

Spotlight

Catalytic Activities of Fluorescent Covalent Organic Frameworks

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Zahra Alishahi was born in 1999 in Qom, Iran. She received her B.Sc. in applied chemistry (2021) from Qom University and M.Sc. in Organic Chemistry (2023) from Bu-Ali Sina University under the supervision of Professor Mohammad Ali Zolfigol. She is currently working towards her Ph.D. under the supervision of Professor Mohammad Ali Zolfigol and Professor Saeid Azizian at Bu-Ali Sina University. Her research interest is the design, synthesis and catalytic applications of magnetic nanoparticles and porous organic polymers in organic transformations.

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1. Introduction

The seminal work conducted by Yaghi and his colleagues [1] in 2005 led to the development of a novel class of crystalline porous organic materials, termed covalent organic frameworks (COFs). These frameworks are composed of organic building blocks connected by strong covalent bonds to form two (2D) and/or three-dimensional (3D) networks [2-5].

These 2D or 3D networks give rise to a wide variety of morphological structures, including cavities, nanosheets, films, pores, spheres, membranes, tubes, shuttles, foams, belts, and fibers [6-7]. This discovery opened new horizons, as the flexibility of covalent bonds allowed chemists to turn their conceptual molecular architecture into reality. The most common reactions lead to the formation of covalent linkages such as B-O, B-N, C-N, C=C, C≡C, and C-O [8]. Nevertheless, most classic COFs suffer from low stability in harsh conditions, unconjugated chemical structures, and limited potential

applications. For this purpose, a new strategy including multicomponent synthesis of COFs to achieve highly stable and conjugated linkages such as quinoline, thiazole, imide, dioxane, carbamate, oxadiazole, and benzofuran-linked COFs has been reported [9-10]. These crystalline materials exhibit remarkable structural diversity, and their properties, such as photophysical behavior, adsorption capacity, and chemical stability, depend mainly on their constituent units [11-12].

Thanks to their customizable skeletons and cavities, designable monomer structures, high specific surface area, excellent thermal stability, low density, and ease of functionalization, COFs have diverse applications in various fields, including catalysis, photocatalysis, gas adsorption and separation, drug delivery, fuel cells, pollutant removal, and fluorescence sensing [13-22]. In recent years, COFs have proven highly effective for applications in the catalytic field.

To date, a wide range of catalytic applications has been reported for the aforementioned COFs, including

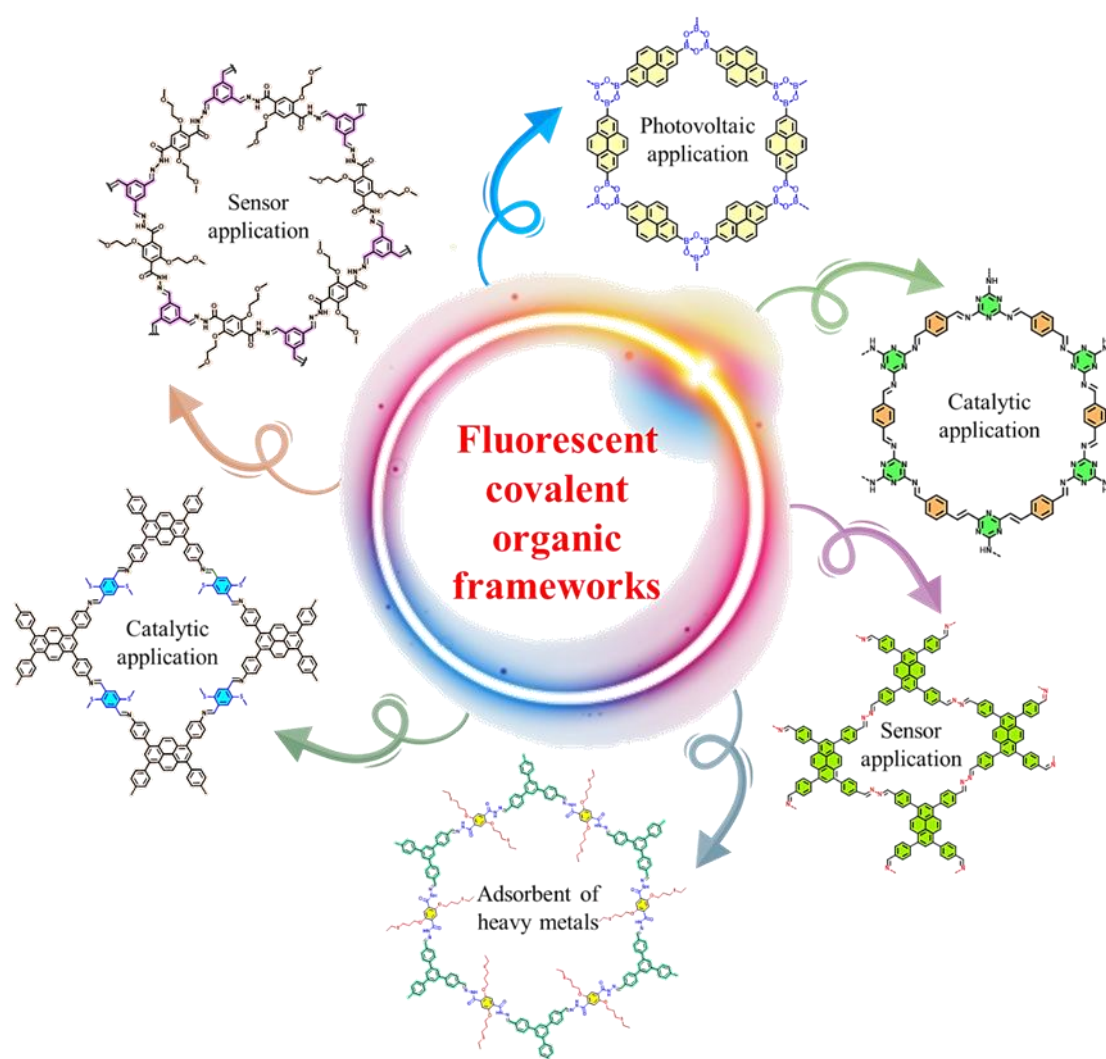
photocatalytic reactions, coupling reactions, electrocatalytic processes, degradation processes, oxidation/reduction reactions, asymmetric catalysis, and multicomponent reactions [23-24]. Another subset of covalent organic frameworks is fluorescent COFs, which have gained significant attention owing to the rational integration of well-designed organic building blocks, endowing them with highly promising properties for advanced applications.

Recently, fluorescent COFs have exhibited considerable promise, especially in fluorescence sensors, because they have shown great potential for sensor applications, since the large number of active sites within the framework can effectively transmit and amplify the sensing signals [25-29]. The porous structure of COFs creates a high specific surface area and enables impressive

interaction of the analyte with the recognition sites, which enhances the sensitivity and selectivity of the sensors.

Due to the fantastic benefits of fluorescent COFs, these materials were broadly applied in catalytic transformations, detecting solvents, pollutants, metal ions, and biomolecules [30-35].

The unrivaled combination of porosity, structural stability, and optical responsiveness has made fluorescent COFs versatile and applicable materials in the fields of chemistry and materials. Some fluorescent COFs with their application can be seen in Scheme 1. Herein, the catalytic applications of fluorescent COFs in organic transformations were investigated, and this study can open new avenues to discover the applications of photoactive COFs.

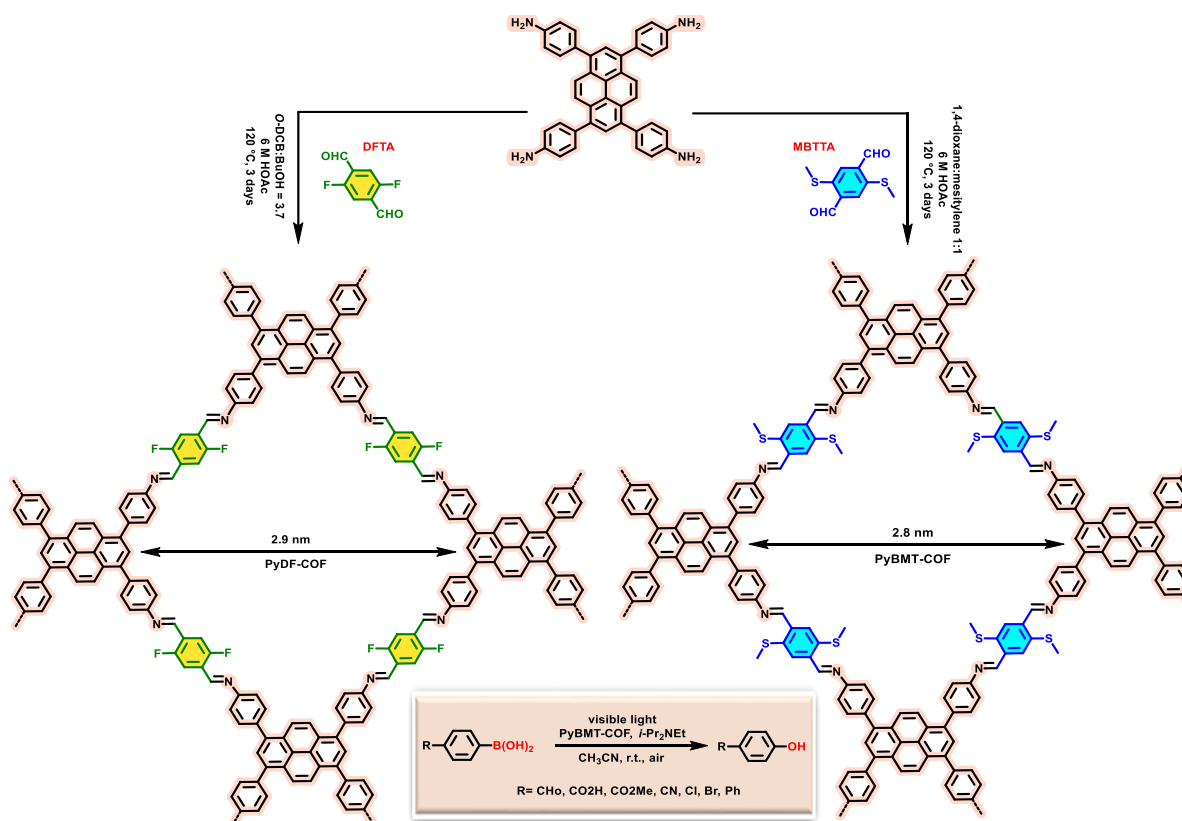


Scheme 1. A number of fluorescent COFs

Abstract

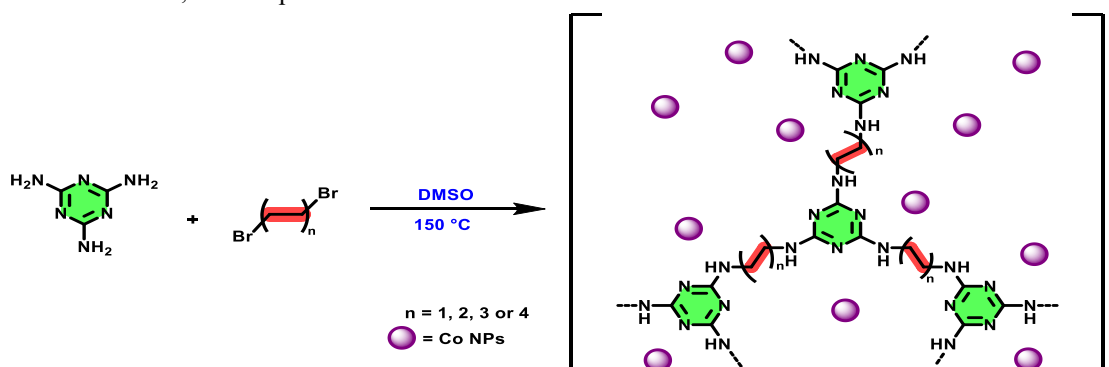
(A) In 2023, Baiwei Ma's research group reported the synthesis of two novel pyrene-based conjugated COFs, namely PyDF-COF and PyBMT-COF. These materials efficiently catalyze the hydroxylation of arylboronic acids with high catalytic activity. The PyBMT-COF framework exhibits superior catalytic performance in the hydroxylation reaction compared with the PyDF-COF framework. This enhancement is attributed to the

electron-donating thiomethyl groups in PyBMT-COF, which enhance the electron cloud distribution more effectively than the electron-withdrawing fluorine substituents in PyDF-COF. As a result, PyBMT-COF demonstrates more efficient hole–electron (h^+/e^-) separation, stronger visible-light absorption, a narrower bandgap, a higher photocurrent response, a longer fluorescence lifetime, and a lower electrochemical impedance [36].



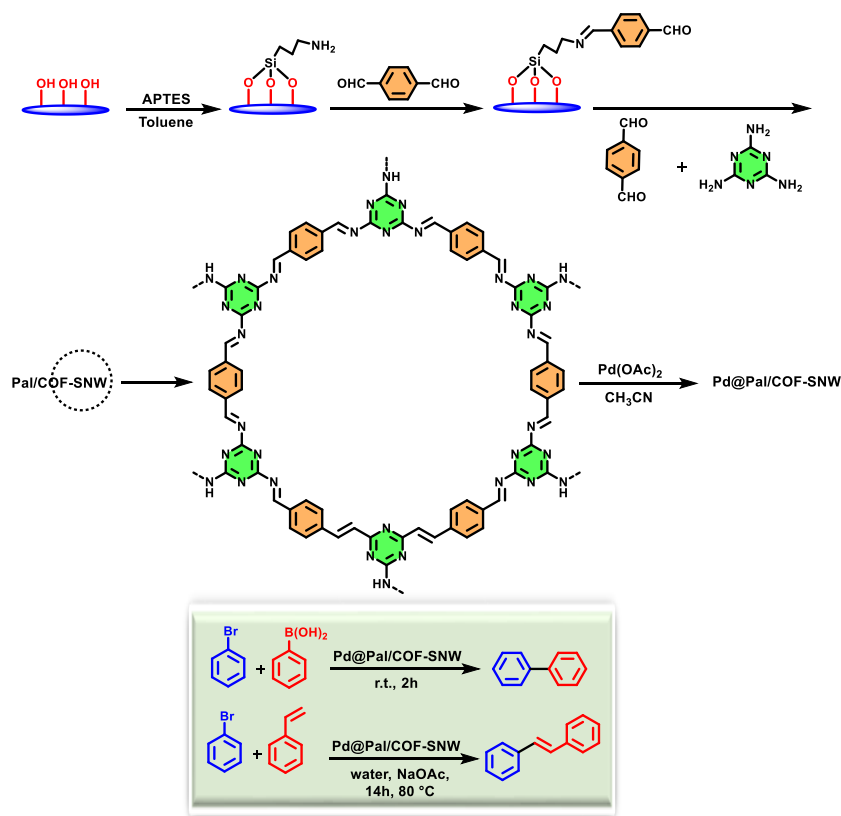
(B) In 2016, a series of COFs based on melamine and dibromoalkanes $[Br(CH_2)_nBr]$ with different chain lengths ($n = 2, 4, 6,$ and 8) was synthesized. These materials (COF-1,2, COF-1,4, COF-1,6, and COF-1,8) were constructed with dimethyl sulfoxide as solvent under reflux conditions. The color of COFs depends on the number of carbon atoms (n), appearing as light yellow, deep yellow, brown, and dark brown, respectively. The COF-1,2 and COF-1,4 samples were further

functionalized with cobalt and employed as catalysts for hydrogen generation via $NaBH_4$ hydrolysis. The reported results indicated that COF-1,2–Co exhibited superior catalytic performance and higher electrical conductivity. In addition, the mentioned COFs displayed fluorescence properties, and their emission wavelengths decreased in the presence of cobalt nanoparticles and with increasing alkyl chain length (n) [37].



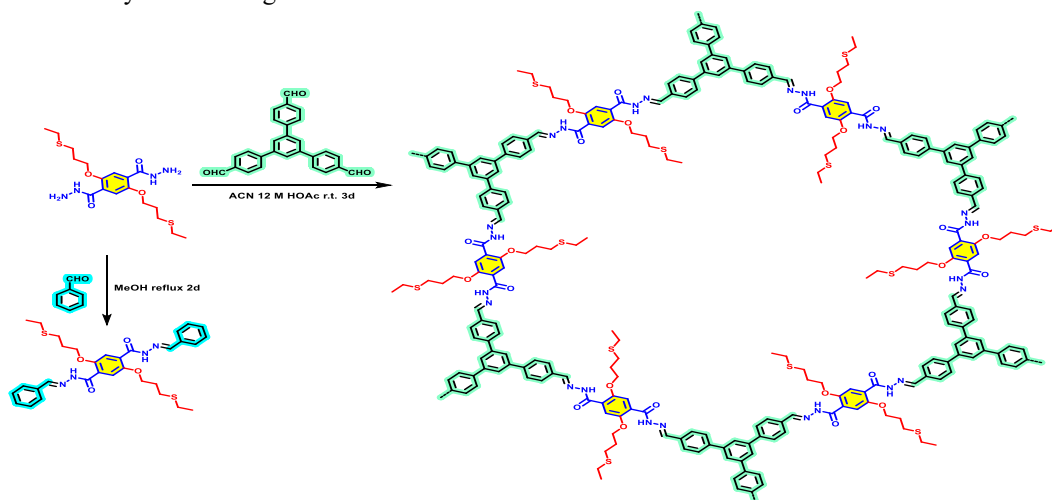
(C) In 2025, a fluorescent material, Pal/COF-SNW, was synthesized by covalently attaching fluorescent covalent organic frameworks (COF-SNW) to the surface of palygorskite. The resulting compound exhibited high fluorescence intensity in THF solution and effectively detected palladium metal ions (Pd^{2+}). Changes in fluorescence intensity before and after the addition of Pd^{2+} enabled rapid detection of Pd^{2+} without the need for

complex methods. In addition to the detection properties, Pd-COF-SNW demonstrated high catalytic activity in Suzuki–Miyaura and Heck coupling reactions, with excellent yield of products. Furthermore, the performance of the reported catalyst was preserved over seven consecutive cycles without a significant reduction of palladium [38].



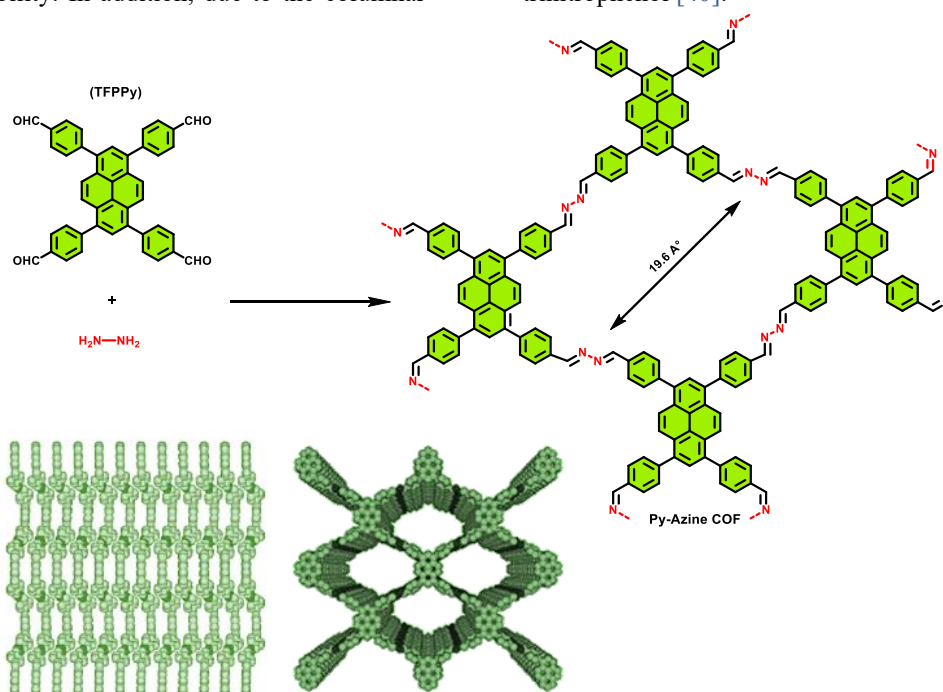
(D) In another investigation, a COF named TFPB-DHzDs was synthesized at room temperature using acetic acid as a catalyst. The reported COF has good crystallinity and strong luminescence properties. This material shows excellent selectivity in detecting Cu^{2+} ions. Experimental results showed that Cu^{2+} ions significantly quenched the fluorescence intensity of the material and could also be effectively adsorbed by it. The organic framework of

TFPB-DHzDs can detect a small amount of copper (up to 47.8 nanomolar) and adsorb copper ions from water (up to 203 mg/g of material). The fabricated COF could be reused at least six times without any noticeable loss of performance. Finally, this study showed that TFPB-DHzDs can act as both a sensitive fluorescence sensor and an efficient reusable adsorbent for heavy metals [39].



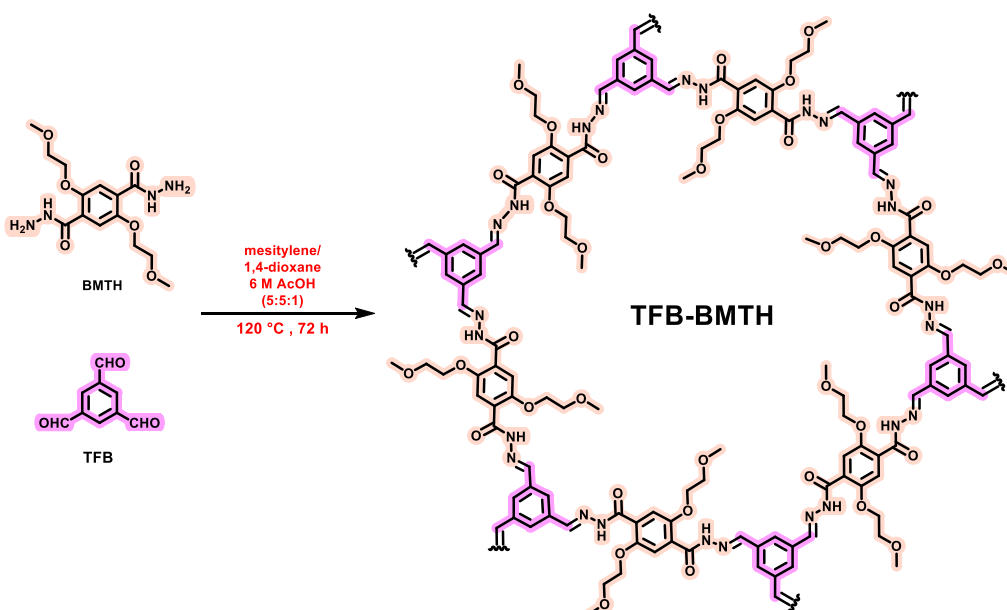
(E) A highly crystalline 2D COF composed of pyrene units and diazabutadiene linkers, termed Py-Azine COF, has been fabricated. The reported framework has a layered structure and was created from ordered pyrene columns and one-dimensional microporous channels. Py-Azine COF has remarkable porosity, high specific surface area, and chemical stability. In addition, due to the columnar

arrangement of pyrene units, this structure exhibits intense luminescence, and the azine groups also provide active sites for hydrogen bonding. Given the characteristics, this framework has a very high sensitivity and selectivity in chemical sensing; for example, it can be used for the selective detection of the explosive compound of 2,4,6-trinitrophenol [40].

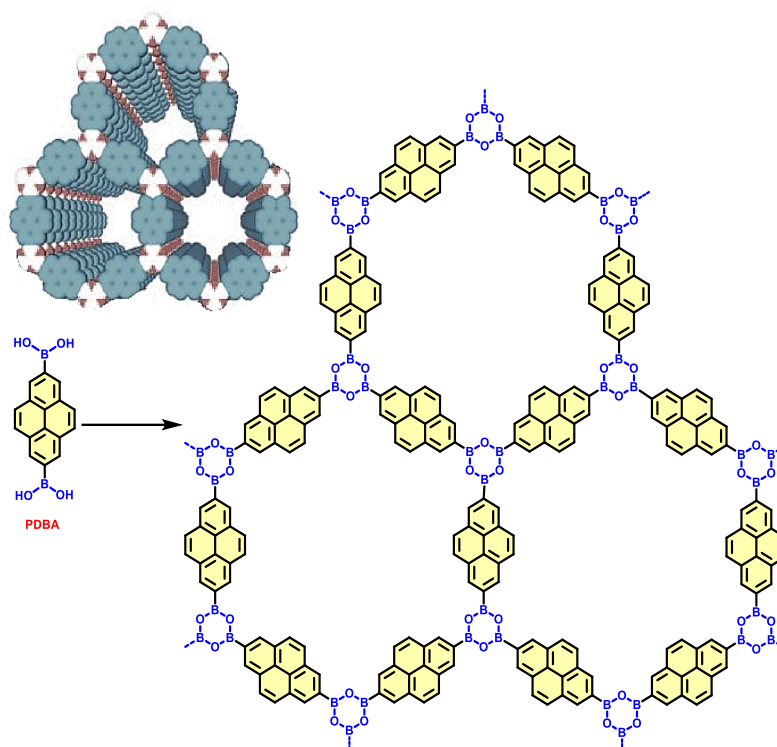


(F) In the manuscript reported by Qiaolin Wu's group, a hydrazone-based COF (TFB-BMTH) has been synthesized via the condensation of BMTH and TFB under solvothermal conditions. TFB-BMTH exhibits a high crystallinity, excellent porosity (BET specific surface area = 632 m^2/g), and good thermal and chemical stability. The resulting compound exhibited high photocatalytic activity in the oxidative hydroxylation of

aryl boronic acid. Its high photocatalytic efficiency is attributed to strong light absorption, effective generation, transport, and separation of photogenerated charges. In addition, TFB-BMTH quenches its fluorescence for the detection of Cu^{2+} ions, whose interaction with the ions was confirmed by XPS and FT-IR. This study demonstrates the development of multifunctional COFs for catalysis and sensing [41].



(G) In 2009, Donglin Jiang and coworkers reported a photoconductive COF (PPy-COF) in which its structure has been synthesized via the self-condensation of pyrene diboronic acid. The sheets composed of the building blocks are stacked in an eclipsed arrangement, which significantly improves the migration of excitons and the transport of charge carriers. The resulting material can



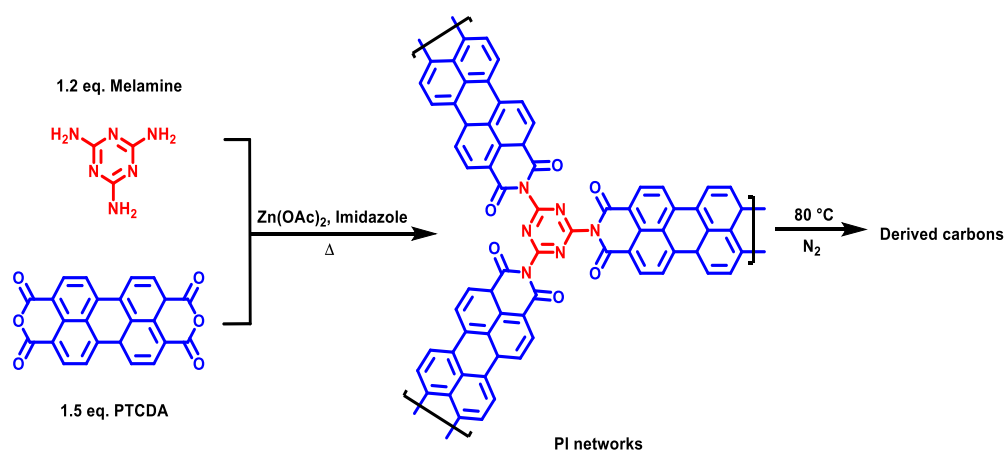
absorb visible light and rapidly generate photocurrent. PPy-COF enables repetitive on-off switching of the photocurrent without degradation and exhibits a very high on-off ratio.

Such unprecedented properties open a new approach for the application of COFs in optoelectronic and photovoltaic systems [42].

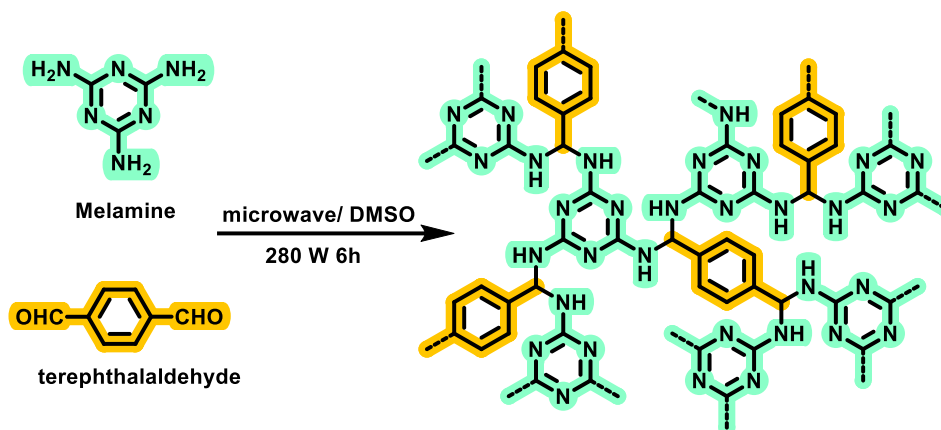
(H) Carbon dioxide (CO₂) capture from point sources can help control CO₂ emissions and reduce global warming. Currently, adsorbents with high CO₂ adsorption capacity that are reversible, highly selective, chemically and thermally stable, and low-cost are required for CO₂ separation. In 2015, Yaozu Liao's research group reported a microporous composite via the condensation of

perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and melamine for the first time.

These materials have strong fluorescence and are effective adsorbents for CO₂ with high capacity (15 wt%), and a very high selectivity factor of 240 over N₂, and their fluorescence properties can be exploited for simple sensing [43].



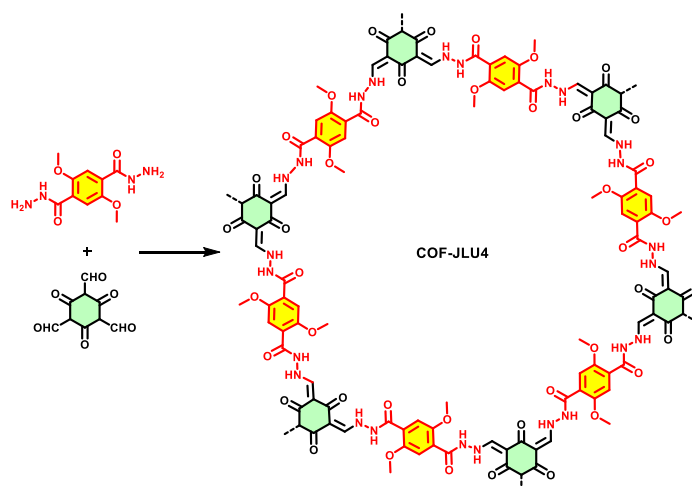
(I) In research by Ling-Guang Qiu and co-workers, a new COF called SNW-1 based on melamine was developed as a fluorescent nanomaterial. Microwave-assisted synthesis is a simple and highly efficient method compared with other conventional methods. The mentioned SNW-1 has been synthesized using a microwave-assisted method for



6 h. The resulting compound, in addition to its very high sensitivity and selectivity, reacts rapidly with nitroaromatic explosive compounds such as TNT, Tetryl, and picric acid. Due to its nanoscale size and porous structure, it exhibits a fast response, free of interference, in the presence of organic solvents [44].

(J) Yuwei Zhang's research group reported a COF with β -ketoenamine linkages, named COF-JLU4, through a condensation reaction between 2,5-dimethoxyterephthalohydrazide and triformylphloroglucinol. COF-JLU4 exhibits a high

crystallinity, suitable porosity, photoluminescent properties, and good wettability toward water. Therefore, this material is significant as the first COF-based fluorescent pH sensor in aqueous media [45].



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Competing Interests

The authors declare no competing interests.

Availability of Data and Materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflict of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



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