

Organic Covalent Interaction based Frameworks as Emerging Catalysts for Environment and Energy Applications: Current Scenario and Opportunities

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Abstract

The term "covalent organic framework" (COF) refers to a class of porous organic polymeric materials made from organic building blocks that have been covalently bonded. The preplanned and predetermined bonding of the monomer linkers allow them to demonstrate directional flexibility in two- or three-dimensional spaces. COFs are modern materials, and the discovery of new synthesis and linking techniques has made it possible to prepare them with a variety of favorable features and use them in a range of applications. Additionally, they can be post-synthetically altered or transformed into other materials of particular interest to produce compounds with enhanced chemical and physical properties. Because of its tunability in different chemical and physical states, post-synthetic modifications, high stability, functionality, high porosity and ordered geometry, COFs are regarded as one of the most promising materials for catalysis and environmental applications. This study highlights the basic advancements in establishing the stable COFs structures and various post-synthetic modification approaches. Further, the photocatalytic applications, such as organic transformations, degradation of emerging pollutants and removal of heavy metals, production of hydrogen and Conversion of carbon dioxide (CO₂) to useful products have also been presented. Finally, the future research directions and probable outcomes have also been summarized, by focusing their promises for specialists in a variety of research fields.

1. Introduction

With the rapid increase in the industrial sectors, the consumption of natural resources such as oil, gas, and coal are not only a concern for sustainability but also a serious threat to environmental pollution and global warming ^[1]. To cope with these challenging issues over the

years, different techniques have been developed to explore greener and sustainable sources of energy. In the context of these monumental efforts, solar light-directed chemical processes comprise CO₂ reduction, water splitting, and photocatalytic degradation. However, Photocatalysis is regarded to be the most fascinating area of research and has been extensively explored as a reliable and cleaner source of energy. Therefore, the development of photocatalysts with remarkable photocatalytic features is the need of society, and is highly appealing ^[2].

In 1960s, Doerffler first time reported the photocatalytic oxidation of carbon monoxide on ZnO surfaces ^[3], however the most revolutionary research work was done by Fujishima et al. in 1972 employing titanium dioxide electrode as a catalyst for water splitting ^[4]. After the gap of four years, Carey and coworkers exploited the performance of the same TiO₂ catalyst for the photocatalytic decomposition of organic contaminants ^[5]. In the past few decades, significant advancement has been developed in the area of photocatalysis by using different inorganic semiconductors *e.g.* TiO₂, ZnO, CdS, SiC and GaP for various applications ^[6]. Owing to the low cost, easy accessibility and reliability, TiO₂ is the highly eminent photocatalyst. Nonetheless, the wide band gap of 3.2 eV confined its utility to be used as the photocatalyst ^[7]. Correspondingly, sulfides and oxides of transition metals as well as Ag₃PO₄ and CdS with appropriate band gap could also be manipulated/applied as photocatalytic materials, however due to the poisonous nature of the heavy metals and their vulnerability to photo-corrosion limit their practicability ^[8]. Moreover, photocatalysts of organic based semiconductors such as graphitic carbon nitride ^[9], transition metal carbides and nitrides (MXenes)^[10] and molecular-organic frameworks ^[11] have also been exploited with magnificent photocatalytic efficiency. Despite of facile availability and high stable nature of g-C₃N₄, its limitation in structural diversity and employing extremely elevated temperature (4500 °C) during its preparation restraint their practical usage ^[12]. However, there are

some documented reports in which g-C₃N₄ has been synthesized using urea or melamine as precursors at relatively low calcination temperature, such as 550 °C ^[13]. Similarly, MOFs synthesized from transition metals and organic skeletons gained immense interest because of their greater porosity, wider surface area, and huge diversity in structural frameworks ^[14]. However, certain drawbacks are associated such as their instability and decomposition on exposure to moisture ^[11b].

In the recent years, covalent organic frameworks (COFs) unfolded as a new type of crystalline and porous organic molecular constituents that are attached with each other's through covalent bonds. These structurally diverse and robust COFs materials displayed great potential in different applications, especially serve as a promising novel photocatalytic candidate in the visible light driven hydrogen production ^[15]. In 2005, Yaghi et al. first time reported COF material ^[16], thereafter different elegant strategies have been established for structuring of COFs and explored their utilities in the fields of sensing ^[17], gas separation and adsorption ^[18], energy storage ^[19], heterogeneous catalysis ^[20] ^[21], photothermal ^[22], photo- and electrocatalysis ^[23]. Bettina Lotsch and coworkers also contributed significantly ^[24] and numerous new COFs have been synthesized by the incorporation of various structural units and linkages into their main skeleton or combined with another semiconductors such as g-C₃N₄, TiO₂ and CdS ^[25]. However, regarding the discovery and synthesis of COFs-based semiconducting materials, pioneering work is done by Jiang et al. by exploring new window for the potential application of COFs in heterogeneous photocatalytic system ^[26]. The presence of orderly arranged π -columns and greater crystallinity of COFs leading to the systematic paths which promote the transmission of charge and avoid rejoining of charge in the photoexcited states, thereby enhanced efficiency is achieved by the employment of COFs materials as photocatalyst in optoelectronic appliances. Beside this, the COFs are highly durable

due to the existence of covalent bond which imparts greater chemical and thermal stability and increases their lifetime as photocatalysts ^[27]. Additionally, the vast diversity found in the molecular frameworks of COFs which can be conveniently constructed and modified by the incorporation of versatile linkages, functionalization of building blocks and functional groups manipulation compared to other organic and inorganic semiconductors ^[28]. Based on these unique features of COFs such as ease of synthesis with tunable backbones, high crystallinity, greater porosity, enhanced stability and semiconducting properties, the applications of COFs as photocatalyst have been thoroughly investigated by different research groups ^[29]. Therefore, a review on the design, preparation and fundamental concept of COFs as photocatalysts is timely needed. This review gives a detailed insight about the enormous progress made in the diverse and emerging research field of COFs as photocatalysts. Various elegant synthetic approaches and new development for the construction different versatile linkages of COFs and their utility as photocatalysts have been discussed. Moreover, various strategies for the synthesis of COFs powders have also been included. It is subsequently ensued by the basic conceptions of COFs photocatalysis and their immense applications as photocatalyst. Eventually, concluding remarks and future prospective about the exploration of COFs as photocatalysts are bestowed, anticipating motivating the researchers for the advancement of more efficient and multifunctional versatile COFs as vibrant photocatalysts for various applications.

2. Construction of Versatile Linkages of COF Photocatalysts

Due to the immense importance of COFs as influential photocatalysts, various efficient synthetic methods have been developed for the construction of valuable organic architectures ^[30]. The versatile covalent linkages formed between numerous building blocks endow crystalline porous

COFs materials with tolerable stability and high tunability. Based on these covalent linkages, they are classified into many types such as illustrated in **Fig. 1**.

2.1. Triazine-Linked COFs

Thomas and coworkers first time documented the most stable and versatile triazine-based COFs. The presence of nitrogen atoms in these linkages make them extremely vital for different practical purposes. Over the years many synthetic strategies such as Friedel-Crafts reaction, ionothermal trimerization, P_2O_5 and superacid catalyzed synthesis, and amidine bound polycondensation have been developed ^[31]. By employing ionothermal trimerization, Song research group reported the construction of amorphous triazine-linked COF (CTF) and employed as a promising catalyst photodegradation of methylene blue ^[32]. Correspondingly, Ph-triazine oligomers were synthesized by Lotsch group and they obtained comparatively better results than carbonization process ^[33]. Different reliable photocatalysts were also synthesized by using superacid catalytic strategy which showed excellent performance in water splitting ^[25b, 34] and many useful organic reactions ^[35]. In 2015, Wu et al. documented the synthesis of various monomers and it was examined that CTF-T1 exhibited evolution of hydrogen gas under sunlight ^[34]. However, later on Su group developed the facile method for sulfur doped CTF-T1 which displayed superior photocatalytic efficacy for the generation of H_2 as compared to non-doped CTF-T1 ^[25b]. Tan et al. reported the construction of CTFs using aldehyde and amidine dihydrochloride as starting materials. This amidine polycondensation strategy conducted at low temperature resulted in the formation of Schiff base ensued by successful Michael addition reaction ^[36]. The developed method reduced the elevated temperature and successfully controlled the formation of unwanted carbonaceous materials as in the case of the ionothermal trimerization process ^[33]. Furthermore, it also avoided the usage of corrosive acid which was the key issue in superacid-catalyzed approach ^[34]. Hence, the designed

CTFs obtained by this strategy containing the versatile organic frameworks with high thermal stability. Similarly, the same research group described the elegant formation of CTFs with enhanced photocatalytic efficiency through conversion of alcohols into aldehyde monomers by the *in-situ* oxidation [37]. To explore the efficiency of organocatalysts for the reduction of CO₂ under visible light, Chakraborty et al. developed the construction of highly reusable triazine linked COF photocatalyst by using 1,3,5-tris-(4-aminophenyl) triazine with 4,4'-biphenyldicarbaldehyde as reaction substrates. The designed catalyst bore a vast surface area (1260 m² g⁻¹) and successfully employed for the reduction of CO₂ into methanol. This metal free and greener process provided facile access to the formation of methanol by applying 20 W white LED irradiation with highest turnover number (TON) of 141. It was also investigated that under the sunlight a TON of approximately 10 was achieved by using ambient conditions [38].

2.2. Imide-Linked COFs

Yan research group described the formation of a novel class of imide-based polymeric crystalline porous COFs [39]. They demonstrated that imidization reaction can be applied to synthesize a wide variety of polyimide (PI)-based COFs having a pore size of 42 x 53 Å. They obtained the large area up to 2,346 m² g⁻¹ and regarded considerably greater compared to the amorphous porous polyimide materials and documented the highest among 2D COFs. Further, these PI-COFs sustain temperature up to 530 °C, and can be easily accessed with diversified structures and applications. In 2015, the same research group unprecedentedly established the formation of two 3D porous PI-COFs through an imidization reaction. They displayed high thermal stability of 450 °C and 460 °C for PI-COF-4 and PI-COF-5, respectively. These PI-COFs also showed a very high surface area up to 2403 m² g⁻¹. For the characterization of PI-COFs, scanning electron microscopy (SEM) and FT-IR techniques were used. Due to the high loading and excellent release control properties, they

are successfully used for drug delivery functions ^[40]. In 2018, Li and coworkers developed a promising protocol for the formation of microporous 2D poly(imide-benzoquinone) bound COF through the *in-situ* polymerization reaction on graphene (PIBN-G). The PIBN-G-COF was utilized in Li-ion batteries as a cathode because of facile transfer of charge between PIBN and graphene. Moreover, because of the excessive electron conduction and Li⁺ ions diffusion, the redox reaction of the carbonyl functionalities is promoted. Owing to this unique property, it displayed exceptionally high reversible capabilities of 271.0 and 193.1 mAh g⁻¹ at 0.1 and 10 C, respectively with retention of higher than 86% are obtained after 300 cycles ^[41]. In 2017, Xian and coworkers employed solvothermal method for the fabrication of fluorescence PI-COF by the reaction of tetra(4-aminophenyl)porphyrin with perylenetetracarboxylic dianhydride. The developed porous PI-COF material showed excellent crystallinity and high thermally stability up to greater than 500 °C. Further, these materials can be easily fabricated into the multilayered PI-CONs (Ns = nanosheets) which were analyzed by various methods such as transmission electron microscopy (TEM) and atomic force microscopy (AFM). An enhancement in the luminous intensity of PI-CONs was observed compared to PI-COF. The PI-COF served as an effective fluorescence probe and used for the effective detection of 2,4,6-trinitrophenol. Moreover, these multilayered nanosheets showed an excellent linear response varying from 0.5 to 10 μM with a limit of detection of 0.25 μM ^[42].

2.3. Imine-Linked COFs

Yaghi et al. for the first time reported the construction of imine-linked 3D-COF by using amines and aldehydes as starting materials. The imine linkages (C=N) were established by the reaction of tetrahedral tetra-(4-anilyl)-methane with linear terephthalaldehyde. The X-rays diffraction (XRD) technique was employed to confirm the crystal structure of 3D-COF which displayed 5-

independent diamond skeletons. The designed COF has the porosity of 7.2 Å with surface area of 1360 m² g⁻¹ [43]. Wang research group documented a novel imine-bound COF for catalytic applications. The synthesized 2D COF can be easily attached with metal ions due to the eclipsed layer geometry. The Pd/COF catalyst was prepared through a post-treatment process which displayed high performance in the Suzuki-Miyaura reaction. The catalytic efficiency was checked in numerous chemical reactions and furnished the corresponding products in high conversion (96–98%) with excellent catalyst stability and recovery [44]. It is highly demanding to design novel COFs with improved structural diversity and new topologies. In this regard, Zhao et al. described the synthesis of COFs containing three types of distinct pores via hetero-structural mixed linker process. This methodology based on the condensation reaction of tetraamine substrate with dialdehydes. The structure of COFs bearing three pores was elucidated by XRD and pore size distribution techniques. Further, thermogravimetric analysis (TGA) was conducted which showed that as-prepared polymers are thermally high stable up to 450 °C [45]. COFs with hexagonal and tetragonal features are frequently explored. Nevertheless, the design and synthesis of COFs with triangular topologies are still underexplored area. Jiang and coworkers reported the formation of new triangular COFs with the smallest porosity up to 12 Å. Owing to the high crystallinity and conductive nature of COFs, they showed facile π -cloud delocalization with a high hole mobility. For thermal stability, TGA technique was used which showed that the COFs did not decompose even up to 550 °C [46]. The conversion of carbon dioxide into useful chemicals and green energy has recently emerged as most exciting area of research. In this context, Dong et al. designed the formation of versatile imine bound COFs as heterogeneous photocatalysts for the reduction of carbon dioxide. The as-synthesized COFs displayed excellent photocatalytic performance and production rates of 951 and 157 $\mu\text{mol/g.h}$ were obtained for CO and H₂, respectively. Moreover,

they also examined that catalytic efficiency is mainly influenced by the planarity and the presence of various conjugation in the COF materials ^[47].

2.4. β -Ketoenamine-Linked COFs

Dichtel and coworkers prepared β -Ketoenamine-based 2D COFs and employed as efficient materials in the charge storage devices due to the micro- or mesoporous nature, large surface area, and their capabilities to facilitate the arrangement of redox-active moieties. The designed COFs demonstrated excellent reversible electrochemical process due to the presence of anthraquinone subunits and showed greater chemical stability the highly acidic electrolyte as compared to boroxines and boronate esters. The experimental results displayed that the redox-active COF fabricated electrodes exhibited greater capacitance relative to the non-redox-active COF modified electrodes despite 5000 charge-discharge cycles ^[48]. In order to solve the instability issue of COF, Banerjee and coworkers described the formation of newly synthesized ketoenamine bounded 2D COFs. These COFs were formed by the condensation reaction of 1,3,5-triformylphloroglucinol with 2,5-*p*-phenylenediamine or *p*-phenylenediamine, respectively. The initially formed Schiff base then underwent irreversible enol-to-keto tautomerism to achieve the stable bond. The introduction of stable bond enhanced the stability of the synthesized COFs and showed high resistance when exposed to aqueous, basic and acidic media, respectively. Further, due to the presence of sheet like petals pattern in the nanomaterials, it can be used as a supportive material for the doping of nanoparticles to employ for catalytic functions. However, in the case of β -ketoenamine based COFs comparatively lower crystallinity are obtained to that of imine analogue due to the irreversible phenomenon which might be responsible for impediment of error correction in the COF crystal lattice ^[49]. Further, Banerjee et al. also investigated that the presence of keto functional group in β -ketoenamine framework assisted to enhance triplet excited state lifespan ^[50].

Thomas et al. also reported the formation of chemically reliable and highly porous β -ketoenamine linked COFs by the incorporation of diacetylene moieties. The designed COFs were employed as efficient photocatalyst to produce hydrogen from water. It was observed that the introduction of diacetylene functionality enormously enhanced the photocatalytic of the COF and produced hydrogen at much higher rate of $324 \pm 10 \text{ h}^{-1}/\text{g}$ in contrast to 1,3,5-triformylphoroglucinol-4,4'-(ethyne-1,2-diyl)dianiline^[51]. Correspondingly, Zhang and coworkers described the acid mediated thioether based COF formation by reacting Tp with diamine bearing thioether moiety. The developed COF displayed greater crystal nature with formation of cavities which confirmed that the presence of thioether moiety facilitated the size control of nanoparticles (NPs). As a resulted highly stable and recyclable PdNPs and PtNPs are obtained which showed remarkable catalytic capability in the reduction of nitrophenol and Suzuki-Miyaura coupling reaction, respectively. Further, PXRD technique was used to confirm the crystallinity of the thio-COF. However, the uniform distribution of the ultrafine PdNPs and PtNPs in COF are validated through TEM images^[52]. Due to greater polarization of the imine-based COFs, they showed poor π -delocalization. In this regard, Perepichka reported the synthesis of β -ketoenamine bound COFs with much improved π -delocalization. The desired COFs were constructed by the reaction of β -ketoenols with aryl amines via Michael addition-elimination. Due to the effective intramolecular H-bonding between keto and HN-moieties, the developed COFs displayed greater hydrolytic stability. Further, the extensive π -electrons delocalization led to the formation of narrow band gap with reversible electrochemical doping and light-emitting features. The FT-IR analysis technique was used which showed that the stretching bands for C–N and N–H (1206 , 3420 and 3470 cm^{-1}) were disappeared wherein the emergence of a newly C–N stretching band around 1200 cm^{-1} revealed the formation of the β -ketoenamine bound COFs^[53]. The construction of β -ketoenamine bound COFs with high

durability and redox potential is a big challenging task. Lang and coworkers described the assembling of 2D β -ketoenamine bounded COFs by using 2,4,6-triformylphloroglucinol (Tp) and 4,7-bis(4-aminophenyl)-2,1,3-benzothiadiazole (BTD) as structural units. The process was carried out at 150, 120 and 25 to furnish eclipsed, staggered and interlayer stacked Tp-BTD materials. The experimental results demonstrated that Tp-BTD-25 showed high photocatalytic proficiency for the selective amine oxidation compared to others. Interestingly, to enhance the catalytic performance and stability, 5 mol% of 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) was used which significantly facilitated the oxidation process due to the facile transfer of electrons and protons. Thus, an elegant method has been developed for conversion of amines into imines via cooperative photocatalysis of Tp-BTD-25 with redox mediator (TEMPO) by using blue light emitting diodes [54]. Zhang group first time reported the formation of heterogeneous photocatalyst by interacting molybdenum sulfide catalyst (MS-c) with β -ketoenamine based COFs and used effectively for the production of hydrogen with high catalytic performance. The designed photocatalyst showed high stability and produced H_2 at the rate of $528 \mu\text{mol g}^{-1} \text{h}^{-1}$ which is 4.7 times greater compared to previously reported value. DFT study was conducted which demonstrated that N-atoms in β -ketoenamine based COF lose electrons which markedly increased the attracting capability of H^* adsorption wherein the on the hand the sulfur atoms in MS-c concurrently obtain electrons. This simultaneous loss and gain of electrons enhanced the formation of H^* along with rapid production of H_2 . It was observed that due to the enormous active sites of MS-c and better transfer and separation of photo-induced charges in the β -ketoenamine linked COF, the manufactured photocatalyst displayed excellent catalytic efficiency [55].

2.5. Azine-Linked COFs

In 2013, Jiang and coworkers first time developed the construction of novel azine based COFs by using 1,3,5,8-tetrakis(4-formylphenyl)pyrene and hydrazine as start materials. The designed versatile COFs showed greater stability, excellent crystal nature with high porousness. The incorporation of the C_2 geometric pyrene groups provided access to the synthesis of rhombic shaped 2D COFs with microporous and luminescent features. Further, it was studied that introduction of azine unit provided the active docking sites for H-bonding interactions. Thus, the developed azine linked COFs function as highly sensitive chemosensors for the judicious sensing of trinitrophenol ^[56]. In 2016, Smaldone and coworkers described the formation of new azine bound COF with high adsorption potential. The COF material is based on the six-fold symmetrical aldehyde by the functionalization with the monomer of hexaphenylbenzene. The as-prepared COFs is bearing a very small porosity (1 nm) and greater surface area (1200 m²/g) exhibited outstanding adsorption ability for carbon dioxide (20 wt.%) and methane (2.3 wt.%) at a temperature of 273 K under 1 atmospheric pressure ^[57]. The fabrication of COFs with desirable character by the introduction of heterogeneous pores is highly underexplored area. In 2015, Zhang research group reported the formation of orderly arranged 2D COFs materials having periodic defects. The COFs possess large surface area, and 1.06 to 1.96 nm microspores were formed which were confirmed through pore size distribution technique (PSD). In addition to PSD, the theoretical simulation and PXRD studies further validated the formation of various hexagonal pores. Thus, it provides new window to the facile formation of 2D COFs with heterogeneous porosities ^[58]. The generation of H₂ by the photocatalysis of water is considered the most emerging and greener source of energy. Lotsch research group documented the fabrication of 2D azine-linked COFs by reacting hydrazine with triphenylarene aldehydes. These water and photo reliable azine-bound COF structures demonstrated excellent performance for the light-assisted hydrogen evolution due the

presence of excessive nitrogen moiety in the skeletons. Different analytical techniques such as SEM, TEM, gas sorption and PXRD were applied to study the morphology and structural features of the designed COFs ^[59]. The same research group extended the previous concept and designed the formation of pyridine-bound COFs. In this study, it was demonstrated that modifying the COF structure on molecular scale significantly changed the morphology and optoelectronic features which were evident from the XRPD pattern. As a result of these variations, lower porosity and crystallinity are obtained which markedly affected the photocatalytic efficiency producing hydrogen compared to azine-bound COF ^[60]. Most of the 2D COFs needed high energy light such as white, green and blue for photocatalytic reactions. In 2022, Wang and coworkers reported an easy approach for the synthesis of robust 2D azine linked COF by reaction of hydrazine hydrate with 5,10,15,20-tetrakis(4-benzaldehyde)porphyrin. The as-synthesized COF bearing a surface area of 1586 m²/g displayed greater reliability even using 9 M HCl or 12 M aqueous NaOH solution. Owing to the greater durability and good recyclability, the designed COF was used as a potent photocatalyst especially for the aerobic oxidative coupling of bezylamines under the irradiation of red light ^[61].

2.6. Hydrazone-Linked COFs

In 2011, Yagi et al first time documented the construction of two porous 2D hydrazone based COFs. The COFs were obtained by the reaction of the 2,5-diethoxyterephthalohydrazide with 1,3,5-triformylbenzene or 1,3,5-tris(4-formylphenyl)benzene. It was examined during the study that variation in solvent or pH of the acid controlled the crystallinity of the COFs. The two COFs having pore sizes of 23 Å and 38 Å were in close range with the size of the pore in the crystal structure simulations. PXRD confirmed the crystal nature whereas during the activation of pores TGA technique was applied which displayed that no significant loss in weight till the

decomposition occurred at 280 °C ^[62]. To access multilayered 2D COF, Dichtel et al. reported the synthesis of hydrazone linked COF polymeric substances ^[63]. It was examined that the COF samples on exposure to methanol, toluene, chloroform and tetrahydrofuran maintained their diffraction whereas amorphous pattern are obtained in dimethyl formamide, water, and dioxane. Owing to the minimum interlayer energy interactions, 2D COF polymers with high aspect ratio are achieved which offered a new method for the preparation of multilayered COF. Further, the facile access and greater diversity of the hydrazone linked COFs make them reliable candidate to be successfully employed in different applications. Exploring the photocatalytic potential of COF, Lotsch and coworkers unprecedentedly designed the construction of hydrazone bound COF by the reaction of 2,5-diethoxyterephthalohydrazide with 1,3,5-tris-(4-formyl-phenyl)triazine ^[24]. The as-prepared COF was used for the production of H₂ from water in the presence of platinum under visible light without any deterioration. The experimental results demonstrated that under the optimized alkaline conditions, the quantity of hydrogen product is 1970 μmol/h g which is significantly greater compared to the reported g-C₃N₄/Pt-modified amorphous melon ^[64]. Subsequently, Wu et al. reported operationally simple and highly sustainable methodology for the formation of thermally and chemically stable hydrazone linked COF. Using the solvothermal process, the COF was prepared by the reaction of 1,3,5-triformylbenzene and 2,5-dimethoxyterephthalohydrazide. A very large area of 1501 m²/g was measured with excellent crystallinity and high porosity. Thus, it was proved to be an efficient photocatalyst for the coupling reactions of tetrahydroisoquinolines with different nucleophiles for instance phenylethyl ketone, acetone, and nitromethane with high catalyst recovery ^[65]. Recently the 2D COFs found widespread applications in various research fields such as water splitting ^[66], organic transformations ^[67] and CO₂ reduction ^[68]. However, certain issues are associated with which limit

their usage as photocatalysts ^[69]. In this respect, Lang's group documented the formation of 2D hydrazone-bound COF by the reaction of 5,10,15,20-tetrakis(4-benzaldehyde)porphyrin with 2,5-dimethoxyterephthalohydrazide. This hydrazone-based COF displayed excellent photocatalytic functioning in the aerobic oxidation of benzylamines to imines with excellent selectivity under the irradiation of red light. Additionally, the designed COFs are highly tunable with wider functional groups tolerance and can be reused after the five consecutive cycles ^[70]. To construct multifunctional photocatalysts with enhanced thermodynamic stability and greater charge separation capacity, Yang and coworkers described the construction of hydrazone-bound macrocyclic COFs by the reaction of 1,3,5-tricarbaldehyde, 2,5-dimethoxyterephthalohydrazide, and diverse pillararene skeleton. The introduction of the different ratios of pillararene units in the COFs produced the orderly arranged layers with electron-rich confined cavities. As a result of this phenomenon, the light adsorption capability of the photo-induced electron-hole pairs is enhanced due to the significant improvement in the charge migration performance. The developed COF materials were efficiently employed for the oxidative aerobic coupling of benzylamines with improved conversion and remarkable selectivity ^[71]. The development of COFs having excessive porosity and greater sensing capability for the removal of specific analytes is emerged as one of the most vibrant area of research. In 2022, Wu and coworkers employed isothermal protocol for the formation of hydrazone-bound COF. The COF material was prepared from 2,5-bis(2-methoxyethoxy) terephthalohydrazide and 1,3,5-triformylbenzene, and successfully utilized to furnish arylboronic acid through the photocatalytic hydroxylation oxidation process. The resulting COF also showed greater thermal stability, excellent crystal nature with surface area up to 632 m²/g was obtained. Moreover, it was examined that impressive photocatalytic performance demonstrated by the hydrazone-based COF was possibly because of the facile generation, transfer

and isolation of photo-induced charges. Furthermore, the synthesized COF also displayed remarkable fluorescence sensing ability for the detection of Cu^{2+} which was confirmed through XRPS and FTIR techniques ^[72].

2.7. Boron-Linked COFs

Lavigne et al. described the construction of boronate ester-based COF by the self- or co-condensation reaction of boronic acid with catechol. This dehydration process resulted in the formation of highly porous sheets with infinite 2D hexagonal materials. PXRD technique was used which confirmed that the stacking pattern between ester-bound sheets developed in such a way that the adjoining lies over each other. The developed COF material displayed high thermal durability with greater surface area up to $1260 \text{ m}^2/\text{g}$ and $0.29 \text{ cm}^3/\text{g}$ volume of micropore ^[73]. Yaghi and coworkers also established synthesis of boron-bound COFs by the dehydration reaction of phenyl diboronic acid with hexahydroxytriphenylene. To investigate about the crystal geometry, PXRD analysis was conducted which showed extended graphitic layers with porous nature. These layers were present both in eclipsed and staggered forms. These strong interactions among boron, carbon and oxygen atoms tightly bounded the crystal structure with high rigidity. Furthermore, they showed high thermal reliability ($500\text{--}600^\circ\text{C}$), high porosity, and large surface area ($1590 \text{ m}^2/\text{g}$) ^[16]. The greater vulnerability of the boron linked COF to the nucleophilic attack of water is the key issue responsible for its decomposition. This problem was circumvented through the addition of less than 1% pyridine which stabilizes the COF skeleton without any sign of decomposition on exposure to moisture ^[74]. However, later on the same research carried out the detailed study and it was examined that pyridine (Py) formed a mixture of Lewis and Bronsted boron (B) complexes (Py–B) along with un-complexed boron sites in the skeleton. Thus, further increasing the loading of the pyridine converted the unused B in COF into Lewis B and caused the

decomposition of COF. This study confirmed that the stability of boron linked COFs in the humid air could be controlled by the addition of low dose of pyridine ^[75]. To further improve the hydrolytic stability, Bredas et al. also synthesized boronate ester based COF by the reaction 2,3,6,7,10,11-hexahydroxytriphenylene with 1,4-phenylenebis(boronic acid). They conducted the DFT study to provide complete insight of the boron linked COF stability in humid condition ^[76]. Thus, the construction of a spiroborate bound COFs bearing anionic boron centers, the boronate linked COFs with alkylated edge moiety or their post-synthetic structural modifications efficiently enhanced their stability in the humid environment. The boronates or boroxines based-COFs usually show lesser stability in the humid conditions which limit their applicability as photocatalysts. In 2022, Pan et al. described the formation of two newly arylboron linked COFs and used to produce H₂ through the splitting of water under the irradiation of visible light ^[77]. The synthesized boron-linked COFs evolved hydrogen at the rate of 666.4 mmol/g h which subsequently reached to the maximum value of 1140 after the lengthy cycle stability. It was noticed that the introduction β -ketoamine functionality significantly boosted the isolation and transportation capacity of the photo-created charge carriers. However, DFT calculations confirmed that the presence of arylboron moiety facilitated the intramolecular charge transfer which consequently increased the carrier transfer for the photocatalytic production of H₂. These results demonstrated that excellent photocatalytic performance displayed by boron-bound COFs was presumably due to the synergistic outcome of the arylboron and β -ketoamine double acceptors.

2.8. Multicomponent reactions

Multicomponent reaction approach (MCRs), with their unique sustainable properties, have recently drawn a great deal of interest in the development of various synthetic routes to produce COFs materials ^[78]. The MCRs approach has many benefits over stop-and-go combinations,

including step efficiency, facile workup, bond, increased yield of the end product, decreased reaction step and transformation time, employment of environmentally benign media, and operational simplicity etc. ^[79]. Ugi, Strecker, Petasis, Mannich, Gewald, Asinger, Groebke-Blackburn-Bien aymé, Debus-Radziszewski, and Povarov are all examples of the various reaction types that fall under the MRCs ^[78]. Using the Debus-Radziszewski reaction, Wang and colleagues ^[80] synthesized imidazole-linked COFs by condensing tertbutylpyrene tetraone and aromatic aldehyde in the presence of NH_4^+ OAc, dioxane, and mesitylene at 150 °C for 5 days. Using styrene, DMTPA, and TAPB in the presence of DDQ and BF_3OEt_2 , Dong and colleagues ^[81] fabricated solid COFs materials (**Fig. 2a**). As shown in **Fig. 2b** ^[82], ultrastable pyrimidazole-based COFs have been made by reacting aminopyridine, isocyanide, and aldehyde for 5 days at 120 °C. In another approach, Wang and coworkers disclose for the first time the use of a photocatalytic multicomponent reaction to build COFs. At room temperature, the photoredox-catalyzed multicomponent Petasis reaction successfully synthesizes a sequence of COFs with exceptional crystallinity, stability, and permanent porosity. The resulting Cy-N3- COF is highly photoactive and recyclable, allowing for the oxidative hydroxylation of arylboronic acids to be propelled by visible light. In addition to enhancing current COF synthesis techniques, the idea of photocatalytic multicomponent polymerization provides a novel pathway for the construction of COFs that may not be feasible using thermally driven MCRs ^[83]. Dong et al. ^[81] formulated an intriguing study that employed a one-pot MCR approach to construct COFs via one of the earliest MCRs, discovered in 1850 and appropriately designated the Strecker reaction. In this sophisticated study, trimethylsilyl cyanide, 1,3,5-tri(4 aminophenyl)benzene (TAPB), and 2,5-dimethoxy terephthalaldehyde (DMTPA) (molar ratio, 1.5: 1: 2) were subjected to the Strecker reaction in

solvothermal conditions at 120 °C for 72 hours in an o-DCB/nBuOH mixture (1: 1, v/v) to produce α -aminonitrile-linked COFs ^[81].

In a different study, ethyl vinyl ether was used to create tetrahydroquinoline-linked COFs (QH-COF-1) in the Povarov reaction rather than styrene. In the presence of Yb(OTf)₃ and Sc(OTf)₃, the reaction between 1,3,5-tris(p-formylphenyl)benzene ethyl vinyl ether and benzidine, was conducted in a combination of 1,2-dichlorobenzene and n-butyl alcohol. By combining with a chiral secondary amine, the obtained QH-COF-1 was used in the photocatalytic asymmetric MacMillan reaction with high enantioselectivity, high activity, and good recyclability ^[84]. A quinoline-linked COF was obtained in another research by performing a one-pot 3CR of aldehyde, amine, and alkyne derivatives with DDQ as the oxidant and B(C₆F₅)₃ as a Lewis acid catalyst; the resulting 2D COF product was highly stable in both bases and acids ^[85].

2.9. Post-functionalization methods

Since most COF applications involve linking external substances to the internal and outer interfaces of the pore zones and intrapore, it is crucial to identify and control crucial COF aspects such as the intrapore chemical behavior and inner structure. COF alterations can be made either before or after synthesis, or even in lieu of it. Adding the appropriate functional groups to the frames is an example of a pre-synthetic modification. Depending on the functional groups, it may be challenging to ensure their stability under sensitive conditions and keep them from impeding the COF crystallization procedure ^[86]. In situ modifications typically involve substrates that engage with the growing COF and cause crystallization to be impeded. These anchoring structures persist from early on in development, allowing the COF to polymerize around them to form a composite substance that can be either organic or inorganic, depending on the host. COFs have the advantage of being amenable to additional functionalization processes after they have been made, which is

not the case for all classes of polymer. Post-synthesis reactions in non-porous polymer architectures are difficult because of insufficient solvent and reagent access to the active reaction locations and constrained mass transfer mechanisms. However, COFs' long porous networks and large surface areas provide preferred access to solvent and reagents, allowing for straightforward post-functionalization and remarkable versatility.

To achieve a covalent post-synthetic modification, the initial step of the process involves adding reactive sites to the initial monomers. Under the new post-synthetic reaction conditions, the COF needs to be sufficiently chemically stable, which could ultimately result in a difficult balance (boroxine or boronic ester type COFs are especially susceptible to hydrolysis, making them extremely unstable in aqueous solutions). The process of functionalization starts with the COF being prepared and includes a mixed reaction.

The reaction must be profitable, high yielding, and create the least number of byproducts. COFs also possess a special characteristic known as post-synthetic modification, which has caused this class to be categorized as both products and starting reagents for organic synthesis. Another well-liked technique for post-synthetic functionalization is click reactions mediated by Cu(I). The used monomers' molecules contain alkynyl groups. Alkynyl groups are not reactive during the COF synthesis, but they subsequently become reactive, allowing for addition reactions. A 5-atom heterocyclic ring with the desired functional group is produced when the COF interacts with an organic azide in the presence of Cu(I). Click reactions, which can typically be carried out under a moderate reacting environment and have an acceptable rate of yielding products, enable the incorporation of various functional compounds, such as amine, carboxyl, hydroxyl, acetate, or ethyl groups. Ring-opening reactions involving succinic anhydride are an alternative post-synthetic technique for introducing carboxylic groups (COOH) into COFs materials, for instance.

Developed COFs Polymers with OH functional groups in their constituents can be treated with succinic anhydride to generate ester and carboxylic acid groups. Since the presence of acidic groups may be possibly unfavorable to the normal COF crystallization mechanism, the post-synthetic functionalization of these groups is of even greater importance. Many applications have been explored that involve adding amine groups to the porous framework of COF. Since the presence of these amine groups in COF preparation disrupts the predicted symmetric structure, they usually hinder the development and growth of COFs, especially imine- or ketoenamine-type COFs. It is possible to use monomers containing nitro groups and then transform those nitro groups into NH_2 groups using metal catalysts, following the production of the COF. Treating the COF with SnCl_2 makes it easy to produce amine-functionalized COFs, as NH_2 groups may ultimately serve as the reaction sites for further functionalization. It has been observed that chemical conversion can introduce new groups like ether, thiol, amidoxime, quaternary amines, and amide into COFs wall precursors. By adding dioxane, sodium chlorite, and 2-methylbut-2-ene to AcOH, amine-based COFs can be converted to amide-based frameworks through an oxidation process. For the production of thiazole-type COFs, sulfur is combined with 2,5-diaminehydroquinone in the presence of water, DMF, and molecular oxygen.

Linkers formed during the polymerization reaction serve as the ligands in the first class of COFs that incorporate metal species in a post-synthetic phase. Crystalline frameworks can have catalytically active cores synthesized by the method of linker metalation. COFs with imine linkages are the most typical types. As ligands for transition metals, imines are common because they donate a nitrogen lone pair to create a dative bond. In reality, Schiff bases can stabilize a wide variety of metals in a variety of oxidation states, allowing for precise regulation of metal performance in a wide range of valuable catalytic transformations^[87]. Therefore, Pd^{2+} , FeII , Co^{2+} ,

and Ni^{2+} have been effectively bound by COFs based on imine moieties. The Suzuki-Miyaura coupling ^[44], hydrogenation of nitrobenzene to aniline ^[88], and cross coupling reactions between silanes and aryl halides are all catalyzed by compounds with immobilized Pd^{2+} , which have been the subject of the most research ^[89]. It's worth noting that the Pd ions are effectively coordinated with two nitrogen atoms from separate layers of the COFs, and that they're located between adjacent layers. In COFs featuring an eclipsed layered-sheet arrangement with interlaminar distances enabling an efficient π - π stacking, this form of coordination is very effective. The equivalent salicylaldehyde benzoyl hydrazone (SBH) ligand is produced by reacting terephthalohydrazide with 1,3,5-triformylphloroglucinol. Strong coordination between the enamine nitrogen atom and ligand's two oxygen atoms allows these ligands to effectively order molybdenum sites into the channel walls of COFs. However, the thermal stability of these metalated COFs is slightly lower than that found for the metalated COFs mentioned above; their decomposition begins at around 260 °C. Hydrogen bonding in the 2D structure is broken, which accounts for this behavior ^[90].

3. Synthesis of COF Powder

There is a demanding curiosity in the synthesis of sustainable materials for numerous applications. Properties of these materials depend upon crystallinity, surface area, porosity and surface functionalities ^[91]. COFs are an evolving type of crystalline and porous organic materials. Owing to their greater porosity and surface area, it is applied in various applications ^[92]. However, properties of the COF powder depend upon their extent of crystallinity and porosity. Various types of building units are available but synthesizing COFs with high crystallinity and porosity is difficult task. To maintain a balance between synthesis and crystallinity of the COF powder, suitable conditions of temperature, pressure and solvent combination are needed ^[93]. COFs are

fabricated by adopting various synthetic procedures including ionothermal, microwave assisted, room-temperature and solvothermal synthesis. Normally, the COFs are used over thin film attached on the surface of support or as a bulk material ^[94]. Generally, crystalline COFs are constructed through imide, Knoevenagel and spiroborane condensation ^[15b, 95], however their direct crystallization is not developed till date. Once the COFs are synthesized then the organic skeleton can be modified, and the porous networks are used as a coordination positions for various catalytic centers. However, the main problem related to the COFs materials like borate and boroxine are their poor stability in humid conditions as their linkages are cleaved when exposed to moisture conditions. Hence new synthetic approaches are growing in a search of synthetic technique which could lead to the production of ideal hybrid composite COFs.

3.1. Solvothermal Synthesis

Solvothermal method is mostly used for the construction of various COFs. In this strategy the starting materials in a sealed vessel are heated at various temperatures ranging from 80 to 120 °C for various days ^[94]. The reaction output, porosity and crystallinity are affected by temperature and pressure of the reaction system ^[93]. In addition, reaction rate, crystal growth rate as well as crystal nucleation are affected by the solvent ^[96]. Hence, selecting a suitable solvent system for the synthesis of COFs with crystalline structure is a challenging task. Usually, a binary solvent mixture with an acidic catalyst is utilized to synthesize COFs. For instance, Ding et al., used DMAc-o-dichlorobenzene to fabricate COFs linked with boronate ester ^[97] while Cote et al., used dioxanemesitylene for the COFs fabrication ^[98]. Wei et al., in 2018, used microfluidic solvothermal conditions and synthesized extremely stable crystalline and porous TpPa-COF ^[99]. This synthesis takes less time as compared to conventional solvothermal synthesis.

Xiong recently reported the synthesis of triphenylamine-derived COFs via solvothermal method by means of Schiff base reaction between tris(4-aminophenyl) amine and tris(4-formylphenyl) amine for the supercapacitors ^[100]. TPA-COFs displayed a large specific area surface area of 398.59 m² g⁻¹. The porous architecture of the synthesized TPA-COFs leaks more active sites of TPA to the solution of electrolyte during the process of charge-discharge. In addition, it also accelerates the ions transport in the active layer. Solvothermal synthesis is frequently used method in laboratories as it results in the synthesis of good qualities COF however, it possesses certain limitations. The main limitation is their slow reaction rate and difficult scale-up to the industrial applications. Thus, search for the alternative techniques which are safe, green and efficient synthetic approaches is the hot topic among the researchers.

3.2. Ionothermal Synthesis

In ionothermal methodology, ionic liquids and molten metal salts are employed to establish ionothermal environment for the COF preparation. Generally, CTFs are synthesized through ionothermal conditions by trimerization of aromatic nitriles. For example, Thomas et al., used ionothermal strategy for the synthesis of crystalline porous and highly durable CTFs by reversible cyclotrimerization of nitriles structural frameworks at 400 °C by employing ZnCl₂ as a catalyst also as solvent ^[31]. Compared to organic solvents, ionic liquids are advantageous for the COF synthesis due to their reusability, environment friendly nature and alteration in their properties through counter ions ^[101]. Maschita et al. in 2020, reported synthesis of crystalline and porous PI-COFs through ionothermal synthesis using ZnCl₂ and eutectic salt mixture ^[102]. In comparison to solvothermal method, the reaction time was greatly reduced and also it did not require soluble starting materials. XRPD technique was applied which indicated that the synthesis of salt adducts with crystalline intermediates and thus it led to the synthesis of COFs powder. Due to harsh

conditions used in ionothermal conditions, the CTFs synthesized in this method have shortcoming of crystallinity governor in comparison to COFs prepared via solvothermal process. Further, due to elevated reaction temperature, the ionothermal synthesis is limited to range of building blocks.

3.3. Microwave-Assisted Synthesis

Compared to conventional heating methods, microwave heating has advantages due to their higher product yield, milder reaction condition, accelerated reaction rates, improved selectivity, and higher product yields during the chemical reaction. Hence rapid microwave-assisted synthesis is regularly utilized for the synthesis of COFs. For instance, Cooper and his team has synthesized 2D COF-5 and 3D COF-102 in 20 minutes through rapid microwave synthesis and their surface area were higher than those synthesized by solvothermal synthetic method in 72 h ^[103]. Wei et al. described the construction of microwave assisted solvothermal formation of 2D enamine-linked COFs with excellent yield in less time and comparatively low temperature ^[104]. The synthesized COF was observed to possess excellent crystalline nature, greater BET surface area, and higher stability with remarkable CO₂ intake. Microwave heating synthesis is rapid and cleaner in comparison to the solvothermal approach.

3.4. Mechanochemical Synthesis

Synthesis at room-temperature is cost-effective and facile method for the COFs synthesis. It mainly consists of two techniques, solvent method and mechanochemical grinding at room temperature. Mechanochemical grinding is an environmentally benevolent approach in which bond formation and cleaving as well as morphology changes happens while grinding ^[105]. Mechanochemical approach has the advantages of environmental friendliness, facile operation and mild conditions and therefore has widely been exploited in the preparation of porous organic

materials ^[106]. Biswal and his team reported the synthesis of 1,3,5-triformylphloroglucinol-diamine via solvent-free and rapid Mechanochemical grinding using a mortar and pestle ^[107]. Color change from yellow to orange and finally to dark-red confirms the synthesis of the COFs. About 90% yield was obtained with 40 min grinding. Although the COF synthesized displayed excellent thermal and chemical stability however, low crystallinity and BET surface area in comparison to the one prepared with solvothermal method. In another research work, a solvent-assisted mechanochemical grinding method was applied during the grinding of monomers by introducing solution of catalyst to the mortar. The developed technique due to enhanced reactant homogeneity increases the crystallinity and reaction rate ^[108]. The shortcoming of this technique includes the synthesis of COF with low surface area, porosity and crystallinity. However, it is advantageous especially for sensitive monomers and substances as the synthesis is carried down at room temperature. Shiraki and coworkers documented COFs synthesis at room temperature from 1,4-phenylenedimine and 1,3,5-benzenetricarbaldehyde ^[109]. Compared with solvothermal approach, COFs synthesized with this technique presented greater surface areas and thermal stability due to higher crystallinity. In another study, Matsumoto coworkers disclosed the room temperature synthesized of 2D imine COFs in 10 minutes by using triflate catalyst ^[110]. The BET surface areas were 2175 m² g⁻¹ which was superior to one synthesized with solvothermal method in 24 h. in the following year, a very fast method for the construction of 3D ionic liquid containing COFs from 1-butyl-3-methylimidazolium bis-((trifluoromethyl) sulfonyl)imide ([BMIm][NTf₂]) at atmospheric pressure and temperature were developed in which synthesis of COFs was carried out only in 3 minutes as compared to synthesis in 3–7 days via solvothermal method ^[93]. However, their applications for the large-scale synthesis of COFs are thought-provoking due to the need of expensive catalysts such as ionic liquid or metal-triflate. Zhao et al. used ball milling

mechanochemical method for the synthesis of TpMA COF in a relatively short time at ambient temperature. The as synthesized TpMA COF was used for the degeneration of phenol and methyl orange through photocatalytic process, and the performance were comparable with counterpart synthesized through solvothermal method ^[111].

4. Basic Concepts of Covalent Organic Framework Photocatalysis

Photocatalysis occurs when semiconductors capture photons with energies greater than their band gap, resulting in electrons and holes moving into the semiconductors conduction and valence band, respectively. In this way, the stimulated holes and electrons may continue the oxidation-reduction reaction with the suitable electron donors and acceptors in the surrounding environment ^[112]. COFs are periodic organized organic polymers with good permeability and crystallinity which are formed by the covalent bond connection of chosen organic blocks, such as ketoenamines, azines, hydrazones, boronic esters, imine bonds, or boroxines, among others^[59, 113].

COFs have recently been hailed as intriguing photocatalysts capable of achieving difficult chemical and material objectives. Using COFs as a photocatalyst has various advantages:

- 1) By adding diverse molecular building components, the topographies, channels, and band architecture of COFs may be readily altered.
- 2) Because of its persistent and nanoscale pore structure, it has a greater surface area and hence enormous active sites, allowing substrates easy entree to COF photocatalytic active sites.
- 3) COFs have high chemical and thermal durability due to the covalent link connection between the building blocks, which extends the lifespan of photocatalysts. The strong and sturdy structure also allows photoactive building components to be stabilized.

- 4) Electron donor-acceptor (D-A) constituents are common in COFs used as photocatalysts.

The segregation performance of photogenerated electron-hole pairs is enhanced by transferring electrons from source to acceptor.

- 5) The conjugated systems regularly organized columnar arrays enhance electronic delocalization, giving COFs exceptional electron-transporting properties and noticeable photoconductivity. [17, 114].

To absorb photons and form excitons, photoinduced charges must be absorbed into a chemical system. The exciton state is then split into isolated charges, which are then transported to a location for the commencement of a redox process triggered by light capture [115]. As a result, the important processes impacting photocatalytic performance are light capturing, E_g , photogenerated charge isolation of charges, and their ultimate transfer. Semiconductor photocatalytic activity is primarily determined by their capacity to trap light, along with the mobility and isolation efficiencies of photogenerated electron-hole pairs. The optical response range and absorption intensity are two characteristics of light harvesting capabilities. A semiconductor's optical response range is largely related to its (E_g) known as energy band gape. According to band gape theory, COFs E_g is determined by the energy gap difference between its highest occupied molecular orbital (HOMO) lower energy state and lowest unoccupied molecular orbital (LUMO) levels higher energy level, which correspond to Valence Band and Conduction Band when we talk about inorganic semiconductors, respectively. Photons are absorbed by electrons, which then shift from a lower energy state to a higher energy state as a result of the energy absorption from the incident photon. There are two sorts of transitions that can occur: $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$. The $\sigma \rightarrow \sigma^*$ transition necessitates light absorption in the range of 10~400 nm, which is in the ultraviolet area, whereas the $\pi \rightarrow \pi^*$ transition necessitates absorption between the

limit of 380~780 nm, which actually present in the visible region of light ^[116]. The pi-conjugated groups in the building blocks of covalent organic framework play a crucial part in the light capturing ^[117]. Theoretical ideas for all covalent organic frameworks are summarized in **Fig. 3**. In photocatalysis, an electron from the HOMO orbital receives energy in the form of light and is transferred to the LUMO orbital. If we can capture this electron, we can use it for a variety of catalytic purposes. The problem is that recombination of electron holes is a common occurrence. To overcome this problem, we can use the donor-acceptor molecule interaction illustrated in **Fig.3 (b)**. The energy and probability of electron-hole recombination are reduced acceptor and donor molecules interact for hybridization. There are numerous types acceptor and donor molecules for this purpose **Fig.3 (a)** also shows that $\pi \rightarrow \pi^*$ requires lower energy than corresponding $\sigma \rightarrow \sigma^*$ transition.

The application of photocatalysts to transfer natural solar energy into useable, cleaner, and greener energy is a new growing topic that demands attention, acknowledgment, and consideration. This sector has the ability to bring attention in a short amount of time to the problem of pollution creation from conventional methods and the development of sustainable energy for use, with photocatalysts being the most important component of this technology. A photocatalytic process, in general, entails a series of photogenerated chemical reactions that must be followed in order, including (i) photon acquisition by the system, (ii) electron-hole pair production and detachment in the system, (iii) charged particles are relocated to the surface, and (iv) these charges eventually initiate a redox reaction on the surface. This all has to happen in one molecular system, so all steps in the sequence can happen in the same phase and charges can be transferred to the surface for redox reaction initiation. For water splitting with a light photon of 1100 nm, the lowest band gap is generally 1.23eV.

Photogenerated carriers have better charge separation and migration. The relatively poor photocatalytic effectiveness of present photocatalysts is majorly because of to the quick rejoining of charged particle carries, which is a severe problem. A co-catalyst and an electron donor that is sacrificial in nature are typically utilized to solve this problem. A co-catalyst aids in proton reduction, which is critical, and an electron donor provides an electron source that aids in photocatalytic material regeneration by irreversibly disintegrating and transferring electron back to the material.

Other parameters, aside from those stated above, that influence photocatalyst activity include pore size, crystalline nature, and structural features, all of which are hypothesized to have an impact on the separation of charged species in the system. COFs have more active sites for reaction than amorphous photocatalysts, and their large range and π - π conjugated layers have transport characteristics. Covalent organic frameworks also have expanded light range and promoted transfer of exciton in the system. Furthermore, their characteristics can be tuned easily based on their structurally diverse and modification induced nature, and thus they exhibit remarkable photocatalytic properties.

Furthermore, we can combine diverse photoactive materials with covalent organic frameworks to create composite materials and structures with better properties than their predecessors. COFs were a versatile material for photocatalytic applications due to their qualities and characteristics ^[118].

5. Photocatalytic Applications of COFs

Chemical and thermal stability, improved surface properties, enlarged pores size, π -conjugated structure, strong absorption of visible light spectrum, and isolation of charged particles

are some of the distinguishing characteristics of covalent organic frameworks that make them ideal for this application. Furthermore, the structure of COFs may be altered by combining appropriate building materials, developing an increased conjugated extended system, and introduction of electron-donor and acceptor units into the structure of COFs through various physiochemical changes ^[119]. COFs have vast number of features that make them ideal candidature for organic chemical synthesis, dye elimination, water splitting, carbon dioxide degradation, and a variety of other applications. Research progress on COF photocatalysts is extensive and its advancement in past few years in major field of interest is wide. This article summarizes some of the most recent advancements in this sector as a result of studies.

5.1. COFs as Heterogeneous Photocatalyst for Organic Transformation

Organic chemical synthesis and transformation, in particular, is a time-consuming process that generates a great deal of pollutants. The usage of visible light to drive chemical synthesis reactions has received a lot of interest in recent decades; this technology is easy, sustainable, and economically benign ^[120]. Photocatalyst design and construction have traditionally had a central role in photocatalysis research, which aims to improve photocatalytic performance. Due to their high absorbance and excellent redox properties in the excited state, numerous photocatalytic systems such as inorganic semiconductors ^[121], organometal complexes ^[122], and pure organic dyes ^[123] have been intensively explored in photo-redox processes up to today. In recent years, polymeric material-based photocatalysts ^[124], MOFs ^[125] and dye-sensitized mesoporous silica ^[126] have already been investigated for a variety of photocatalytic organic syntheses in an attempt to improve the major drawbacks of the above-mentioned homogeneous photocatalysts, such as high cost, laborious separation, and low recyclability. Many of these have demonstrated excellent results, but porous organic polymer-based materials have gained widespread recognition for their

excellent reusability, good catalytic characteristics even when illuminated with visible light, and are regarded to have magnificent results in organic chemical transformation (**Fig. 4a-d**)^[127].

Using visible light-induced reactions is both economically cheaper and environmentally friendly. The fundamental reaction pattern of organic chemical synthesis caused by visible light is as follows:

- I. Production and isolation of photocatalyzed e^-/h^+ pairs,
- II. Transformation of molecular oxygen to superoxide oxygen radical anion ($\bullet\text{O}_2^-$) and singlet oxygen $^1\text{O}_2$ ^[128], and
- III. Oxidation of materials by h^+ or active species.

Excellent yield of desired products, quick chemical conversion, high selectivity, moderate conditions, and recyclability of catalysts are all advantages of photocatalytic-driven organic synthesis. Many COFs based compounds have been employed as catalysts in chemical synthesis processes such as hydrogen addition, oxidation, and linked organic reactions. Under illumination visible light, COF-JLU5 showed outstanding photocatalytic activity for the coupling reaction of *N*-phenyltetrahydroisoquinolines under aerobic conditions with certain nucleophiles^[129]. The construction of COF-JLU5 and catalyzed reaction of COF-JLU5 aerobic photocatalytic C–H functionalizations. Photocatalyzed e^-/h^+ pairs initiate the production of the radical anion COF-JLU5 $\bullet^-$, which transfers electrons to molecular oxygen to give $\bullet\text{O}_2^-$ radical anion. Radical anion $\bullet\text{O}_2^-$ has a crucial function in H^+ transport and intermediate production. Finally, nucleophiles were added by functionalization of C–H through oxidation. COF-JLU5 has a high heating stability up to the range of 450 °C. Even in organic solvents, strong acids or alkalis, their structure, crystallinity, may be preserved. In the recycling process, there is no fundamental modification in activity or structure.

Li research group described the synthetic methodology for the construction of a completely conjugated Py-BSZ-COF, which has electron-donating pyrene units as well as electron-accepting benzothiadiazole units to form a donor-acceptor skeleton with excellent stability and increased charge isolation efficiency. This extended conjugated donor-acceptor Py-BSZ-COF may create superoxide radical anion ($\bullet\text{O}_2^-$) in air saturated with acetonitrile under visible light irradiation, which promotes transformation amine via oxidative coupling and photocatalytic annulation of thioamide to furnish 1,2,4-thiadiazole in fair to excellent yield with reusability. Py-BSZ-COF has been reported to offer 99 % yield for photocatalytic oxidative amine coupling of benzylamine under moderate air and 520nm LED light conditions. For oxidative photocatalytic cyclization of thioamide to 1,2,4-thiadiazole, Py-BSZ-COF showed up to 91 percent yield in 20 hours. **Fig. 5** Demonstrate the suggested mechanism for the two-reactions of cyclization and amide coupling indicated above. **Table 1** mentioned and summarizes some of the recent advancement in organic transformation photocatalyzed reactions.

5.2. Degradation of Organic Materials Using COFs Based Photocatalyst

Various anthropogenic activities are contaminating fresh water and water reservoirs. Major pollutants of the water resources include antibiotics, metal ions ^[130], ^[131], dyes ^[132], phenolic compounds ^[133] and various other pollutants ^[134]. This makes the water inapt for humans and other aquatic life. The removal of the pollutant materials like antibiotics ^[135], phenol ^[136], and poisonous dyes ^[137] has become a severe concern because of result of the extensive use of chemical products in everyday life. For the last several decades, a variety of strategies for eliminating organic contaminants ^[91b, 138] have been utilized, including physicochemical adsorption, separations using membrane, bioremediation, and photocatalytic pollutant degradation. Among these approaches, photocatalyst removal of pollutant has proved to be an efficient, energy-effective, and ecologically

acceptable means of removing contaminants. The pollutant was degraded using a range of photocatalysts, including MOFs ^[139], g-C₃N₄^[140], ZnO ^[141], Ag^[142], TiO₂ ^[143], and Bi₂WO₆ ^[144].

The photocatalysts disadvantages, such as their poor photochemical stability, unapproachable catalytic active sites, restricted limit for the absorption of light spectrum, less charge mobility effectiveness, and greater reunite speed of electron-hole pairs in the frameworks, minimized their future applicability. On the other hand, COF-material photocatalysts with strong stability and outstanding photoelectronic characteristics, providing a potential pathway for the successful removal of organic contaminants. For instance, mechanochemically synthesized durable TpMA-COFs with keto-enol tautomerism were made by the reaction of melamine (MA) with 1,3,5-triformylphloroglucinol (Tp) ^[111]. TpMA-COF has better photocatalytic ability for decomposing methyl orange and phenol as compared to g-C₃N₄ ^[145].

When illuminated light energy excels or becomes identical to the bandgap of the COF photocatalyst, e⁻-h⁺ couples are formed and isolated from each other. Adsorbed O₂ might capture photogenerated e⁻ in CB to form superoxide radical anions (•O₂⁻), which could then combine with hydrogen ion to produce hydroxyl radicals (•OH). Organic contaminants may be effectively degraded due to the significant oxidizing power of the produced •O₂⁻ and •OH. Concurrently, the h⁺ may efficiently exit from the catalyst and thus absorb contaminants or bring about water oxidation, results in successful isolation of charge. Organic material contaminant are initially adsorbed on the surface, where reduction oxidation reactions take place, and then the resultant products are detached off the surface and transferred again into the solution form (**Fig. 6a**) ^[146].

Only a minor quantity of COF progressively deteriorated beyond 100 °C, and owing to the volatilization of water molecules absorbed, a little weight loss was seen at ambient temperature. In the elimination of dye, Fe-porphyrin based COFs (UPC-CMP-1) demonstrate very effective

degrading and recyclability capability. $\bullet\text{O}^{2-}$ is more liable to be a reactive species when it comes to dye degradation. Furthermore, UPC-CMP-1 has a high selectivity for Congo red degradation when compared to a number of dyes for instance methyl orange, methyl red and Rhodamine B [147]. CTF-Th@SBA-15 is recently discovered to have excellent photocatalytic activity for dye degradation and alcohol oxidation [148]. The dye molecule was simpler to absorb owing to silica's hydrophilic characteristics. CTF-Th@SBA-15 has also shown effective catalytic activity of photocatalyst in solid as well as in metal-free mediums. Air pollution is caused by NO_x , which is created by automotive or industrial emissions. Recently it is revealed that CTF (CTF-HUST-HCl) with high crystallinity and facets (001) displayed exceptional NO_x photocatalytic efficacy [37b]. When compared to both amorphous and $\text{g-C}_3\text{N}_4$ CTF (CTF-HUST-1), the crystalline CTF-HUST-HCl produced fewer harmful byproducts (such as NO_2) during the photocatalytic processes.

In recent decades, there has been high and enormous advancement in photodegradation of pollutants using COFs photocatalysts; recently, it is reported that the presence of heterocyclic Nitrogen in specified COF-photocatalyst increase its efficiency for Cr (VI) photodegradation, Escherichia coli inhibitions, and paracetamol removal and degradation, for testing this four COF-based photocatalyst with heterocyclic Nitrogen at a different position is manufactured and tested. One COF without heterocyclic nitrogen atom is also tested. It is noted that COF-PDZ which possesses two heterocyclic nitrogen atoms at ortho position showed highest efficiency. In contrast, the lowest efficiency for COF-1 without the presence of heterocyclic nitrogen atom and all others have satisfactory results in eliminating or degrading pollutants (**Fig. 6b**) [149].

Furthermore, it is recently reported that vinylene bound-COF developed by different triazine and diacetylene scaffolds have effective removal and degradation efficiencies for phenol, norfloxacin and bacterial disinfection and shown to have >96 percent photocatalytic degradation

activity in just 15 minutes, providing a powerful foundation for the rational modification of the chemical architecture of COFs to upgrade their photocatalytic performance, thereby expanding the application.

It is also reported that COFs based inorganic semiconductors is thought to be an effectual strategy to increase the catalytic efficacy of photocatalysts for the destruction of organic contaminants. By co-precipitation, 3D covalent triazine bound COF was transferred with 2D layered BiOBr nanosheets to form a novel BiOBr/CTF-3D composite photocatalyst. Under visible light irradiation, the improved BiOBr/CTF-3D-2% photodegraded tetracycline hydrochloride (TC) delivered the photodegradation efficiency of 90.9 percent in 50 minutes. $\bullet\text{O}_2^-$ radicals produced by the reduction of O_2 with photo-excited electrons had a substantial function in the degradation of TC in the photocatalytic experiment. The low band gap of BiOBr/CTF-3D-2% (2.78 eV) boosted the absorption of visible light and enhanced the photocatalytic performance as compared to pure BiOBr (2.85 eV) (**Fig. 6c**)^[150].

Liu, et al.^[151] also proposed new COF-PD/AgI composites made by the precipitation of AgI on the exterior of COF-PD (**Fig. 7a**). This as-synthesized COF-PD/AgI blend-composites demonstrate outstanding VLD photocatalytic activity for *E. coli* disinfection along with decomposition of ACTP and RhB. Under the illumination of visible light, the COF-PD/AgI could entirely inhibit 1.5×10^6 CFU mL⁻¹ of *E. coli* in 40 minutes, whereas 5 mg/L of RhB and ACTP could be photocatalytically eliminated in 80 and 160 minutes, respectively. **Table 2** covers some of the most current research in the field of photocatalytic decomposition of organic contaminants.

The pharmaceutical industry has seen rapid growth, and pharmaceutical utilization is increasing day by day in order to maintain a healthy lifestyle. However, incorrect medication disposal into the aquatic system is wreaking havoc on our nature^[135]. Pharmaceuticals poisonous,

teratogenic, and mutagenic effects (ampicillin, diclofenac, sulfamethazine, and so on) pose a serious hazard to human health. COFs have been found to have the capacity to absorb medicines in the past few decades. Because COFs are hydrophobic, they are attracted to organic compounds ^[152]. Different adsorption methods, such as hydrogen bonding, affinities, pore size effect, electrostatic and pi- pi-interactions, and hydrophobic characteristic interactions, may be implicated in the adsorption approach between COF and medicines ^[153]. Mellah and colleagues created the fluoro integrated COF (TpBD-(CF₃)₂), by covalent bonding of 3,3'-bis(trifluoromethyl)benzidine with triformylphloroglucinol, and used for ibuprofen with adsorption capability of 119 mg/g (120 min). COF may be regenerated using isopropanol. The adsorption of ibuprofen on COF was aided by hydrophobic interactions ^[154].

Covalent organic framework had a number of problems at first due micro-crystalline structure, one of which was the separation of COFs following absorption in solution form. Modified COFs containing magnetic particles were synthesized for this purpose, which was accomplished by adding magnetic particles into the sekeleton of COFs. ThiS is accomplished by combining magnetic nanoparticles with a covalent organic framework and encasing them within the COF core shell. A recent publication said that magnetic COFs were produced by immersing TPB-DMTP-COFs in Fe³⁺/Fe²⁺ containing solutions. This COF was used as is for diclofenac and sulfamethazine adsorption. In 50 and 80 minutes, they found that for diclofenac the adsorption capability is 109 mg g⁻¹ wherein a sulfamethazine adsorption potential of 113.2 mg g⁻¹, respectively. The magnetic COF has a high segregation capacity from the solution. The adsorption phenomenon was attributed to the C–H interaction between COF and both medications ^[155].

Various photocatalytic systems have been used to photodegrade a variety of pharmaceutical-based pollutants ^[156]. However, photocatalysts have a number of limitations,

including a small surface area, low stability, and rapid hole and electron interaction ^[146b]. COFs have reportedly been employed to photocatalyzed the breakdown of contaminants ^[157]. COFs are highly porous polymeric materials with a high crystalline framework and a covalently bonded component structure. COFs construction units are held together in layers via interactions whereas few COFs have extensive networks. They are porous materials with a greater surface area, variable pore dimension, and great stability, therefore they are ideal photocatalysts ^[146b]. COFs were sensitive to visible light because they had a modest band gap and conjugation ^[158]. Changes in conjugation and the addition of other features may be used to create a band gap. COF has a distinct advantage over other catalysts in that it can isolate photo-generated charges via arrays and pores, allowing matter to be transferred. Triazine building blocks operate as light-harvesting sites in COFs, increasing electron release and decreasing electron-hole recombination ^[159]. Furthermore, COFs give considerable electron delocalization in the related families of olefins, benzimidazole, amides, and dioxins ^[160]. Under moderate reaction conditions, photo-excitation of COFs resulted in the formation of different reactive species for the activation of organic molecules. Electrons are frequently transferred between the catalyst and the substrate.

A triazine-bound COF material was generated by the incorporation of BiOBr nanoflake with a covalent triazine framework using a co-precipitation approach (CFT-3D). The CFT-3D/BiOBr demonstrated photocatalytic performance when exposed to light and might efficiently decompose ciprofloxacin and tetracycline. The photocatalytic performance of the composite containing 2% CFT-3D was exceptional. Superoxide radicals were active intermediates in the degeneration process, as demonstrated by the use of a trapping approach for intermediates. The increased photocatalytic activity was achieved due to the broad limit of optical adsorption. The presumably isolated electrons and holes formed photoactive electrons and holes in a synergistic

photocatalytic process, which increased antibiotic adsorption and transfer. Combining COFs with inorganic materials, according to this study, might open up new paths for pollution reduction ^[150]

5.3. Hydrogen Production Via COF-based Photocatalysts

Photocatalytic reduction systems produce H₂, which provides a huge chance to get tenable fuels, reduce the emission of greenhouse gases, and solve the problem of energy ^[161]. Many photocatalysts such as inorganic metal complexes ^[162] and amorphous conjugated polymers ^[93, 163], have also been investigated in order to enhance photocatalytic hydrogen production efficiency during the last few decades. However, their weak photocatalytic characteristics limit their applicability in hydrogen production ^[140a]. COFs offer a novel platform for H₂ evolution photocatalytic devices as a growing kind of crystalline, porous, and adjustable frameworks. Predesigned building blocks (**Fig. 8a**) connected by strong covalent connections enable high physicochemical stability, enhanced electrical and structural characteristics, and better photocatalytic activity ^[164].

Water splitting using photocatalyst is a novel technology for producing sustainable and clean energy from water by splitting photons (**Fig. 8b**). It is a step toward green and sustainable and renewable energy ^[165]. Photogenerated electron and hole pairs that subsist reunite travel in the direction of the photocatalytic surface, where OER and HER will occur, when exposed to light ^[166]. Movement of an electric field related to the electrolytes/semiconductor and co-catalyst/semiconductor interfaces allow photoinduced charge haulers to move to surface-active sites. These non-recombining carriers may oxidize and reduce water molecules to produce oxygen and hydrogen. To control the Gibbs free energy for hydrogen production, the photocatalyst must have a band gap of more than 1.23 eV, whereas > 1.6 eV band gap is required for the gas production and electron transfer phases ^[115].

At this time, a smaller number of COFs based materials have been studied for the reaction of water splitting. In preliminary studies, Stegbauer and co-workers manufactured solvothermally a newly synthesized hydrazone-based crystalline (TFPT)-COF through condensation reaction of 2,5-diethoxy-terephthalohydrazide with TFPT, which is considered to be first COF employed for the production of hydrogen by photocatalysis under visible light. After 52 hours of irradiation of visible light, TFPT-COF demonstrated incessant evolution of hydrogen from H₂O. In the photocatalytic process, the triazine in TFPT-COF played an important function. The photo-active TFPT-COF is a suitable system for investigating and controlling the photocatalytic process due to its high porosity, precise modular structure, and exact molecular organization ^[24]. As the degree of conjugation in the system grows, the delocalization of pi-electrons increases. As a result, functional conjugated chromophores are vital and important for transfer of charge over the COF surface. The very first COFs-based material employed for water splitting present a full conjugation network of type A₃B₂ structure^[167]. This COF showed long-term photostability, with a constant (HER) rate of up to 20 hours. Not only does the structure fit the redox potential of water when combined with the band gap, but it also has long-term stability. Due to presence of excess delocalized electrons positioned in the py, px, orbitals of N, the triazine unit is chosen as a fundamental building block in various azine-based COF. N₃-COF has gradually improved the activity of photocatalyst for hydrogen evolution when compared to N₁-COF and N₂-COF ^[59].

Zhao, et al. ^[168] reported the successful construction of vigorous COFs (NKCOFs = Nankai University COFs) premised on electron acceptor and donor matrices in which the donor functionalities of pyrenes can be employed for trapping of light, inspired by the configuration feature of photosystem I in the environment. Meanwhile, several functional groups of benzothiadiazole were used as electron acceptors to modify the capacity of light adsorption by

COFs. The NKCOF-108 is considered one of the most potent COFs without hybridization with other materials for photochemical hydrogen production under the visible light. Due to its unusual skeletal characteristics and broad range response to visible light, NKCOF-108 has a high hydrogen generation rate. The donor–acceptor configuration may facilitate the splitting of photogenerated carriers, and thoroughly organized layered structure guarantees that enough active positions are available for hydrogen generation.

2D ketoenamine-linked COF (TpPa-1-COF) containing single platinum atom with greater loading capacity were documented by Dong, et al. ^[169] (**Fig. 8c**). The optimized Pt1@TpPa-1 catalyst displays a greater photocatalytic production rate of hydrogen (719 mol/g h), an increased Pt loading of 0.72 wt. % and a 19.5 h⁻¹ turnover frequency, with 48- and 3.9-times activity equivalent to that of platinum nanoparticles/TpPa-1, respectively. The effective photogenerated charge mobility and isolation, along with thorough distribution of active sites of single platinum atom, are credited with the increased photocatalytic performance for H₂ evolution.

5.4. COF-based Photocatalysts for CO₂ Conversion

Owing to the high usage of fossil fuels, the rate of carbon dioxide in the atmosphere has grown tremendously. As a result, the emission of carbon dioxide as a by-product of fossil fuel combustion causing severe threat to the environmental and the greenhouse effect. Collecting and converting carbon dioxide into other valuable products as soon as feasible is critical. One key strategy for reaching this goal is photocatalytic transformation of CO₂ into methane and other valuable compounds utilizing COFs-based photocatalyst. Photocatalytic selective CO₂ reduction allows for the efficient use of solar energy and the production of environmentally benign solar fuels. For carbon dioxide conversion and reduction, a new generation 2-dimensional covalent organic framework with outstanding π -columnar array and a better framework have recently been

designed. Another breakthrough in this research is the invention of a COF based on the triazine structure, which has emerged as an artificial system of photosynthesis with outstanding carbon dioxide to formic acid conversion efficiency ^[170]. The modification of 2-dimensional CTF with β -NAD⁺ and corresponding rhodium complex, allowed visible light to be harvested while allowing electron transport from the CTF structure to the Rh center in an organized π -electron channel system. This COF has shown impressive stability and reusability, with a comparable conversion rate maintained across three cycles and no unusual reduction products discovered. Furthermore, no formic acid was formed in the absence of CO₂ or photocatalyst, this emphasizes the fact that carbon dioxide was the source of the product's production. In addition, when paired with Rh complex (Re (bpy)(CO)₃Cl) (**Fig. 8d**), another modified 2-dimensional COFs based triazine material converts carbon dioxide into CO with good efficacy and selectivity ^[119, 171].

The conversion of CO₂ into real-value products using solar energy offers a possible path to resolving the energy problem and reducing global warming ^[172]. The conventional photocatalyst based on the molecular and amorphous polymeric materials are facing some challenging difficulties such as poor selectivity, weak gas adsorption, and restricted active sites, and therefore it markedly affects the catalyst efficiency to reduce CO₂. On the other hand, COFs with special features gave a novel way to make CO₂ reduction photocatalyst (**Fig. 9a**) ^[173]. Because of their distinct chemical structures connected by covalent bonds, the bulk of COFs displayed exceptional stability in the different solvents, in comparison to the relatively poor endurance of most metal-organic frameworks in water. Photocatalytic CO₂ reduction systems benefit from the highly porous skeletons with enhanced surface-active sites for carbon dioxide capture and stabilization. Nevertheless, in highly crystalline COFs, organized building blocks and systematic layer stacking aids charge separation and photogenerated electron transport. For aqueous electrochemical CO₂

reduction, imine-bound COFs with cobalt porphyrin catalysts were produced as structural units^[172]. Notably, adding adjustable molecular moieties to COFs increased the efficacy of carbon dioxide reduction to carbon monoxide with excellent performance and selectivity. The research suggests that photocatalytic materials based on COFs might be used to reduce carbon dioxide. Under visible-light irradiation, azone-based COFs were used as photocatalysts to catalyze the reaction of carbon dioxide with water to produce methanol without the need for sacrificial agents^[127b, 164].

Many breakthroughs in COF-based photocatalysts have recently been achieved, and their adjustment has made them more capable and adaptable for usage in CO₂ conversion to valuable products. The synthesis of benzothiazole-linked COFs (TTzTp and BTzTp) with two distinct configurations of tris-benzothiazole triamine (TTz) or bis-benzothiazole diamine (BTz) with triformylphloroglucinol (Tp), the COFs manufactured from benzothiazole main units with comparatively double the gap in their pore sizes, showing great affection with carbon dioxide and light-harvest. The greater pore size of BTzTp had a higher transformation rate of carbon dioxide to carbon monoxide compared to TTzTp, owing to improved photocatalytic driving force, a broader band gap with prolonged isolated charge lifetime, and better charge carrier transfer due to enhanced crystalline percentage present in the framework (**Fig. 9b**)^[174]. Another notable advancement in this field is the synthesis of COFs catalysts that operate in solvent-free or solvent-less environments. In this regard, the synthesis of a 3-Dimensional-COF modified with zinc (II) catalyst (Zn@RIO-1) (**Fig. 9c**), which demonstrates an effective approach for producing alkylidene cyclic carbonates and oxazolidinones from propargylic alcohols by chemical conversion of carbon dioxide, both kinds of catalytic reactions are facilitated due to the microporous material, which has a large surface area (312.61 m² g⁻¹) at atmospheric CO₂ pressure.

More significantly, solvent-free circumstances provided fair to excellent conversions of desirable carbonates and oxazolidinone derivatives using readily recyclable and reused catalysts. From a sustainable standpoint, they were relevant and crucial due to the solvent-free circumstances and high conversion rate ^[175].

Ding, et al. ^[176] used a three-component one-pot Povarov reaction to create a porphyrin and imidazolium-ionic liquid (IL)-decorated and quinoline-bound COF (abbreviated as COF-P₁₋₁). The metallized COF-PI₂ is produced through post-synthetic metallization of COF-P₁₋₁ with Co (II) ions (**Fig. 9d**). When exposed to visible light, COF-PI₂ shows greater selectivity for CO₂ adsorption as well as a strong photothermal conversion capacity (T = 26 °C). The photothermal conversion of the Co (II)–porphyrin COF following visible light irradiation provides the required thermal energy for the reactions. More crucially, the CO₂ cyclization described here is a "window ledge" reaction that may continue easily in the presence of natural sunshine.

6. Conclusion and future prospective

Despite various recognized synthesis techniques and applications, the development of COFs is still in its early stages. Compared to many other porous framework materials, COFs are more adaptable and have a variety of chemical and physical characteristics. As they are created by strong covalent connections between linkers, COFs have a high degree of thermal and chemical stability. Additionally, COFs can be simply altered to fit a variety of applications. Materials made from COF are also crucial for a variety of purposes, such as environmental remediation. Organic linkers that may contain specific FGs are polymerized to create COFs. COFs can, however, also be post-synthetically functionalized to change their chemical and physical characteristics, enhancing their stability and effectiveness.

The latest high-quality publications included in this study show how COF-based materials are transforming environmental remediation and energy conversion research. They offer performance appraisal in a number of disciplines with significant environmental and energy implications because of their highly regular porous nature and durability. The most common uses of COFs include photocatalytic degradation of environmental pollutants including pharmaceuticals, organic materials, heavy metals and organic transformations as well production of hydrogen and conversion of CO₂. Contrary to MOFs, COFs do not include metals, which is an important distinction because numerous metals are thought to be poisonous or damaging to the surroundings and human health. This offers COFs an added advantage when used in environmental remediation. The use of COFs in energy and environmental science is still in its infancy despite their high potential because of their delayed development relative to other porous materials and complicated chemistry. As a result, a number of projects and difficulties must be resolved. First, it is currently difficult to synthesize highly organized COF structures, particularly those with high porous nature. Therefore, simple COF synthesis techniques ought to be created.

Second, for COFs, there is still no clear correlation between performance and structure. More research should be done on the assembly of COF-linked functional materials and the manipulation of their environment-related applications based on a perception of performance structure interrelationship (as observed, for example, in MOFs).

Third, COFs' ability to progress is additionally hampered by the fact that their antecedents, or COFs linkers, are sometimes exceedingly expensive. Linkers should be chosen with cost and ensemble approach in mind. COFs may become less expensive as research on COFs continues.

Fourth, the risks related to COF usage have not yet been evaluated. In order to estimate the viability of COFs for actual environmental utilization, assessments of their environmental risks should be made with increasing attention to the environmental applications of COFs.

Fifth, concerns for the ongoing development of COFs include the reuse and regeneration of COF-based products as well as the follow-up processing. The improved COFs can be used for effective energy conversion and effective degradation, of selected contaminants when the recyclability has been established.

Finally, by using the information gained with MOFs, COFs may be used in environmental cleanup more effectively. A fascinating type of porous crystalline materials with promising futures in energy and environmental applications is made up of both COFs and MOFs ^[177]. As a result, COF/MOF hybrids might be used, or some applications could make use of both materials advantages ^[178].

With additional research, COFs will be better understood, and more scientists will be motivated to use COF-based products. Because COFs are becoming increasingly popular, precursor materials and related technologies will eventually be more widely accessible and less expensive. Given everything said above, COFs have excellent potential as materials for environmental rehabilitation.

Conclusively, we have outlined current developments in photocatalytic COF reactions for energy and environmental applications in this review. As one of the most important advancements in photocatalytic applications, we first outlined the design and construction of COFs, including techniques for powder synthesis and chemical modification of COFs for simpler handling. Then, for environmental and energy applications, we discussed current developments in organic transformations, degradation of various pollutants, hydrogen evolution, and CO₂

conversion reactions. We expect that our analysis will help researchers better grasp the current progress and potential future applications of COF-based photocatalysts.

Acknowledgement

The King Fahd University of Petroleum and Minerals, Saudi Arabia is thankfully acknowledged for providing literature services. Author did not receive any funding to furnish this work.

Keywords

Covalent organic frameworks

CO₂ Conversion; hydrogen production

Organic transformations;

Powder COFs

Pollutants degradation

Conflict of interest disclosure

The representative authors have no conflict of interest to disclose in ant capacity, either competing or financial.

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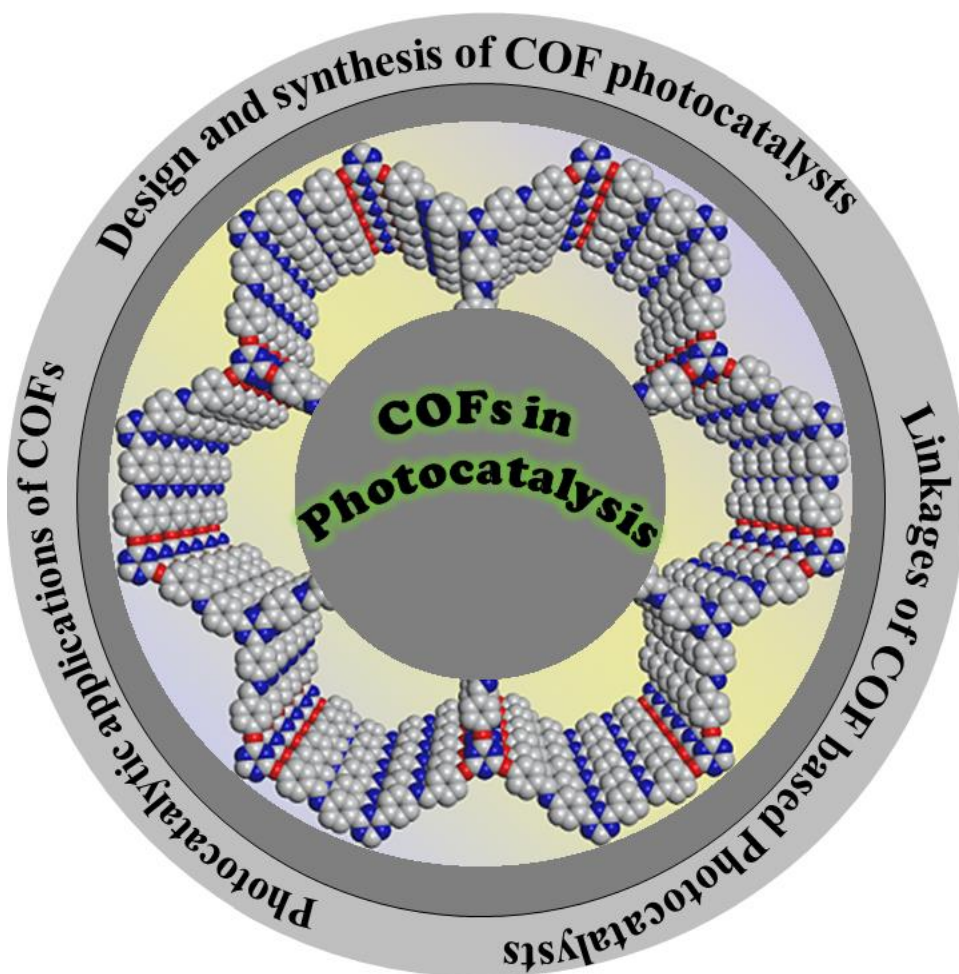
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TOC



The advancements in establishing the stable COFs structures and various post-synthetic modification approaches, along with the photocatalytic applications, such as organic transformations, degradation of emerging pollutants and removal of heavy metals, production of hydrogen and Conversion of carbon dioxide (CO_2) to useful products.

Figures

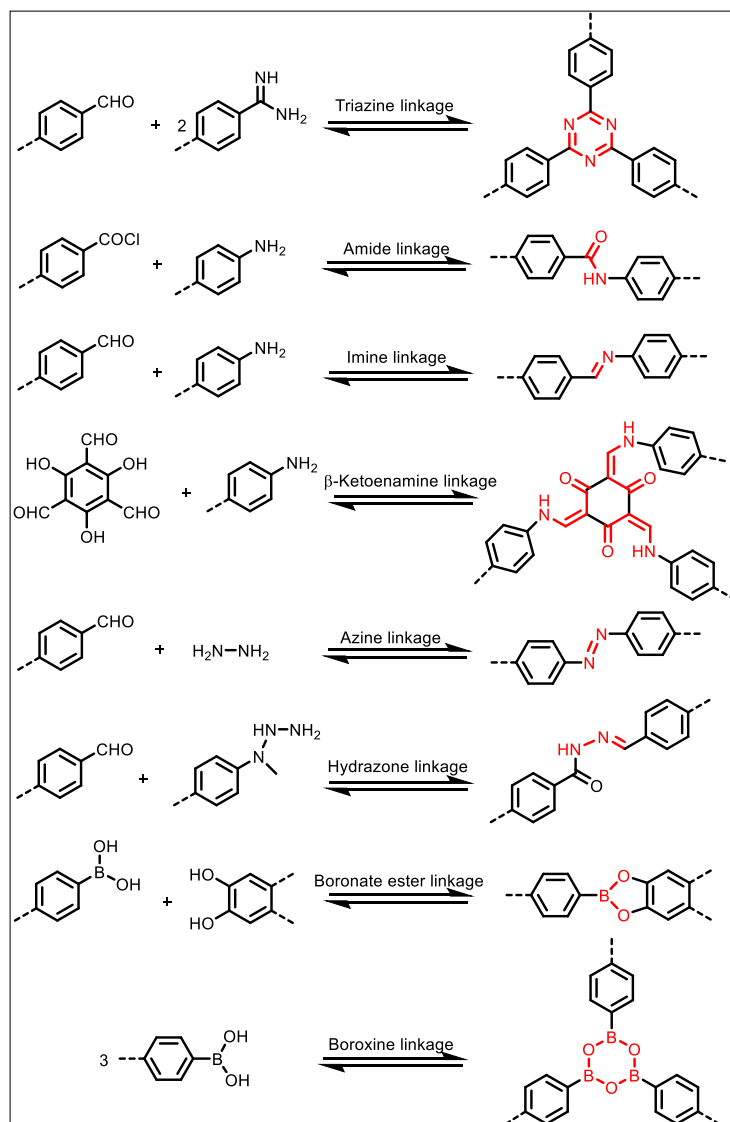


Fig. 1. Different types of linkages for the construction COFs.

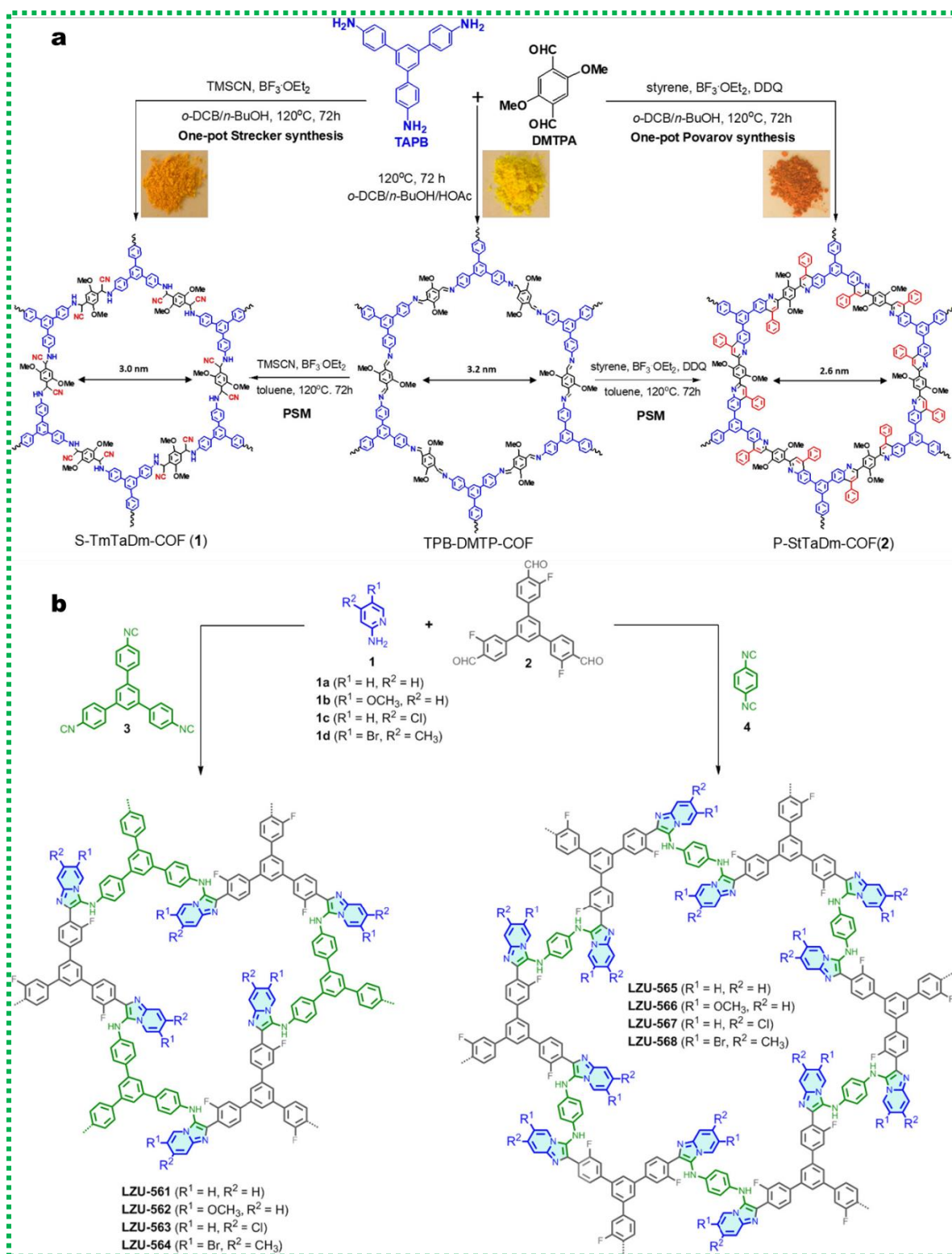


Fig. 2 (a) Synthesis of S-TmTaDm-COF (1) and P-StTaDm-COF (2) via One-Pot *In Situ* Approach and PSM, with the Corresponding Sample Photographs Shown in the Insets. Adopted from ref.^[81]

(b) Construction of Pyrimidazole-Based COFs via the One-Pot GBB Reaction among Isocyanides, 2-Aminopyridines, and Aldehydes. Adopted from ref.^[82]

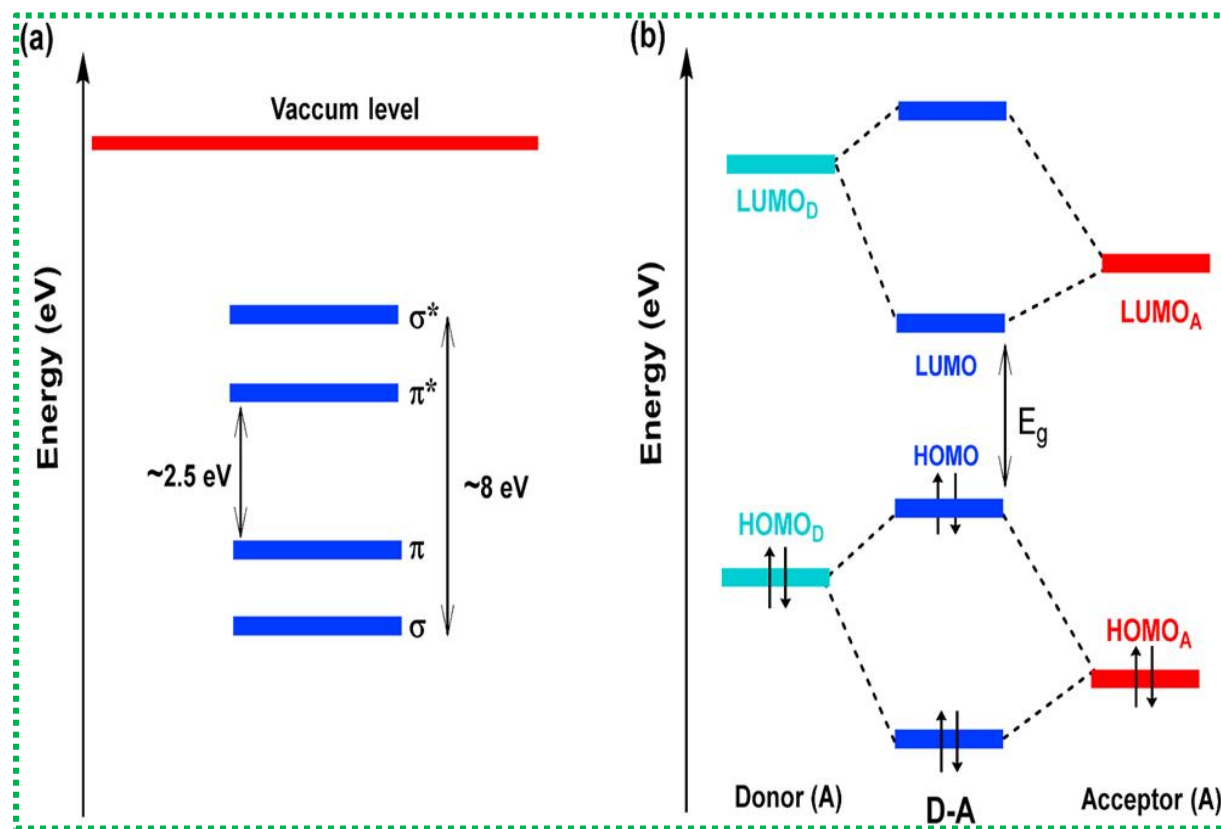


Fig. 3. (a) Lower energy level HOMO and high energy level LUMO shift in a pi-conjugated system; (b) Representation of the hybridization of molecular orbital levels in donor-acceptor (D-A) system through donor-acceptor intramolecular interplay^[146b].

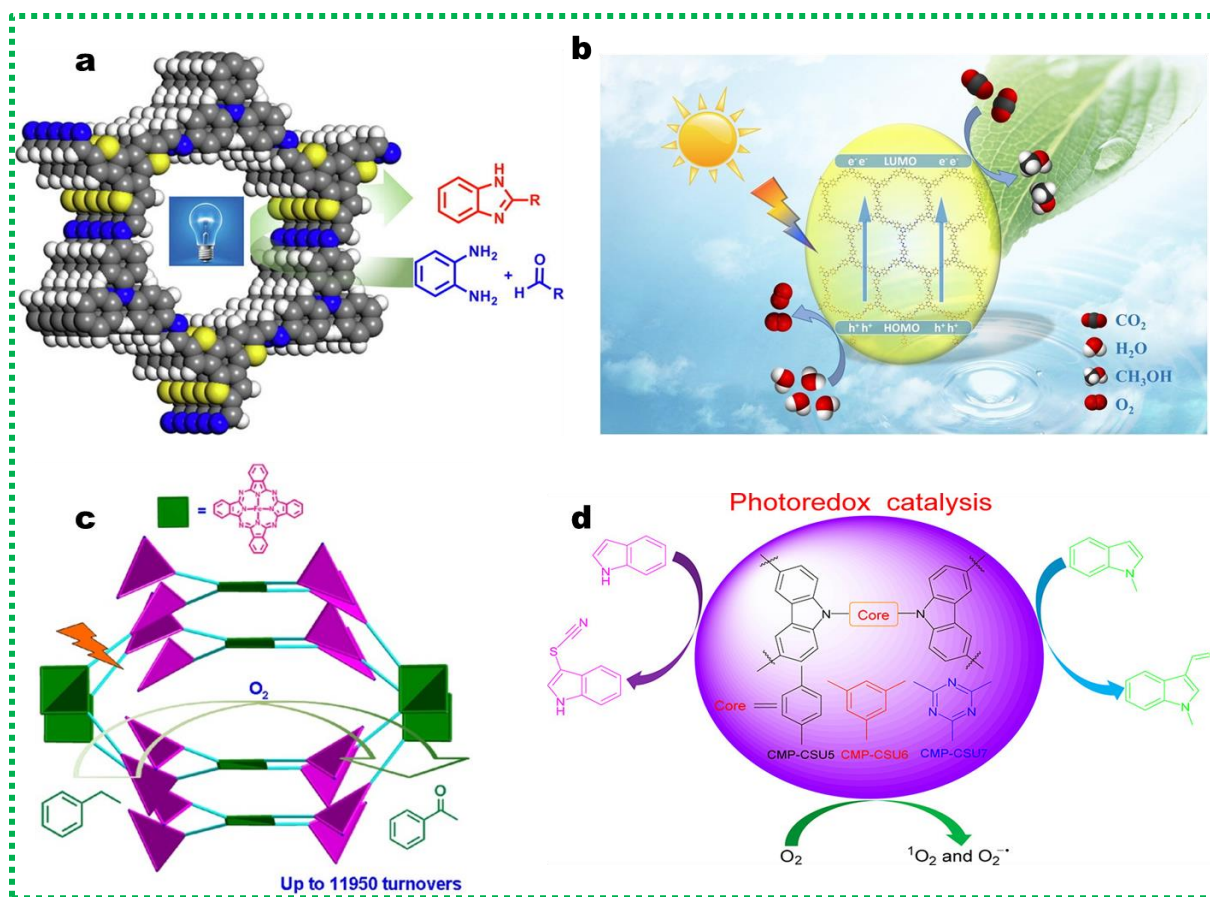


Fig. 4 (a) Schematic illustration of benzotrithiophene and triphenylamine based covalent organic frameworks as heterogeneous photocatalysts for benzimidazole synthesis. Adopted from ref. ^[127a]. (b) Illustration of Azine-based covalent organic frameworks as metal-free visible light photocatalysts for CO_2 reduction with H_2O . adopted from ref. ^[127b]. (c) illustration of CZJ-30 for highly efficient photocatalytic oxidation of arylalkanes. Adopted from ref. ^[127c]. (d) Illustration of Visible Light-Driven C-3 Functionalization of Indoles over Conjugated Microporous Polymers. Adopted from ref. ^[127d].

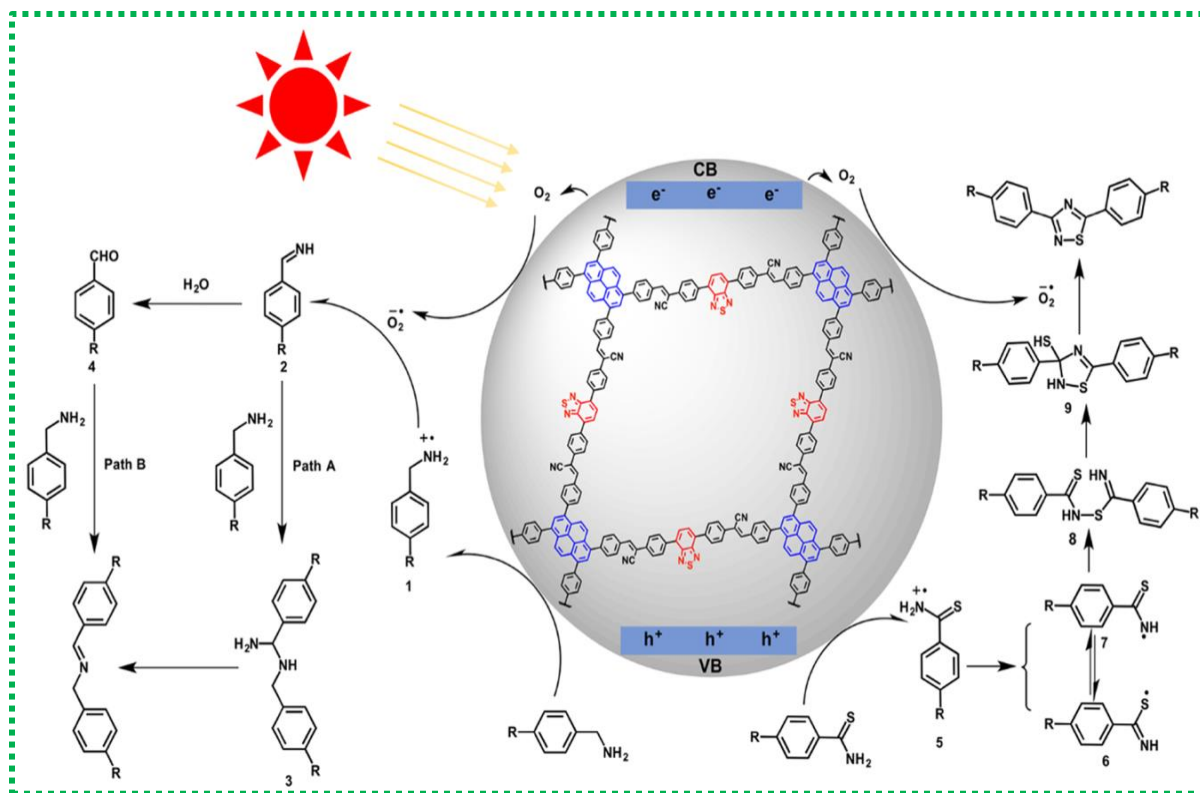


Fig. 5. The insight proposed photocatalytic mechanisms of Py-BSZ-COF mediated oxidative amine coupling and photocatalytic cyclization of thioamide to 1,2,4-thiadiazole ^[179].

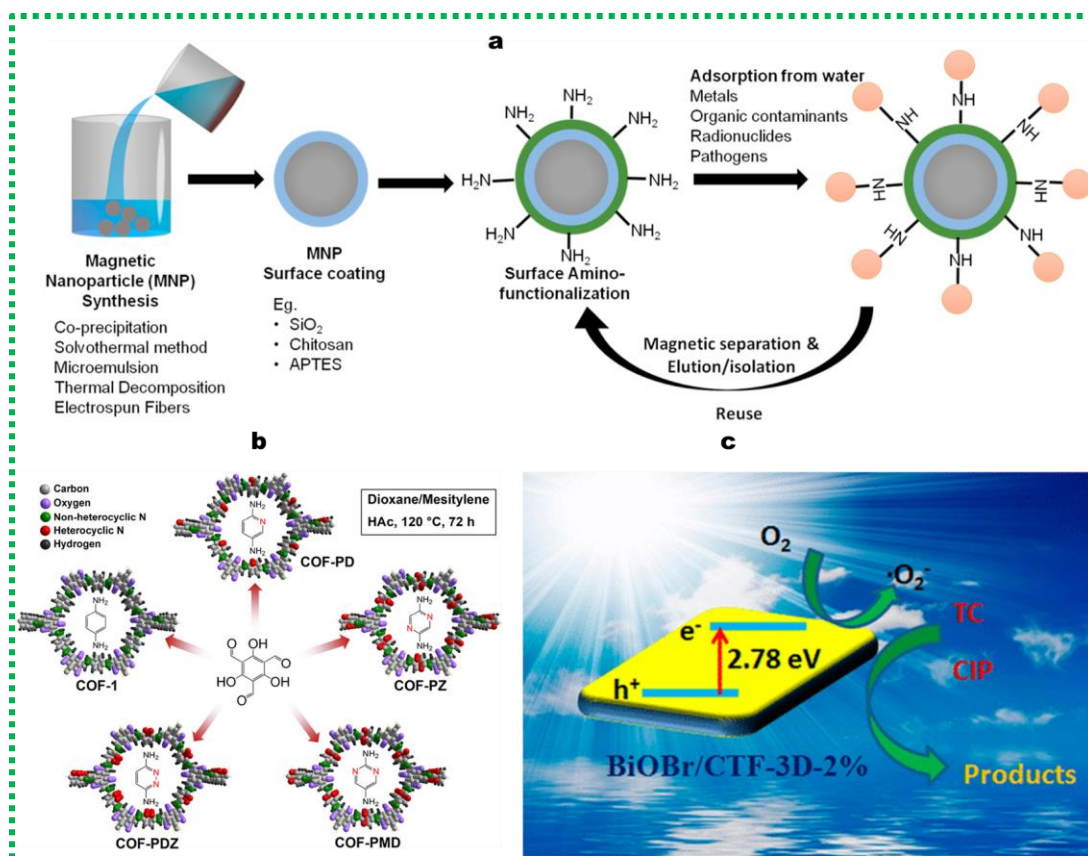


Fig. 6 (a) Synthesis of magnetic nanoparticles and surface functionalization to achieve aminated MNPs for water remediation. Adopted from ref. ^[146a]. (b) Synthesis and Chemical Structures of COF-1, COF-PD, COF-PZ, COF-PMD, and COF-PDZ. Adopted from ref. ^[149]. (c) Illustration of covalent Triazine Framework Modified BiOBr Nanoflake with Enhanced Photocatalytic Activity for Antibiotic Removal. Adopted from ref. ^[150].

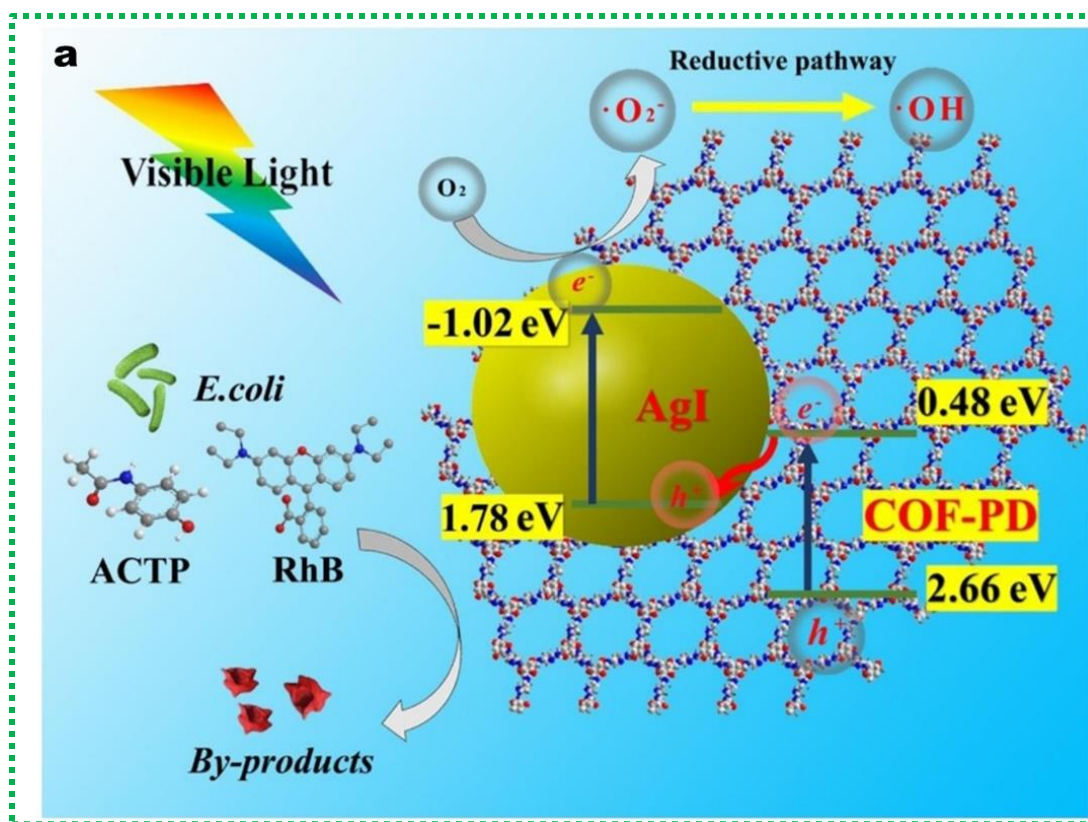


Fig. 7 (a) Illustration of AgI modified covalent organic frameworks for effective bacterial disinfection and organic pollutant degradation under visible light irradiation. Adopted from ref. [151].

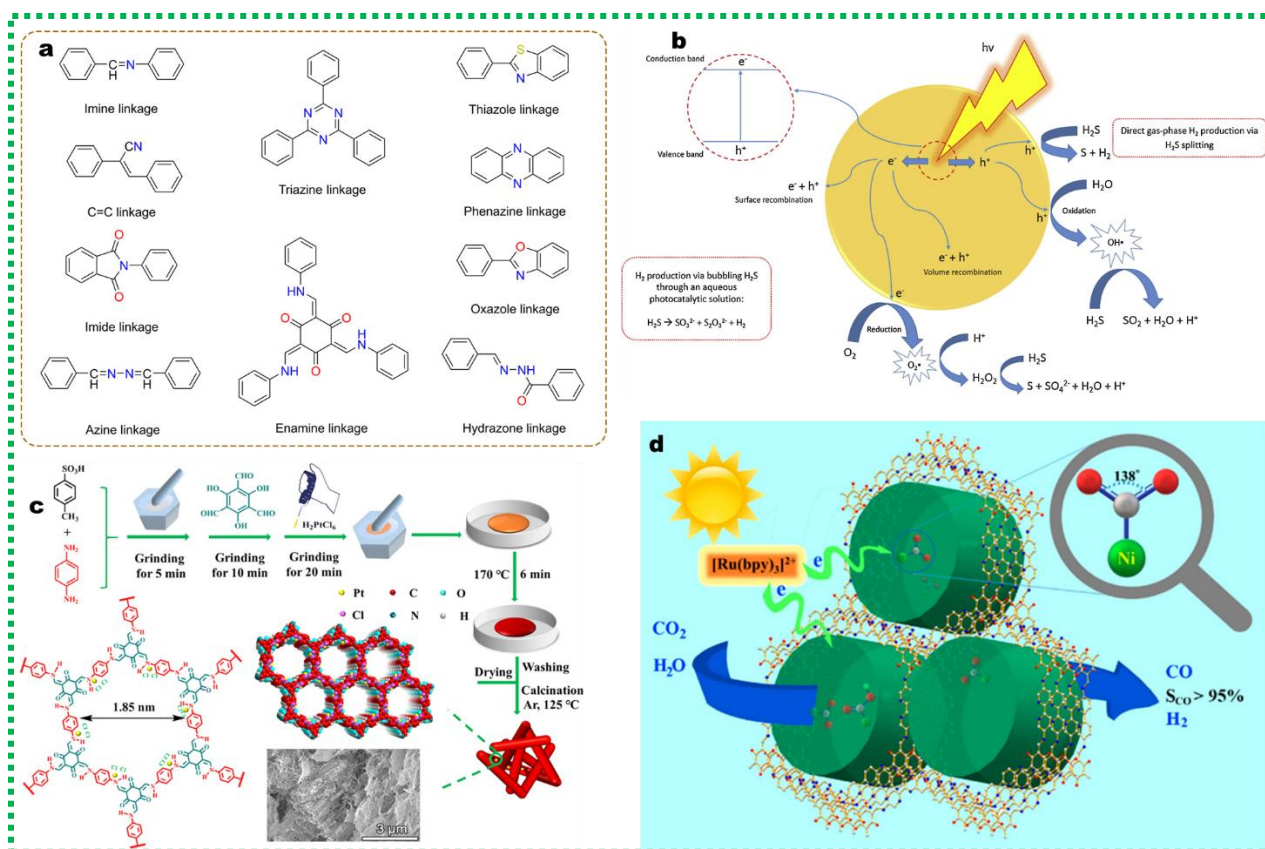


Fig. 8 (a) Various linkage modes in COFs applied in photocatalytic reactions. Adopted from ref. [164]. (b) Schematic of the fundamental mechanisms and reactions involved in the photocatalytic removal of gaseous H₂S as well as production of hydrogen. Adopted from ref. [165]. (c) Schematic Illustration for the Preparation of Single-Atom Pt Anchored on TpPa-1-COF. Adopted from ref. [169]. (d) Schematic diagram of photocatalytic selective reduction of CO₂ over Ni-TpBpy. Adopted from ref. [171].

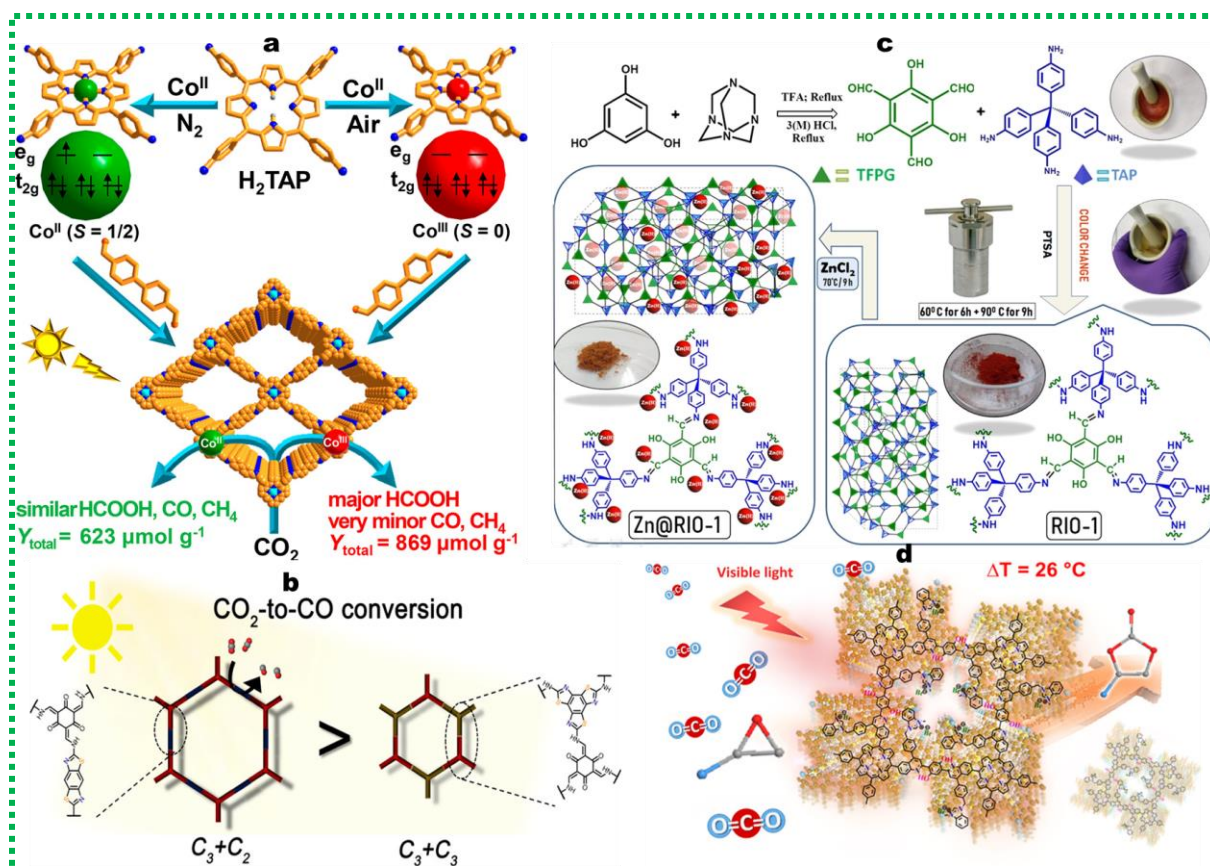


Fig. 9 (a) Rational Fabrication of COF-367-Co Featuring Different Spin States of Co Ions toward Photocatalytic CO₂ Reduction. Adopted from ref. ^[173]. (b) Benzothiazole-Based Covalent Organic Frameworks with Different Symmetrical Combinations for Photocatalytic CO₂ Conversion. Adopted from ref. ^[174]. (c) Synthesis Route of the Zn@RIO-1 Catalyst. Adopted from ref. ^[175]. (d) Illustration of Catalytic CO₂ Cycloaddition via Visible-Light-Induced Photothermal Conversion. Adopted from ref. ^[176].

Tables

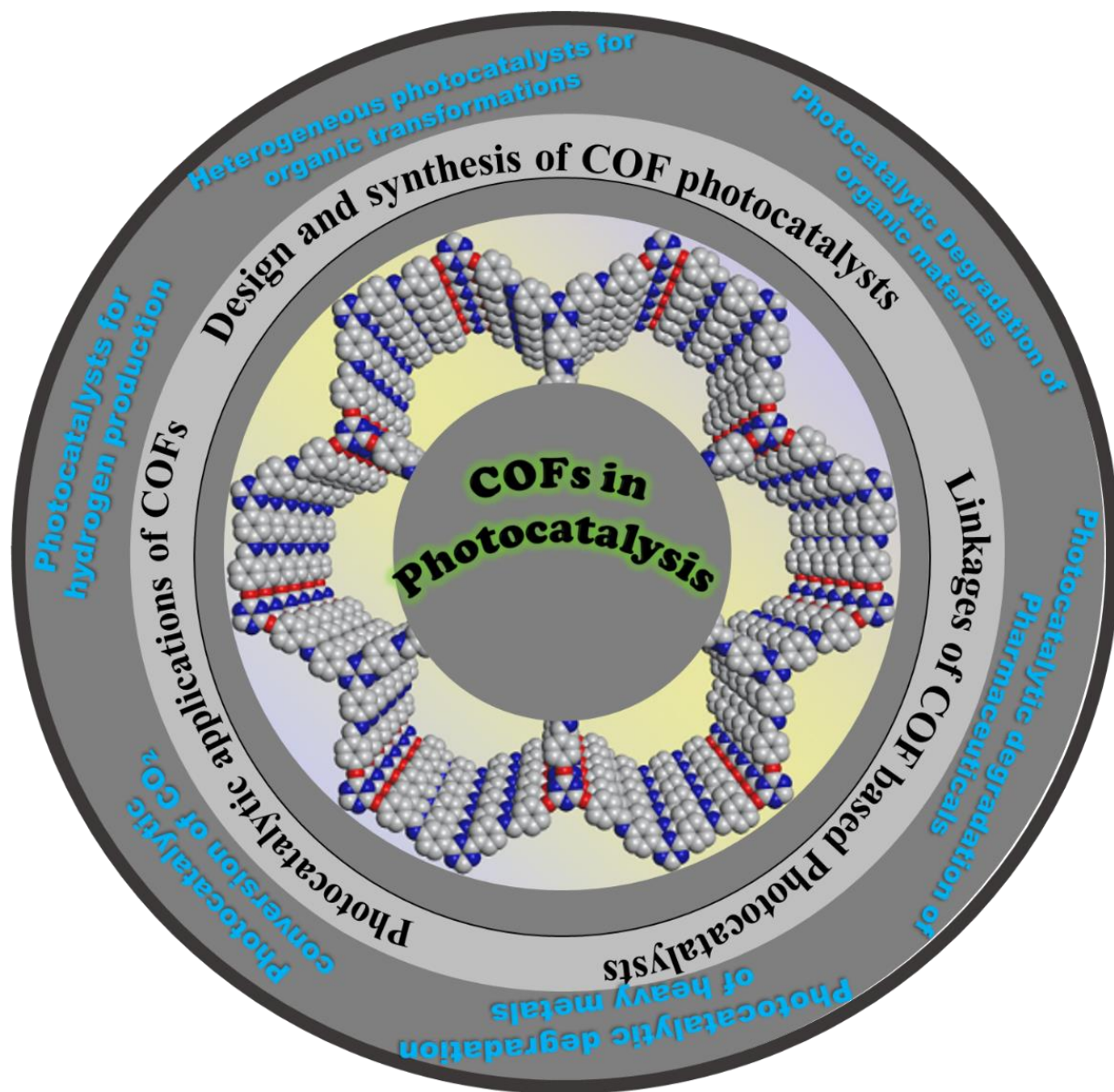
Table 1. Advancement in Catalytic Transformations of Organic Compounds using Photocatalyst System in recent times.

COF Photocatalyst	Catalyzed Reaction	Illumination	Conversions/Yield	Reference
Ir,Ni@Phen-COF	Cross-Coupling of Potassium Benzyltrifluoroborates and Aryl Bromides	Blue LEDs, 23 W, 450 nm	90%	[181]
Py-BSZ-COF	Photocatalytic Oxidative Amine Coupling and Thioamide Cyclization	LED light 520nm	99%	[179]
AQ-COF	Photocatalytic Selective Oxidation of Sulfides	300 W Xe lamp (400~780 nm)	99%	[182]
TTR-COF	Photocatalytic Hydrogen Production from Seawater	300 W xenon lamp (420 nm)	501 $\mu\text{mol g}^{-1}$ Hydrogen production in 4 hours	[111]
2D–2D SnS ₂ /TpPa-1-COF heterojunction Photocatalyst	Enhanced Solar-Driven Hydrogen Evolution	Visible light up to 600nm	37.11 $\mu\text{mol h}^{-1}$ Hydrogen Production	[183]
NCTF-1	Photocatalytic Conversion of CO ₂ into CH ₄	Visible Region	Conversion up to 85%	[184]

UiO-66- NH ₂ @Au@COF Core-Shell	Selective Oxidation of Amines into Imines	Visible light induced	66.9% yield of imines	[185]
TBPA-sp ² C-COF, TPA-sp ² C-COF	photocatalytic oxidative organic transformations reactions	23 W white LED bulb	Approximately more than 90% conversion for all reactions	[186]
TFB-BMTH	Oxidative hydroxylation of arylboronic acids	Blue LED lamp (30 W, $\lambda = 454$ nm)	99% yield	[72]
Por-DETH-COF	Selective aerobic oxidation of benzylamine to imines	Blue LED of $\lambda_p =$ 460nm	93% conversion and 99% selectivity	[70]
TFPG- DAAQ-COF with Co-Catalyst	formic acid synthesis through carbon dioxide reduction	445nm visible light source	-----	[187]
QH-COF-1 and QH-COF-2	asymmetric α - alkylation of aldehydes	30 W blue LEDs	QH-COF-1 = 75% yield and 91% ee yield QH-COF-2 = 60% yield and 91% ee	[84]
TiO ₂ @CTF-Py	Photoreduction of CO ₂ to CO with H ₂ O	Visible light source	-----	[188]

Table 2. Some of recent works on COFs based photocatalytic degradation of organic contaminants.

Framework	Pollutants	Light source	vc	Degradation (%)	Catalyst (mass)	References
Ag ₃ PO ₄ /TpPa-1-COF	Pesticide pymetrozine (PYM) and Rhodamine B (Rh. B)	300 W Xe lamp ≥ 420 nm	1	PYM =99.3% and Rh.B = 96.7%	20 mg	[189]
DA-CTF	Rhodamine B (RhB) and methylene blue (MB)	Visible light (380–750 nm)	1	RhB = 92.3% and MB = 99.2%	8 mg	[190]
COF-PRD	5 bisphenols (BPA, BPB, BPF, BPZ, BPAP)	Visible light driven	2.5	n.a	18 mg	[191]
MoS ₂ /COF	Tetracycline (TC) and Rhodamine B (RhB).	300W Xeon Lamp	0.5 for RhB 1 for TC	RhB = 98% and TC =85.9%	10 mg	[192]
EDA-TMT, TDA-TMT and EDA-TMT	MB, bacterial disinfection, norfloxacin and phenol	Visible light	0.25 for BDA-TMT	BDA-TMT=>96% degradation activity		[193]



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Dr. Tahir Rasheed is currently working as a researcher at Interdisciplinary Research Center for Advanced Materials, King Fahd University of Petroleum and Minerals, Saudi Arabia. Dr. Rasheed completed his Ph.D. degree and postdoctoral research in Polymer Chemistry from the School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, China. His research interests focus on multiple disciplines including controllable synthesis, characterization and Self-assembly of Polymeric materials, polymer-based composites, nanomaterials & nanocomposites, hybrid nanocomposites, with special emphasis on their potential applications in the field of sensing and biosensing, electrocatalysis, degradation and quantification of various emerging pollutants and energy storage devices.



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