidation of amines with oxygen coupling, achieving an apparent quantum efficiency of up to 32.3% at 420 nm.



Figure 1.17 (a) Synthesis routes of TAPPy-TPTA-COF, TAPPy-BTDP-COF, and TAPPy-DBTDP-COF, respectively.⁴⁷



Figure 1.18 (a) Schematic diagram of the photoexcited electron-transfer process in the D–A system and D– π –A system.⁴⁸ (b) Scheme of synthesis of CTF-1 and A-CTF-2 following acid-catalyzed trimerization.

1.2.4 Constructing π -conjugated and Coplanar System

The construction of π -conjugated systems plays a crucial role in the photocatalytic applications of COF materials. π -delocalization not only adjusts molecular properties but also increases stability by lowering electron energy. Additionally, the degree of π -delocalization is critical for tuning the HOMO-LUMO energy levels (bandgap). To gain deeper insight into the π -conjugated systems of 2D materials, Gutzler and Perepichka systematically evaluated the theoretically calculated bandgaps of various one-dimensional (1D) and two-dimensional (2D) polymers derived from the same parent monomeric units.⁵⁰ The results demonstrated that in 1D materials, the reduction in the HOMO-LUMO gap (HLG) diminishes as the number of repeating units increases. In 2D materials, the HLG contraction becomes faster for increasing oligomer size. Moreover, the π - π stacking interactions between the layers of 2D COFs are stronger than the interlayer electronic interactions generated by cross-conjugated planar frameworks. This enhanced stacking facilitates more efficient charge transport in the out-of-plane direction. Like 1D systems, the coplanarity of conjugated units strongly

influences the electronic delocalization within 2D polymers. Due to torsional hindrance, the interlayer conjugation in two-dimensional polymers can be significantly affected, limiting the extent of π -overlap. This structural distortion reduces the efficiency of π - π stacking, thereby impacting the electronic delocalization and charge transport across layers. Therefore, when constructing conjugated systems, the planarity of the conjugated units must also be carefully considered.

1.2.5 Defect Engineering

Defects in COFs may arise from the absence of certain organic components, resulting in incomplete binding sites between adjacent complementary monomers, or from poorly connected comonomers. Additionally, defects can originate from irregularities in the crystalline structure or imperfections in the stacking and folding of the polymeric framework.⁵¹ At the same time, defect engineering serves as an effective strategy to tune the electronic and band structure of semiconductor materials. Wang and coworkers synthesized TAPT-COF with varying structural defect ratios, denoted as TAPT-COF-X.⁵² Electrochemical impedance spectroscopy revealed that TAPT-COF-7, with an optimized defect ratio, exhibited the highest photocatalytic activity and charge separation efficiency, achieving a maximum hydrogen evolution rate of 33,910 μ mol h⁻¹ g⁻¹. In 2024, Qiu and colleagues applied this strategy to the field of photocatalytic fine chemical synthesis.⁵³ As shown in **Figure 1.19**, they selected low-cost monomers, including 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAPT), 2,5dihydroxybenzaldehyde (Dhb), and 2,5-dihydroxyterephthalaldehyde (Dha), to synthesize a stable, highly porous, crystalline, and defect-rich COF (COF-HNU30-x). Among these, COF-HNU30-10, with moderate defects introduced into the framework, exhibited excellent photocatalytic activity. The catalytic efficiency of COF-HNU30-10 in oxidative coupling of C-H bonds (OCCR) was significantly higher than that of the defect-free COF-HNU30-0. The product yield increased from 49% for COF-HNU30-0 to over 99.9% for COF-HNU30-10.

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Figure 1.19 (A) Schematic representation for the production process of defective COF-HNU30-*x*. (B–D) PXRD patterns, FTIR and N₂ sorption isotherms of COF-HNU30-*x*. (E and F) SEM images COF-HNU30-0 and COF-HNU30-30. (G) High-resolution XPS spectra of deconvoluted N 1s of COF-HNU30-0 and COF-HNU30-30. ⁵³

1.3 Photocatalytic Applications of COFs

1.3.1 Photocatalytic Hydrogen Peroxide Production

Hydrogen peroxide (H_2O_2) has probably received the most attention in recent years among the various valuable chemicals synthesized by photosynthesis. H_2O_2 is an important green oxidant and energy carrier, and it has a wide range of applications in the fields of chemical industry, medical, environmental protection, and energy.⁵⁴ In industrial synthesis, H_2O_2 is widely used in bleaching, oxidation and wastewater treatment; in the environmental field, it is used as a green oxidant for degrading organic pollutants, replacing traditional chlorine-based oxidants, and reducing secondary pollution.⁵⁵ Currently, the primary industrial method for producing H_2O_2 is the anthraquinone process. However, this method is energy-intensive, operationally complex, and generates organic waste, posing challenges for sustainable development.⁵⁶ In view of this, photocatalytic synthesis of H_2O_2 is a recently developed alternative route for H_2O_2 production.⁵⁷

1.3.1.1 Principles of Photocatalytic H₂O₂ Generation

Theoretically, the complete photocatalytic H₂O₂ formation pathway consists of two complementary half-reactions: the oxygen reduction reaction (ORR) and the water oxidation reaction (WOR).⁵⁸ In the ORR pathway, H₂O₂ is produced either *via* two successive single electron transfers as shown in Eq (1-2) or *via* a direct two-electron transfer ORR pathway as shown in Eq (3),⁵⁹ where NHE is the normal hydrogen electrode. Similarly, H₂O₂ can also be produced by an oxidation reaction via the 2 e⁻ WOR (Eq. 4). The 4 e⁻ WOR to oxygen in Eq (5), which happens at 0.83 V (vs NHE, pH = 7) is a competitive reaction to the 2 e⁻ WOR to H₂O₂ (happening at 1.35 V vs NHE, pH = 7) Eq (4). However, the 4 e⁻ process is kinetically more sluggish than the 2 e⁻ process. In addition, the photogenerated holes can oxidize H₂O via the one-electron process to form OH• which then combines with each other to produce H₂O₂. However, this stepwise one-electron water oxidization process requires high concentrations of OH• to form desired H₂O₂, limiting the H₂O₂ production yields.⁶⁰

- (1) $O_2 + e^- \rightarrow O_2^{\bullet-} (E^\circ = -0.33 \text{ V vs. NHE, pH=7})$
- (2) $O_2^{\bullet-} + 2H^+ + e^- \rightarrow H_2O_2$ ($E^\circ = +0.91 \text{ V vs. NHE, pH=7}$)
- (3) $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ ($E^\circ = +0.28 \text{ V vs. NHE, pH=7}$)
- (4) $2H_2O + 2 h^+ \rightarrow H_2O_2 + 2H^+$ (E° =+1.35 V vs. NHE, pH=7)
- (5) $2H_2O + 4 h^+ \rightarrow O_2 + 4H^+$ (E° =+0.83 V vs. NHE, pH=7)

1.3.1.2 Reaction Systems

Photocatalytic H₂O₂ production typically occurs in suspensions of COFs in oxygen-

saturated water, While the experimental setup appears straightforward, the process faces significant challenges that limit its efficiency and scalability. One primary issue is the poor solubility and slow diffusion rate of oxygen in water, leading to inefficient mass transfer. Additionally, photo-induced decomposition of H_2O_2 often occurs, further reducing the overall yield. A key limitation also lies in the reverse half-reaction of the oxygen reduction process, specifically the oxidation of H_2O to O_2 . This reaction is notably sluggish and often becomes the rate-limiting step of the overall redox cycle, which includes the reduction of O_2 to H_2O_2 and the oxidation of H_2O to O_2 . To address this, sacrificial agents such as ethanol (EtOH), isopropanol (IPA), and benzyl alcohol (BA), are added to act as hole scavengers. However, the use of sacrificial reagents introduces additional challenges, as their oxidation can generate unwanted byproducts that complicate the downstream processing of H_2O_2 . Such byproducts are especially problematic in industrial applications where direct utilization of high-purity H_2O_2 is critical.

This issue can be addressed using a biphasic system, specifically a water-organic (immiscible) biphasic system. Our group recently reported four pyrene-based COFs for photocatalytic H_2O_2 production.⁶¹ We discovered that pyrene units serve as active sites for H_2O_2 generation, but their dense proximity can induce undesired H_2O_2 decomposition. A biphasic reaction system consisting of water and benzyl alcohol (BA) was employed to mitigate this issue, which effectively prevented unnecessary product loss. In this setup, the hydrophobic COFs spontaneously dispersed in the BA phase, while the generated H_2O_2 rapidly diffused into the water phase. This spatial separation between H_2O_2 and the COFs was shown to effectively inhibit the decomposition of H_2O_2 . Simultaneously, BA acted as a sacrificial hole scavenger, addressing the challenges of both H_2O_2 stability and charge recombination. This dual functionality highlights the potential of biphasic systems to overcome key obstacles in photocatalytic H_2O_2 production while maintaining efficiency and scalability.

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1.3.1.3 COFs for photocatalytic H₂O₂ production

In 2020, our group first reported the use of imine-linked COFs for photocatalytic H_2O_2 production. By reacting the electron-rich N,N,N', N' -tetra(4-aminophenyl)-1,4-phenylenediamine (TAPD) with either 2,5-dimethyl-1,4-benzenedicarbaldehyde or 2,5-dimethoxy-1,4-benzenedicarbaldehyde, we synthesized two-dimensional (2D) imine-linked COFs. The resulting TAPD-(Me)₂ COF exhibited photocatalytic activity, achieving a production rate of 97 µmol h⁻¹ g⁻¹ for H₂O₂ under visible light irradiation. The redox-active TAPD units, which functioned as Wurster-type systems, played a crucial role in the process. They facilitated the reduction of molecular oxygen to form superoxide radical anions ($\bullet O_2^-$), which are essential intermediates for H₂O₂ generation. This highlights the importance of redox-active building blocks in designing efficient photocatalytic COFs for sustainable H₂O₂ production (**Figure 1.20**).⁶² Since then, numerous strategies have been developed to enhance the efficiency of photocatalytic H₂O₂ production. The strategies discussed in the earlier sections of this review can also be systematically applied to the generation of hydrogen peroxide.



Figure 1.20 Synthesis of TAPD-(Me)₂ and TAPD-(OMe)₂ COFs forming a dual pore Kagome lattice. ⁶²

Lan's group synthesized an imine-linked TTF-BT-COF by rationally designing a donoracceptor structure, combining tetrathiafulvalene (TTF), which provides oxidation sites, with benzothiazole (BT), which offers reduction sites.⁶³ This design enabled efficient electron-hole separation and provided suitable photoredox capabilities. The unique electronic structure allowed oxygen to readily accept electrons from the BT units, forming H₂O₂, while water was oxidized at the TTF sites to produce H₂O₂ as well. This simultaneous completion of the oxygen reduction reaction (ORR) and the water oxidation reaction (WOR) significantly enhanced the overall photocatalytic performance (**Figure 1.21**). The TTF-BT-COF achieved an impressive H₂O₂ production rate of 2760 μ mol h⁻¹g⁻¹, which is three times higher than that of the COF without the D–A structure. The TTF-BT-COF demonstrates the potential of donor-acceptor strategies in achieving efficient and synergistic photoredox processes for H₂O₂ production.



Figure 1.21 (a) Schematic representation of the oxidation-reduction molecular junction COF photocatalyst for full reaction photosynthesis of H_2O_2 . (b) UV/Vis

absorption spectra. (c) Tauc plot for band gap calculation. (d) Photocatalytic activity of TTF-BT-COF, TTF-pT-COF and TPE-BT-COF for H_2O_2 production in pure water and O_2 atmosphere. ⁶³

Introducing functional groups into COF materials is another effective strategy to enhance the rate of H₂O₂ production. For instance, Han's group achieved a significant improvement in photocatalytic performance by modifying the COF backbone with cyano groups.⁶⁴ This modification enhanced the photosensitivity of the COF material and tuned the electronic properties of the organic π -conjugated system. The cyanofunctionalized CN-COF increased the intersystem crossing (ISC) efficiency from the singlet to the triplet state, thereby activating O_2 to generate singlet oxygen ($^{1}O_2$). This improvement resulted in a remarkable H_2O_2 production rate of 2623 µmol h⁻¹ g⁻¹, which is significantly higher than that of the non-cyano-functionalized H-COF, which achieved a production rate of 1640 μ mol h⁻¹ g⁻¹. Subsequently, Ni and co-workers discovered that the number of cyano groups could be tuned to control the number of charge transfer channels between the donor-acceptor units in COFs.⁶⁵ Specifically, the dicyano-functionalized COF (COF-2CN) exhibited up to four charge transfer channels, leading to highly efficient exciton separation and transfer, as well as enhanced surface catalytic reactions. Under visible light irradiation, COF-2CN achieved a high H₂O₂ production rate of 1601 μ mol g⁻¹ h⁻¹ without requiring any sacrificial agents (Figure **1.22**).



Figure 1.22 (a) Chemical structure of COF-0CN, COF-1CN and COF-2CN. (b) Photosynthesis of H_2O_2 by the fabricated COFs, g-C₃N₄ and P25. (c) The apparent quantum yield (AQY) of COF-2CN as a function of wavelength. (d) H_2O_2 yield for 5-reused cycles by COF-2CN with natural sunlight irridation

Post-modifications that convert imine linkages into more robust thiazole or quinoline linkages can enhance the stability of COFs, increase π -conjugation, and improve visible light absorption. Our group recently reported a study involving the synthesis of a thiazole-linked COF through post-modification and its application in photocatalytic H₂O₂ production.⁶⁶ In this work, an imine-linked COF, 4PE-N, derived from 4,4',4",4"'-(ethylene-1,1,2,2-tetrayl)tetrabenzamine, was treated with a post-synthetic sulfurization process to form a thiazole-linked COF (4PE-NS). The sulfurized COF exhibited enhanced conjugation in both x and y direction, which significantly improved its photocatalytic performance. In pure water, 4PE-NS achieved a photocatalytic H₂O₂ production rate of 1574 µmol g⁻¹ h⁻¹, approximately 5.8 times higher than that of the pristine 4PE-N COF. Thomas's research group recently synthesized a quinoline-4-carboxylic acid-functionalized COF, DMCR-1NH, using a three-component Doebner reaction.⁶⁷ The results demonstrated that DMCR-1NH exhibit superior photocatalytic activity and photostability for H₂O₂ production

compared to their imine-linked COF. The enhanced activity of DMCR COFs is attributed to their extended conjugated structure, which provides excellent light-harvesting capabilities, and the presence of additional oxygen adsorption sites (-COOH). These features synergistically improve both the photocatalytic efficiency and the stability of the COF, making it a promising candidate for sustainable H₂O₂ production under visible light irradiation.

Doping modifications, such as incorporating nanoparticles or nanoclusters, are effective strategies to regulate active sites. However, stabilizing isolated metal clusters through physical methods often compromises the catalyst's stability during catalytic processes. To address this issue, Guo and colleagues reported a novel fluorinated COF strategy to stabilize Pd isolated clusters (Pd ICs).⁶⁸ They found that the introduction of fluorine groups enhanced the metal-support interactions between Pd ICs and the COF framework (**Figure 1.23**). This not only significantly improved the photocatalytic H₂O₂ production performance but also provided remarkable stability. The resulting TAPT-TFPA@Pd ICs exhibited an impressive H₂O₂ production rate of 2143 μ mol g⁻¹ h⁻¹ and outstanding stability for over 100 hours. This opens up a new strategy for simultaneously enhancing photocatalytic performance and stability.



Figure 1.23 Schematic diagram of TAPT-PBA COFs@Pd ICs (physical confinement of Pd ICs) and TAPT-TFPA COFs@Pd ICs (fluorination of COFs for reinforcing the confinement of Pd ICs). ⁶⁸

1.3.2 Photocatalytic Organic Transformations

Visible light photoredox catalysis uses clean, renewable solar energy or inexpensive LED light to drive chemical reactions, providing an environmentally friendly method for producing valuable fine chemicals. In recent years, it has become a powerful tool for developing transformations that are often challenging or impossible to achieve with traditional thermal methods.⁶⁹ Typical homogeneous transition metal oxide photocatalysts have disadvantages such as toxicity, selectivity, water instability, and poor recyclability.⁷⁰ COFs, as structurally tunable, environmentally friendly, and recyclable heterogeneous photocatalytic catalysts, can be successfully used to convert organic matter into valuable chemicals. COFs have been demonstrated to be useful for a variety of organic transformations such as oxidation, reduction, cross-coupling reactions, C-H activation, and cyclization under UV/visible light irradiation.

1.3.2.1 Oxidation Reactions

Photocatalytic oxidation is one of the most important reactions, including sulfide oxidation, conversion of alcohol to aldehyde, aryl boronic acid oxidation, benzyl alcohol oxidation, and oxidative coupling of amines. The general mechanism of these reactions typically involves the generation of photoinduced holes or reactive oxygen species (ROS, such as O_2^- and 1O_2) to facilitate specific organic transformations.

(1) Selective oxidation of sulfides

The aerobic oxidation of sulfides to sulfoxides holds significant importance in organic synthesis. The generation of singlet oxygen (${}^{1}O_{2}$) plays a crucial role in this reaction, yet the selective production of ${}^{1}O_{2}$ remains a challenge. An effective strategy to address this issue involves modifying the coordination environment around the catalytic sites. To this end, Jiang and colleagues utilized Ni-porphyrin COFs with pore walls functionalized by groups exhibiting different electron-donating or electron-withdrawing characteristics (e.g., -CN, -CF₃, -COOMe, -H, and -OMe) to fine-tune the outer microenvironment for ${}^{1}O_{2}$ generation.⁷¹ As the electron-donating ability of the

functional groups increased, the tailored microenvironment activated catalytic activity (**Figure 1.24**). Methoxy-functionalized COFs, with strong electron-donating properties, achieved an outstanding yield of 98%. In contrast, cyano-functionalized COFs, with strong electron-withdrawing properties, exhibited nearly zero yield. DFT calculations revealed that the primary factor responsible for the differences in photocatalytic activity for the oxidation of sulfides is the variation in excitonic behavior. This behavior is influenced by the outer microenvironment tuning, which modulates the COF's band energy levels and orbital composition.



Figure 1.24 Outer sphere microenvironment modulation of Ni sites in COF-366(Ni)-R (-R=, -CN, -CF3, -COOMe, -H, -OMe) for photocatalytic oxidation of thioether. ⁷¹

Fully conjugated sp²-carbon-based COFs have made remarkable contributions to enhancing the stability of COFs. Lang and colleagues synthesized two olefin-linked COFs (TTO-COF and TBO-COF) using 2,4,6-trimethyl-1,3,5-triazine (TMT) with either 2,4,6-tris(4-formylphenyl)-1,3,5-triazine (TFPT) or 1,3,5-tris(4-formylphenyl)-benzene (TFPB) as precursors (**Figure 1.25**).⁷² These COFs were applied for blue-light-driven oxidation of thioethers to sulfoxides. The TTO-COF nanotubes, constructed from two triazine-based structural units, exhibited superior photocatalytic performance due to more efficient charge carrier separation and higher charge mobility. Remarkably, TTO-COF achieved a 98% conversion rate within just one hour. Subsequently, additional π conjugated rigid units (acetylene) were incorporated into the olefin-linked COF, resulting in TBPA-COF with an extended π -conjugated structure that facilitates efficient charge transfer.⁷³ Compared to TBP-COF, which lacks acetylene units, TBPA-COF demonstrated superior performance in the selective photocatalytic oxidation of sulfides. Mechanistic studies revealed that the enhanced selectivity of TBPA-COF in photocatalytic sulfide oxidation arises from the synergistic contributions of both electron and energy transfer pathways.



Figure 1.25 (a) Synthesis of olefin-linked TTO-COF and TBO-COF. (b) Photocatalytic oxidation of thioether under various wavelengths of LEDs via TTO-COF. ⁷²

(2) Oxidative Coupling of Amines

The oxidation of benzylamine to its derivatives plays a critical role in the chemical and pharmaceutical industry. Lan and co-workers proposed a strategy to rationally design a series of three-motif molecular junction catalysts, resulting in a COF (PY-BT COF) with dual photosensitizers and redox-active molecular junctions, specifically tailored for the photocatalytic oxidation of benzylamine to imines.⁷⁴ In the PY-BT COF, pyrene and triphenylamine units function as effective photosensitizers and photo-oxidation sites, while the thiadiazol group acts as a reduction site. For comparison, the authors synthesized three other COFs: one containing only a single photosensitizer site, another with dual photosensitizers but no reduction site, and a third with only a single dual photosensitizer site (**Figure 1.26a**). Among these samples, PY-BT COF demonstrated the highest conversion efficiency, achieving 99.9% benzylamine conversion within 2.5 hours (**Figure 1.26b**). This result highlights the superiority of the three-motif molecular junction design in photocatalysis.



Figure 1.26 (a) Synthesis of dual photosensitizer coupled redox molecular junction COFs, including the PY-BT COF, PY-BDAT COF, BATA-BT COF, and BATA-BDAT. (b) Photocatalytic performance of benzylamine oxidative coupling reactions a by the PY-BT COF. ⁷⁴

In 2022, Jiang and co-workers synthesized a photo-responsive o-COF by integrating porphyrin photosensitizers with diarylethene switches.⁷⁵ By utilizing UV and visible light to modulate the open/closed forms of the diarylethene units, they achieved isomerization of the COF, thereby regulating the generation of singlet oxygen. Under blue light irradiation, the open form of the COF exhibited significantly enhanced catalytic performance for the selective oxidative coupling of benzylamine. Remarkably, the COF maintained a conversion efficiency of over 99% across five consecutive runs, demonstrating excellent stability and reusability.

(3) Aryl Boronic Acid Oxidation

Phenols are key intermediates in pharmaceuticals, agrochemicals, and polymer industries. The selective oxidative hydroxylation of aryl boronic acids provides a direct route to phenolic compounds. There is substantial evidence indicating that superoxide radicals ($\cdot O_2^-$) are the most important ROS involved in the photocatalytic oxidation of aryl boronic acids.⁷⁶ In 2018, Wang and colleagues developed a series of highly stable benzoxazole-based COFs and applied them to the hydroxylation of aryl boronic acids into phenols.⁷⁷ These COFs demonstrated remarkable catalytic efficiency, achieving yields as high as 99%. Among them, LZU-190 stood out for its unprecedented

recyclability: the catalyst retained its activity and crystallinity even after at least 20 consecutive cycles, showcasing its excellent stability and durability. This study highlights the potential of benzoxazole-based COFs as robust and efficient photocatalysts for organic transformations, especially in processes requiring high yield and catalyst longevity. Zhou and his co-workers synthesized three olefin-linked COFs by incorporating different functional groups (-H, -F, and -OMe) into the framework.⁷⁸ Among these, the methoxy-containing COF exhibited broader visible-light absorption and superior charge transfer efficiency. As a result, it demonstrated better photocatalytic performance compared to TBT-COF and F-TBT-COF. This methoxy-functionalized COF showed excellent photocatalytic activity and recyclability in the aerobic conversion of aryl boronic acids to phenols.

1.3.2.2 C-X Coupling Reactions

Carbon-carbon (C-C) and carbon-heteroatom (C-X) cross-coupling reactions play a crucial role in various fields, including the synthesis of fine chemicals, pharmaceuticals, and medical drugs. Recently, Maji and co-workers synthesized a fully conjugated sp²-COF (Bpy-sp²c-COF) through a Knoevenagel condensation reaction between 1,3,6,8tetrakis(4-formylphenyl) pyrene (TFPPy) and 5,5'-dicyano-2,2'-bipyridine (BPDAN).⁷⁹ The bipyridine monomer within the COF were subsequently functionalized with nickel (II) chloride centers, resulting in Ni@Bpy-sp²c-COF. Notably, a single Ni@Bpy-sp²c-COF exhibited excellent catalytic performance across eight distinct visible-light-mediated C–X (X = B, C, N, O, P, S) cross-coupling reactions, achieving high yields ranging from 61% to 99%. The anchored COF framework prevented the formation and leaching of nickel black, enabling selective coupling of substrates with varying steric and electronic properties. This design maintained high catalytic efficiency, evidenced by high turnover numbers (TONs) and turnover frequencies (TOFs), as well as excellent reusability. High-connectivity COFs have become a research hotspot in recent years. Recently, Lan's group reported a hierarchical expansion strategy to create 16connected building blocks for constructing 3D COFs with sqc topology.⁸⁰ By condensing

16-connected carbazolyl dicyanobenzene-based building blocks (CzTPN) with linear diamine linkers, they successfully synthesized two 3D COFs ([16 + 2] structures), referred to as CzBD COF and CzBpy COF. Among them, the bipyridine-containing CzBpy COF demonstrated the ability to chelate Ni atoms, enabling photoredox-catalyzed C(sp³)-C(sp²) cross-coupling reactions. This catalytic system achieved an impressive maximum conversion rate of 98%, showcasing the potential of high-connectivity 3D COFs in facilitating challenging organic transformations.

In the context of cross-coupling reactions, C–N cross-coupling is particularly significant for the synthesis of various important pharmaceutical compounds. β-Ketoenamine-linked COFs, known for their excellent stability, have been explored for such applications. Maji and colleagues developed a bimetallic hybrid material by postsynthetic metallization of a crystalline porous TpBpy COF.⁸¹ The modification involved incorporating $[Ir(ppy)_2(CH_3CN)_2]PF_6$ and NiCl₂ into the COF framework, resulting in a dual-metallic Ni-Ir@TpBpy COF (Figure 1.27). The bipyridine units within the COF coordinated with the nitrogen, effectively anchoring the metals to the framework. Under visible light irradiation, the Ni-Ir@TpBpy COF exhibited remarkable photocatalytic performance in C–N cross-coupling reactions between (hetero)aryl iodides and amines (including aryl, heteroaryl, and alkyl amines) across a variety of substrates. In the coupling reaction of iodobenzene with aniline, the catalyst achieved a high yield of 89%. More importantly, this reaction can be conducted on a gram-scale with high conversion efficiency and excellent recyclability, making it suitable for the late-stage functionalization of pharmaceutical derivatives. Thomas group reported a series of acridine-based COFs synthesized by reacting a novel acridine structural unit with various hydroxyl-functionalized benzene-1,3,5-trialdehyde derivatives.⁸² These COFs, with nickel metal photocatalytic sites, were employed for photocatalytic metalmediated C-N cross-coupling reactions between pyrrolidine and monohalogenated benzene derivatives under blue and green LED irradiation. Among the synthesized COFs, the fully β -ketoenamine-linked Tp-Acr-COF exhibited the highest photocatalytic activity and reusability. It achieved a yield of up to 91% within 16 hours. The enhanced

catalytic activity of Tp-Acr-COF was attributed to its larger surface area and planar structure, which facilitated efficient electron/hole transfer kinetics.



Figure 1.27 (a) Synthesis of dual metal-installed Ni-Ir@Tp-Bpy COF. (b) Timedependent photocatalysis C–N cross-coupling reaction kinetics profile. (c) Late-stage diversification of bioactive compounds and the synthesis of drug molecules by Ni-Ir@Tp-Bpy COF.⁸¹

1.3.2.3 C–H Functionalization

C–H functionalization offers innovative ways to construct and modify molecules. Its importance spans fundamental research, industrial applications, and sustainable development. The photocatalytic synthesis of α -trifluoromethylated ketones is an important route for obtaining various fluorinated compounds but has been rarely reported in heterogeneous photocatalytic systems. To address this, Cai and co-authors reported a fully conjugated, olefin-linked, two-dimensional COF based on triazine groups (TTO-COF).⁸³ This COF exhibits high planarity and conjugation, enabling efficient photocatalytic trifluoromethylation of C-H bonds in arenes and heteroarenes, achieving moderate to high yields. TTO-COF not only facilitates the generation of reactive oxygen species (ROS) but also directly participates in substrate activation

under photoexcitation, demonstrating its dual functionality in the photocatalytic process. Liu et al. synthesized a novel triazine-based imine-linked COF (COF-JLU32) with a donor-acceptor structure.⁸⁴ Subsequently, they transformed the imine bonds into more stable amide bonds through post-synthetic modification, creating COF-JLU33. Under green LED illumination, COF-JLU33 exhibited commendable yields in the photocatalytic synthesis of α-trifluoromethylated ketones. Furthermore, after four consecutive cycles of use, both the conversion rate and yield remained consistent, demonstrating the excellent stability and recyclability of COF-JLU33 in photocatalytic applications. His research group also prepared three novel isostructural pyrene-based 2D COFs (COF-JLU23, COF-JLU24, and COF-JLU25) with different linker groups.⁸⁵ Among these, COF-JLU24, which exhibits donor-acceptor electronic characteristics, demonstrated the best photocatalytic activity for the C-3 functionalization of indoles, surpassing even the metal-free photocatalyst g-C₃N₄. More importantly, COF-JLU24 showed broad substrate adaptability and excellent recyclability as a metal-free photocatalyst.

1.3.3 Photocatalytic Degradation of Pollutants

Harmful pollutants from industrial wastewater, agricultural runoff, and medical waste residues are increasingly contaminating our environment and posing threats to human health. In recent years, significant efforts have been devoted to the efficient removal of various pollutants from water. Photocatalysis is considered an environmentally friendly and effective method to degrade organic pollutants into non-toxic molecules such as CO₂ and H₂O. During oxidative photodegradation, reactive species such as superoxide radicals, hydroxyl radicals, and holes (h⁺) are recognized as the primary active agents driving the process. For example, Tong et al. synthesized two COFs with strong donor-acceptor (D-A) characteristics, COF-TD1 and COF-TD2, by condensing electron-donating units (1,3,4-thiadiazole or 1,2,4-thiadiazole rings) with electron-accepting units (quinone).⁸⁶ Due to the presence of easily excitable electrons in the 1,3,4-thiadiazole ring, COF-TD1 exhibited more effective electron-hole

separation through the push-pull electronic effect compared to COF-TD2, leading to superior photocatalytic degradation of acetaminophen. COF-TD1 also demonstrated efficient photocatalytic degradation of acetaminophen in complex water matrices, including river water, lake water, and wastewater. Furthermore, to enhance recyclability and facilitate reuse, COF-TD1 was immobilized on indium tin oxide (ITO) glass substrates. This supported COF retained high photocatalytic performance and was capable of effectively degrading acetaminophen, diclofenac, bisphenol A, naproxen, tetracycline hydrochloride, and other emerging contaminants. TpMA COF synthesized via mechanochemical ball-milling of 1,3,5-triformylphloroglucinol (Tp) and melamine (MA) demonstrated high efficiency in the photocatalytic degradation of phenol.⁸⁷ After four cycles of reuse, the TpMA COF retained 87.6% of its photocatalytic activity, indicating excellent recyclability and stability achieved through the mechanochemical approach. Mechanistic studies revealed that superoxide radicals (O_2^{-}) and hydroxyl radicals (OH) play dominant roles in the photocatalytic decomposition of phenol. Qiu and coworkers synthesized novel vinyl-linked COFs (BDA-TMT, EDA-TMT, and TDA-TMT) through an alcohol-aldehyde condensation reaction,⁸⁸ incorporating diacetylene monomer and triazine blocks for photocatalytic degradation of organic pollutants and antibacterial applications. The results demonstrated that the introduction of diacetylene moieties enhanced the delocalization of conjugated π -electrons, optimized the electronic band structure, and improved charge separation efficiency. Among these, BDA-TMT exhibited exceptional photocatalytic performance, achieving ultrafast degradation of phenol and norfloxacin under visible light, with degradation rates exceeding 96% within 15 minutes. The reaction rate constants for phenol and norfloxacin degradation were 0.1675 and 0.1764 min^{-1} , respectively, making BDA-TMT the best-performing COF among those synthesized.

In addition to photocatalytic degradation of organic pollutants, COFs can also serve as photocatalysts for the removal of heavy metals from wastewater. Among heavy metal pollutants, Cr (VI) is one of the most common and poses significant threats to

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environmental ecosystems and human health due to its carcinogenic and mutagenic effects, leading to irreversible damage. Cr (III) is an essential nutrient for the human body. Compared to the more traditional techniques to remove Cr (VI), like membrane separation, chemical reduction, electrolysis, and ion adsorption, the photocatalytic reduction of Cr (VI) has gained more and more attention. Reduction of Cr (VI) to Cr (III) has another important advantage, since Cr (III) is readily removed, for instance by precipitation as carbonate, sulfide or sulfate. Sheng and Liu synthesized three halogen (F, Cl, and Br) functionalized porphyrin-based COFs (Figure 1.28a),⁸⁹ which demonstrated excellent visible light absorption performance (420 nm $\leq \lambda \leq$ 780 nm) according to UV-vis diffuse reflectance spectroscopy. These COF materials exhibited good crystallinity, isoporous structures, and suitable band structures. The halogen groups were utilized to modulate the band structure and carrier distribution of the COFs. With the increase in electronegativity of the functional groups (Br < Cl < F), the conduction band (CB) potential of the COFs became more negative (Figure 1.28b), and carrier separation was enhanced, providing sufficient driving force for the photoreduction of Cr (VI) to Cr (III). Notably, due to the strong electronegativity of the F substituent, TAPP-2F showed nearly 100% conversion efficiency and the highest reaction rate constant. Quenching experiments revealed that photogenerated electrons (e⁻) and superoxide radicals ($\cdot O_2^{-}$) were the main active species involved in the photoreduction process (Figure 1.28c). This strategy of introducing highly electronegative substituents offers a new approach for designing novel photocatalysts for the degradation of organic pollutants.

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Figure 1.28 (a) Synthesis of halogen (F, Cl, and Br) functionalized porphyrin-based COFs. (b) Band positions of C_3N_4 , TAPP-2F, TAPP-2Cl, and TAPP-2Br. (c) Mechanism illustration of the photoreduction of Cr (VI) to Cr (III) by TAPP-2F. ⁸⁹

Similarly, Lv's group also optimized the efficiency of Cr (VI) reduction by tuning the electronic environment.⁹⁰ They incorporated three different substituents (-Br, -OMe, -OH) into triazine-based COFs, synthesizing a series of visible-light-responsive Triazine-COFs-R families (**Figure 1.29**). Compared to COFs-H, the introduction of substituents with electronic effects narrowed the band gaps and improved electron-hole separation efficiency. The electron-withdrawing substituent (-Br) significantly lowered the LUMO and HOMO energy levels of COFs-R, enhancing the oxidative ability of h⁺ and thereby improving the photocatalytic degradation of tetracycline. On the other hand, the

electron-donating substituent (-OMe) significantly raised the energy levels of COFs-R, boosting the reduction ability of photogenerated electrons and enhancing the catalytic reduction of Cr (VI). This work provides a molecular-level strategy for band structure modification and fine-tuning of COFs' photocatalytic redox activity, contributing to the elucidation of the structure-performance relationship of COFs in photocatalysis. Ding et al. investigated the impact of different heterocyclic nitrogen positions in COFs on the photocatalytic reduction of Cr (VI).⁹¹ They synthesized five COFs through a one-pot reaction of 1,3,5-triformylphloroglucinol and various phenylenediamines with differing numbers or positions of heterocyclic nitrogen atoms, denoted as COF-1, COF-PD, COF-PZ, COF-PMD, and COF-PDZ. Among these, COF-PDZ, with two orthopositioned heterocyclic nitrogen atoms, exhibited the best performance. COF-PMD and COF-PZ, with two meta- and para-positioned heterocyclic nitrogen atoms, respectively, demonstrated moderate performance, while COF-PD, with a single heterocyclic nitrogen atom, and COF-1, without any heterocyclic nitrogen atoms, showed the lowest performance. The study found that an increase in heterocyclic nitrogen atoms suppressed the recombination of h^+ and e^- . Consequently, the Cr (VI) reduction kinetics of COF-PD, which has a single heterocyclic nitrogen atom, were lower than those of COFs with two heterocyclic nitrogen atoms.



CHO-R-monomer

Figure 1.29 Syntheses of four COFs by introducing R (R=H, OH, OMe, Br) substituents with different electronic effects for photocatalytic Cr (VI) reduction. ⁹⁰

1.4 Assessing the Industrial Feasibility of COF-Based Photocatalysis

Despite the remarkable progress in the development of COFs for applications such as photocatalytic hydrogen peroxide (H_2O_2) production, organic pollutant degradation, and fine chemical synthesis, most research efforts remain confined to fundamental studies. These typically focus on internal comparisons among COF structures, rather than evaluating their practical competitiveness against established industrial processes. So systematic comparisons with existing industrial-standard processes are often lacking, which creates uncertainty when evaluating their feasibility for real-world applications. Therefore, it is essential to place the performance of COFs within a broader industrial context to better understand their advantages and limitations, and to set realistic expectations for future technological development.

A representative case is the photocatalytic production of H_2O_2 . Currently, over 95% of global H_2O_2 is produced via the anthraquinone process. This process operates through a cyclic redox mechanism involving several key steps: (i) Hydrogenation: 2-alkyl-anthraquinone or its derivatives dissolved in an organic solvent (a mixture of aromatic hydrocarbons and alcohols), is hydrogenated to form the corresponding anthrahydroquinone. This step is catalyzed by palladium (Pd) supported on alumina under elevated temperature (40–60 °C) and pressure (2–4 MPa H₂). (ii) Oxidation: The anthrahydroquinone solution is then oxidized with air or pure oxygen at similar temperatures, regenerating the anthraquinone and producing H_2O_2 in the solvent phase. (iii) Extraction: The H_2O_2 is extracted from the organic phase into water using a liquid–liquid extraction step. (iv) Purification and Concentration: The aqueous H_2O_2 is purified and typically concentrated to commercial grades. This process is well-optimized, with yields exceeding 90%, production rates typically over 1 g·L⁻¹·h⁻¹ (approximately 30 mmol·L⁻¹·h⁻¹), and plant-scale output reaching hundreds of tons per day.

Nevertheless, the anthraquinone method poses notable drawbacks: it is energy- and resource-intensive, requires high-pressure hydrogen and thermal management,

involves complex multi-step infrastructure, and depends on noble metal catalysts. Safety concerns related to the flammable H_2/O_2 mixtures further complicate its operation. Moreover, its centralized nature limits flexibility for decentralized or ondemand production scenarios.

In contrast, COF-based photocatalysts offer a fundamentally greener approach, using only water, oxygen, and light—often under ambient temperature and pressure. They avoid the need for organic solvents or noble metals and thus present a highly sustainable and potentially low-cost alternative. However, the major bottleneck lies in the reaction rate. To date, most COF systems report H_2O_2 production rates in the range of 50-500 µmol·L⁻¹·h⁻¹ under conventional aqueous batch conditions, and only a few systems surpass 1 mmol·L⁻¹·h⁻¹, even under optimized conditions such as high-intensity light, pure oxygen flow, and sacrificial agents to mitigate decomposition pathways.

Notably, biphasic systems have recently emerged as an effective strategy to enhance both H_2O_2 yield and stability. In such systems, hydrophobic COFs are dispersed in the organic phase, while the generated H_2O_2 is continuously extracted into the aqueous phase, minimizing its exposure to reductive or degradative pathways. This separation significantly suppresses H_2O_2 decomposition and facilitates its accumulation over time. For example, certain COFs designed with hydrophobic channels or surface functionalization have achieved H_2O_2 production rates exceeding 10 mmol·g⁻¹·h⁻¹, with cumulative concentrations reaching tens of millimolar (>50 mM) within several hours of visible-light irradiation.

Future research should not only deepen the understanding of structure–property relationships in COFs, but also place greater emphasis on evaluating their performance within the context of existing industrial processes. Incorporating standardized evaluation metrics (such as industrial-level reaction rates, stability testing protocols, and cost-effectiveness analyses) into experimental research can provide a more rigorous and comparable foundation for transitioning COF materials from fundamental exploration to real-world applications.

1.5 Objectives of this Thesis

COFs, as semiconducting materials with tunable structures, ordered frameworks, and advantageous optical properties, exhibit tremendous potential in photocatalysis. Most importantly, their ordered structures allow the precise construction of structureperformance relationships, although research in this area is still in its infancy. The inherent tunability of COF materials enables the pre-design and modulation of their structures. Rational design strategies can precisely control and predict the properties of photocatalysts at the molecular and/or atomic levels. As summarized in our earlier discussions, the photocatalytic performance of COFs is influenced by various factors, such as their bonding types, conjugation strength, introduction of heteroatoms, microenvironmental modifications, donor-acceptor relationships, and coplanarity.

In this thesis, we aim to further understand the relationship between photocatalytic activity, photophysical properties and the synthesis parameters, in order to design tailor-made COF-based photocatalysts. Properties such as charge separation, band gap, and photo-response density are critical parameters in photocatalysis. We also need to characterize these properties. In each research chapter, we selected COFs with the similar topological structure to better compare the effect of each parameters mentioned above to the photocatalytic performance.

In Chapter 2, our primary objective was to explore the impact of ligands with different degrees of conjugation on the photocatalytic performance of COFs. To this end, we synthesized two COFs containing benzothiadiazole units along with phenyl and triazine linkages and conducted a comprehensive study of their photophysical and electrochemical properties. The ability of these materials to produce H₂O₂ from water without the use of a sacrificial agent was evaluated. The triazine-based COF demonstrated superior photo-induced charge separation and significantly reduced charge recombination due to its enhanced conjugation. After confirming the crucial role of conjugation in COF materials, we moved on to **Chapter 3** to explore the impact of donor-acceptor architecture on charge transfer. Three pyrene-based COFs (Py-Por-
COF, Py-Py-COF, and Py-Etta-COF) were synthesized for photocatalytic amine oxidative coupling in this chapter. Among the three COFs, the Py-Por-COF with D-A structure exhibits the highest photocatalytic performance (99% yield) and demonstrates a remarkable apparent quantum efficiency of 11.3 % at 420 nm. Moreover, the catalyst exhibited a good recyclability, with no significant decrease in catalytic activity after four cycles. It has been proven that the construction of donor-acceptor systems is indeed beneficial for electron transfer in the x-y direction. Therefore, we retained this strategy in **Chapter 4** and enhanced the conjugation along the z-axis by introducing highly planar building blocks through p-orbital overlap. In this chapter, a highly planar TEB-COF was constructed using triazine (acceptor) and ethynyl (donor) linkages. Through the C=C connections and highly conjugated interlayer stacking, the TEB-COF achieved efficient charge separation and excellent charge carrier mobility across all three dimensions. We also synthesized two additional COFs (TFB-COF and TPB-COF) with poorer planarity for comparison. The synthesized COFs were tested for the photocatalytic reduction of Cr (VI) and simultaneous one pot degradation of dyes under the irradiation of visible light.

By modulating the conjugation strength, optimizing the donor-acceptor designs, and enhancing the coplanarity of the materials, we systematically explore the effects of these variables on photocatalytic hydrogen peroxide production, photocatalytic organic transformations, and pollutant degradation. The more detailed discussion is presented in the following three chapters.

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Chapter 2.

Understanding photocatalytic hydrogen peroxide production in pure water for Benzothiadiazole-based Covalent Organic Frameworks



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Abstract

Photocatalytic production of hydrogen peroxide (H₂O₂) presents a promising and sustainable alternative to the current industrial anthraquinone route. Recent years have witnessed the emergence of covalent organic frameworks (COFs) as excellent photocatalysts, owing to their tunable band gaps, structural versatility and functional tunability. However, the current activity of COFs is limited and often relies on sacrificial agents to scavenge the holes in the photo-excited COFs. In this study, we introduce two benzothiadiazole-based COFs with tunable electronic structures and electron affinities for photocatalytic H₂O₂ production. The triazine-containing material, TAPT-BT-COF, exhibits outstanding charge separation and achieves a H₂O₂ production rate of $1363 \pm 10 \,\mu$ mol·h⁻¹·g_{cat}⁻¹ in pure water, nearly twice as high as the benzene-containing TAPB-BT-COF (731±10 μ mol·h⁻¹·g_{cat}⁻¹). Moreover, TAPT-BT-COF demonstrates a remarkable apparent quantum efficiency of 4.9% at 420 nm. This study underscores the significance of framework conjugation and provides valuable insights for the design of advanced photocatalytic framework materials with efficient charge separation.

2.1. Introduction

Hydrogen peroxide (H_2O_2) is a vital chemical compound with widespread applications in pharmaceutical industries, water treatment, chemical synthesis, and even fuel cells for electricity generation.¹⁻³ Currently, the industrial production of H_2O_2 relies on the anthraquinone method, which employs noble metals such as Pd, Pt, Ag, and Au as catalysts.⁴ However, this multistep process is highly energy-intensive and generates harmful catalytic waste, necessitating the development of environmentally friendly and energy-efficient techniques. Consequently, there is a growing research focus on the exploration of sustainable alternatives that can address these challenges. Recently, there has been significant attention directed towards photocatalytic production of hydrogen peroxide through the oxygen reduction reaction (ORR), primarily due to its utilization of clean resources such as oxygen, water, and sunlight.⁵ In this method, H_2O_2 is produced either *via* two successive single electron transfers as shown in Eq (1-2) or *via* a direct two-electron transfer ORR pathway as shown in Eq (3), where NHE is the normal hydrogen electrode.

(1) $O_2 + e^- \rightarrow O_2^{\bullet-}(E^\circ = -0.33 \text{ V vs. NHE, pH=7})$

(2) $O_2^{\bullet-} + 2H^+ + e^- \rightarrow H_2O_2$ (E° = +0.91 V vs. NHE, pH=7)

(3) $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ ($E^\circ = +0.28 \vee vs. \text{ NHE, pH=7}$)

In recent years, many photocatalysts have been designed for such H_2O_2 production, e.g., TiO₂, graphic carbon nitride (g-C₃N₄), and metal-organic compounds and their derivatives.⁶⁻⁹ However, it has been observed that some of these photocatalysts exhibit challenges related to light-harvesting efficiency and photostability, which can impact their overall performance in H_2O_2 production.¹⁰ In this context, covalent organic frameworks (COFs) have emerged as a promising alternative owing to their remarkable ability to efficiently harvest visible light, their well-organized structure, exceptional chemical stability, customizable topology, and tunable bandgap properties. COFs have been employed in numerous photocatalytic applications such as hydrogen evolution,¹¹ reduction of carbon dioxide,¹² pollutants degradation,¹³ H_2O_2 production,¹⁴ etc. Nevertheless, the full potential of COFs for photocatalytic H_2O_2 production is not yet well-explored.

In 2020, we reported the first successful utilization of COFs as photocatalysts for H₂O₂ production through ORR, employing N,N,N',N'-tetrakis(4-aminophenyl)-1,4phenylenediamine as the linker. Our initial findings demonstrated a maximum H₂O₂ production rate of (only) 97 μ mol·h⁻¹·g_{cat}⁻¹.¹⁵ Subsequently, in 2023, we investigated the use of a biphasic system consisting of benzyl alcohol and water, which led to an enhanced activity of pyrene-based COFs for photocatalytic H₂O₂ production, effectively preventing undesired in situ decomposition. Furthermore, our study revealed the significant influence of the COF surface area and optimal decoration of pyrene units on the photocatalytic performance, resulting in a remarkable maximum H_2O_2 production rate of 1242 µmol·h⁻¹·g_{cat}⁻¹.¹⁶ Building upon these findings, in a subsequent publication, we demonstrated that extending the π -conjugation in COFs through post-synthetic sulfurization can significantly enhance their photocatalytic performance for H₂O₂ production as well.¹⁷ Around 30 papers have appeared since 2020 on the use of COFs as photocatalysts for H_2O_2 , by ORR or the water oxidation reaction (WOR) or both. Some of these papers are briefly discussed below, others are summarized in Table S2.2. For instance, acetynyl triazine-based COFs,¹⁸ fluorinated COFs¹⁹, vinylene-linked triazine-based COFs,²⁰ bipyridine-based²¹ and Ni single-atombased COFs²² were all explored for photocatalytic H₂O₂ production. These studies showed that COFs bearing a triazine unit exhibited a high H_2O_2 production performance. Still, a majority of studies uses sacrificial hole scavengers such as ethanol and benzyl alcohol, or metals to improve the H₂O₂ generation rate. A recent study involving 60 COFs made by mutually pairing 22 different linkers conducted by the Cooper group confirmed that triphenylbenzene or triphenyltriazine units displayed better photoactivity for H_2O_2 production due to their extended π -conjugation.²³ Also, benzothiadiazole (BT) is a well-known chromophore and BT-based COFs have shown excellent photocatalytic activities in hydrogen evolution,²⁴ organic transformations²⁵ and dye degradation²⁶ due to their highly efficient charge separation and strong

electron affinity. In these COFs, the BT moieties act as the O₂ reduction sites for H_2O_2 production.²⁷ These studies collectively emphasize the importance of specific functional groups with their electron-donating or -withdrawing properties, as well as the effects of their oxophilicity and hydrophilicity (or -phobicity). Furthermore, they highlight the significance of structural alignment and overall surface area of the COFs in achieving efficient photocatalytic H_2O_2 production. Consequently, the next crucial step is to develop a comprehensive understanding of the materials' underlying structure-property relationships. This knowledge will enable the fine-tuning of their photophysical and electrochemical properties, ultimately facilitating sacrificial agent-free photocatalytic H_2O_2 production.

Drawing inspiration from this concept, our work places a specific emphasis on exploring the photo-responsive charge separation and transfer efficiency of COFs. By correlating these essential photophysical properties with the corresponding photocatalytic H_2O_2 production efficiency in pure water, we aim to establish a comprehensive structure-property relationship. To achieve this, we combined the beneficial features of the BT moiety (4,4'-(benzothiadiazole-4,7-diyl)dibenzaldehyde) with triphenyltriazine linker (1,3,5-tris-(4-aminophenyl) triazine (TAPT)) and triphenylbenzene linker (1,3,5-tris(4-aminophenyl) benzene (TAPB)) to produce two COFs, TAPT-BT-COF and TAPB-BT-COF. The presence of a triazine unit significantly influenced the efficiency of charge separation and transfer, thus leading to an augmented H_2O_2 formation rate.

2.2. Experimental section

2.2.1. Materials and characterization

The chemicals were bought from TCI Europe or Sigma-Aldrich and used as received. X-ray diffraction (XRD) was carried out on a Bruker D8 Advance diffractometer equipped with a Cu-K α source (40 kV, 30 mA, λ = 1.5406 Å). Fourier transform infrared (FTIR) spectroscopy measurements were recorded on a Thermo Nicolet 6700 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) was conducted using a PHI 5000 VersaProbe II spectrometer equipped with a monochromatic AI K_{α} X-ray source (hv = 1486.6 eV). During analysis, the samples were excited with an X-ray beam (size: 200 μ m) over an area of 500 x 500 μ m² at a power of 50 W. Wide range survey scans and high-resolution spectra were recorded with a pass energy of 187.85 eV and 23.5 eV and a step size of 0.8 eV and 0.1 eV respectively. All spectra were acquired at a takeoff angle of 45° relative to the sample surface in the XPS chamber where the pressure was constantly maintained below 10⁻⁶ Pa. Nitrogen adsorption experiments were performed on a 3P instrument micropore analyzer. Before analysis, the samples were degassed at 120 °C for 24 h. The solid UV-vis absorption curve was obtained from diffuse reflectance spectra (DRS) measured on a Shimadzu UV-3101PC spectrophotometer. BaSO₄ was used as the reflectance standard. Thermogravimetric analyses (TGA) were carried out on a Netzsch STA 449 F3 Jupiter instrument using a heating rate of 10 °C/min in an N₂ atmosphere. Photoluminescence experiments were conducted on a spectrofluorometer (Edinburgh FLSP920), with a photomultiplier detector operating in the 200–900 nm wavelength range at room temperature.

2.2.2. Synthesis of TAPT-BT-COF

TAPT-BT-COF was synthesized according to the literature using some minor modifications.²⁴ A Pyrex tube (10 mL) was charged with 1,3,5-tris-(4-aminophenyl) triazine (TAPT, 17.72 mg 0.05 mmol), 4,4'-(benzothiadiazole-4,7-diyl) dibenzaldehyde (BT, 25.8 mg, 0.075 mmol, see synthesis in supporting information), and o-dichlorobenzene/n-butyl alcohol (1:1 v/v, 1 mL). The resulting mixture was sonicated for 15 minutes to obtain a yellow suspension. Subsequently, 0.1 mL of acetic acid (6 M) was added. After sonicating for 5 minutes, the tube was flash-frozen at 77 K, degassed by three freeze-pump-thaw cycles, sealed and heated at 120 °C for 3 days. The collected yellow powder was washed with N, N-dimethylformamide (DMF), tetrahydrofuran (THF), acetone, and methanol, respectively and dried at 80 °C under vacuum for 12 h (~69% isolated yield).

2.2.3. Synthesis of TAPB-BT-COF

A Pyrex tube (10 mL) was charged with 1,3,5-Tris(4-aminophenyl) benzene (TAPB, 17.57 mg 0.05 mmol), BT (25.8 mg,0.075 mmol), and o-dichlorobenzene/n-butyl alcohol (1:1 v/v, 1 mL). The mixture was sonicated for 5 minutes to obtain a yellow suspension. Subsequently, 0.1 mL of acetic acid (6 M) was added. The tube was flash-frozen at 77 K and degassed by three freeze-pump-thaw cycles. Hereafter, the tube was sealed and heated at 120 °C for 3 days. The collected yellow powder was washed with DMF, THF and methanol, respectively. The product was dried at 80 °C under vacuum for 12 h to obtain the corresponding yellow powder in ~75% isolated yield.

2.2.4. Photoelectrochemical measurements

The photoelectrochemical measurements were performed on a computercontrolled electrochemical workstation (BioLogic VSP Potentiostat) in a standard three-electrode system using a Pt plate and a saturated Ag/AgCl electrode (in 1 M KCl) as the counter and reference electrode, respectively. The COF was used as the working electrode and a Na₂SO₄ solution (0.1 M) was applied as the electrolyte. A 300 W Xe lamp (filtered to $\lambda > 420$ nm) was used as the visible light source. Fluorine-doped tin oxide (FTO) glasses were cleaned by sonication in ethanol for 30 min and dried at 85 °C for 24 h. 5 mg of the COF sample was dispersed in 1 mL ethanol and sonicated for 20 min to get a slurry, which was coated afterwards on the piece of FTO glass (1 × 1 cm²). The FTO glass coated with the sample was dried in air (See details in supporting information).

2.2.5. Photocatalytic experiment

The photocatalytic H₂O₂ production experiments were carried out in a 20 ml sealed glass vial. 5 mg of the photocatalyst was dispersed in 10 ml Milli-Q water to form a homogeneous suspension. The resulting mixture was bubbled with oxygen and stirred in the dark for 30 min to obtain an adsorption-desorption equilibration environment

before irradiation with a 300 W Xenon lamp ($\lambda > 420$ nm). The temperature was maintained at 25 °C using a condenser. The distance between the reactor and the lamp was set at 15 cm, the stirring speed was kept at 800 rpm, and the intensity of the irradiation light was 20.5 mW/cm² (420 nm).

2.3. Results and discussion

2.3.1. Structure characterization

TAPT-BT-COF and TAPB-BT-COF were synthesized under conventional solvothermal conditions. To confirm the crystallinity of the synthesized COFs, the powder X-ray diffraction (PXRD) pattern was measured and compared against theoretical simulations (Figure 2.1a). As seen in Figure 2.1b and 2.1c, the PXRD patterns of both COFs show highly intense diffractions, suggesting a high crystallinity. The PXRD of TAPT-BT-COF possesses an intense peak at $2\vartheta = 2.5^{\circ}$ assigned to the (100) plane, and diffraction peaks at 5.1, 6.7, and 11.6° (2ϑ), which originate from the (200), (210), (140) planes, respectively. The broad peak at 2ϑ = 24.5° suggests the formation of twodimensional layers through π - π stacking. In comparison, the position of the first intense peak of TAPB-BT-COF is located at $2\vartheta = 2.0^\circ$, which indicates that the two COFs have different crystal structures. Subsequently, the structure of the two crystalline COFs was verified by structureless profile fits (Pawley refinement) of the PXRD patterns. The Pawley refinement (red curves) is in excellent agreement with the peak assignment (Figure 2.1b and 2.1c). We have simulated the most frequently observed stacking models (AA, AA-d, AB, ABC, eclipsed, etc.) and the simulated AA-d stacking model corresponds the best to the experimentally obtained PXRD profile of TAPT-BT-COF (Figure S2.2-S2.8). The "d" in "AA-d" refers to some distortions in the regular AA stacking, particularly in the hexagonal pores of the material. This means that while the layers are largely organized directly above one another, there may be some slight deviations or distortions from this perfect alignment, particularly in the regions of the material where the hexagonal pores are located. And the AA- stacking model

corresponds well to the PXRD profile of TAPB-BT-COF (**Figure 2.1e**), indicating that both COFs crystallized in eclipsed stacking mode but possess different structures with different penetrating pores.



Figure 2.1. (a) Schematic overview of the synthesis of TAPT-BT-COF and TAPB-BT-COF. PXRD profile fits (Pawley method) of TAPT-BT-COF (b) and TAPB-BT-COF (c). Top view (left) and side view (right) of the A–A packing mode of TAPT-BT-COF (d) and TAPB-BT-COF (e).

The detailed chemical composition and structure of both COFs were investigated using FTIR and XPS. As shown in **Figure S2.9**, compared to the pristine monomers, a new peak appeared at 1621 cm⁻¹ in the FTIR spectra of both COFs, which can be attributed to the C=N stretching. This indicates the formation of imine linkages. In addition, retention of the characteristic N-S (890 cm⁻¹) stretching bonds in the spectra of the synthesized COFs confirmed the preservation of the benzothiadiazole functional group. As presented in **Figure 2.2**, The XPS survey spectra of TAPT-BT-COF and TAPB-BT-COF show the presence of C, N and S. The high-resolution C 1s XPS spectrum of TAPT-BT-COF can be deconvoluted into four peaks with binding energies at 287.3, 286.4, 285.5 and 284.9 eV, which can be assigned to the C=N in BT, triazine and imine, and aromatic sp² carbon, respectively. In contrast, TAPB-BT-COF did not show any XPS peak for the C=N in triazine, whereas the C=N of the BT unit appeared at 286.8 eV. This

0.5 eV shift with respect to TAPT-BT-COF inferred that the electron affinity of BT is weaker in TAPB-BT-COF than in TAPT-BT-COF. In the N 1s region of the TAPT-BT-COF, three peaks appearing at 398.6, 399.4, and 400.3 eV can be attributed to the Ns of triazine rings, BT and imine bonds, respectively. Compared to that, TAPB-BT-COF possessed only two peaks at binding energies 399.5 and 400.5 eV arising from the Ns in BT and imine C=N linkages. The result distinguishes the two COFs very well. On the other hand, the high-resolution S 2p XPS spectrum of both COFs showed typical doublets (at 165.7 and 166.9 eV), which is characteristic of the benzothiadiazole ring.²⁸ These XPS data further confirmed the successful synthesis of the two COFs, endorsing the FTIR data. The porosity of the TAPT-BT-COF and TAPB-BT-COF was evaluated by nitrogen adsorption measurements at 77 K (Figure S2.10 and S2.11). The Brunauer-Emmett–Teller (BET) surface area of TAPT-BT-COF and TAPB-BT-COF is 186 and 80 m²g⁻ ¹, respectively. Moreover, the pore size distribution obtained by the Quenched-Solid Density Functional Theory method (QSDFT) revealed that the average pore size of TAPT-BT-COF is 2.8 nm, while TAPB-BT-COF possessed an average pore size of 4.1 nm. These results further confirm the theoretically obtained pore size distributions calculated from the structure model.



Figure 2.2. XPS spectra of the TAPT-BT-COF and TAPB-BT-COF: (a) survey; (b) C 1s; (c) N 1s; and (d) S 2p.

The thermal stability of the COFs was investigated using TGA. Both samples were stable up to 500 °C under a nitrogen atmosphere (**Figure S2.12**), proving their high thermal stability. On the other hand, the morphologies and elemental distribution of TAPT-BT-COF and TAPB-BT-COF were revealed by transmission electron microscopy (TEM) and scanning transmission electron microscopy energy-dispersive X-ray spectroscopy (STEM-EDS) elemental mapping (see details in supporting information). Both COFs show nanowire structures (**Figure S2.13**) and the elements C, N and S are uniformly distributed (**Figure S2.14** and **Figure S2.15**).

2.3.2. Optical and electrochemical properties

The optical properties of the photocatalysts are of paramount importance for their catalytic performance. Initially, the optical absorptions of the COFs were investigated

by UV-Vis DRS (Figure 2.3a). Both COFs showed a strong visible light absorption capability. The absorption edges of TAPT-BT-COF and TAPB-BT-COF were 552 and 531 nm, respectively. The slight redshift in the absorption edge of TAPT-BT-COF compared to that of TAPB-BT-COF indicated a better visible light absorption ability of the former. Moreover, a broadening and red-shift in the photo-absorption tail of TAPT-BT-COF around 550-650 nm range compared to its phenyl analogue was observed. This further suggested that the triazine containing COF manifests a subset of charged species that have a lower band gap oscillator strength, i.e., a higher degree of excited state charge separation efficiency, which would be beneficial for photocatalysis. An augmented framework conjugation in the TAPT-BT over TAPB-BT can be ascribed as the reason behind this observation. The optical band gaps (E_{BG}) of TAPT-BT-COF and TAPB-BT-COF were calculated to be 2.35 and 2.43 eV, respectively from the corresponding Tauc plots. Mott-Schottky (M-S) analyses were conducted to obtain the conduction band potentials of both COFs at their respective isoelectric points (Figure S2.16, see details in supporting information). As depicted in Figure S2.17 and S2.18, the positive slope indicated that both COFs are n-type semiconductors, justifying their use in ORR. The flat-band potentials (E_{FB}) of TAPT-BT-COF and TAPB-BT-COF were calculated to be -0.88 and -0.81 V vs. Ag/AgCl (-0.68 and -0.61 V vs. NHE) respectively. Based on these, the valence band (VB) position of TAPT-BT-COF and TAPB-BT-COF were calculated to be 1.67 and 1.82 V (vs. NHE), respectively (Figure 2.3b). Evidently, the conduction band (CB) values of the synthesized COFs were more negative than -0.33 V and 0.28 V (vs. NHE), indicating that they are thermodynamically capable of producing H_2O_2 via a direct or indirect 2e⁻ ORR pathway. On the other hand, the VB potentials were also thermodynamically suitable for oxidizing water to O_2 , thereby completing the redox cycle. Hence, both COFs can theoretically be used as effective photocatalysts for the photo-production of H₂O₂ from pure water.



Figure 2.3. (a) UV-vis diffuse reflectance spectra, (b) Band-structure diagram, (c) Electrochemical impedance spectra (EIS) of TAPT-BT-COF and TAPB-BT-COF, (d) Transient photocurrents of TAPT-BT-COF and TAPB-BT-COF under visible light irradiation, (e) Photoluminescence emission spectra (λ_{ex} = 385 nm) and (f) transient fluorescence lifetime decay profile of TAPT-BT-COF and TAPB-BT-COF.

Furthermore, the charge transfer rates and the separation efficiency of the photogenerated electrons and holes were analyzed by impedance spectroscopy (EIS) and transient photocurrent response (TPR) measurements (see details in supporting information). As illustrated in **Figure 2.3c**, the TAPT-BT-COF shows a smaller semicircular radius of the Nyquist curve compared to TAPB-BT-COF. This indicates a lower interfacial charge transfer resistance of TAPT-BT-COF, which is more favorable to electron and hole transfer. The impedance spectra were fitted using the equivalent Randle circuit $R_s+(Q_{Bulk}/R_{Bulk})+(Q_{CT}/R_{CT})$, where R_s is the solvent resistance, R_{Bulk} is the bulk resistance, and R_{CT} is the charge transfer resistance. The R_{CT} value of TAPT-BT-COF (299 Ω) was much lower than in the case of TAPB-BT-COF (1255 Ω) (**Table S2.1**). The transient photocurrent density of TAPT-BT-COF was also recorded to be higher than in the case of TAPB-BT-COF (Figure 2.3d). In general, the photocurrent response intensity

is positively correlated to the separation efficiency of the photogenerated electrons and holes. This result confirms that TAPT-BT-COF prevents the recombination of charge pairs to a great extent, which is in good agreement with the results obtained from the EIS and UV-Vis measurements, and a justifiable due to the enhanced framework conjugation.

To further endorse these results, photoluminescence (PL) spectra and the fluorescence lifetime decay profile of both COFs were determined. As seen in **Figure 2.3e**, the emission peak maximum of TAPB-BT-COF appeared at 523 nm. Compared to that, TAPT-BT-COF exhibited a red shift (35 nm) and quenched intensities (40%), suggesting lower recombination of photogenerated carriers. The PL peaks can be further deconvoluted into two segments, one centering around 520 nm and the other one significantly redshifted. This indicated the simultaneous existence of two recombination processes.

To better understand the photoexcited charge recombination mechanism and assess the potential for efficient charge separation, the lifetime of the PL decay was measured. A longer lifetime is generally considered beneficial for photocatalysis as it implies a greater chance for charge carriers to participate in chemical reactions. The fluorescence lifetime decay profile (**Figure 2.3f**) revealed two distinct decay patterns, characterized by faster decay constants (τ 1) and relatively slower ones (τ 2). The values of τ 1 were calculated to be 1.18 µs for TAPT-BT-COF and 0.87 µs for TAPB-BT-COF, while the τ 2 values were 9.42 µs and 8.22 µs, respectively. These longer lifetimes (τ 2) in the microsecond range indicate significant phosphorescence in both COFs. The presence of a significant phosphorescent component suggests that the materials possess a higher population of triplet excitons, resulting in a more efficient singlet-to-triplet intersystem charge transfer. Importantly, the triazine-containing COF (TAPT-BT-COF) exhibits a higher efficiency in this process compared to its benzene-based counterpart (TAPB-BT-COF). It is worth noting that the existence of a triplet state in BT is well-documented in the literature, which further supports these observations.^{29, 30}

For a detailed understanding of the excited state charge dynamics in this material,

we further analyzed TAPT-BT-COF by femtosecond transient absorption (TA) spectroscopy and correlated the obtained data with the UV-Vis DRS and PL results. As shown in Figure 2.4a, the TA map is dominated by a spectrally shaped and transiently decaying photo-induced absorption feature ($\Delta A > 0$), which gradually depleted from 2 to 1000 ps. This wavelength range corresponds well to the charge separation band observed in the UV-Vis spectra of TAPT-BT and its PL maximum, which translates as the ground state bleaching of the COF in TA spectra. Furthermore, two excited state absorbance (ESA) peaks were observed at around 675 nm 800 nm in the TA spectra. Considering the high charge transfer efficiency of the material, as already substantiated using other photo-electrochemical analysis, the peak at 675 nm can be ascribed to a probable strong ESA of the excited TAPT-COF radical cation,^{31, 32} whereas the further low-energy one at 800 nm is originating plausibly from the thermal relaxation of the ESA. As shown in Figure 2.4, the peak at 800 nm decreased rapidly in a femtosecond scale (τ_0 = 650 fs), which can justify the small energy requirement of the thermal relaxation of the ESA. The ESA peak then gradually decayed in a twocomponent exponential fashion with lifetimes of 5.6 ps (τ_1) and 150 ps (τ_2), respectively. These two-components can be explained considering that τ_1 is possibly originating from the inter-system crossing in BT, whereas τ_2 is due to direct quenching of the ESA. The TA analysis together with UV-Vis, PL, and the electrochemical analysis endorsed the superiority of TAPT-BT-COF as a photocatalytic material.



Figure 2.4. (a) fs-TA contour spectra of TAPT-BT-COF (b) fs-TA kinetics and the corresponding fitting results (c) fs-TA contour spectra of TAPT-BT-COF at different time scale showing the time

constants.

2.3.3. Photocatalytic activity

The photocatalytic H₂O₂ production was carried out under visible light irradiation. As shown in Figure 2.5a, in the absence of any sacrificial agents, both COFs showed photoactivity with H₂O₂ generation rates of 1363 ± 10 and 731 ± 10 μ mol·h⁻¹·g_{cat}⁻¹ in pure water for TAPT-BT-COF and TAPB-BT-COF respectively. The amount of H_2O_2 increased steadily on prolonging the irradiation time. It is worth noting that the H₂O₂ production rate of TAPT-BT-COF is either comparable or has surpassed most of the similar materials reported to date (Table S2.2). The higher H₂O₂ formation by TAPT-BT-COF can be justified by considering the enhanced charge separation and transfer efficiency of the material. The hydrogen peroxide production performance and the apparent quantum yield (AQY, see details in supporting information) of TAPT-BT-COF were measured under different irradiation wavelengths as well (Figure 2.5b). It showed a remarkable apparent quantum efficiency of 4.9% at 420 nm, and the hydrogen peroxide production rate reached 1214 µmol·h⁻¹·g_{cat}⁻¹. On increasing the wavelength from 420 nm, a noticeable decrease in the H₂O₂ generation activity was observed. As the COF has only a nominal photo-absorbance at higher wavelengths, this observation is understandable. Furthermore, the stability of the TAPT-BT-COF was studied through recycling experiments (Figure 2.5d). The H₂O₂ production rate of the TAPT-BT-COF only showed a slight decrease in activity after successive runs. Furthermore, PXRD (Figure S2.20 and S2.21) and FTIR (Figure S2.22 and S2.23) analysis were performed after catalysis to verify the stability of the TAPT-BT-COF material. The minor changes in both spectra indicate that the crystallinity and the chemical structure of the TAPT-BT-COF remained intact after photocatalysis.



Figure 2.5. (a) H_2O_2 production of the two COFs during three hours of reaction. (b) The H_2O_2 production rate and the apparent quantum yield (AQY) of TAPT-BT-COF under different wavelengths (c) and different atmospheres. (d) Recycling of TAPT-BT-COF for 5 cycles.

To investigate the mechanism of H_2O_2 production, a series of control experiments were carried out using TAPT-BT-COF as the probe catalyst. As shown in **Figure 2.6a**, no hydrogen peroxide was detected when the reaction was carried out in the dark, suggesting the need of light for the catalytic process. As shown in **Figure 2.5c**, TAPT-BT-COF showed the highest H_2O_2 production rate in the presence of pure O_2 . In air, a significant decrease in the hydrogen peroxide production rate is observed while there was no H_2O_2 production in the presence of Ar. These results suggest that O_2 is required for photocatalytic H_2O_2 production. Furthermore, the H_2O_2 production was evaluated by introducing different scavengers into the reaction system, including *tert*-butyl alcohol (TBA, •OH scavenger), benzoquinone (BQ, electron scavenger) and ethanol (hole scavenger). When BQ was introduced into the reaction system, the H_2O_2

production was completely guenched. This suggested that BQ guenched the excited electron and thereby suppressed the generation of $O_2^{\bullet-}$, which, in turn, reduced H_2O_2 formation. When combined with the effect of O₂, this observation emphasized the significant role of electrons in the photocatalytic ORR. In contrast, the presence of TBA did not influence the H_2O_2 formation, indicating that $\cdot OH$ radicals did not participate in the photocatalysis. When ethanol was added as a hole scavenger, a noticeable increase in the H₂O₂ production rate was observed. Based on these results, we can conclude that H₂O₂ is produced at the CB via a stepwise two-electron ORR route $(O_2 \rightarrow O_2^- \rightarrow H_2O_2)$. WOR is the only possible counter-reaction to complete the redox process in pure water. To confirm the WOR, TAPT-BT-COF and AgNO₃ (as an electron scavenger) were added to water and the entire reaction system was placed under an N₂ atmosphere to suppress the ORR and enhance the counter oxidation. After 6 hours of irradiation, only O_2 was detected (**Figure S2.24**). This proves that the reaction at VB is the water oxidation to O₂. Based on these results a plausible reaction mechanism is proposed in Figure 2.6b. Upon visible light irradiation, the photoexcited COF generates electron-hole pairs. The photogenerated electrons of the COF migrate from VB to CB leaving holes in the VB. The electron-deficient VB then oxidizes water to generate oxygen and a proton. At the same time, electron-rich CB reduces the oxygen to produce $O_2^{\bullet-}$, which takes up protons from the medium to form H_2O_2 .



Figure 2.6. Mechanism studies. (a) Photocatalytic H₂O₂ production of TAPT-BT-COF under different conditions. (b) Schematic diagram of the catalytic reaction mechanism.

We performed further theoretical calculations to better understand the photocatalytic behavior of the COFs. The Density Functional Theory (DFT) optimized molecular analogue of both COFs provided interesting insights. The total electron density of the materials mapped for their potential energy surface showed that the Satom of BT is the most active center in both COFs (Figure 2.7a). This indicated that the sulfur of BT would function as the catalytic center in a reaction. Accordingly, the HOMO (Highest Occupied Molecular Orbital)-LUMO (Lowest Unoccupied Molecular Orbital) distribution also showed that the LUMO is mostly located on the BT for both compounds with similar energy values, whereas the HOMO is delocalized over the entire repeating unit and has significantly different energies for the two materials (Figure 2.7b and 2.7c). For the triazine-containing unit, the HOMO energy is lower than in the case of TAPB. This led to a higher bandgap of TAPB-BT than TAPT-BT, which agreed well with the experimental bandgap and photophysical property trend. Moreover, in line with the potential energy surface mapped total electron density, these results also suggested that ORR would take place on the BT, more specifically on the S-center of the BT.



Figure 2.7. (a) DFT-B optimized structure and corresponding total electron density mapped against respective potential energy surface for TAPB-BT (top) and TAPT-BT (bottom), isovalue 0.0004; and corresponding HOMO-1, HOMO, LUMO and LUMO+1 distribution with respective energies (in vacuum) for (b) TAPB-BT and (c) TAPT-BT, isovalue 0.02; (d) the change in free energy for the H₂O₂ production *via* ORR by the two materials.

With this knowledge and the experimental observation that the H_2O_2 production progressed *via* stepwise electron transfer, we calculated the theoretical free energies of the reaction for both TAPB-BT-COF and TAPT-BT-COF. As shown in **Figure 2.7d**, the change in free energy during the first electron transfer to generate the superoxide intermediate at the S-center of the BT (*OOH) was found to be +0.35 eV and -0.14 eV for TAPB and TAPT respectively, whereas that for the second electron transfer (*H₂O₂) is -0.69 eV and -0.15 eV. This suggested that both electron transfers during ORR are thermodynamically favorable for the triazine containing COF, whereas the first step is thermodynamically uphill for TAPB-BT-COF justifying the better catalytic performance of the former. This further endorsed our claimed correlation between the catalytic activity and photo-physical properties of the COFs.

2.4. Conclusion

In summary, two BT-based COFs, containing phenyl and triazine nodes, respectively, were synthesized and their photophysical and electrochemical properties were thoroughly studied. The triazine-containing COF manifested superior photo-induced charge separation and many-fold diminished recombination. The materials were investigated for sacrificial agent-free photocatalytic H₂O₂ production from water. The results showed that the triazine-based COF significantly outperformed the phenyl analogue, which is attributed to the better photophysical properties of the former. This study revealed the importance of framework conjugation for metal-free materials and provides insights into the design of advanced photocatalytic framework materials for augmented charge separation.

2.5. References

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2.6. Supplementary Information

2.6.1. The apparent quantum yield (AQY) measurement

The apparent quantum yield of TAPT-BT-COF was measured under 300 W Xe lamp irradiation (with a bandpass glass filter of 420 nm). The light intensity at 420 nm is measured by an optical power meter. The AQY was calculated as follows:

$$AQY(\%) = \frac{(\text{Number of produced H2O2 molecules}) \times 2}{\text{number of incident photons}} \times 100$$
$$= \frac{(\text{Number of produced H2O2 molecules}) \times 2}{ISt\lambda/hc}$$
(1)

Where *I* = light power intensity (W cm⁻²); S = the irradiation area (cm²); *t* = reaction time (s); λ = wavelength (m); *h* = 6.63×10⁻³⁴ m² kg s⁻¹(Planck's constant); c = 3×10⁸ m s⁻¹ (speed of light).

2.6.2. Electrode preparation

To prepare the working electrodes, 5 mg ground sample was dispersed in 1 mL asprepared solution (ethanol: Nafion =100:1). After sonication for 10 min, the solution was dropped on the surface of FTO glass with an exposed area of 1×1 cm², and then dried in air at 40°C. This step was repeated three times to achieve a uniform coverage.

2.6.3. Transmission electron microscopy (TEM) and scanning transmission electron microscopy energy-dispersive X-ray spectroscopy (STEM-EDS) mapping

The samples were dispersed in ethanol at room temperature and drop cast on an amorphous carbon coated Cu TEM grid. TEM images were collected on a JEOL JEM-2200FS transmission electron microscope with a HAADF detector, and operated at 200 kV and equipped with a *C*_s corrector. The composition of the materials was studied using EDS in the HAADF-STEM mode.

2.6.4. Electrochemical impedance spectroscopy (EIS) and Mott-Schottky

measurement

All electrochemical measurements were performed in a standard three-electrode system. Pt foil served as the counter electrode and Ag/AgCl was used as reference electrode. The working electrodes were immersed in the electrolyte for 60 s before any measurement was conducted. Impedance measurements were collected in a 0.1 mol/L Na₂SO₄ solution at a bias potential of -0.5 V over a frequency range from 10⁶ to 10⁻¹ Hz. The photocurrents were tested under 300 W Xe lamp irradiation with light on-off cycles at a time interval of 30 s and the scan rate was 150 mV/s, while the working electrodes were irradiated from the back side to minimize the influence of the thickness of the semiconductor layer. The Mott–Schottky plotswith frequency of 1 kHz, 2 kHz, 3 kHz in dark condition to determine the flat-band potential. The applied potentials vs. Ag/AgCl were converted to NHE (Normal Hydrogen Electrode) or RHE (Reversible Hydrogen Electrode) potentials using the following equations:

$$E_{\rm NHE} = E_{\rm Ag/AgCl} + E^{\theta}_{\rm Ag/AgCl} \left(E^{\theta}_{\rm Ag/AgCl} = 0.199 \, \rm V \right)$$
(2)

$$E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.0591 \text{pH} + E_{\rm Ag/AgCl}^{\theta} \left(E_{\rm Ag/AgCl}^{\theta} = 0.199 \text{ V} \right)$$
(3)

2.6.5. Quantification of H₂O₂

The concentration of H₂O₂ was quantified using the Ti reagent solution by UV-visible spectroscopy. An aqueous Ti reagent solution was prepared by diluting 640 mg of Titanium (IV) oxysulfate-sulfuric acid hydrate in sulfuric acid (40 mL, 16 M) with milli-Q water to give 750 mL of solution (TiOSO₄.xH₂O+H₂SO₄). This acidic aqueous solution of titanium oxysulfate reacts in the presence of H₂O₂, resulting in the formation of a yellow peroxotitanium complex $[Ti(O_2)OH(H_2O)_3]^+_{aq}(Eq. S4-5)$, the absorbance of which can be measured at 409 nm.

$$TiOSO_{4(s)} + 5H_2O \leftrightarrow [Ti(OH)_3(H_2O)_3]^+_{(aq)} + HSO_4^-_{(aq)}$$
(Eq. S4)

 $[Ti(OH)_{3}(H_{2}O)_{3}]^{+}_{(aq)} + H_{2}O_{2} (aq) \leftrightarrow [Ti(O_{2})OH(H_{2}O)_{3}]^{+}_{(aq)} + 2H_{2}O$ (Eq. S5)

After the photocatalytic reaction, we transferred 1 mL of sample solution (after syringe filtration to remove photocatalysts) into a quartz tube and then add 1 mL of Ti reagent

solution. Then measure the absorbance of this solution by using Shimadzu UV-1800 UV-visible scanning spectrophotometer (see Fig. S19).

2.6.6. Zeta potential measurement

The isoelectric point was determined using a Malvern Panalytical Zetasizer Ultra equipped by zeta potential measurements. To this end, 2 mg of COFs was dispersed in 2 ml Milli-Q water and sonicated for 1 h to give a mixed solution. Then 1 ml of mixed solution was used for a zetapotential titration measurement. The pH was adjusted to either acidic or basic values using aqueous HCl (0.01 M) or aqueous NaOH (0.01 M) respectively, starting each time from the natural pH to minimise salt loading.

2.6.7. Femtosecond transient absorption (TA) spectroscopy

TA experiments are carried out using a 5 kHz Yb:KGW laser source (1030 nm, Carbide, Light Conversion) where pump light is generated through third harmonic generation in a sequence of BBO crystals and probe light is generated by focusing the fundamental into a sapphire crystal of 5 mm thickness. In short, a 220 fs pump pulse at 343 nm excites a thin film of the COF system under ambient conditions. At a time delay *t* (0-1000 ps) generated through a mechanical delay line, a broadband probe pulse measures the change in absorption ΔA over the wavelength range from 525 to 850 nm. Due to the high optical density (OD) of the film above the band gap, no direct bleach of the band gap transitions can be observed in transmission.

2.6.8. Synthesis of 4,4'-(benzothiadiazole-4,7-diyl)dibenzaldehyde (BT)



4,4'-(benzothiadiazole-4,7-diyl)dibenzaldehyde was synthesized according to a previously reported procedure¹. Generally, 4,7-dibromo-2,1,3-benzothiadiazole (4 mmol, 1.18 g), 4-formylphenylboronic acid (12 mmol, 1.8 g) sodium carbonate (24

mmol, 2.55 g), and tetrakis(triphenylphosphine)palladium(0) were introduced into a 100 mL three-neck flask and degassed for three times. Then, dioxane/water (50 mL, v/v = 4/1) was slowly added into the flask under a N₂ atmosphere. After reflux for 48h under N₂, the mixture was poured into distilled water. The yellow solid was filtered and washed with water giving the crude compound which was further purified by flash chromatography with dichloromethane as eluent to afford the title product as a yellowish green powder (1.03 g, 73%). 1H NMR (400 MHz, CDCl3): δ 10.07 (s, 2H, CHO), 8.12 (d, 4H, Ph-H), 8.02 (d, 4H, Ph-H), 7.85 (s, 2H, Ph-H) ppm.

2.6.9. Supplementary Tables and Figures



Figure S2.1. 1H NMR spectrum of 4,4'-(Benzothiadiazole-4,7-diyl)dibenzaldehyde (BT) in CDCl3 (The peak at 7.2 ppm originates from CDCl3).


Figure S2.2. Comparison of the experimental PXRD pattern of TAPT-BT-COF with the simulated possible stacking models, where the AA-d, AB-d, AA, AB, and ABC stackings are related to the formation of regular hexagonal pores. The AA-d stacking model represents the distortions of TAPT-BT-COF.



Figure S2.3. Comparison of the experimental (black) and simulated AA-d stacking PXRD patterns of TAPT-BT-COF and the top view of the simulated structure of AA-d stacking.



Figure S2.4. Localized unit cell structure of TAPT-BT-COF in AA-d stacking to demonstrate the rotation (ca. 30°) of the benzene rings due to repulsion between hydrogen atoms.



Figure S2.5. Comparison of the experimental (black) and simulated AB-d stacking PXRD patterns of TAPT-BT-COF and the top view of the simulated structure of AB-d stacking.



Figure S2.6. Comparison of the experimental (black) and simulated AA stacking PXRD patterns of TAPT-BT-COF and the top view of the simulated structure of AA stacking.



Figure S2.7. Comparison of the experimental (black) and simulated ABC stacking PXRD patterns of TAPT-BT-COF and the top view of the simulated structure of ABC stacking.



Figure S2.8. Comparison of the experimental (black) and simulated ABC stacking PXRD patterns of TAPT-BT-COF and the top view of the simulated structure of ABC stacking.



Figure S2.9. FT-IR spectra of TAPT-BT-COF and TAPB-BT-COF and their monomers.



Figure S2.10. N_2 adsorption-desorption analyses and pore size distribution of TAPT-BT-COF



Figure S2.11. N₂ adsorption-desorption analyses and pore size distribution of TAPB-BT-COF



Figure S2.12. TGA curves of TAPT-BT-COF and TAPB-BT-COF under (a) N_2 and (b) air.



Figure S2.13. TEM images of TAPT-BT-COF (left) and TAPB-BT-COF (right).



Figure S2.14. STEM-EDS element mapping of TAPT-BT-COF. (a) TEM image, (b) Carbon



element, (c) Nitrogen element and (d) Sulfur element.

Figure S2.15. STEM-EDS element mapping of TAPB-BT-COF. (a) TEM image, (b) Carbon element, (c) Nitrogen element and (d) Sulfur element.



Figure S2.16. Zeta potential of TAPT-BT-COF and TAPB-BT-COF as a function of pH showing the isoelectric point of the COFs around pH 6.



Figure S2.17. Mott-Schottky plots of TAPT-BT-COF.



Figure S2.18. Mott-Schottky plots of TAPB-BT-COF.



Figure S2.19. (a) The absorption spectra of different concentrations of H_2O_2 in the presence of Ti reagent solution at wavelengths of 325-550 nm. (b) The H_2O_2 concentration-absorbance calibration curve.



Figure S2.20. PXRD patterns of TAPT-BT-COF before and after catalysis.



Figure S2.21. PXRD patterns of TAPB-BT-COF before and after catalysis.



Figure S2.22. FTIR of TAPT-BT-COF before and after catalysis.



Figure S2.23. FTIR of TAPB-BT-COF before and after catalysis.



Figure S2.24. GC chromatogram of TAPT-BT-COF. A vial was charged with 3 mM AgNO₃

aqueous solution (5 mL) and 10 mg COF. Oxygen is removed by bubbling N_2 in dark condition. Before starting the reaction, the gas headspace of the vial was measured by GC to ensure that no oxygen was present in the vial.

Table S2.1. The charge transfer resistance (R_{CT}) and the bulk resistance (R_{Bulk}) of the COFs.

Material	R _{bulk} (Ω)	R _{CT} (Ω)
ТАРТ	32	299
ТАРВ	43.3	1255

Table S2.2. Comparison with other representative materials in photocatalytic H_2O_2 production.

Matorial	H ₂ O ₂ production Irradiation		Solvent	Poforonco			
Wateria	rate	conditions		ons	Solvent	herefelle	
	07.umol a ⁻¹ b ⁻¹	λ	> 4	420	$H_2O: EtOH =$	c1	
TAPD-(IME)2-COP	97 µmorg - n -	nm			9:1	51	
	$(OM_{0})_{1} COE = 01 \text{ umpl} a^{-1} h^{-1}$		> 4	420	$H_2O: EtOH =$	c1	
TAPD-(UNIE)2-COP	μποιg π	nm			9:1	51	
	$516 \mu m o l \sigma^{-1} b^{-1}$	λ	> 4	400	$H_2O: EtOH =$	c)	
n-cor	στο μποι g π	nm			9:1	SZ	
TE COE 1220 umal a ⁻¹ h ⁻¹		λ	> 4	400	$H_2O: EtOH =$	c)	
11-001	1239 µ1101 g 11	nm			9:1	52	
TENCOE	$1720 \text{ uppol} \text{ g}^{-1} \text{ b}^{-1}$	λ	> 4	400	$H_2O: EtOH =$	c)	
1150-001	1755 µinorg n	nm			9:1	52	
	2006 upol $a^{-1}b^{-1}$	λ	> 4	400	$H_2O: EtOH =$	62	
	2090 μποι g - π	nm			9:1	55	
	1851 umol $a^{-1} b^{-1}$	λ	> 4	400	$H_2O: EtOH =$	62	
COPC-DAB-COP	1651μποι g π	nm			9:1	55	
	1920 umpl $a^{-1} b^{-1}$	λ	= 4	420	$H_2O: EtOH =$	c.4	
		nm			9:1	s4	

CTF-NS-5BT	1630 μmol g ⁻¹ h ⁻¹		>	420	H ₂ O: BA = 9:1	s5	
СОҒ-ТfpВpy	1042 µmol g ⁻¹	λ nm	>	420	H ₂ O	s6	
	606 μ mol g ⁻¹ h ⁻¹ (O ₂ -presaturated						
	water)	λ	>	420		- 7	
TPB-DMTP-COF	1565 µmol g ⁻¹ h ⁻¹	nm			H ₂ O	s/	
	(continuous O ₂						
	bubble)						
	07	λ	>	420		0	
CIF-BDDBN	97 μmol g ⁻¹ h ⁻¹				H ₂ O	SX	
g-C ₃ N ₄ /PDI-BN0.2-		λ	>	420		_	
rGO _{0.05}	30.8 μmol g ⁻¹ h ⁻¹	nm			H₂O	<u>s</u> 9	
		λ	>	420	H2O: BA =		
Py-Da-COF	1242µmol g ⁻¹ h ⁻¹	nm			9:1	s10	
TTF-BT-COF	2760 µmol g ⁻¹ h ⁻¹	λ nm	>	420	H ₂ O	s11	
Вру-ТАРТ	4038 µmol g ⁻¹ h ⁻¹	λ nm	>	420	H ₂ O	s12	
FS-COFs	3904 µmol g ^{−1} h ^{−1}	λ nm	>	420	H ₂ O	s13	
		λ	>	420			
TpDz	7327 μmol g ⁻¹ h ⁻¹	nm			H₂O	s14	
ТрMd	6034 μmol g ⁻¹ h ⁻¹	λ nm	>	420	H ₂ O	s14	
ТрРz	1418 μmol g ⁻¹ h ⁻¹	λ nm	>	420	H ₂ O	s14	

TaptBtt COF	1407 μmol g ⁻¹ h ⁻¹	λ > 420 nm	H ₂ O	s15
TAPT-TFPACOFs@Pd ICs	2143 μmol g ⁻¹ h ⁻¹	λ > 420 nm	H ₂ O	s16
TD-COF	4620 μmol g ⁻¹ h ⁻¹	λ > 420 nm	H ₂ O	s17
TAPT-BT-COF	1360 ± 30 μ mol g ⁻¹ h ⁻¹	λ > 420 nm	H ₂ O	This work
TAPB-BT-COF	730 ± 30 μ mol g ⁻¹ h ⁻¹	λ > 420 nm	H ₂ O	This work

Table S2.3. Comparison of reaction rates under different solvent, gas and lightconditions.

Entry	catalyst	Solvent system ₅	Gas	Irradiatio n conditions	H ₂ O ₂ production rate(umol/g/h)	
1	Blank	Water	O ₂	Light	0	
2	TAPT-BT-COF	Water	Ar	Light	0	
3	TAPT-BT-COF	Water	O ₂	Dark	0	
Λ		Wator	BQ: radical	Light	0	
4		water	scavenger		0	
5	ταρτ.βτ.ΟΓ	Water	AgNO ₃ : electron	Light	26	
J		Water	scavenger		20	
6	TAPT-BT-COF	Water	O ₂	Light	1363	
7		Water/EtO	0.	Light	1740	
/		H=9:1	02		1740	
8		Water	TBA: hydroxyl	Light	1257	
0		water	radical scavenger		1227	

TAPT-BT-COF				
		Trigonal <i>, P3</i> (143)	
	<i>a</i> = <i>b</i> = 40).156568 Å, c = 3.	537274 Å	
Atom Johol		$r = 6 = 90^{\circ}, \gamma = 120^{\circ}$		_
Atom label	Atom type	X	У	2
C1	C	0.55942	0.02756	0.52211
C2	С	0.51663	0.01380	0.52533
C3	С	0.48920	0.97165	0.47022
C4	С	0.49949	0.04199	0.55580
C5	С	0.51974	0.08095	0.38729
C6	С	0.50217	0.10611	0.39153
C7	С	0.46560	0.09502	0.58222
C8	С	0.44401	0.05502	0.73430
С9	С	0.46060	0.02868	0.71966
C10	С	0.54110	0.19519	0.62935
C11	С	0.58047	0.22849	0.56927
C12	С	0.58568	0.26460	0.40338
C13	С	0.55056	0.26658	0.29602
C14	С	0.51103	0.23212	0.34202
C15	С	0.50581	0.19542	0.49920
C16	С	0.62765	0.30028	0.36286
N17	N	0.46411	0.16189	0.55641
C18	С	0.44655	0.12180	0.60348
N19	N	0.70547	0.36626	0.36375
C20	С	0.50383	0.94450	0.40337
C21	С	0.54639	0.95820	0.38536
C22	С	0.57395	0.00051	0.45022

 Table S2.4. Unit cell parameters and atom positions of the TAPT-BT-COF crystal

 structure fitted by Material Studio.

C23	С	0.55909	0.92711	0.29578
C24	С	0.53166	0.89202	0.09243
C25	С	0.53979	0.86016	0.03316
C26	С	0.57295	0.85955	0.20273
C27	С	0.60257	0.89596	0.38089
C28	С	0.59578	0.92948	0.42829
N29	Ν	0.61368	0.01740	0.44378
S30	S	0.63797	0.07118	0.54307
C31	С	0.48101	0.77328	0.24688
C32	С	0.43860	0.75070	0.19245
C33	С	0.42065	0.71235	0.01556
C34	С	0.44622	0.69699	0.10448
C35	С	0.48934	0.72125	0.06753
C36	С	0.50747	0.76067	0.09544
C37	С	0.37538	0.68856	0.02583
N38	Ν	0.55205	0.78427	0.12763
C39	С	0.57961	0.82339	0.18006
N40	N	0.47749	0.41216	0.58183
N41	N	0.29150	0.64482	0.02499
H42	Н	0.54919	0.09216	0.25162
H43	Н	0.51723	0.13518	0.24279
H44	Н	0.41434	0.04384	0.86488
H45	Н	0.44339	0.00186	0.83469
H46	Н	0.53712	0.16830	0.77925
H47	н	0.60670	0.22619	0.65123
H48	Н	0.55365	0.29441	0.17810
H49	Н	0.48461	0.23392	0.25604
H50	Н	0.41445	0.10409	0.66595

H51	Н	0.50375	0.88903	0.02191
H52	Н	0.51987	0.83457	0.15130
H53	Н	0.63080	0.89880	0.48348
H54	Н	0.61869	0.95718	0.56657
H55	Н	0.49445	0.80151	0.41052
H56	Н	0.41985	0.76305	0.28772
H57	Н	0.43313	0.66667	0.22515
H58	Н	0.50849	0.70944	0.16504
H59	Н	0.61130	0.83254	0.21258
H60	Н	0.45687	0.96009	0.47918
H61	Н	0.48195	0.91268	0.36546

Table S2.5. Unit cell parameters and atom positions of the TAPB-BT-COF crystalstructure fitted by Material Studio.

TAPB-BT-COF				
Trigonal <i>, P3</i> (143) α = b = 49.890085 Å, c = 3.630779 Å α = β = 90°, γ = 120°				
Atom label	Atom type	x	У	z
C1	С	0.65174	-0.69832	0.81069
C2	С	0.68075	-0.67923	0.80834
С3	С	0.63672	-0.73019	0.72857
C4	С	0.60595	-0.74654	0.69272
C5	С	0.59167	-0.77694	0.63502
C6	С	0.60768	-0.79169	0.61618
С7	С	0.63860	-0.77524	0.64128
C8	С	0.65290	-0.74483	0.69839
N9	Ν	0.59174	-0.82318	0.57228
C10	С	0.60181	-0.84085	0.63931

C11	С	0.53924	-0.98586	0.39321
C12	С	0.52882	-0.96754	0.51913
C13	С	0.49930	-0.98119	0.63425
C14	С	0.54783	-0.93492	0.53706
C15	С	0.57688	-0.92193	0.66461
C16	С	0.59430	-0.89137	0.69248
C17	С	0.58312	-0.87305	0.59460
C18	С	0.55418	-0.88588	0.46376
C19	С	0.53673	-0.91650	0.43546
N20	N	0.56538	-0.97678	0.27202
S21	S	0.56980	-0.00685	0.13165
H22	Н	0.59286	-0.73590	0.71416
H23	Н	0.56791	-0.78918	0.61236
H24	Н	0.65190	-0.78556	0.61557
H25	Н	0.67666	-0.73281	0.72242
H26	Н	0.62372	-0.83247	0.74644
H27	Н	0.58601	-0.93536	0.75105
H28	Н	0.61646	-0.88203	0.79636
H29	Н	0.54499	-0.87231	0.38397
H30	Н	0.51458	-0.92581	0.33170
C31	С	0.35054	-0.30216	0.50350
C32	С	0.31959	-0.31640	0.50368
C33	С	0.36873	-0.26918	0.50218
C34	С	0.39714	-0.25464	0.34967
C35	С	0.41422	-0.22394	0.35349
C36	С	0.40306	-0.20687	0.49588
C37	С	0.37479	-0.22101	0.64783
C38	С	0.35800	-0.25175	0.65446

N39	N	0.42136	-0.17538	0.49433
C40	С	0.41170	-0.15691	0.47996
C41	С	0.48085	-0.01196	0.62523
C42	С	0.49092	-0.03074	0.50006
C43	С	0.52021	-0.01755	0.38277
C44	С	0.47081	-0.06323	0.49414
N45	N	0.53247	-0.03154	0.25283
C46	С	0.44139	-0.07515	0.38420
C47	С	0.42231	-0.10560	0.38168
C48	С	0.43227	-0.12482	0.48496
C49	С	0.46163	-0.11303	0.59540
C50	С	0.48062	-0.08256	0.60256
H51	Н	0.30898	-0.30331	0.50371
H52	Н	0.40615	-0.26676	0.21881
H53	Н	0.43598	-0.21334	0.23551
H54	Н	0.36606	-0.20841	0.77329
H55	Н	0.33696	-0.26167	0.78904
H56	Н	0.38838	-0.16483	0.44852
H57	Н	0.43322	-0.06091	0.29581
H58	Н	0.39978	-0.11419	0.29461
H59	Н	0.46980	-0.12732	0.68216
H60	Н	0.50285	-0.07416	0.69893
H61	Н	0.49046	-0.96799	0.73998
H62	Н	0.45857	-0.02117	0.72424

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Chapter 3.

Donor-Acceptor Pyrene-Based Covalent Organic Framework for Blue Light Photocatalytic Oxidative Coupling of Amines



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Abstract

Covalent organic frameworks (COFs) with a donor-acceptor (D-A) architecture have been investigated as prospective semiconducting materials, particularly for photocatalytic processes. The incorporation of electron donating and accepting moieties into the COF backbone creates nano heterojunctions, enhancing efficient light absorption, charge separation, and charge transport. Herein, three pyrene-based COFs were well designed for the aerobic coupling of amines under air atmosphere with blue-LED irradiation. Among the three COFs, the Py-Por-COF with D-A structure exhibits the highest photocatalytic performance and demonstrates a remarkable apparent quantum efficiency of 11.3 % at 420 nm. In addition, the Py-Por-COF maintains a good level of crystallinity and high yield even undergone four cycles, showcasing the exceptional potential of D-A structure COFs in the field of photocatalytic organic transformation.

3.1. Introduction

Visible light driven photocatalysis is one of the most promising and environmentally friendly routes for the conversion of organic compounds into valuable intermediates and chemical products¹⁻³. Imines are essential intermediates in the synthesis of organic compounds and are widely used in the pharmaceutical industry owing to their high reactivity and notable antibacterial effects⁴⁻⁶. The traditional synthesis of imines via condensation of amines with carbonyl compounds suffers a few drawbacks such as a long reaction time and the need for a high reaction temperature⁷. Therefore, photocatalytic aerobic oxidative coupling of amines could be a promising alternative. In the last decades, a wide class of materials have been optimized and tested for the photocatalytic synthesis of imines, such as inorganic semiconductors^{8, 9}, metal oxides^{10, 11}, organometallic compounds^{12, 13} and metal-organic frameworks (MOFs)¹⁴.

Recently, another family of very lightweight metal-free semiconducting materials with high surface area, porosity, high chemical stability, and tunable bandgaps have emerged, the so-called Covalent Organic Frameworks (COFs).¹⁵⁻¹⁹ COFs have been widely applied in organic transformation such as selective oxidation of aromatic alcohols²⁰, selective oxidation of sulfides²¹, C-C coupling²², C-N coupling²³, C-O coupling²⁴, and aerobic oxidative coupling of amines²⁵. As for efficient photocatalysts, the suitable bandgaps, strong photo-response ability, and good reusability are very essential. The rational design of COF structures or the introduction of functional groups with special needs have been demonstrated as very effective strategies to enhance the photocatalytic activity of COFs. For example, acetylene-bridged covalent triazine frameworks (A-CTF-2), as reported by Bai et al., revealed that the functional group acetylene moiety plays a crucial role in the inhibition of e^- h⁺ recombination and in minimizing the exciton binding energy, thereby enhancing photocatalytic activity²⁶. In particular, the construction of donor-acceptor (D-A) COFs is documented as a powerful method to adjust charge separation and transformation.^{27, 28}

Pyrene is well-known as a strong electron donor²⁹⁻³¹. Considering its strong light-

harvesting and large π -conjugated structure, we selected pyrene as the electron donor part. We designed three pyrene-based COFs with 5,10,15,20-Tetrakis(4-aminophenyl) porphyrin (Por-NH₂), 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl) tetraaniline (Py-NH₂), and 4,4',4'',4'''-(Ethene-1,1,2,2-tetrayl) tetraaniline (Etta-NH₂), all featuring identical crystal topology. Among the three synthesized COFs, the one containing porphyrin ligands can construct a D-A type COF with Pyrene ligands. For comparison, the other two are D-D type COFs (Py-Py-COF and Py-Etta-COF). Their structural and optoelectronic properties were fully characterized, and the photocatalytic performance of aerobic oxidative coupling amines of all three COFs was explored. The Py-Por-COF with the donor-acceptor pairs displayed the best performance of 99% yield in air under blue LED irradiation, and it still maintains high activity after four cycles. The photocatalytic performance is higher than that of most similar materials, reported to date (**Table S3.1**). The high performance of Py-Por-COF might be contributed to the regular arrangement of D-A moieties and the strong absorption in all visible light region.

3.2. Results and Discussion

3.2.1. Structure characterization

Employing Py-CHO as a fixed building unit, the three imine-linked COFs, namely Py-Por-COF, Py-Py-COF, and Py-Etta-COF were synthesized under solvothermal conditions via Schiff base condensation with different amino building blocks (e.g., Por-NH₂, Py-NH₂, and Etta-NH₂, respectively) (**Figure 3.1**). The crystalline structures of the synthesized COFs were verified by powder X-ray diffraction (PXRD). As presented in **Figure 3.2a-c**, the Py-Por-COF exhibited two diffraction peaks in the 4-7° region at 4.9° and 5.6°, which are assigned to the (011) and (01-1) planes, respectively, and other peaks at 9.9° and 20.8° are assigned to the (200) and (001) planes, respectively. The experimental PXRD of Py-Py-COF showed a sharp peak at 5.0°, which is assigned to the

(100) facet, and other peaks at 7.1°, 10.2°, 15.2°, and 22.5° are attributed to the (110), (200), (210), and (001) planes, respectively. A similar PXRD pattern was observed for Py-Etta-COF. The simulated models were geometrically optimized, and good agreements were observed for Py-Por-COF (6.59% for R_{wp} and 4.98% for R_p), Py-Py-COF (4.62% for R_{wp} and 2.73% for R_p), and Py-Etta-COF (5.65% for R_{wp} and 3.50% for R_p), respectively.



Figure 3.1. Schematic illustration of the pyrene-based COFs.

The chemical structure of the synthesized COFs was further confirmed by Fourier transform infrared (FT-IR) spectroscopy. As shown in **Figure S3.1-S3.3**, a new peak at 1623 cm⁻¹ that belongs to the C=N stretching appeared in the FT-IR patterns of the synthesized COFs, indicating the successful formation of imine linkage. On the other hand, a remarkable attenuation of the C=O stretching vibration intensity at 1690 cm⁻¹ was observed in the FT-IR patterns of COFs compared to the aldehyde monomer counterparts. This reduction suggests that a high condensation degree between the

aldehyde and amino groups. The porosity and specific surface area of Py-Por-COF, Py-Py-COF, and Py-Etta-COF were evaluated by N₂ adsorption/desorption isotherm measurements at 77 K. As shown in Figure 3.2d-f, all three COFs showed a rapid adsorption increase in the low-pressure range ($P/P_0 < 0.05$). This observation is indicative of a type I isotherm, which is a characteristic feature associated with the intrinsic microporosity of these three COFs. The Brunauer-Emmett-Teller (BET) surface area and total pore volume of Py-Por-COF, Py-Py-COF, and Py-Etta-COF are 896 m² g⁻¹, 0.54 cm³ g⁻¹, 1078 m² g⁻¹, 0.68 cm³ g⁻¹, and 1246 m² g⁻¹, 0.72 cm³ g⁻¹, respectively. The pore size distribution (PSD) analysis results for Py-Por-COF, Py-Py-COF, and Py-Etta-COF were obtained by the quenched solid density functional theory (QSDFT) method. The average pore sizes of Py-Por-COF, Py-Py-COF, and Py-Etta-COF were calculated to be 1.7 nm, 1.6 nm, and 1.4 nm, respectively. These values correspond well with the theoretical calculation (1.6 nm, 1.7 nm, and 1.5 nm). The thermal stability of three COFs was also evaluated by the thermogravimetric analysis (TGA). As shown in Figure S3.4, all three COFs can be thermally stable up to 500 °C under a N_2 atmosphere, which suggests their good thermostability for amine coupling reactions.



Figure 3.2. The PXRD patterns and Pawley refinements of (a) Py-Por-COF, (b) Py-Py-COF, and (c) Py-Etta-COF. N₂ sorption isotherms and pore size distributions (inset) of (d) Py-

Por-COF, (e) Py-Py-COF and (f) Py-Etta-COF.

3.2.2. Optical and electrochemical properties

The optical properties of the COFs were analyzed by solid-state UV-vis diffuse reflectance spectroscopy. As shown in Figure 3.3a, Py-Py-COF and Py-Etta-COF displayed similar absorption curves with the absorption edge at 525 nm and 500 nm, respectively. In contrast, the Py-Por-COF exhibited a broad and strong absorption in the region of 300-700 nm, which could be attributed to the Q-bands of the porphyrin linker leading to augmented light-harvesting properties. (The Q-band is relatively weak and occurs in the visible region, the band typically corresponds to electronic transitions within the porphyrin molecule). Accordingly, the optical bandgaps of these COFs were determined from the Tauc plot. The optical bandgaps of 1.79 eV, 2.38 eV, and 2.5 eV were calculated for Py-Por-COF, Py-Py-COF, and Py-Etta-COF, respectively (Figure 3.3b). To further investigate the electronic properties of all three COFs, Mott-Schottky (M-S) analysis was performed at frequencies of 1000 Hz, 2000 Hz, and 3000 Hz to estimate their band positions. This analysis was carried out at the pH corresponding to the isoelectric point (an approximate pH of 7, Figure S3.5) of the COFs to ensure that surface charges were minimized. The positive slopes observed in the M-S plots (Figure S3.6-S3.8) indicate the n-type semiconductor behavior exhibited by the COFs. The conduction band (CB) potentials of Py-Por-COF, Py-Py-COF, and Py-Etta-COF were observed around -0.67, -0.61, and -0.71 V (vs. Ag/AgCl) respectively. These values are converted to standard hydrogen electrode potentials at -0.47, -0.41 and -0.51 V (vs. NHE, pH=7). Evidently, the CB values of the synthesized COFs were more negative than the redox potential of $O_2/\bullet O_2^-$ (-0.33 V vs. NHE, pH=7). This observation indicates that the synthesized COFs have theoretical feasibility to produce •O₂⁻. In combination with the optical bandgap mentioned above, the valence band potentials (VB) of Py-Por-COF, Py-Py-COF, and Py-Etta-COF were calculated to be 1.12, 1.97, and 1.79 V vs. NHE, pH=7 respectively. Their VB potential supports the oxidation of organic substrates such as benzylamine to a cationic radical (+0.76 V vs. NHE pH=7). The schematic representation of the respective band structure alignments of Py-Por-COF, Py-Py-COF, and Py-Etta-COF is depicted in **Figure 3.3c**.



Figure 3.3. (a) UV-vis spectra DRS of Py-Por-COF, Py-Py-COF and Py-Etta-COF. (b) Band gap determined from Tauc plot, (c) Band-structure diagram, (d) Photoluminescence emission spectra, (e) Transient photocurrents under visible light irradiation (I-T), and (f) electrochemical impedance spectra (EIS).

To further evaluate the charge separation efficiency, the internal resistances for the charge transfer process, and the photo-responsive properties of the three COFs were evaluated by steady-state photoluminescence (PL), electrochemical impedance spectroscopy (EIS), and photo current response (I-t) experiments. The normalized PL spectra showed that Py-Py-COF and Py-Etta-COF have a maximum emission peak at 575 nm and 566 nm, respectively (**Figure 3.3d**). Compared to them, Py-Por-COF showed a significant red shift (50 nm) with the maximum emission at 625 nm and a slightly weakened intensity, suggesting a reduced recombination of photogenerated electrons and holes. As shown in **Figure 3.3e**, the Py-Etta-COF exhibited the weakest photocurrent density response under periodic irradiation. In contrast, Py-Por-COF and Py-Py-COF showed highest current changes, which indicate a more efficiency charge separation. It is remarkable that the Py-Py-COF and Py-Por-COF showed very similar photocurrents, yet show a large difference in photocatalytic activity (vide infra). This lower activity is explained by the fact that the photocurrents of the Py-Por-COF decays significantly slower than Py-Py-COF, so we used the weighted average to calculate the average lifetime of the charge decay (**Figure S3.9**). The τ_{avg} values of Py-Por-COF and Py-Py-COF were fitted to be 5.6 s and 1.8 s, respectively, which suggests the Py-Por-COF can separate the charges better than Py-Py-COF. To further substantiate this observation, electrochemical impedance spectroscopy was conducted to clarify the interfacial properties between the COF and the medium. As depicted in **Figure 3.3f**, the Py-Por-COF showed the smallest arc radius, demonstrating the highest electron mobility and the lowest resistance in charge transportation among the three COFs. The charge transfer resistance (R_{CT}) of Py-Por-COF, Py-Py-COF, and Py-Etta-COF is calculated as 1072 Ω, 1565 Ω, and 3714 Ω respectively, by fitting the equivalent Randles circuit.

3.2.3. Photocatalytic activity

Driven by the remarkable properties demonstrated by Py-Por-COF in terms of lightharvesting capability, charge transfer efficiency, and structural stability, our research aimed to investigate the oxidative coupling of amines to imines under air conditions. The catalytic reaction for the oxidative coupling of benzylamine was first conducted under the irradiation of an energy efficient 34 W blue LED (420-430 nm). After 1 hour of irradiation, an excellent yield (99%) of N-benzylidenebenzylamine was observed (**Table 3.1, entry 1**). This yield corresponds to a high photocatalytic activity of 20 mmol $g^{-1} h^{-1}$, which is one of the highest values reported so far (see **Table S3.1**). In addition, as an important criterion for evaluating photocatalytic performance, the apparent quantum yield (AQY) was also calculated by using Eq (1) in supporting information. Depending on the amounts of N-benzylidenebenzylamine produced by the photocatalytic reaction in 1 h, the power intensity of the light, and the irradiation area, the AQY was calculated to be 11.3 % at 420 nm. The high AQY value implied efficient solar energy conversion by Py-Por-COF, indicating its significant potential of Py-Por-COF for practical application. In contrast, the yields of N-benzylidenebenzylamine were only 6% and 8 % when using Py-Py-COF and Py-Etta-COF under the same reaction conditions (**Table 3.1, entries 2-3**). It is worth noting that when we use *a* 34 W oriel lamp with a 575 nm filter, the benzylamine still produces N-benzylidenebenzylamine with a high yield (90 %) by the Py-Por-COF (**Table 3.1, Entry 4**). This result illustrates that Py-Por-COF still performs well even under longer wavelength light, due to its broad light absorption capacity (**Figure 3.3a**). Furthermore, a series of control experiments were carried out to investigate the process of the amine coupling reaction. N-benzylidenebenzylamine was not detected in the absence of catalyst or light, suggesting the significant role of COFs and light in this reaction (**Table 3.1, entries 5-6**). Moreover, the oxidative coupling reaction could not occur without oxygen, emphasizing its necessity in the reaction process (**Table 3.1, entry 7**).

To identify the key reactive oxygen species, different quenchers were introduced into the reaction system. After separately adding AgNO₃ as an electron or KI as a hole scavenger, the yield dramatically decreased to 2 % and 23 %, respectively, indicating the important role of both generated electrons and holes in the amine coupling reaction (**Table 3.1, entries 8-9**). When adding the *p*-benzoquinone (BQ) as a $\cdot O_2^-$ scavenger, the yield was significantly reduced from 99 % to 1 %, highlighting the dominant role of $\cdot O_2^-$ in this reaction (**Table 3.1, entry 10**). Furthermore, with the addition of either TEMPO ($^{1}O_2$ scavenger) or iso-propanol (\cdot OH scavenger), a negligible decrease of the yield was observed, which excluded the involvement of $^{1}O_2$ and \cdot OH in this catalytic process. (**Table 3.1, entries 11-12**). Moreover, the effect of different solvents was also investigated. The result in **Table S3.2** suggests that acetonitrile is the optimal solvent, probably because the polar nature of acetonitrile can stabilize the radical formed during the reaction.

Table 3.1. Control Experiments for the Photocatalytic Oxidative Amine Coupling of

Benzylamine.

\bigcirc	NH ₂ Air, Py-Por-COF Blue light, RT	N
Entry	Reaction condition	Yield (%) ^[b]
1	Standard conditions ^[a]	99
2	Py-Py-COF as the catalyst	6
3	Py-Etta-COF as the catalyst	8
4	Xenon lamp with a 575 nm filter	90
5	No photocatalyst	5
6	No light	7
7	no O ₂	4
8 ^[c]	AgNO ₃	2
9 ^[d]	KI	23
10 ^[e]	1,4-Benzoquinone	< 1
11 ^[f]	TEMPO	98
12 ^[g]	Isopropanol	96

^[a] Standard reaction conditions: under 1 atm air atmosphere, benzylamine (0.2 mmol), photocatalyst (5 mg), 2 mL of 99.8% anhydrous acetonitrile, and under 34 W blue LED (420-430 nm) irradiation for 1 h at R.T. ^[b] yield was determined by gas chromatography with flame ionization detector (GC-FID) using dodecane as the internal standard. ^[c] Silver nitrate (AgNO₃) as the electron scavenger (1 equivalent). ^[d] Potassium iodide (KI) as the hole scavenger. ^[e] p-Benzoquinone (BQ) as the superoxide scavenger (0.2 equivalent). ^[f] TEMPO used as ¹O₂ radical scavenger. ^[g] Isopropanol (IPA) used as •OH radical scavenger.

Based on the results presented in the above control experiments and supported by the relevant reported literature^{32, 33}, a plausible mechanism has been proposed to illustrate the process of the photocatalytic oxidative coupling of benzylamine to Nbenzylidenebenzylamine with Py-Por-COF. In addition, liquid chromatography-mass spectrometry (LC-MS) analysis was conducted to examine potential intermediate products (**Figure S3.10**). As depicted in Figure 3.4, the photoexcited Py-Por-COF generates abundant electron-hole pairs under blue light irradiation. The photoinduced electrons transfer from VB to CB and react with O_2 to form the reactive oxidation species $\bullet O_2^-$. At the same time, the holes remaining in the VB could oxidize benzylamine into the key radical form. The produced $\bullet O_2^-$ in CB can further react with the benzylamine radical, leading to the formation of the intermediate I and H_2O_2 . The molecular ion peak appears at 106 m/z and is attributed to the intermediate I. After that, the condensation between intermediate I and another benzylamine molecule results in the formation of intermediate II, which is detected as well, from the ion peak at 212 m/z. In the final step, the N-benzylidenebenzylamine is produced with loss of ammonia.



Figure 3.4. Proposed possible mechanism for the photocatalytic oxidative coupling of benzylamines into *N*-benzyl-1-phenylmethanimines over Py-Por-COF.

To further test the wide applicability of the Py-Por-COF under blue light irradiation, the substrate scope of the reaction was investigated. As shown in **Table 3.2**, for benzylamines bearing electron donating groups such as $-CH_3$ and $-OCH_3$ (entries 1-2), high yield (95-98%) were achieved in 1 hour of irradiation. Moreover, by prolonging the irradiation time from 1 hour to 1.5 hours or 2 hours, benzylamines substituted with electron-withdrawing groups such as -F, -CI, -Br, $-CF_3$, and -CN can be converted more than 90%, indicating the excellent catalytic performance of Py-Por-COF. Additionaly, the dibenzylamine was used as substrate for oxidation of secondary amines. As shown

in entry 10 (**Table 3.2**), 89 % dibenzylamine could be converted to Nbenzylidenebenzylamine in 2 hours. Of note, this oxidation goes via similar redox steps but a different mechanism as shown in **Figure S3.11**. Catalyst recycling is also of great importance in the field of heterogeneous catalysis. Keeping this in perspective, recycling experiments were performed to assess the recyclability of Py-Por-COF. As shown in **Figure 3.5**, the Py-Por-COF catalyst exhibited a good recyclability, with conversion and selectivity exceeding 90% over four consecutive operating cycles, a slight decrease in the conversion could be related to the unavoidable weight loss during the recovery process of Py-Por-COF. In addition, the structure of the recycled Py-Por-COF was evaluated by PXRD and FT-IR. As shown in **Figure S3.12-S3.13**, no obvious changes were observed compared to these of the fresh material, indicating its excellent photochemical stability.

	R NH ₂	Air, Py-Por-COF Blue light, RT		R	
Entry	Substrate Product	Time	Conv.	Sel.	
			(h)	(%)	(%)
1	NH ₂		1	99	99
2	H ₃ C NH ₂	N	1	96	99
3	H ₃ CO NH ₂	H ₃ CO OCH ₃	1	98	99
4	F NH ₂	F F	1.5	92	99
5	CI NH2		1.5	90	99

Table 3.2. Substrate scope of Py-Por-COF catalyzed selective oxidation of amines.



Figure 3.5. The recyclability of Py-Por-COF for photocatalytic oxidation of benzylamine.

3.3. Conclusion

In summary, we designed and prepared three pyrene-based COFs with the names Py-Por-COF, Py-Py-COF, and Py-Etta-COF. Our investigations show that all three COFs exhibit good crystallinity, high porosity, and chemical stability. Among the trio of COFs studied for the oxidative coupling of amines, the Py-Por COF proved to be the most active in terms of photocatalytic activity, due to its enhanced ability to absorb visible light and its donor-acceptor structure, which is well suited to facilitate electron

transport. The chemical structure of Py-Por-COF, consisting of electron-rich moieties pyrene as the donor and porphyrin as the acceptor, can efficiently separate the photoinduced charge pairs, the generated electrons can react with O₂ to produce superoxide radicals for photocatalytic oxidation coupling of amines. This study further provides significant insights into the rational design and construction of donor-acceptor COFs for solar-driven organic transformations.

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3.5. Supplementary Information

3.5.1 Materials

The chemicals and solvents were commercially available and used as received. methanol, acetonitrile, N-butyl alcohol, ethanol, 1, 2-dichlorobenzene, chloroform, acetic acid, Tetrahydrofuran (THF) and N, N-dimethylformamide (DMF) were purchased from TCI Europe, Sigma-Aldrich, and Fluorochem. 5,10,15,20-Tetrakis(4aminophenyl) porphyrin was purchased from BLD-pharm. X-ray diffraction (XRD) was carried out on a Bruker D8 Advance diffractometer equipped with an autochanger and LynxEye XE-T Silicon strip Line detector, operated with a Cu-Ka source (40 kV, 30 mA, λ = 1.5406 Å). Fourier transform infrared (FTIR) spectroscopy measurements were conducted on a Thermo Nicolet 6700 FTIR spectrometer equipped with a nitrogencooled MCT detector and a KBr beam splitter. X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5000 VersaProbe II spectrometer equipped with a monochromatic Al K_{α} X-ray source (hv = 1486.6 eV). During analysis, the samples were excited with an X-ray beam (size: 200 μ m) over an area of 500 x 500 μ m² at a power of 50 W. Wide range survey scans and high-resolution spectra were recorded with a pass energy of 187.85 eV and 23.5 eV and a step size of 0.8 eV and 0.1 eV respectively. All spectra were acquired at a take-off angle of 45° relative to the sample surface in the XPS chamber where the pressure was constantly maintained below 10^{-6} Pa. Nitrogen adsorption experiments were performed on a 3P instrument micropore analyzer. Before analysis, the samples were degassed at 120 °C for 24 h. The solid UVvis absorption curve was obtained from diffuse reflectance spectra (DRS) measured on a Shimadzu UV-3101PC spectrophotometer. BaSO₄ was used as the reflectance standard. Thermogravimetric analyses (TGA) were carried out on a Netzsch STA 449 F3 Jupiter instrument using a heating rate of 10 °C/min in an N₂ atmosphere. Photoluminescence experiments were performed on a spectrofluorometer (Edinburgh FLSP920), with a photomultiplier detector operating in the 200–900 nm wavelength range at room temperature.

3.5.2 COF synthesis

Synthesis of Py-Por-COF. The Py-Por-COF was synthesized according to the reported literature with slight changes. An ampule (10 mL) charged with Py-CHO (0.04 mmol, 24.7 mg), Por-NH₂ (0.04 mmol, 27 mg), o-dichlorobenzene (1 mL), *n*-butyl alcohol (1 mL), and aqueous CH₃COOH solution (6 M, 0.2 mL) was sonicated for 10 min, degassed by three freeze–pump–thaw cycles and sealed. The tube was then heated at 120 °C for 3 days. After cooling to room temperature, the precipitate was collected by filtration and washed three times with THF, acetone, and diethyl ether three times and dried at 120 °C under N₂ flow for 8 h.

Synthesis of Py-Py-COF. The Py-Py-COF was synthesized according to the reported literature with slight modifications. A Pyrex tube (10 mL) charged with Py-CHO (0.05 mmol, 30.9 mg), Py-NH₂(0.05 mmol, 28.3 mg), DCB (1 mL), *n*-BuOH (1 mL), and aqueous CH₃COOH solution (6 M, 0.2 mL) was sonicated for 10 min, degassed by three freeze–pump–thaw cycles before sealing. Then the tube was heated at 120 °C for 3 days. After cooling to room temperature, the precipitate was collected by filtration and washed with THF, acetone, and diethyl ether three times and dried at 120 °C under N₂ flow for 8 h.

Synthesis of Py-Etta-COF. The Py-Etta-COF was synthesized by reported literature with slight modifications. A Pyrex tube (10 mL) charged with Py-CHO (0.06 mmol, 37.1 mg), Etta-NH₂(0.06 mmol, 23.7 mg), DCB (1 mL), *n*-BuOH (1 mL), and aqueous CH₃COOH solution (6 M, 0.2 mL) was sonicated for 10 min, degassed by three freeze–pump–thaw cycles before sealing. Then the tube was heated at 120 °C for 3 days. After cooling to room temperature, the precipitate was collected by filtration and washed with THF, acetone, and diethyl ether three times and dried at 120 °C under N₂ flow for 8 h.

3.5.3 Photocatalytic Oxidative Coupling of Amines

In the photocatalytic aerobic oxidative coupling of amines, a 34 W blue LED light with a wavelength of 420-430 nm was used as the light source. Into a 20 mL vial, 2 mL of CH₃CN, 0.2 mmol of substrate, 5 mg of catalyst, and 20 μ L of dodecane were added. After stirring in the dark for 10 minutes, the mixture was irradiated with a blue LED (34 W, 420-430 nm) in air and at room temperature. The distance between the reactor and the lamp was set at 10 cm, the stirring speed was kept at 800 rpm, and the light intensity was 3.5 mW/cm² measured by the optical power meter. The conversion was determined by gas chromatography with flame ionization detector (GC-FID) using dodecane as the internal standard.

3.5.4 Electrochemical measurements.

The photoelectrochemical measurements were conducted using a computercontrolled electrochemical workstation (BioLogic VSP Potentiostat) in a standard three-electrode system. A Pt plate and a saturated Ag/AgCl electrode (in 1 M KCl) served as the counter and reference electrodes, respectively. The COF was utilized as the working electrode, and a Na₂SO₄ solution (0.1 M) served as the electrolyte. A 300 W Xe lamp, filtered to λ > 420 nm, was employed as the visible light source. Fluorinedoped tin oxide (FTO) glasses were cleaned by sonication in ethanol for 30 minutes and dried at 85 °C for 24 hours. For the preparation of the working electrode, 3 mg of the COF sample was dispersed in 0.3 mL isopropanol and sonicated for 20 minutes to form a slurry. After the addition of 30 µL Nafion, the mixture was coated onto a piece of FTO glass $(1 \times 1 \text{ cm}^2)$. The FTO glass coated with the sample was air-dried. Photocurrents were measured under 300 W Xe lamp irradiation with light on-off cycles at a time interval of 30 s, and the scan rate was 150 mV/s. The working electrodes were irradiated from the back side to minimize the influence of the semiconductor layer's thickness. Impedance measurements were carried out in a 0.1 M Na₂SO₄ solution at a bias potential corresponding to their conduction band value, over a frequency range from 10⁶ to 10⁻¹ Hz. The impedance spectra can be designated by the equivalent

Randles circuit $[R_s + (Q_{Bulk}/R_{Bulk}) + (Q_{CT}/R_{CT})]$, where R_s is the solvent resistance, R_{Bulk} is the bulk resistance of the COFs, and R_{CT} is the charge transfer resistance. Mott– Schottky plots were generated with frequencies of 1 kHz, 2 kHz, and 3kHz in dark conditions to determine the flat-band potential.

3.5.5 Geometrical optimization of COFs

Geometrical optimization for all the COFs were performed using Materials Studio (2019) software package. In detail, first build the monomers required for COF and connect them, and then use the ultra-fine mode of the 'Forcite' module to optimize the structure. For all the COFs, AA stacks were considered by creating corresponding unit cells and their geometry were optimized, followed by the imposition of high symmetry. Simulated powder diffraction patterns and refinements of PXRD pattern were calculated using Reflex module of Materials studio. R_p determines the residual of least square refinement whereas R_{wp} is the weighted residue. They are used to evaluate the quality of PXRD fits.

3.5.6 Pore size distribution analysis

The pore size distribution (PSD) analysis results for Py-Por-COF, Py-Py-COF, and Py-Etta-COF were obtained by the quenched solid density functional theory (QSDFT) method. Quenched solid density functional theory (QSDFT) is more optimized compared to non-local density functional theory (NLDFT), although NLDFT is also commonly used in calculating the pore size distribution of porous materials. QSDFT considers the effect of surface roughness and heterogeneity explicitly, which enables a more reliable assessment of porosity and pore size distribution in porous materials (ASiQWin Version 5.2). Specifically, COFs usually do not achieve 100% crystallisation, and the QSDFT approach is more advanced in evaluating the poorly crystallised or disordered portion of COFs. Therefore, we chose QSDFT as the most accurate way to evaluate the overall COF material in this work.

3.5.7 GC measurement and the calculation of conversion and selectivity

The conversion, selectivity, and yield for photocatalytic oxidation of the amines to target product were determined by gas chromatography with a flame ionization detector (GC-FID, Thermo - Finnigan Trace GC Ultra) using high purity He as the carrier gas. Standard GC–FID analysis conditions included an injector temperature of 250°C, detector temperature of 280°C, and a column temperature program from 50°C (held for 1 min) to 280°C (held for 2 min) at a rate of 20°C per minute. In the photocatalytic oxidation of amines to the target product, conversion, selectivity, and yield were calculated as follows:

Conversion (%) = $[(C_0 - C_r)/C_0] \times 100$ Selectivity (%) = $[C_p/(C_0 - Cr)] \times 100$ Yield (%) = Conversion (%) × Selectivity (%) Where C₀ =S_{substrate}/S_{dodecane} C_r = S_{substrate} after reaction/ S_{dodecane} after reaction C_p=S_{product}/S_{dodecane}

3.5.8 The apparent quantum yield (AQY) measurement

The apparent quantum yield of Py-Por-COF was measured under 34 W blue light irradiation. The light intensity at 420 nm is measured by an optical power meter. The AQY was calculated as follows:

$$AQY(\%) = \frac{(\text{Number of produced } N - \text{benzylidenebenzylamine molecules})}{\text{number of incident photons}}$$
$$= \frac{(\text{Number of produced } N - \text{benzylidenebenzylamine molecules})}{ISt\lambda/hc} \qquad Eq (1)$$

Where *I* = light power intensity (W cm⁻²); S = the irradiation area (cm²); *t* = reaction time (s); λ = wavelength (m); *h* = 6.63×10⁻³⁴ m² kg s⁻¹(Planck's constant); c = 3×10⁸ m s⁻¹ (speed of light).

3.5.9 Information of the used Kubelka-Munk function and Tacu plot

The Kubelka–Munk function $F(R)=(1-R)^2/2R$ is used to approximate the absorption coefficient (α) from diffuse reflectance data for powder samples. In many practical cases, especially for powdered or highly scattering samples, measuring direct absorption is difficult. Instead, a diffuse reflectance spectroscopy is performed.

The Tauc plot is used to estimate the optical band gap of semiconducting materials. The Tauc plot method is then applied using $(\alpha hv)^n$ versus hv, where the exponent n depends on the nature of the electronic transition. For direct allowed transitions, n=2 is used, which is why we plot $(\alpha hv)^2$ to estimate the optical band gap. By finding the linear portion of the plot and extrapolating to the photon energy axis, the band gap Eg can be determined.

The Tauc plot method is most reliable when applied to materials with well-defined band structures and sharp absorption edges, typically found in crystalline or semicrystalline semiconductors. In contrast, for amorphous, defect-rich, or multiphase materials, the presence of localized states or broad absorption tails can lead to ambiguous estimations of the optical band gap.

3.5.9 Supplementary Table and Figures



Figure S3.1. FT-IR spectra comparison of Py-Etta-COF, monomers Py-CHO, and Etta-

 $NH_2.$



Figure S3.2. FT-IR spectra comparison of Py-Py-COF, monomers Py-CHO, and Py-NH₂.



Figure S3.3. FT-IR spectra comparison of Py-Por-COF, monomers Py-CHO, and Por-

NH₂.



Figure S3.4. TGA of Py-Por-COF, Py-Py-COF, and Py-Etta-COF under nitrogen atmosphere.



Figure S3.5. Zeta potential of Py-Por-COF, Py-Py-COF, and Py-Etta-COF as a function of

pH.



Figure S3.6. Mott-Schottky plots of Py-Por-COF.



Figure S3.8. Mott-Schottky plots of Py-Etta-COF.



Figure S3.9. Photocurrent lifetime decay profile of Py-Por-COF and Py-Py-COF.



Figure S3.10. The total ions chromatogram (TIC) from LC-MS.



Figure S3.11. Proposed possible mechanism for the photocatalytic oxidative of the dibenzylamine.



Figure S3.12. PXRD patterns of Py-Por-COF before and after catalysis.



Figure S3.13. FT-IR patterns of Py-Por-COF before and after catalysis.

Table S3.1. Comparison with other representative materials in photocatalytic

material	raction conditions	time	yield (%)	catalytic activity (mmol/g/h)	Referenc e
Py-BSZ-COF	0.2 mmol Benzylamine, 5 mg of photocatalyst, 1 atm air	12 h	98	1.7	1
PTZ-TTA- COF	0.1 mmol Benzylamine, 2 mg of photocatalyst, 1 atm air	1 h	>80	20	2
Por-BC-COF	0.2 mmol Benzylamine, 10 mg of photocatalyst, 1 atm air	70 min	97	8.8	3
Por-sp ² c- COF	0.1 mmol Benzylamine, 9.67 mg of photocatalyst, 1 atm air	0.5 h	99	10.2	4
Tp-BTD-25	0.3 mmol Benzylamine, 5 mg of photocatalyst, 1 atm air	25 min	42	30.3	5
BTDA-TAPT	0.1 mmol Benzylamine, 6 mg of photocatalyst, 1 atm oxygen	4 h	97	2.1	6
Тр-ТАВ	0.25 mmol Benzylamine, 10 mg of photocatalyst, 1 atm oxygen	6 h	99	2.1	7
A-CTF-2	0.2 mmol Benzylamine, 8 mg of photocatalyst, 0.1 atm oxygen	4 h	99	3.2	8

oxidative coupling of amines.

CTF-1-400	0.33 mmol Benzylamine, 17 mg of photocatalyst, 1 atm oxygen	12 h	99	0.8	9
TiO2@COF- 5	0.2 mmol Benzylamine, 10 mg of photocatalyst, 1 atm oxygen	8 h	99	1.3	10
Py-Por-COF	0.2 mmol Benzylamine, 5 mg of photocatalyst, 1 atm air	1 h	99	20	This work

Catalytic activity: Calculated as mmol of N-benzylidenebenzylamine produced per gram of catalyst per hour.

Table S3.2. The impact of various solvents on the oxidative coupling of benzylamine
over Py-Por-COF under blue light irradiation.

Entry	Solvent	Catalyst	Yield (%)
1	Acetonitrile	Py-Por-COF	99
2	CH₃OH	Py-Por-COF	51
3	Toluene	Py-Por-COF	73
4	THF	Py-Por-COF	87

Table S3.3. Unit cell parameters and atom positions of the **Py-Por-COF** crystal structurefitted by Material Studio.

Py-Por-COF					
		Triclinic <i>, P1</i> (1)			
	a = 8.357597 Å,	b = 22.599309 Å, c	: = 25.313381 Å		
	$\alpha = 81.17372^{\circ}$	°, β = 95.10722°, γ	= 96.49296°		
Atom label	Atom type	x	у	z	
С	С	-1.07899	-0.55505	-0.31829	
Н	Н	-1.13532	-0.53139	-0.29181	

С	С	-0.99213	-0.52199	-0.35664
Н	Н	-0.98087	-0.47371	-0.35899
С	С	-1.06010	-1.13055	-0.88848
Н	Н	-1.16434	-1.16182	-0.89797
С	С	-0.99337	-1.09342	-0.92898
Н	Н	-1.04834	-1.09578	-0.96892
С	С	-0.24875	-0.63848	-1.08671
Н	Н	-0.24084	-0.68592	-1.07941
С	С	-0.23116	-0.60502	-1.04429
Н	Н	-0.21385	-0.62658	-1.00441
С	С	-1.07726	-1.12062	-0.54617
Н	Н	-0.96327	-1.13438	-0.55275
С	С	-1.08502	-1.08309	-0.50774
Н	Н	-0.97747	-1.06748	-0.48434
N	N	-0.81340	-0.53389	-0.47792
С	С	-1.36521	-0.79365	-0.32275
Н	Н	-1.37893	-0.81428	-0.35960
С	С	-1.41195	-0.82746	-0.27531
С	С	-1.44932	-0.88973	-0.27094
С	С	-1.09856	-0.61718	-0.31386
С	С	-0.92557	-0.54958	-0.39396
С	С	-0.84370	-0.51329	-0.43593
Н	Н	-0.80902	-0.46580	-0.42909
С	С	-1.10811	-1.09888	-0.73532
Н	Н	-1.07005	-1.05860	-0.75979
С	С	-1.12237	-1.15790	-0.74985
С	С	-1.06522	-1.17294	-0.79510
С	С	-1.07047	-1.23234	-0.80283

С	С	-1.00013	-1.25181	-0.84543
Н	Н	-0.91842	-1.22501	-0.87134
С	С	-0.99774	-1.12847	-0.83618
С	С	-0.85947	-1.05254	-0.91851
С	С	-0.71323	-0.97043	-1.14244
Н	Н	-0.76108	-0.98029	-1.18185
С	С	-0.77195	-1.00603	-1.09975
Н	Н	-0.86404	-1.04304	-1.10637
Н	Н	-0.69337	-0.35486	-0.57361
С	С	-0.75786	-0.43673	-0.52802
Н	Н	-0.84242	-0.41754	-0.50744
С	С	-1.28029	-0.91892	-0.33727
Н	Н	-1.18537	-0.88430	-0.32686
С	С	-1.25657	-0.95549	-0.37464
Н	Н	-1.14459	-0.94916	-0.39339
С	С	-0.16101	-0.47163	-0.83101
Н	Н	-0.09560	-0.48166	-0.79319
С	С	-0.15687	-0.50707	-0.87127
Н	Н	-0.08592	-0.54389	-0.86539
N	Ν	-0.78518	-1.01515	-0.95820
С	С	-0.47269	-0.73044	-1.14813
Н	Н	-0.50419	-0.70501	-1.11781
С	С	-0.37300	-0.70232	-1.18780
С	С	-0.28539	-0.64572	-1.18469
С	С	-0.59696	-0.92193	-1.13571
С	С	-0.71979	-0.99376	-1.04830
С	С	-0.78890	-1.03148	-1.00456
Н	Н	-0.84725	-1.07595	-1.01440

С	С	-0.51468	-0.44648	-0.70384
Н	Н	-0.60086	-0.48091	-0.68682
С	С	-0.44991	-0.39298	-0.68181
С	С	-0.46704	-0.38239	-0.63033
С	С	-0.38204	-0.33232	-0.61047
С	С	-0.36762	-0.32304	-0.55592
Н	Н	-0.40760	-0.35490	-0.52375
С	С	-0.56575	-0.42364	-0.59429
С	С	-0.73700	-0.49669	-0.51725
С	С	-0.46304	-1.02612	-0.67544
Н	Н	-0.35204	-1.01814	-0.69480
С	С	-0.48599	-0.98995	-0.63778
Н	Н	-0.39256	-0.95447	-0.62797
С	С	0.33299	-0.58779	-1.11329
Н	Н	0.40292	-0.62487	-1.10711
С	С	0.33003	-0.55263	-1.07292
Н	Н	0.40139	-0.56140	-1.03607
С	С	-0.46021	-1.08861	-0.91585
Н	Н	-0.55808	-1.12348	-0.92282
С	С	-0.39794	-1.05408	-0.95874
Н	Н	-0.44350	-1.06347	-0.99852
С	С	-0.44909	-0.51590	-0.41511
Н	Н	-0.53352	-0.49679	-0.39439
С	С	-0.36349	-0.47980	-0.45238
Н	Н	-0.38147	-0.43327	-0.46025
N	N	-0.76220	-0.96948	-0.54241
С	С	0.30426	-0.26427	-0.67661
Н	Н	0.27520	-0.28870	-0.63902

С	С	0.28420	-0.29374	-0.72347
С	С	0.19494	-0.35011	-0.72730
С	С	-0.57796	-1.07312	-0.68804
С	С	-0.62618	-0.99875	-0.61171
С	С	-0.64488	-0.96055	-0.57146
Н	Н	-0.54914	-0.92263	-0.56737
С	С	0.44385	-0.55068	-1.25112
Н	Н	0.46013	-0.51580	-1.22490
С	С	0.34104	-0.60485	-1.24401
С	С	0.24496	-0.61846	-1.20236
С	С	0.15484	-0.67332	-1.19557
С	С	0.05550	-0.69007	-1.15307
Н	Н	0.02913	-0.66105	-1.12508
С	С	0.24665	-0.57694	-1.16152
С	С	0.23759	-0.50573	-1.07972
С	С	0.27051	-0.44954	-0.85429
Н	Н	0.28626	-0.47189	-0.81470
С	С	0.25153	-0.48306	-0.89655
Н	Н	0.25271	-0.53093	-0.88949
С	С	-0.64151	-0.87671	-0.43292
Н	Н	-0.53379	-0.86137	-0.40951
С	С	-0.63210	-0.91342	-0.47162
Н	Н	-0.51768	-0.92738	-0.47731
С	С	0.02246	-0.35547	-0.65073
Н	Н	0.02715	-0.30731	-0.65380
С	С	-0.05780	-0.38856	-0.61056
Н	Н	-0.10903	-0.36613	-0.58197
С	С	-0.13115	-0.91425	-1.17426

Н	Н	-0.18249	-0.91717	-1.21457
С	С	-0.19831	-0.95199	-1.13393
Н	Н	-0.30150	-0.98396	-1.14285
N	N	0.23281	-0.46973	-1.03952
С	С	-0.46761	-1.21149	-0.85273
Н	Н	-0.39191	-1.19181	-0.88388
С	С	-0.50212	-1.17625	-0.81362
С	С	-0.46465	-1.11391	-0.81744
С	С	0.27174	-0.38796	-0.86167
С	С	0.23341	-0.45631	-0.94812
С	С	0.22198	-0.49247	-0.99191
Н	Н	0.20632	-0.54137	-0.98135
С	С	-0.85550	-0.89942	-0.31526
Н	Н	-0.86112	-0.93535	-0.34003
С	С	-0.81454	-0.83821	-0.33159
С	С	-0.78717	-0.81694	-0.38313
С	С	-0.74284	-0.75702	-0.39608
С	С	-0.85550	-0.89942	-0.31526
Н	Н	-0.86112	-0.93535	-0.34003
С	С	-0.81454	-0.83821	-0.33159
С	С	-0.78717	-0.81694	-0.38313
С	С	-0.74284	-0.75702	-0.39608
С	С	-0.71078	-0.73219	-0.44813
Н	Н	-0.74070	-0.75427	-0.48377
С	С	-0.78608	-0.85853	-0.42382
С	С	-0.76874	-0.93298	-0.50262
N	N	-0.15957	-0.27933	-0.77561
N	N	-0.30574	-0.28416	-0.63970

Ν	-1.17742	-1.19588	-0.70927
Ν	-0.34794	-0.35857	-0.71561
С	-1.50772	-0.91831	-0.22445
С	-1.42749	-0.79605	-0.23154
Н	-1.11902	-0.58212	-0.22140
С	-1.19577	-0.62351	-0.22614
С	-1.36289	-0.73518	-0.23222
Н	-1.52742	-0.96665	-0.22023
	N N C C H C C H	N -1.17742 N -0.34794 C -1.50772 C -1.42749 H -1.11902 C -1.19577 C -1.36289 H -1.52742	N-1.17742-1.19588N-0.34794-0.35857C-1.50772-0.91831C-1.42749-0.79605H-1.11902-0.58212C-1.19577-0.62351C-1.36289-0.73518H-1.52742-0.96665

Table S3.4. Unit cell parameters and atom positions of the **Py-Py-COF** crystal structurefitted by Material Studio.

Ру-Ру-СОГ						
	Monoclinic <i>, P21</i> (4) a = 24.664757 Å, b = 26.028010 Å, c = 3.940542 Å					
	<i>α</i> = 87.84501	°, <i>6</i> = 83.99819°,	y = 93.31863°	I		
Atom label	Atom type	x	У	Z		
C1	С	0.39812	0.55092	0.30983		
C2	С	0.44929	0.55082	0.39666		
C3	С	0.47581	0.60007	0.44720		
C4	С	0.36498	0.59802	0.32210		
C5	С	0.38026	0.64704	0.13385		
C6	С	0.34739	0.69380	0.17285		
С7	С	0.29764	0.69250	0.40030		
C8	С	0.28050	0.64297	0.57778		
С9	С	0.31397	0.59675	0.54165		
C10	С	-0.10629	0.05109	0.36952		
C11	С	-0.05319	0.05065	0.42810		
C12	С	-0.02516	0.09961	0.46163		
C13	С	-0.13750	0.09922	0.35610		

C14	С	-0.18968	0.10400	0.55838
C15	С	-0.21996	0.15226	0.54967
C16	С	-0.19861	0.19743	0.33935
C17	С	-0.14735	0.19260	0.13199
C18	С	-0.11804	0.14433	0.14164
C19	С	-0.22548	0.24750	0.32963
N20	N	-0.26944	0.26014	0.56604
H21	Н	0.46069	0.63787	0.41198
H22	Н	0.41607	0.64996	-0.02899
H23	Н	0.36028	0.72887	0.03626
H24	Н	0.24399	0.63977	0.73713
H25	Н	0.30070	0.56218	0.68250
H26	Н	-0.04064	0.13763	0.43832
H27	Н	-0.20598	0.07252	0.71837
H28	Н	-0.25737	0.15416	0.70045
H29	Н	-0.13051	0.22413	-0.02632
H30	Н	-0.08128	0.14337	-0.00724
H31	Н	-0.21060	0.27533	0.13980
C32	С	0.47485	0.50000	0.44658
C33	С	0.37568	0.50000	0.24347
H34	Н	0.34026	0.50000	0.16063
H35	Н	0.16790	0.00000	0.72708
C36	С	0.13066	0.00000	0.66950
C37	С	0.02642	0.00000	0.53654

Table S3.5. Unit cell parameters and atom positions of the **Py-Etta-COF** crystalstructure fitted by Material Studio.

CHAPTER 3. Pyrene-Based COFs for photocatalytic oxidative coupling of amines

Py-Etta-COF						
Triclinic, P1 (1)						
	a = 22.413787 Å, $b = 20.263604$ Å, $c = 4.611950$ Å					
Atom label	Atom type	x	у	Z		
C1	С	0.36990	0.55232	0.43870		
C2	С	0.43264	0.55556	0.47763		
C3	С	0.46281	0.61631	0.49022		
C4	С	0.33283	0.61077	0.35949		
C5	С	0.35053	0.65239	0.13174		
C6	С	0.31624	0.70716	0.05676		
C7	С	0.26221	0.71971	0.19815		
C8	С	0.24289	0.67746	0.41902		
С9	С	0.27806	0.62327	0.49943		
C10	С	0.95018	0.07402	0.43869		
C11	С	0.89185	0.04981	0.39147		
C12	С	0.84557	0.08940	0.29204		
C13	С	0.85466	0.15611	0.24192		
C14	С	0.91032	0.18366	0.30417		
C15	С	0.95738	0.14327	0.39852		
C16	С	0.80851	0.19293	0.08546		
N17	N	0.78113	0.23988	0.20119		
H18	Н	0.43908	0.66272	0.48430		
H19	Н	0.39099	0.64245	0.01144		
H20	Н	0.33109	0.73896	-0.11790		
H21	Н	0.20106	0.68635	0.52951		
H22	Н	0.26290	0.59165	0.67385		
H23	Н	0.88050	-0.00054	0.40867		
H24	Н	0.80279	0.06704	0.24310		

H25	Н	0.91861	0.23539	0.26051
H26	Н	1.00048	0.16664	0.41679
H27	Н	0.78754	0.16865	-0.09717
C28	С	0.62157	0.56408	0.57713
C29	С	0.55873	0.56149	0.54298
C30	С	0.52443	0.61920	0.51805
C31	С	0.65552	0.62639	0.62175
C32	С	0.63874	0.67074	0.84065
C33	С	0.67191	0.72788	0.88923
C34	С	0.72358	0.74041	0.72794
C35	С	0.74158	0.69598	0.51336
C36	С	0.70766	0.63926	0.46026
C37	С	0.00474	0.02912	0.49433
C38	С	0.06083	0.06431	0.60164
C39	С	0.11935	0.05474	0.49471
C40	С	0.16837	0.08687	0.61670
C41	С	0.16056	0.13292	0.83707
C42	С	0.10324	0.14472	0.94351
C43	С	0.05459	0.10946	0.83257
C44	С	0.21285	0.16382	0.97146
N45	N	0.23719	0.21343	0.86018
H46	Н	0.54477	0.66752	0.51465
H47	Н	0.60032	0.66077	0.97620
H48	Н	0.65802	0.76177	1.05804
H49	Н	0.78136	0.70520	0.38656
H50	Н	0.72189	0.60554	0.29161
H51	Н	0.12980	0.02580	0.31063
H52	Н	0.21270	0.07613	0.53640

H53	Н	0.09642	0.17938	1.11919
H54	Н	0.01110	0.11823	0.92283
H55	Н	0.23864	0.13463	1.12188
C56	С	0.62696	0.44408	0.52956
C57	С	0.56359	0.44018	0.52878
C58	С	0.53305	0.37962	0.52505
C59	С	0.66771	0.38853	0.45427
C60	С	0.66838	0.32845	0.60670
C61	С	0.70801	0.27816	0.52602
C62	С	0.74918	0.28866	0.30192
C63	С	0.75098	0.34952	0.16108
C64	С	0.71017	0.39863	0.23353
C65	С	0.00203	0.96004	0.48881
C66	С	0.05139	0.91873	0.36481
C67	С	0.07763	0.93788	0.10550
C68	С	0.12945	0.90782	0.00555
C69	С	0.15031	0.84983	0.13404
C70	С	0.11844	0.82329	0.36934
C71	С	0.06901	0.85747	0.48321
C72	С	0.20385	0.81883	0.00625
N73	N	0.22989	0.76983	0.11354
H74	Н	0.55620	0.33312	0.51717
H75	Н	0.63878	0.32049	0.78888
H76	Н	0.70619	0.23105	0.63643
H77	Н	0.78216	0.35790	-0.01474
H78	Н	0.71128	0.44464	0.11403
H79	Н	0.06124	0.98090	-0.00158
H80	Н	0.15221	0.92901	-0.17967

H81	н	0.13221	0.77740	0.46842
H82	Н	0.04628	0.83738	0.67058
H83	н	0.22333	0.84096	-0.18552
C84	С	0.37276	0.43295	0.52067
C85	С	0.43625	0.43464	0.52287
C86	С	0.47102	0.37705	0.54155
C87	С	0.33638	0.37383	0.59814
C88	С	0.34128	0.31341	0.44984
C89	С	0.30667	0.25905	0.53427
C90	С	0.26506	0.26531	0.75945
C91	С	0.25743	0.32627	0.89565
C92	С	0.29313	0.37984	0.81790
C93	С	0.94968	0.92226	0.60560
C94	С	0.91905	0.94654	0.84670
C95	С	0.86288	0.92180	0.91842
C96	С	0.83905	0.86724	0.77556
C97	С	0.87247	0.83727	0.55429
C98	С	0.92725	0.86500	0.46805
C99	С	0.77834	0.84653	0.86160
N100	N	0.75436	0.79365	0.78345
H101	Н	0.45125	0.32885	0.56191
H102	Н	0.37166	0.30823	0.26870
H103	Н	0.31266	0.21212	0.42575
H104	Н	0.22560	0.33165	1.07092
H105	Н	0.28761	0.42602	0.93308
H106	Н	0.93607	0.98948	0.95582
H107	Н	0.83637	0.94583	1.08196
H108	Н	0.85509	0.79498	0.43879

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H109	Н	0.95016	0.84389	0.28343
H110	Н	0.75421	0.87666	1.01617
C111	С	0.46607	0.49646	0.50827
C112	С	0.34126	0.49137	0.46647
H113	Н	0.29313	0.48904	0.44498
C114	С	0.52950	0.49935	0.52946
C115	С	0.65415	0.50548	0.57025
H116	Н	0.70234	0.50764	0.59046

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Chapter 4.

Totally Conjugated and Coplanar Covalent Organic Frameworks as Photocatalysts for Water Purification: Reduction of Cr (VI) while Oxidizing Water Borne Organic Pollutants



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Linyang Wang, Jeet Chakraborty, Kuber Singh Rawat, Maojun Deng, Jiamin Sun, Yifan Wang, Veronique Van Speybroeck, Pascal Van Der Voort*. Totally conjugated and coplanar covalent organic frameworks as photocatalysts for water purification: Reduction of Cr (VI) while oxidizing water borne organic pollutants, *Separation and Purification Technology*, **2024**, *359*, 130368.

Abstract

Covalent organic frameworks (COFs) have emerged as photocatalytic materials with bandgaps in the visible region. Imine-based COFs, which have been extensively explored, often suffer from limited stability and poor conjugation, hindering their photocatalytic activities. The chemical and hydrolytic stability and the photocatalytic performance of COFs is drastically enhanced by constructing 2D COFs that are fully conjugated in the x,y plane, that have alternating donor-acceptor (D-A) units for better charge separation and that have enhanced conjugation in the z-axis by p-orbital overlap by using highly planar building blocks. In this study, we introduce three highly crystalline sp² COFs that are able to photocatalyticlly reduce highly toxic Cr (VI) species to much less toxic and easily removable Cr (III) residues, while simultaneously oxidizing water borne organic pollutants. One of them, the TEB-COF, with the integration of the acetylene group, exhibited excellent photocatalytic activity due to its superior planarity and extended conjugation. TEB-COF is able to completely remove the model dye Rhodamine B and Cr (VI) (10 mg/L) in less than 30 minutes. This research provides valuable insights into the development of recyclable metal-free photocatalysts for wastewater treatment.

4.1. Introduction

Water pollution is a critical global problem. In many cases the pollutants are diverse and include both toxic metals and organic compounds. Adsorption or precipitation/flocculation are the most common techniques to remove such pollutants.¹⁻⁴ Degradation or functionalization into non-toxic (or less toxic) molecules is an elegant alternative that also neutralizes the sorbed components. Photo-degradation is an interesting technique that is both low-cost and environmentally friendly.

Hexavalent chromium (Cr (VI)) is a common and highly toxic contaminant due to its widespread use in industries such as electroplating, leather tanning, printing, and pigment production.⁵ The limitation for total chromium in drinking water is 0.05 mg/L according to the World Health Organization (WHO).⁶ This limit includes the sum of all Cr-species, typically trivalent chromium (Cr (III)) and hexavalent chromium (Cr (VI)). However, Cr (VI) is over 500 times more toxic than Cr (III).⁷ Reduction of Cr (VI) to Cr (III) has another important advantage, since Cr (III) is readily removed, for instance by precipitation as carbonate, sulfide or sulfate. Compared to the more traditional techniques to remove Cr (VI), like membrane separation, chemical reduction, electrolysis, and ion adsorption,⁵⁻⁷ the photocatalytic reduction of Cr (VI) has gained more and more attention.⁸⁻¹⁰ Various photocatalysts have been developed for water treatment, including inorganic semiconductors, graphene oxide, and metal-organic frameworks.¹¹⁻¹⁵ However, many of these photocatalysts have limitations such as poor light-harvesting capabilities, low Cr(VI) reduction efficiency, slow kinetics, or low water stability.¹⁶ Additionally, some metal-based photocatalysts may lead to secondary contamination by leaching heavy metals. Therefore, the development of efficient metal-free photocatalysts is a logical next step.

Covalent organic frameworks (COFs) are excellent porous photocatalysts due to their large surface area, structural regularity, tailorable functionalities, and strong light-harvesting properties.^{17, 18} However, most studied COFs in the photocatalytic

reduction of Cr (VI) are connected by dynamic bonds. Examples are imine bonds and arylhydrazone bonds, which generally exhibit limited π -electron delocalization and have insufficient chemical stability.¹⁹⁻²¹ More stable COFs are vinylene-linked COFs with C=C linkages. They offer important other benefits, such as an excellent in-plane π -electron delocalization throughout the framework, high efficiency in exciton separation, excellent thermal and chemical stability, and a good photocatalytic activity.²² It is widely recognized that incorporating coplanar backbones and constructing electron donor-acceptor (D-A) structures can improve photocatalytic activity by further extending the π -conjugation, creating local polarization, reducing the exciton binding energy and facilitating electron-hole mobility.²³⁻²⁸ Thus, the integration of these two strategies should greatly enhance the photocatalytic performance.

So we chose the triazine moiety as the electron accepting building unit because of its planarity, high electron affinity, and conjugated nature.²⁰ The electron donating building group is the coplanar electron-rich acetylene group.^{29, 30} In this study, we designed and synthesized three fully conjugated triazine-based 2D COFs, designated as TPB-COF, TEB-COF, and TFB-COF by linking 2,4,6-trimethyl-1,3,5-triazine (TMT) with 5'-(4-Formylphenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarbaldehyde (TFPB), 4,4',4''-(Benzene-1,3,5-triyltris(ethyne-2,1-diyl))-tribenzaldehyde (TAEB), and [1,1:4,1:3,1:4,1-Quinquephenyl]-4,4-dicarboxaldehyde, 5-(4-formyl[1,1-biphenyl]-4-yl)-(DAFB), respectively (Figure 4.1). The structure and photochemical properties of the three COFs were comprehensively characterized. The COFs were tested for the photocatalytic reduction of Cr (VI) and simultaneous one pot degradation of dyes under the irradiation of visible light. The D-A structure in TEB-COF proved favorable for the photocatalytic reduction of Cr (VI) and degradation of dyes. Photoelectronic experiments further confirmed the enhanced mobility of charge carriers in TEB-COF.

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4.2. Experiment section

4.2.1 Materials and characterization

The chemicals were purchased from TCI Europe or Sigma-Aldrich and used without further purification. X-ray diffraction was carried out on a Bruker D8 Advance diffractometer equipped with a Cu-K α source (40 kV, 30 mA, λ = 1.5406 Å). Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurements were recorded on a Thermo Nicolet 6700 FTIR spectrometer. Nitrogen adsorption experiments were performed on a 3P instrument micropore analyzer. Before the analysis, the samples were degassed at 120 °C for 24 h. The solid UV-vis absorption curve was obtained from the diffuse reflectance spectra (DRS) measured on a Shimadzu UV-3101PC spectrophotometer. BaSO₄ was used as the reflectance standard. Luminescence excitation and emission spectra were collected using an Edinburgh Instruments FLSP920 UV-vis-NIR spectrometer setup. The thermogravimetric analyses (TGA) were carried out on a Netzsch STA 449 F3 Jupiter instrument using a heating rate of 10 °C/min in an N₂ atmosphere. The isoelectric point was determined using a Malvern Panalytical Zetasizer Ultra, which was equipped for zeta potential measurements. The detection of oxygen was analyzed using a micro-GC (Agilent 990 Micro Gas Chromatograph Micro Gasifier) with Ar (99.99%) as the carrier gas.

The lake water is taken from Blaarmeersen, Ghent, Belgium. Seawater is taken from the North Sea at Oostende coast, Belgium. Prior to use, the lake water and seawater were filtered using a vacuum filter with 0.22 μ m acetate cellulose film and used for subsequent experiments.

4.2.2 Synthesis of TPB-COF

TPB-COF was synthesized according to reported literature²⁰. In detail, TMT (12.3 mg, 0.1 mmol), TFPB (39.04 mg, 0.1 mmol), *n*BuOH (1.4 mL), *o*-DCB (0.6 mL), and KOH (16.8 mg) were placed in an ampoule. The mixture was sonicated for 15 minutes and then degassed via a freeze-pump-thaw procedure for 3 cycles. The ampoule was

flame-sealed and heated at 120 °C for 72 hours. The resulting precipitate was collected by filtration, washed with acetone, methanol three times, subjected to Soxhlet extraction with methanol and tetrahydrofuran for 24 h for each solvent, and then dried at 100 °C under vacuum to produce the TPB-COF in 83 % isolated yield.

4.2.3 Synthesis of TEB-COF

TEB-COF was synthesized according to reported literature²⁸. In detail, TMT (12.3 mg, 0.1 mmol), TAEB (46.2 mg, 0.1 mmol), mesitylene (0.9 mL), 1,4 -dioxane (0.9 mL), and acetonitrile (0.1 mL) were placed in an ampoule. The mixture was subjected to sonication for 15 minutes, and then TFAA (0.4 mL) was added. Subsequently, the ampoule was subjected to a freeze-pump-thaw procedure for 3 cycles to remove oxygen. The sealed ampoule was heated at 150 °C for 72 hours. The resulting precipitate was collected by filtration, followed by Soxhlet extraction with methanol and tetrahydrofuran for 24 h for each solvent, and then dried at 100 °C under vacuum to produce the TEB-COF in 79 % isolated yield.

4.2.4 Synthesis of TFB-COF

TFB-COF was synthesized according to reported literature²⁸. In detail, TMT (12.3 mg, 0.1 mmol), DAFB (61.8 mg, 0.1 mmol), mesitylene (0.9 mL), 1,4 -dioxane (0.9 mL), and acetonitrile (0.1 mL) were placed in an ampoule. The mixture was subjected to sonication for 15 minutes, and then TFAA (0.4 mL) was added. Subsequently, the ampoule was subjected to a freeze-pump-thaw procedure for 3 cycles to remove oxygen. The sealed ampoule was heated at 150 °C for 72 hours. The resulting precipitate was collected by filtration, followed by Soxhlet extraction with methanol and tetrahydrofuran for 24 h for each solvent, and then dried at 100 °C under vacuum to produce the TFB-COF in 81 % isolated yield.

4.2.5 Photocatalytic Experiment

In the photocatalytic experiments of Cr (VI) reduction and degradation of organic
pollutes, a 300 W Xe lamp with a 420-700 nm wavelength was employed as visible light source. 10 mg of catalyst was dispersed into 30 mL of the reaction aqueous solution under ceaselessly stirring. Prior to light illumination, the reaction suspension was initially stirred under Ar condition for 45 min to reach an adsorption-desorption equilibrium. After a certain time of illumination, the solution was extracted with a 0.22 µm syringe. The absorbance of RhB was detected at 554 nm. The concentration of Cr (VI) was determined by 1,5-diphenylcarbazide method. In 1 mL of the supernatant, 9 mL of sulfuric acid solution (0.2 M) and 0.2 mL of 1,5-diphenylcarbonohydrazide (DPC, 2.5 mg mL⁻¹) were added in turn. A purple complex is formed between Cr (VI) and DPC. This reaction has high selectivity for Cr (VI) versus Cr (III). After allowing to stand for 10 min, the absorbance of the Cr (VI)-DPC complex at 540 nm was detected immediately using an UV spectrophotometer.

4.3. Results and Discussion

4.3.1 Structural Characterization

The three vinylene-linked COFs (TPB-COF, TEB-COF, and TFB-COF) were prepared by linking the aldehyde monomers (TFPB, TAEB, and DAFB) and electron-deficient TMT via the acid-catalyzed solvothermal method (**Figure 4.1**, see Supporting Information for more details). To validate the crystalline structures of the synthesized COFs, powder X-ray diffraction (PXRD) analysis was conducted, and the results are shown in **Figure 4.2a-c**. The TPB-COF showed a sharp peak at 2 ϑ =5.8°, which is assigned to the (100) plane, and other peaks at 10.4°, 11.8°, 15.7°, and 25.4° are attributed to the (110), (200), (210), and (001) facets, respectively. TEB-COF exhibited five prominent diffraction peaks, with the most intensive one at 4.5° and the four other peaks at 7.9°, 9.3°, 12.4°, and 25.8°, corresponding to the reflections from the planes (100), (110), (200), (210), and (001), respectively. Similar PXRD pattern could be found for TFB-COF except the peak corresponding to the (100) plane was located at 2 ϑ = 4.0°, The shift of the main peak to a lower angle can be attributed to the insertion of the long-chain linker DAFB. Pawley refinements of the simulated AA-eclipsed model against the experimental PXRD pattern of the three COFs were performed using Material Studio. Refined parameters for the unit cell were revealed as a = b = 17.92 Å, c = 3.52 Å, and $\alpha = 6 = 90^\circ$, $\gamma = 120^\circ$ for TPB-COF; a = b = 22.12 Å, c = 3.63 Å, $\alpha = 6 = 90^\circ$, $\gamma = 120^\circ$ for TEB-COF; and a = b = 25.51 Å, c = 3.55 Å, $\alpha = 6 = 90^\circ$, and $\gamma = 120^\circ$ for TFB-COF. High correlation and negligible differences were found between the experimental data and the simulated AA-eclipsed structure ($R_{wp} = 4.25\%$ and $R_p = 3.96\%$ for TPB-COF; $R_{wp} =$ 2.62% and $R_p = 2.25\%$ for TEB-COF; and $R_{wp} = 4.32\%$ and $R_p = 2.59\%$ for TFB-COF).



Figure 4.1. Synthesis scheme for TPB-COF, TEB-COF, and TFB-COF.

In order to confirm the chemical structure of the synthesized COFs, Fouriertransform infrared (FT-IR) analysis was conducted. FT-IR spectra of TPB-COF, TEB-COF, and TFB-COF as well as their corresponding building blocks are shown in **Figure S4.1**. A new vibration peak at 1628 cm⁻¹ that belongs to the C=C stretching was observed in the FT-IR spectra of the three COFs while lacking in the FT-IR spectra of the monomers, confirming the formation of the vinylene linkages in the three COFs. At the same time, the characteristic absorbance at 1695 cm⁻¹ of C=O stretching disappeared in the three COFs, which indicated their high polymerization degree.

The three COFs were further subjected to X-ray photoelectron spectroscopy (XPS) analysis. The XPS survey spectra reveal the presence of C and N elements in all three COFs (**Figure S4.2**). The high-resolution C 1s XPS spectrum of TEB-COF (**Figure S4.3a**) could be resolved into four peaks with binding energies at 284.5, 285.2, 286.7, and 288.9 eV, which corresponded to C=C (sp²), C=C (sp), N-C=N in the triazine ring, and π - π *, respectively.³¹ The very broad and weak π - π * feature is unspecific and is often associated with shake-up processes, which occur when an electron is ejected from a core level and simultaneously excites another electron to a higher energy state.³⁵ The high-resolution C 1s XPS spectrum of TFB-COF and TPB-COF (**Figure S4.3b-c**) can be deconvoluted into three peaks centering at 284.6, 286.5, and 288.9 eV, which originates from the C=C (sp²), N-C=N in the triazine ring, and π - π *, respectively. TEB-COF, TFB-COF, and TPB-COF (**Figure S4.3d-f**) exhibit similar N 1s spectra with a distinct peak around 399.4 eV, assigned to the nitrogen atom in the triazine moiety.

Nitrogen adsorption experiments at 77 K were performed to evaluate the permanent porosity and surface area of these vinylene-linked COFs. As shown in **Figure 4.2d-f**, all three COFs displayed a type-I isotherm indicated by the sharp rise in the low-pressure region (P/P₀ <0.05), suggesting the presence of micropores in the COFs. The surface areas of TPB-COF, TEB-COF, and TFB-COF were calculated to be 265 m² g⁻¹, 1150 m² g⁻¹, and 1085 m² g⁻¹ respectively, by employing the Brunauer-Emmett-Teller

(BET) model. The lower surface area of the TPB-COF is mainly due to a lesser crystallinity compared to the two other COFs, which is also apparent from the smaller signal-to-noise ration and the higher Rp value in the XRD patterns. Fitting the N₂ adsorption branch data with a quenched solid density functional theory (QSDFT)^{32, 33} cylindrical pore model resulted in a pore size distribution with prominent distribution peaks at 1.28 nm, 1.45 nm, and 1.72 nm for TPB-COF, TEB-COF, and TFB-COF, respectively, which matched well with the theoretical values (1.1 nm, 1.5 nm, and 1.8 nm) shown in **Figure4.2g-i**. The total pore volume (at P/P₀ = 0.99) of TPB-COF, TEB-COF, and TFB-COF, and TFB-COF, and TFB-COF, and TFB-COF, and TFB-COF, TEB-COF, T



Figure 4.2. The PXRD patterns and Pawley refinements of (a) TPB-COF, (b) TEB-COF, and (c) TFB-COF in AA stacking modes. N₂ sorption isotherms and pore size distributions (inset) of (d) TPB-COF, (e) TFB-COF, and (f) TEB-COF. Images of the crystal structures of the hexagonal structure (g) TPB-COF, (h) TFB-COF, and (i) TEB-COF.

The thermogravimetric analysis (TGA) was performed to evaluate the thermal stability of the prepared COFs. As illustrated in **Figure S4.4**, TEB-COF and TFB-COF showed less than 5% weight loss up to 400 °C under a nitrogen atmosphere, indicating a good thermal stability. The morphologies of TEB-COF, TFB-COF, and TPB-COF were then examined by scanning electron microscopy (SEM). As shown in **Figure S4.5a-c**, TEB-COF and TFB-COF are spherical, whereas the TPB-COF is more fibrous. The chemical stability of the synthesized COFs was assessed by immersing them into common organic solvents (N,N-dimethylformamide, tetrahydrofuran, methanol,) HCl (12 M in water) and NaOH (12 M in water) for three days. There was no significant change in the PXRD pattern (except for TPB-COF that loses some crystallinity in 12 M HCl) after the treatment by different solvents (**Figure S4.6**), which indicated their excellent chemical stability.

4.3.2 Optical properties

The optical properties of the as-prepared photocatalysts were investigated by ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS). As shown in **Figure 4.3a**, the absorption edges of TPB-COF, TEB-COF, and TFB-COF were observed at 470 nm, 585 nm, and 592 nm, respectively, indicating a strong absorption in both the ultraviolet and visible region. Subsequently, the optical bandgaps calculated from the respective Tauc plots are 2.65 eV, 2.40 eV, and 2.43 eV for TPB-COF, TEB-COF, and TFB-COF, respectively (**Figure 4.3b**). The band structures of the photocatalysts were validated by Mott–Schottky measurements at their corresponding isoelectric points (**Figure 54.7**). The flat-band potentials (E_{FB}) of TPB-COF, TEB-COF, and TFB-COF are estimated to be -1.10, -0.64, and -0.62 V (vs. Ag/AgCl) at pH=7, respectively, which convert to standard hydrogen electrode potentials of -0.90, -0.44, and -0.42 V (vs. NHE) at pH=7. Furthermore, we have indicated the conduction band minimum (CBM) as being the flat band potential -0.1V, according to Choong and Jang at al.,³⁴ although opinions on this differ and many papers also use the flat band as the CBM.^{35, 36} The

CBM potential was calculated to be -1.0, -0.54, and -0.52 for TPB-COF, TEB-COF, and TFB-COF, respectively. (Figure S4.8-10). All three CBMs are more negative than Cr (VI)/Cr (III) (+0.95 V vs. NHE) at pH = 7, indicating that all of them have the potential to facilitate Cr (VI) reduction. Based on the optical bandgaps, the valence band maximum (VBM) of TPB-COF, TEB-COF, and TFB-COF were calculated to be 1.65, 1.86, and 1.91 V (vs. NHE) at pH = 7, as illustrated in the band-structure diagrams in Figure 4.3c.

The capability to effectively separate photoinduced electrons and holes is another crucial factor that influences the catalytic performance of photocatalysts. This capability is often positively correlated with the intensity of the transient photocurrent response (TPR). As depicted in Figure 4.3d, the TEB-COF exhibited much higher photocurrent intensity compared to TPB-COF and TFB-COF, suggesting more efficient charge separation in TEB-COF. Moreover, electrochemical impedance spectroscopy (EIS) revealed that TEB-COF possesses the smallest arc radius in the Nyquist plot (Figure 4.3e), indicating the lowest interfacial charge transfer resistance. The charge transfer resistance (R_{CT}) values after fitting to the Randel circuit were calculated to be 2515 Ω , 816 Ω , and 1733 Ω for TPB-COF, TEB-COF, and TFB-COF, respectively. This trend is in good agreement with the TPR results. Furthermore, photoluminescence (PL) spectra were carried out to assess the efficiency of photoinduced charge separation. As shown in Figure 4.3f, upon excitation at 360 nm, the emission peaks of TPB-COF and TFB-COF were approximately located at 570 nm. In contrast, the TEB-COF displayed a redshift of 30 nm, which is attributable to its larger π -extended structure, which lower the energy between the excited state to ground state, leading to longer wavelength. Additionally, the TEB-COF showed significantly lower intensity than TPB-COF and TFB-COF, indicating a reduction of undesired recombination of photogenerated charges, which is favorable to the photocatalytic activity.



Figure 4.3. (a) UV-vis DRS spectra of TPB-COF, TEB-COF, and TFB-COF, (b) Bandgaps determined from the Tauc plots, (c) Band-structure diagram, (d) Transient photocurrents under visible light irradiation, (e) electrochemical impedance, and (f) Photoluminescence emission spectra (λ_{ex} = 360 nm).

4.3.3 DFT calculation

Density functional theory (DFT) calculations were further conducted to understand the effect of chemical structure on the optoelectronic properties of these COFs. All calculations were performed at the PBE-D3(BJ) level using the VASP package (more details are given in the SI). Our geometry optimization study suggests that the inclined AA-stacking configuration is energetically more favorable than the eclipsed AAstacking configuration by 0.18 eV, 0.23 eV, and 0.36 eV for TPB-COF, TFB-COF, and TEB-COF, respectively. Therefore, we continue with the inclined AA-stacking for further investigation. The results also show that in TPB-COF and TFB-COF, the strong spatial interactions between hydrogen atoms on neighboring benzene rings induce a twisting of the backbone. This interaction leads to the formation of dihedral angles that reduce the overall planarity of the structure (**Figure 4.4a**). For TPB-COF, the average dihedral angles between the benzene ring and the adjacent triazine ring and between the benzene rings are 10.67° and 17.49°, respectively. In contrast, TFB-COF exhibits increased average dihedral angles of 31.40° and 30.01° between the benzene rings and decreases between the benzene ring and the adjacent triazine ring to 4.58°. However, introducing acetylene building units in TEB-COF eliminates this steric effect, resulting in a highly coplanar structure with a negligible dihedral angle of 2.22°. The highly planar backbone structure has been verified to enhance π -conjugation, thereby accelerating electron separation.²⁶⁻²⁸

Figure 4.4b shows that TEB-COF has the smallest band gap, aligning well with experimental values. This supports the structural analysis conclusion that TEB-COF's coplanar structure enhances π - π interactions, reducing the band gap. The HOMO (the highest occupied molecular orbital) and LUMO (the lowest unoccupied molecular orbital) value of TFPB, DAFB, and TAEB monomer was calculated to estimate the donor strength of the three linkers. The electron donating ability of a donor monomer is usually related to its HOMO energy level. A high HOMO energy level means that the donor molecule can more easily transfer electrons to the acceptor molecule. As shown in Figure S4.11, the HOMO values of TFPB, DAFB, and TAEB are calculated to be -7.52, -7.22, and -7.29 eV respectively, indicating the stronger donor ability of TAEB and DAFB monomer. Furthermore, the primary contribution to the HOMO of all three COFs mainly originates from the benzene ring and alkynyl chain (Figure 4.4c), whereas the LUMO of TEB-COF and TFB-COF primarily concentrated on the electron-accepting triazine fragment. In contrast, for TPB-COF, it remains distributed over the entire backbone. The reduced overlap between the HOMO and LUMO orbitals in TEB-COF and TFB-COF demonstrates the effective construction of the D-A structure, thereby minimizing charge recombination.

Furthermore, the effective masses (m*) were calculated to evaluate the mobility rate of charge carriers, extrapolated from the calculated band structures (**Table 4.1**). The

calculated effective electron mass (m_e^*) of charge carriers in TEB-COF is significantly smaller than TFB-COF and TPB-COF, indicating faster charge carrier transfer in TEB-COF. Conversely, the effective hole mass (m_h^*) of charge carriers is larger for TEB-COF than the other COFs, resulting in a larger difference between the effective masses of holes and electrons. This leads to a larger relative effective mass ratio (m_h^*/m_e^*) of TEB-COF indicates its higher carrier separation efficiency.





COF. (a) The top and side view of optimized structures with dihedral angles (°) at the PBE-D3(BJ) level of theory. (b) Band structure and total density of states at HSE06 level of theory and (c) HOMO and LUMO. The valence band maximum (VBM) is shifted to zero and indicated by the grey dashed line, and the VBM and conduction band minimum (CBM) are indicated by green and red dots, respectively.

Table 4.1. Calculated band gap (E_g) , effective mass of the electron (m_e^*) and hole (m_h^*) using HSE06 functional. The relative effective mass is defined as $R = m_h^*/m_e^*$. All values of masses are expressed in terms of the free-electron mass m_0 . The K-points ((Y-T), (Y-G), (U-R) etc.) denote the directions in which the electrons and holes move within the band structure.

COFs	E_g (eV)	m_e^*	m_h^*	R
TPB-COF	2.57	8.09 (Y-T)	-4.15 (Z-G)	0.51
		2.289 (Y-G)	-1.45 (Z-T)	
TFB-COF	2.65	1.67 (U-R)	-2.48 (Z-G)	1.48
			-2.13 (Z-T)	
TEB-COF	2.49	0.77 (U-R)	-10.49 (R-V)	13.62
			-8.226 (R-U)	

4.3.4 Photocatalytic performance

The experiments of the photocatalytic reduction of Cr (VI) were carried out under the irradiation of a 300 W xenon lamp (with a 420 nm cut-off filter, to use only visible light). The concentration of Cr (VI) was determined by the 1,4-diphenylcarbazide (DPC) method (see details in supporting information). Prior to the photocatalytic tests, the suspension was stirred for 45 min in dark to reach the adsorption-desorption equilibrium (**Figure S4.12**). In the acid condition (pH=3), the adsorption capacity of TEB-COF for Cr (VI) increases compared to neutral conditions. The calculated equilibrium for adsorbed Cr (VI) is 8.95 mg/g in pH=3. The results show that only a small fraction of Cr (VI) was adsorbed on the catalyst, confirming the dominant role of

photocatalysis in Cr (VI) removal. The photocatalytic performance of the three COFs was assessed by measuring the reducing efficiency of Cr (VI) (10 mg/L) within the same period. As shown in Figure 4.5a and Figure S4.13, after 40 min of irradiation, 99%, 65%, and 52% of Cr (VI) was removed by TEB-COF, TFB-COF, and TPB-COF, respectively (Eq. (S1)). TEB-COF exhibits excellent photocatalytic reduction capabilities for Cr (VI) compared to some previously reported porous materials (Table S4.1). The determination of the reaction rate constant (k) can be achieved by using Eq (S2), assuming that the photoreduction of Cr (VI) follows pseudo-first order kinetics.^{37, 38} As depicted in Figure S4.14, the k value for TEB-COF was calculated to be 0.092 min⁻¹, which is 5.4 times and 4.2 times higher than that of TPB-COF (0.017 min^{-1}) and TFB-COF (0.022 min⁻¹), respectively. This is a significant discrepancy in the photocatalytic reaction rate between TEB-COF and TFB-COF even though they possess comparable bandgaps, suggesting that the bandgap may not be the primary driver impacting in photocatalytic reduction of Cr (VI). The superior performance of the TEB-COF is attributed to the fact that i) the establishment of a donor-acceptor architecture with the electron deficient triazine moieties and strong electron donating alkynyl building blocks and ii) as show earlier in the manuscript, the TEB-COF is the most coplanar system, with negligible dihedral distortion, as there has the best Z-axis conjugation as well. Both features facilitate the charge separation and charge mobility towards the surface of the catalyst. The effect of initial pH on the photocatalytic reduction of Cr (VI) was investigated and the results are shown in Figure 4.5b. When the pH is decreases from 7 to 3, the photocatalytic reduction efficiency of Cr (VI) is significantly enhanced. We can explain this as follows: first, the photocatalyst has a positive charge under acidic conditions (Figure S4.7), which is favorable for the adsorption of the $Cr_2O_7^{2-}$, CrO_4^{2-} , and $HCrO_4^{-}$ anions. Secondly, as the pH decreases, there is a simultaneous increase in the concentration of H⁺, a crucial reactant in the Cr (VI) reduction reaction under acidic and neutral conditions ($Cr_2O_7^{2-}$ + 14H⁺ + 6e⁻ \rightleftharpoons 2Cr³⁺ +7H₂O).^{39, 40} On the other hand, under alkaline conditions, the photocatalytic efficiency of Cr (VI) reduction was severely inhibited, resulting in a removal rate of only 40 % after 60 minutes of irradiation. In alkaline conditions, the catalyst surface is charged negatively (as indicated in the zeta potential plots in **Figure S4.3**), resulting in the electrostatic repulsion of the anionic $Cr_2O_7^{2-}$, CrO_4^{2-} , and $HCrO_4^{-}$. Moreover, the reduction of Cr (VI) proceeds as $CrO_4^{2-} + 4H_2O + 3e^{-} \rightleftharpoons Cr(OH)_3 \downarrow + 5OH^{-}$ under alkaline conditions, The formation of $Cr(OH)_3$ precipitates could obscure active sites on the TEB-COF, leading to the inhibition of the reaction.



Figure 4.5. (a) Photocatalytic performance of TPB-COF, TEB-COF, and TFB-COF for the photocatalytic Cr (VI) reduction. The effects of the (b) initial pH, and (c) different water matrix on the photocatalytic Cr (VI) reduction performance of TEB-COF. (d) Recycling tests of TEB-COF in photocatalytic Cr (VI) reduction.

We additionally assessed the photocatalytic Cr (VI) reduction efficiency of TEB-COF in seawater and lake water and the results are shown in **Figure 4.5c**. Compared to milli-Q water, the photocatalytic efficiency of TEB in seawater and lake water exhibit negligible changes, which illustrates the feasibility of TEB-COF for practical applications.

The recovery and reuse of catalysts is very important for ecological and economic reasons. Therefore, the reusability of TEB-COF was evaluated by recycling experiments (**Figure 4.5d**). After five consecutive runs, TEB-COF still performed very well with a removal efficiency of over 87%, demonstrating the good stability of the photocatalyst. The slight decrease in removal efficiency can be mainly attributed to the inevitable weight loss of TEB-COF during the filtration and recycling process, as we work with low masses of photocatalysts.

We also checked the structural features of the spent catalysts after three runs. The crystalline structure of TEB-COF was conserved, as indicated by the PXRD pattern (Figure S4.16). Moreover, no evident changes were observed in the FT-IR spectrum nor the surface area of the recycled photocatalyst (Figure S4.17-18), indicating the robust structural and chemical stability of TEB-COF. As shown in Figure 4.6a, the XPS survey spectra of TEB-COF after the photocatalytic reaction (pH=7) shows the presence of the element Cr, which was not present before the reaction. Additionally, the binding energies of C 1s and N 1s remain consistent with those before the reaction (Figure 4.6b-c). The high-resolution Cr 2p spectra of TEB-COF after photocatalytic reaction was composed of two peaks located at 287.2 and 577.3 eV, which are attributed to Cr (III)2p1/2 and 2p3/2, respectively (Figure 4.6d).^{41, 42} The results of the XPS spectra demonstrate that the Cr (VI) absorbed on the surface of the COF has been efficiently reduced to Cr (III).



Figure 4.6. (a) Survey XPS spectrum of TEB-COF, high-resolution spectra of TEB-COF in the region of (b) C 1s, and (c) N 1s before and after the reaction. (d) High-resolution XPS spectrum of Cr element on the surface of TEB-COF after the reaction.

4.3.5 Photocatalytic mechanism

In order to shed more light on the photocatalytic mechanism, we performed a series of control and trapping experiments were performed. As shown in **Figure 4.7a**, in the absence of a photocatalyst or light, the concentration of Cr (VI) does not change. When the O₂ was replaced with an Ar atmosphere, the efficiency of Cr (VI) reduction decreased very significantly. So oxygen plays a significant role in the reaction, although the Cr (VI) reduction also seems to proceed through oxygen-free pathways. We also conducted trapping experiments to determine active intermediate species. $K_2S_2O_8$, butylated hydroxytoluene (BHT), sodium azide (NaN₃), tert-butyl alcohol (TBA), and ethanol (CH₃CH₂OH) served as the scavenger of e^- , $\bullet O_2^-$, O_2^-1 , $\bullet OH$, and h^+ ,

respectively. It can be seen from **Figure 4.7b** that the introduction of $K_2S_2O_8$, TBA, and BHT suppresses the photoreduction of Cr (VI), indicating the e⁻, •OH, and •O₂⁻ serve as the dominant active species in the photocatalytic reduction of Cr (VI). On the contrary, the capture of holes by CH₃CH₂OH impedes the recombination of photogenerated electron-hole pairs, consequently improving the reaction rate. These results indicate that the main reactive oxygen species (ROS) in the Cr reduction reaction are $\bullet O_2^-$ and $\bullet OH$. The $\bullet OH$ can be formed by reducing H₂O₂. We further conducted the H₂O₂ measurement to check the pathway of ROS formation. After the photocatalytic Cr (VI) reduction reaction in air condition, we transferred 1 mL of sample solution (after syringe filtration to remove photocatalysts) into a quartz tube and then mixed with 1 mL of Ti reagent solution. Then measure the absorbance of this solution by using UV spectrophotometer. There was an obvious peak at 409 nm, confirming the formation of H₂O₂ (see **Figure S4.19**). We could not detect H₂O₂ after adding the $\bullet O_2^-$ scavenger, indicating that hydrogen peroxide is generated through an indirect two-electron(2e⁻) ORR pathway.



Figure 4.7. (a) Controlled experiments for the reduction of Cr (VI) under different conditions and (b) trapping experiments with different scavengers.

Based on the band structure of TEB-COF and the radical trapping experiments, a plausible mechanism was proposed in **Figure 4.9** and **Figure S4.20**. Under visible light irradiation, electron-hole pairs (excitons) are generated, that separate into charges

that further migrate to the surface of the photocatalyst. The photocatalytic reduction of Cr (VI) typically proceeds through the following three pathways: (i) the photoexcited electrons directly reduce Cr (VI) to Cr (III), (ii) oxygen in the air can also be trapped by electrons to produce superoxide radicals to reduce Cr (VI) indirectly,^{43, 44} and (iii) The H_2O_2 was generated by O_2^- through two-electron(2e⁻) ORR pathway, the formed H_2O_2 further reduce to •OH, which participate in the Cr reduction reaction. This was confirmed by the corresponding radical quenching experiment results using K₂S₂O₈, TBA, and BHT. For the oxidation reaction, the photoexcited holes oxidize water to produce oxygen. To confirm the oxygen evolution at the VB, a control experiment was performed. AgNO₃ was used as an electron scavenger, and the experiment took place in a nitrogen atmosphere to inhibit the oxygen reduction reaction (ORR) while promoting the counter oxidation. Only O2 was observed after 6 hours of irradiation, thereby providing evidence for the generation of O_2 on the VB of TEB-COF (Figure **S4.21**). When ethanol or organic pollutants are present that oxidize more easily than water, the organics will be oxidized without oxygen generation, hereby facilitating the overall redox reaction.

4.3.6 Simultaneous photocatalytic degradation of organic pollutants and

Cr (VI) reduction

We simulated the simultaneous photoreduction of Cr (VI) and the photooxidation of water borne organics, choosing Rhodamine B (RhB) as the model pollutant. We first studied the oxidation half reaction separately. The absorbance wavelength of pure RhB were at 554 nm. As illustrated in **Figure S4.22**, the removal efficiency of RhB reaches 99 % after 30 min under visible light irradiation. The degradation efficiency of TEB-COF towards RhB is exceptional compared to some previously published porous materials (**Table S4.3**).

Similarly, the radicals trapping tests were also conducted at pH=7 to further investigate the mechanism in photocatalytic RhB degradation (**Figure 4.8a**). In the presence of EDTA-2Na (h^+ scavenger) and BHT ($\bullet O_2^-$ scavenger), the degradation

efficiency reduced significantly, indicating the dominant role of h^+ and $\bullet O_2^-$ in the degradation process. Conversely, the introduction of TBA ($\bullet OH$ scavenger) resulted in only a minor reduction in degradation efficiency, implying that $\bullet OH$ was not the key active species. The results of the trapping experiments revealed that the h^+ and $\bullet O_2^-$ were the primary active species responsible for the degradation of RhB.

We subsequently ran the tests of the full system, introducing both the Cr (VI) as the dyes, using the TEB-COF as the active photocatalyst (**Figure 4.8b**). Nearly all RhB was removed within a 20-minute irradiation, at an even faster rate compared to the single half reaction. Similarly, 99% reduction of Cr (VI) was achieved after 30 min of irradiation, again an improvement of the rate as 50 min were required in the isolated half reaction. This rate increase is due to the fact that the dyes (and most organics) will oxidize easier than water, improving the overall rate of the full redox system. Consequently, the recombination of photogenerated electrons and holes is effectively mitigated, resulting in an enhancement of photocatalytic efficiency.



Figure 4.8. (a) the effect of trapping experiments with different scavenger on photocatalytic degradation of RhB. (b) Comparison of TEB-COF performance for removal of single or mixed pollutants.

The photocatalytic mechanism is proposed in **Figure 4.9**, Cr (VI) is reduced to Cr (III) mainly by photo-excited electrons in the CB. On the one hand, electrons can also

participate in the reduction of O_2 to $\bullet O_2^-$ and $\bullet O_2^- \to H_2O_2 \to \bullet OH$, thereby further accelerating the photocatalytic reduction of Cr (VI). Organic pollutants (RhB) serve as sacrificial agent to consume the photogenerated holes left in the VB, thus effectively inhibiting photoelectron-hole recombination. Some of the generated $\bullet O_2^-$ is also beneficial for pollutants degradation confirmed by the radical capture experiments.



Figure 4.9. Proposed mechanism for photocatalytic Cr (VI) reduction and organic pollute degradation.

4.4. Conclusion

We prepared three fully conjugated 2D COFs to perform the photocatalytic reduction of Cr (VI) with simultaneous degradation of organic pollutants. The very coplanar TEB-COF, based on triazine (acceptor) and acetylene (donor) linkers shows the best performance, due to the fact that the acetylene groups is a strong donor and to the fact that this COFs showed the highest planarity in the z-axis (dihedral angle only 2°), allowing good charge separation and good charge transfer mobility in all 3 dimensions. The oxidation of organics present in the water is not only an efficient pollutant removal strategy, but it also strongly enhances the rate of the Cr (III) reduction due to the favorable oxidation potential of many organic species. The reduced Cr (III) is easily removed by precipitation techniques. This study exemplifies an effective strategy for the development of durable and metal-free photocatalysts designed for the treatment of water pollutants.

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4.6. Supplementary Information

4.6.1. Photoelectrochemical Measurement

The photoelectrochemical measurements were performed on a computercontrolled electrochemical workstation (BioLogic VSP Potentiostat) in a standard three-electrode system using a Pt plate and a saturated Ag/AgCl electrode (in 1 M KCl) as the counter and reference electrode, respectively. The COF was used as the working electrode and a Na₂SO₄ solution (0.2 M) was applied as the electrolyte. A 300 W Xe lamp (filtered to λ > 420 nm) was used as the visible light source. Fluorine-doped tin oxide (FTO) glasses were cleaned by sonication in ethanol for 30 min and dried at 80 °C for 12 h. 3 mg of the COF sample was dispersed in 0.3 mL isopropanol and sonicated for 20 min to get a slurry, which was coated afterwards on the piece of FTO glass (1 × 1 cm²). The FTO glass coated with the sample was dried in air. Impedance measurements were collected in a 0.2 mol/L Na₂SO₄ solution over a frequency range from 10⁶ to 10⁻¹ Hz. The impedance plots can be modeled by the equivalent Randle circuit $[R_s + (Q_{Bulk}/R_{Bulk}) + (Q_{CT}/R_{CT})]$, where Rs is the solvent resistance, R_{Bulk} is the bulk resistance of the COFs, and R_{CT} is the charge transfer resistance. The photocurrents were tested under 300 W Xe lamp irradiation with light on-off cycles at a time interval of 30 s and the scan rate was 150 mV/s, while the working electrodes were irradiated from the back side to minimize the influence of the thickness of the semiconductor layer. The Mott–Schottky plots with frequency of 1 kHz, 1.5 kHz, 2 kHz in dark condition to determine the flat-band potential.

4.6.2. Photoluminescence Measurements

Luminescence excitation and emission spectra were collected using an Edinburgh Instruments FLSP920 UV-vis-NIR spectrometer setup, which employed a 450 W xenon lamp for steady-state excitation. Emission signals were detected with a Hamamatsu R928P photomultiplier tube. All emission spectra presented in the manuscript were adjusted for detector response. Colloidal suspensions of the COFs were measured in quartz cuvettes with a path length of 10 mm.

4.6.3. Zeta potential Measurement

The isoelectric point was determined using a Malvern Panalytical Zetasizer Ultra, which was equipped for zeta potential measurements. For this purpose, 2 mg of COFs was dispersed in 2 mL of Milli-Q water and sonicated for 1 hour to create a uniform solution. Subsequently, 1 mL of this solution was used for a zeta potential titration measurement. The pH was adjusted to both acidic and basic values by adding either aqueous HCI (0.01 M) or aqueous NaOH (0.01 M), respectively. In each case, the adjustment was initiated from the natural pH to minimize salt loading.

4.6.4. Micro-GC measurements

The detection of oxygen was carried out in a 40 ml vial filled with a 3 mM AgNO₃ aqueous solution (10 mL) and 10 mg COF. Oxygen was removed by purging with highpurity N₂ (99.99%) before illumination. Prior to initiating the reaction, the gas headspace in the vial was analyzed by micro-GC to ensure the absence of oxygen in the reactor. Subsequently, the suspension was exposed to a 300 W Xe lamp (λ > 420 nm). After 4 hours of irradiation, 5 ml of the gas phase sample in the reactor was analyzed using a micro-GC (Agilent 990 Micro Gas Chromatograph Micro Gasifier) with Ar (99.99%) as the carrier gas.

4.6.5. Removal efficiency calculation

The removal efficiency was calculated using the following equation:

Removal efficiency (%) = $\frac{C_0 - C}{C_0} \times 100$ (Eq. S1)

Assuming Cr (VI) photoreduction and pollutes degradation follows the pseudo-firstorder reaction, its kinetics can be represented as the following equation:

$$ln(C_0/C_t) = kt$$
(Eq. S2)

where C_0 and C_t represent Cr (VI) concentrations at the dark adsorption equilibrium and the irradiation time *t*, respectively. k and *t* represented the reaction rate constant and reaction time, respectively. The adsorption capacity at equilibrium (q_e(mg/g)) of Cr (VI) was calculated based on the following equation:

$$q_e = \frac{(C_0 - C) \times V}{M} \tag{Eq. S3}$$

 C_0 and C were the initial and equilibrium Cr (VI) concentration. M (g) was the weight of photocatalysts and V (L) was the volume of the Cr (VI) solution.

4.6.6. Computational Details

All the DFT calculations were performed using the projector augmented wave (PAW)¹ with Vienna ab initio simulation package (VASP).²⁻⁵ The Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was used to describe the electron exchange-correlational interaction.⁶ The plane-wave basis cutoff energy was set to 500 eV. All the structures were optimized until the change in energy between successive iterations dropped below 1×10^{-5} eV and the atomic forces on each atom reached smaller than 0.01 eV Å⁻¹. The Γ-centered $1 \times 1 \times 5$ grids were used to sample the Brillouin zone for TPB-COF. For TFB-COF and TEB-COF, a Γ-centered $1 \times 1 \times 7$ grids were used to sample the Brillouin zone. The Grimme's D3 with Becke-Johnson damping was used in our calculations to consider the non-covalent interactions.^{7, 8} The hybrid functional (HSE06) was used to calculate the band structure and density of states. The k-path for bands structure and effective mass were originated using SUMO.⁹

4.6.7. H₂O₂ measurement

We use the titanium oxysulfate method to confirm the formation of H_2O_2 . An aqueous Ti reagent solution was prepared by diluting 640 mg of Titanium (IV) oxysulfate-sulfuric acid hydrate in sulfuric acid (40 mL, 16 M) with milli-Q water to give 750 mL of solution (TiOSO₄.xH₂O+H₂SO₄). This acidic aqueous solution of titanium oxysulfate reacts in the presence of H_2O_2 , resulting in the formation of a yellow peroxotitanium complex

 $[Ti(O_2)OH(H_2O)_3]^+_{aq}$, the absorbance of which can be measured at 409 nm.

 $TiOSO_{4(s)} + 5H_2O \leftrightarrow [Ti(OH)_3(H_2O)_3]^+_{(aq)} + HSO_4^-_{(aq)}$

 $[\mathsf{Ti}(\mathsf{OH})_3(\mathsf{H}_2\mathsf{O})_3]^+_{(\mathsf{aq})} + \mathsf{H}_2\mathsf{O}_2 \text{ (aq)} \leftrightarrow [\mathsf{Ti}(\mathsf{O}_2)\mathsf{OH}(\mathsf{H}_2\mathsf{O})_3]^+_{(\mathsf{aq})} + 2\mathsf{H}_2\mathsf{O}$

After the photocatalytic Cr (VI) reduction reaction, we transferred 1 mL of sample solution (after syringe filtration to remove photocatalysts) into a quartz tube and then add 1 mL of Ti reagent solution. Then measure the absorbance of this solution by using Shimadzu UV-1800 UV-visible scanning spectrophotometer.

4.6.8. Supplementary Tables and Figures



Figure S4.1. FT-IR spectrum of the aldehyde linkers, TPB-COF, TEB-COF, and TFB-COF.



Figure S4.2. Survey XPS spectrum of TPB-COF, TFB-COF, and TEB-COF.



Figure S4.3. XPS high-resolution spectra of (a)TEB-COF, (b) TFB-COF, and (c) TPB-COF in the region of C 1s, and high-resolution N element XPS spectra of (d)TEB-COF, (e) TFB-COF, and (f) TPB-COF.



Figure S4.4. TGA of TPB-COF, TEB-COF, and TFB-COF under nitrogen atmosphere.



Figure S4.5. SEM images of (a) TEB-COF, (b) TFB-COF, and (c) TPB-COF.



Figure S4.6. PXRD patterns of the (a) TEB-COF, (b) TFB-COF, and (c) TPB-COF after treatment in different solvents.



Figure S4.7. Zeta potential of TPB-COF, TEB-COF, and TFB-COF as a function of pH.



Figure S4.9. Mott-Schottky plots of TEB-COF.



Figure S4.11. The HOMO-LUMO calculation of TFPB, DAFB, and TAEB linker.



Figure S4.12. The monitored UV-vis spectroscopy of the Cr (VI)-DPC complex of the adsorption of Cr (VI) on (a) TEB-COF in neutral condition, (b) TEB-COF in pH=3, (c) TFB-COF, and (d) TPB-COF under dark and Ar conditions.



Figure S4.13. UV-vis spectra of Cr (VI)-DPC complex for determination of the

photocatalytic reduction Cr (VI) to Cr (III) using (a) TEB-COF, (b) TFB-COF, and (c) TPB-COF as photocatalyst in milli-Q water. (d) The color change of Cr (VI)-DPC complex for determination of the photocatalytic reduction Cr (VI) to Cr (III) using TEB-COF, TFB-COF, and TPB-COF.



Figure S4.14. Pseudo-first-order kinetic constant for reduction of Cr (VI) with different photocatalysts.

The impact of Cr (VI) concentration (30 ml of 10 mg/L, 20 mg/L, and 30 mg/L with 10 mg of catalyst) on the photocatalytic reduction of Cr (VI) was investigated (**Figure S4.14a**). As shown in **Figure S4.14a**, with an increase in the concentration of Cr (VI) from 10 mg/L to 30 mg/L, the TEB-COF exhibited a decreased photocatalytic reduction rate of Cr (VI). This decline may be attributed to the limited active sites on TEB-COF. In addition, a high concentration of Cr (VI) interferes with the light absorption of the catalyst, which could be another reason for the decrease in the photocatalytic reduction rate. **Figure S4.14b** illustrates the influence of varying photocatalyst dosages (5, 10, 15 mg in 30mL of 10 mg/L Cr (VI)) on the photocatalytic reaction rate. During the first twenty minutes of irradiation, notable disparities in their apparent reaction rates were observed. At a dosage of 15 mg, the apparent rate constant of TEB-

COF is 0.106 min⁻¹, which is higher than that of the dosage of 10 mg (k= 0.092 min⁻¹) and the dosage of 5 mg (k= 0.061 min⁻¹). This is because a higher amount of catalyst renders more surface area and available active sites.

It is worth noting that even using the smallest dosage of 5 mg, more than 95% of Cr (VI) can be removed in one hour. This is further evidence of the excellent photocatalytic performance of TEB-COF.



Figure S4.15. The effects of the (a) initial concentration of Cr (VI) solution, (b) dosage of photocatalyst of TEB-COF in photocatalytic Cr (VI) reduction.



Figure S4.16. PXRD patterns of TEB-COF before and after catalysis.



Figure S4.17. FTIR of TEB-COF before and after catalysis.



Figure S4.18. BET of TEB-COF before and after catalysis.



Figure S4.19. The absorbance spectra of H_2O_2 in the presence of Ti reagent solution.



Figure S4.20. Proposed mechanism for photocatalytic Cr (VI) reduction in water.



Figure S4.21. GC chromatogram of TEB-COF. A 40 ml vial was filled with a 3 mM AgNO₃ aqueous solution (10 mL) and 10 mg COF. Oxygen is removed by bubbling N₂ in dark condition. (a) Before starting the reaction, the gas headspace of the vial was measured by GC to ensure that no oxygen was present in the vial. (b) After 6 hours irradiation, oxygen was detected, indicating the formation of oxygen on VB.


Figure S4.22. Time dependent degradation spectra of RhB solution of TEB-COF.



Figure S4.23. scheme of photocatalysis reactor set-up.

Table S4.1.: Comparison with other representative porous materials in photocatalytic

Cr (VI) reduction.

Matarial	Catalyst	Cr (VI)	Irradiation	Time	Removal	Refere
Wateria	dosage	conc.	conditions	(min)	rate (%)	nce
			300 W Xe-			
UiO-66(NH2)	0.5 g/L	10 mg L ⁻¹	lamp	80	100	10
			(λ > 420 nm)	80		
			300 W Xe-			
	0.5 g/L	8 mg L ⁻¹	lamp	45	100	11
00D(FE)			(λ > 420 nm)	45		
TPB-BT-COF	1 g/l	10 mg ⁻¹	Xenon lamp	75	98	12
TAPT-BT-COF	- 8/ -	10 118 1	(λ> 400 nm)	105	98	
	0.25 ~/		125±1		05	13
COF-PDZ	0.25 g/L	5 mg L ⁻¹	mW/cm ²	20	95	10
			300 W Xe-			
TzDa-COF	0.2 g/L	10 mg L ⁻¹	lamp	100	40.5	14
			(λ > 420 nm)	100		

Au@C2	0.33 g/L	9 mg L ⁻¹	500 W Xe- lamp (λ > 420 nm)	120	98.2	15
PYE-COF	1 g/L	10 mg L ⁻¹	300 W Xe- lamp (λ > 400 nm)	60	100	16
HDU-26	0.16 g/L	10 mg L ⁻¹	300 W Xe- lamp (λ > 420 nm)	60	99.5	17
JOU-7	0.33 g/L	9 mg L ⁻¹	300 W Xe- lamp (λ > 400 nm)	100	95.2	18
Py - SO1	0.1 g/L	10 mg L ⁻¹	300 W Xe- lamp (λ > 420 nm)	90	93	19
TACTF	1 g/L	50 mg L ⁻¹	300 W Xe- lamp (λ > 420 nm)	120	75	20
TEB-COF	0.33 g/L	10 mg L ⁻¹	300 W Xe- lamp (λ > 420 nm)	40	99	This work

Table S4.2.: Parameters of first-order kinetic model for Cr (VI) photocatalytic reduction by synthesized COFs.

	<i>k</i> (min ⁻¹)	R ²
TEB-COF	0.092	0.971
TFB-COF	0.022	0.996
TPB-COF	0.017	0.978
Cr (VI) concentration: 10 mg/L	0.092	0.971
Cr (VI) concentration: 20 mg/L	0.045	0.986
Cr (VI) concentration: 30 mg/L	0.026	0.954
5 mg dosage of TEB-COF	0.061	0.983
10 mg dosage of TEB-COF	0.092	0.971
15 mg dosage of TEB-COF	0.106	0.965

 Table S4.3.: Comparison with other representative porous materials in photocatalytic

degradation of RhB.

Material	Catalyst dosage	RhB conc.	Time	Removal	Reference
			(min)	rate (%)	

g–C ₁₈ N ₃ –COF	0.04 g/L	300 mg L ⁻¹	540	100	21
COF-HFeTBD	0.2 g/L	20 mg L ⁻¹	180	87	22
Au@COF	0.1 g/L	10 mg L ⁻¹	40	100	23
ZnPor- COF	0.33 g/L	20 mg L ⁻¹	100	94.3	24
BiOBr/ZIF-67	1 g/L	20 mg L ⁻¹	120	95.2	25
COFs-Ph@CdS	0.4 g/L	20 mg L ⁻¹	100	82.5	26
MoS ₂ /COF (20)	0.5 g/L	20 mg L ⁻¹	60	85.9	27
NH ₂ -MIL88B/TpPa- 1-COF (40)	0.5 g/L	10 mg L ⁻¹	40	100	28
HDU-105	0.08 g/L	10 mg L ⁻¹	90	99.8	29
TEB-COF	0.33 g/L	10 mg L ⁻¹	30	99.9	This work

Table S4.4.: Unit cell parameters and atom positions of the TPB-COF crystal structure

fitted by Material Studio.

TPB-COF				
	Н	exagonal <i>, P-6</i> (17	4)	
	a = b =	17.9162 Å, <i>c</i> = 3.	5222 Å	
	α	$\theta = \theta = 90^\circ, \gamma = 120^\circ$)°	
Atom label	Atom type	x	У	z
C1	С	1.58089	0.29713	-0.48269
C2	С	1.61651	0.24655	-0.48269
С3	С	1.56384	0.15542	-0.48269
C4	С	1.47735	0.11815	-0.48269
C5	С	1.42762	0.03217	-0.48268
C6	С	1.46349	-0.01790	-0.48269
С7	С	1.54983	0.01882	-0.48270
C8	С	1.59952	0.10478	-0.48270
С9	С	1.40931	-0.10801	-0.48269
C10	С	1.43838	-0.16009	-0.48270
C11	С	1.38343	-0.24988	-0.48270

N12	Ν	1.29996	-0.28345	-0.48270
H13	Н	1.51079	0.26817	-0.48269
H14	Н	1.44708	0.15812	-0.48268
H15	Н	1.35745	0.00258	-0.48268
H16	Н	1.57968	-0.02152	-0.48271
H17	Н	1.66969	0.13438	-0.48271
H18	Н	1.33934	-0.13591	-0.48269
H19	Н	1.50790	-0.13519	-0.48270

 Table S4.5.: Unit cell parameters and atom positions of the TFB-COF crystal structure

fitted by Material Studio.

TFB-COF				
		Trigonal, P3 (143)		
	a = b =	= 25.5131 Å <i>, c</i> = 3.5	5557 Å	
	c	$\alpha = \beta = 90^\circ, \gamma = 120$	o	
Atom label	Atom type	x	У	z
C1	С	0.64151	0.37081	0.78879
C2	С	0.60274	0.30769	0.78397
C3	С	0.53890	0.28194	0.75524
C4	С	0.51306	0.31468	0.59605
C5	С	0.45082	0.28782	0.54231
C6	С	0.41206	0.22729	0.64301
C7	С	0.43691	0.19495	0.81192
C8	С	0.49895	0.22185	0.87110
С9	С	0.34673	0.19693	0.54910
C10	С	0.31551	0.22930	0.54559
C11	С	0.25501	0.20117	0.43499
C12	С	0.22425	0.14010	0.32744
C13	С	0.25503	0.10727	0.34103
C14	С	0.31551	0.13548	0.44780

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C15	С	0.15979	0.11223	0.22053
C16	С	0.12685	0.05600	0.08463
C17	С	0.06128	0.02752	0.03994
N18	N	0.03362	0.06113	0.04062
H19	Н	0.62194	0.39954	0.78850
H20	Н	0.54031	0.35966	0.48238
H21	Н	0.43369	0.31365	0.39961
H22	Н	0.40840	0.14878	0.90468
H23	Н	0.51448	0.19528	1.02029
H24	Н	0.33753	0.27624	0.63168
H25	Н	0.23210	0.22725	0.43450
H26	Н	0.23338	0.05983	0.27122
H27	Н	0.33795	0.10904	0.44269
H28	Н	0.13788	0.13860	0.27199
H29	Н	0.14655	0.02797	0.02840

Table S4.6.: Unit cell parameters and atom positions of the **TEB-COF** crystal structurefitted by Material Studio.

TEB-BT-COF				
	Н	exagonal <i>, P-6</i> (17	4)	
	a = b =	22.0820 Å, <i>c</i> = 3.	6399 Å	
	α	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	D°	
Atom label	bel Atom type x y z			
C1	С	1.63625	0.37257	0.45335
C2	С	1.59703	0.30292	0.45337
С3	С	1.52559	0.27172	0.45329
C4	С	1.46555	0.24548	0.45336
C5	С	1.39410	0.21424	0.45355
C6	С	1.36366	0.25344	0.45355

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С7	С	1.29402	0.22301	0.45368
C8	С	1.25451	0.15336	0.45380
С9	С	1.28531	0.11419	0.45381
C10	С	1.35494	0.14462	0.45368
C11	С	1.18153	0.12315	0.45388
C12	С	1.14032	0.05738	0.45394
C13	С	1.06758	0.02804	0.45399
N14	N	1.03937	0.06742	0.45399
H15	Н	1.61027	0.40605	0.45332
H16	Н	1.39713	0.31290	0.45343
H17	Н	1.26805	0.25649	0.45369
H18	Н	1.25202	0.05472	0.45392
H19	Н	1.38092	0.11114	0.45368
H20	Н	1.15697	0.15791	0.45390
H21	Н	1.16235	0.02042	0.45395

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Chapter 5.

Conclusion and Perspectives



5.1 Conclusion

COFs represent a major milestone in materials science, enabling the design and synthesis of macromolecules with precisely tailored and higher order structures. This breakthrough has established a new molecular platform for the development of multifunctional materials, with photocatalysis emerging as a prominent and dynamic research frontier. This dissertation explores the broad applications of COFs in photocatalysis by regulating their structure and functional design, emphasizing the influence of their structure on their physicochemical properties and functions. In this dissertation, with the aim of revealing a complete picture of photocatalysis with COFs, I first introduce the fundamental principles of photocatalysis and provide a comprehensive overview of the research progress in COF-based photocatalysts. These materials have shown great promise in applications such as photocatalytic hydrogen peroxide production, organic transformations, and pollutant degradation. In addition, potential strategies to enhance the photocatalytic performance of COFs are highlighted, including donor-acceptor structure design, molecular structure modulation, and incorporation of functional groups. Based on these strategies, I have enhanced the light-harvesting capability and physicochemical properties of COFs by designing structures with increased conjugation, constructing donor-acceptor systems, and introducing coplanar ligands. These COFs were then applied separately in photocatalytic hydrogen peroxide production, organic transformations, and pollutant degradation.

In the first work, I designed two isostructural COFs by combining the beneficial features of the BT moiety with TAPT and TAPB, resulting in the formation of TAPT-BT-COF and TAPB-BT-COF. The π -conjugated units in the skeletal structures of COFs play a crucial role in light harvesting. In TAPT-BT-COF, the presence of highly conjugated triazine rings significantly enhances the efficiency of charge separation and transfer, thus leading to an augmented H₂O₂ formation rate. In the second work, after confirming the crucial role of conjugation in COF materials, we selected the pyrene

moiety (py), which also possesses conjugated properties, and synthesized three pyrene-based COFs: Py-Por-COF, Py-Py-COF, and Py-Etta-COF for photocatalytic amine oxidative coupling. Among the three COFs, the one containing porphyrin ligands can construct a D-A type COF (Py-Por-COF) with Pyrene ligands. In contrast, the other two are D-D type COFs (Py-Py-COF and Py-Etta-COF). The construction of a donor-acceptor structure in Py-Por-COF, which is highly favorable for electron transport, enables it to exhibit excellent catalytic performance in photocatalytic amine oxidation. Under blue light irradiation for 1 hour, Py-Por-COF achieved a high yield of 99% for Nbenzylidenebenzylamine, corresponding to a remarkable photocatalytic activity of 20 mmol g⁻¹ h⁻¹. This performance represents one of the highest values reported to date. Although the imine-linked COFs have shown excellent photocatalytic performance in the above work, their chemical stability under strong acidic and basic conditions remains a concern. In the third work, to address this issue, we turned our attention to more stable vinylene-linked COFs with C=C linkages, which offer both excellent π delocalization and enhanced chemical stability. We have recognized that constructing D-A COFs can strengthen in-plane charge transfer from the donor to the acceptor. Additionally, charge transport along the z-axis can be facilitated through ordered π - π stacking. Therefore, we aim to minimize planar distortion and construct co-planar structure, ensuring efficient charge transport in all directions. For this purpose, we designed three highly crystalline sp² COFs , designated as TPB-COF, TEB-COF, and TFB-COF by linking 2,4,6-trimethyl-1,3,5-triazine (TMT) with 5'-(4-Formylphenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarbaldehyde (TFPB), 4,4',4"-(Benzene-1,3,5triyltris(ethyne-2,1-diyl))-tribenzaldehyde [1,1:4,1:3,1:4,1-(TAEB), and Quinquephenyl]-4,4-dicarboxaldehyde, 5-(4-formyl[1,1-biphenyl]-4-yl)-(DAFB), respectively. These COFs were tested for the photocatalytic reduction of Cr (VI) and simultaneous one pot degradation of dyes under the irradiation of visible light. Among the three isostructural COFs, the very coplanar TEB-COF, based on triazine (acceptor) and acetylene (donor) linkers shows the best performance, due to the fact that the acetylene groups is a strong donor and to the fact that this COFs showed the highest

planarity in the z-axis (dihedral angle only 2°), allowing good charge separation and good charge transfer mobility in all 3 dimensions.

Material	Structural feature	Theoretical Effect	Practical Performance
	Conjugated	Enhanced	
(Chaptor 2)	triazino ringo	efficiency of	Augmented H ₂ O ₂ formation
	thazine migs	electron transport	
Py-Por-COF	Donor-acceptor	Favorable for	More efficient amine
(Chapter 3)	structure	charge separation	coupling
TERCOE		Facilitated charge	Moro officient Cr (\/l)
(Chantar 2)	High coplanarity	transport between	reduction rate
		the layers	

Table 5.1. Structure-performance relationship obtained from this thesis.

5.2 Perspectives

Despite the remarkable progress achieved in the development of COF-based photocatalysts, these achievements represent only the initial exploration of an exceptionally promising and evolving field. The structural and functional versatility of COFs opens up immense possibilities for designing advanced photocatalytic systems; however, many challenges remain in realizing their full potential for practical applications. Future research must not only address these challenges but also expand the scope of COF development by exploring new, stable, and scalable frameworks, such as single-crystal COFs or three-dimensional (3D) COFs or other simple and green synthesized COF architectures. In addition, a deeper understanding of the structureperformance relationship and innovative design strategies will also be critical to unlocking new capabilities in COF-based photocatalysis.

1. Overcoming the Challenge of High Crystallinity or Single-Crystal COF Synthesis

Currently, the crystallinity of most COFs is far from ideal, which limits their performance and application potential. Most COFs reported to date exist as polycrystalline powders, limiting the resolution of structural characterization techniques such as single-crystal X-ray diffraction (SCXRD). The lack of satisfactory crystallinity makes it difficult to fully understand their atomic-level configurations and restricts the ability to optimize their structure for targeted photocatalytic functions. Additionally, low crystallinity can lead to increased defect density, which may negatively affect charge transport, stability, and overall catalytic efficiency. Without clear insight into the detailed spatial orientation and intermolecular interactions within COF frameworks, establishing accurate structure-performance relationships becomes difficult. Therefore, improving the crystallinity of COFs is a key challenge that must be addressed for enhancing their performance.

To address this limitation, new synthetic approaches aimed at producing highquality single crystals of COFs should be developed. Strategies such as developing new solvents to assist crystallization, modulated synthesis, and interfacial polymerization hold promises for achieving a better crystallinity. In addition, the use of dynamic covalent chemistry to construct more reversible bond-forming reactions could facilitate error correction during crystallization, leading to higher-quality single-crystal COFs. Single-crystal synthesis will also play a pivotal role in the development of 3D COFs, which often face even greater challenges in achieving long-range order due to their complex topologies and interpenetrated networks. The successful realization of single-crystal 3D COFs would enable direct observation of their three-dimensional charge transport pathways and provide unprecedented opportunities to design isotropic photocatalytic systems with enhanced efficiency.

2. Developing Scalable and Sustainable Synthesis Methods

The scalability of COF synthesis remains a major obstacle to their industrial application. Traditional synthetic methods often require high temperatures, long reaction times, and specific organic solvents—factors that increase production costs

and environmental impact. Additionally, variations in synthesis conditions can lead to structural inconsistencies, such as uneven pore distribution and increased defect density, which adversely affect catalytic performance.

Our research group has recently developed an efficient and convenient method for synthesizing a wide range of imine-linked covalent organic frameworks under mild and environmentally friendly conditions. This approach relies solely on simple aqueous solutions of alkyl alcohols and acetic acid, eliminating the need for harsh organic solvents typically used in conventional solvothermal synthesis. Remarkably, the COFs produced by this method have a crystallinity comparable to or even higher than those obtained by conventional techniques. In addition, the scalability of the process is a significant advantage, allowing more than ten grams of COF material to be produced in a single batch without compromising structural integrity or performance. This breakthrough simplifies the large-scale production of COFs, paving the way for their broader exploration and accelerating their transition from laboratory research to industrial applications. However, it is important to note that this method currently faces limitations when applied to more complex COF architectures or fully conjugated sp² carbon frameworks, highlighting the need for further refinement and adaptation to expand its applicability.

3. Balancing Light Absorption, Redox Potential, and Charge Separation

Achieving an optimal balance between light absorption, redox potential, and charge separation remains a fundamental challenge in COF-based photocatalysis. Efficient solar-to-chemical energy conversion requires broad light absorption to maximize the utilization of the solar spectrum. However, materials with narrow bandgaps often exhibit reduced redox potential and increased charge carrier recombination, both of which are detrimental to photocatalytic efficiency.

To address these challenges, future research should focus on the creation of innovative heterostructures, building on the design strategies discussed in this dissertation, such as enhancing π -conjugation, introducing heteroatom doping to modify the COF microenvironment, constructing donor-acceptor architectures to

facilitate spatial charge separation, and incorporating highly planar ligands to enhance charge transport. Combining COFs with other semiconductor materials (such as MOFs, perovskites, and transition metal oxides) to form heterostructures offers a promising avenue for performance enhancement. In particular, the development of Z-scheme COF heterojunctions, inspired by natural photosynthesis, holds great potential to significantly enhance carrier dynamics by promoting the efficient migration of electrons and holes between different catalytic sites. One of its primary strengths is its enhanced redox capability, as it combines the strong oxidative and reductive potentials of two semiconductors, making it highly effective for complex redox reactions. Moreover, the Z-scheme mechanism promotes efficient charge carrier separation by allowing the recombination of lower-energy electrons and holes while retaining highenergy electrons and holes, which extends the carrier lifetime and boosts photocatalytic activity. Its structural diversity and tunability further allow precise performance optimization through band position adjustment, interface engineering, and surface modification. This approach can be a good solution to the long-standing challenge of balancing strong light absorption and narrow redox potential. By achieving this balance, Z-type COF heterojunctions open up exciting possibilities for designing highly efficient and stable photocatalytic systems.

4. Elucidating Reaction Mechanisms and Expanding Theoretical Understanding

Another critical challenge facing COF-based photocatalysis is the incomplete understanding of its reaction mechanisms. Due to the complexity and heterogeneity of photocatalytic processes in COFs, the detailed pathways of these reactions, particularly in complex organic transformations, are still not well understood. Investigating mass transfer, electron transport, and charge accumulation in these systems is essential for elucidating the underlying mechanisms. By studying the dynamics of these processes, we can gain deeper insights into photochemical transformations across different spatial and temporal scales. Furthermore, advanced characterization techniques such as transient absorption spectroscopy, ultrafast transient spectroscopy, and electron paramagnetic resonance spectroscopy are needed to further explore the photophysical and photochemical properties of COFs.

Future efforts should also focus on developing more advanced theoretical models and computational simulations to predict the electronic structures, band alignments, and exciton dynamics of COFs. Techniques such as density functional theory (DFT) calculations, time-dependent DFT (TD-DFT), and non-adiabatic molecular dynamics can provide deeper atomic-level insights into charge separation and recombination processes.

5. Enhancing Stability for Long-Term Photocatalytic Operation

The long-term stability of COF materials remains a significant concern, particularly under harsh photocatalytic conditions involving strong oxidants, high-energy irradiation, and extended operational times. Although sp² C=C-linked COFs offer enhanced chemical robustness compared to imine and boronate-ester-linked counterparts, their poor reversibility during synthesis often results in low crystallinity, compromising performance.

Future strategies for enhancing COF stability should focus on designing more robust linkages while maintaining high crystallinity. Additionally, the incorporation of protective hydrophobic layers or encapsulation of active sites within stable polymeric matrices could mitigate degradation caused by solvent interactions or photoinduced structural weakening.

6. Expanding the Scope of COF Architectures and Applications

Beyond the existing two-dimensional (2D) frameworks, the exploration of 3D COFs, flexible COFs, and hierarchical hybrid structures represents a frontier in COF research. 3D COFs, with their isotropic pore networks and enhanced mechanical stability, offer unique advantages for applications requiring high diffusion rates and uniform catalytic activity. Their potential for efficient charge transport in all three dimensions makes them ideal candidates for next-generation photocatalysts. Additionally, I would like to explore the potential of COFs in many untapped and emerging photocatalytic applications. One promising area is photocatalytic nitrogen fixation, where COFs can drive the reduction of N₂ to ammonia under mild conditions, taking advantages of their highly tunable active sites and exceptional light-harvesting capabilities. Another exciting direction is the photocatalytic reduction of CO₂ to multi-carbon products, while most current efforts have focused on converting CO₂ into simple molecules like CO or methanol, the ability of COFs to precisely regulate their electronic structures and catalytic environments makes them ideal candidates for the production of more complex hydrocarbons, such as ethylene or ethanol. Furthermore, the application of COFs in fine chemical synthesis as photocatalysts remains in its infancy and requires more extensive exploration to fully harness their potential in driving selective and efficient organic transformations.

In summary, while significant progress has been made in COF-based photocatalysis, the field remains in its early stages with vast opportunities for growth. By addressing current challenges and expanding the scope of COF architectures and applications, future research can unlock the full potential of COFs as next-generation photocatalysts for sustainable energy conversion and environmental remediation. In my future research, I will focus on the construction of Z-scheme heterojunctions based on COF materials, the exploration of 3D COFs with novel topological structures, and the development of COF-based materials for emerging applications.

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