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Metal-organic frameworks: Photocatalytic application in organic syntheses

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Spotlight

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Mahrokh Farrokh was born in Qom, Iran, in 1999. She received her B.Sc. in Applied Chemistry (2022) from Bu-Ali Sina University, Iran. She was also accepted for an M.Sc. in Organic Chemistry under the supervision of Prof. Mohammad Ali Zolfigol at Bu-Ali Sina University. Her research interest is the synthesis, characterization, and applications of homogeneous and heterogeneous reagents and catalysts in organic synthesis.

Introduction

A group of porous and solid materials called metal-organic frameworks (MOF), in which metal atoms are connected by organic bonds in a network and are responsible for creating spaces and holes in the network for the coordination link of the metal-ligand. The stability of MOFs depends on the strength of coordination forces that have average energy between covalent bonds MOFs are excellent materials that can be synthesized with any metal (monometallic or bimetallic) and also have characteristics such as large pore size and surface area, network stability, specific unsaturated metal sites, ease of design, and synthesis, thermal stability, regular and discrete structure, low density are that this class of materials have many catalytic applications. In recent years, metal-organic frameworks (MOFs) have been developed and are widely used in optics, sensors, gas adsorption and separation, gas storage, catalysis, drug delivery, etc MOFs are structurally tunable due to their high porosity and high surface area [1–5]. Photocatalysis is a process of converting solar energy into chemicals, for example, reduction and oxidation reactions initiated by electrons (e^-) and holes (h^+), respectively. Basically, the $e^- - h^+$ excited pair formed after photocatalysts absorb photons with energy higher than its band gap ($Er \geq EBG$), and in turn can initiate oxidation ($D \longrightarrow D^+$) and reduction ($A \longrightarrow A^-$) start. In these reactions, semiconductors are mostly used because of the relatively small and appropriate band gap, which is done by transferring electrons from the valence band to the condensation band and creating the aforementioned holes. The advantages of these types of reactions include less energy consumption, sometimes less reaction time, destruction of pollutants, production of H_2 and O_2, production of less waste, and production of safer materials [6–15]. MOFs, due to their high stability, flexibility, and the variety of blocks they have, as well as the variety of their building blocks, provide the possibility of creating a photoactive catalyst with the help of photoactive organic ligands. This ability of MOFs offers a new approach to heterogeneous catalysts under the title of photocatalysts and photocatalytic transformations.

Due to their high surface area and large number of holes, metal-organic frameworks trap excited electrons in the holes and increase the photocatalytic reaction potential due to their high thermal stability. Metal-organic frameworks have unique characteristics due to their porosity, and due to the possibility of synthesizing them with different metals, they have excellent light transmission capabilities and perform photocatalytic processes well. Environmental issues, energy crises, and global warming have caused concern and encouraged researchers to develop sustainable and clean energy sources. Photocatalytic application is one of the most important applications of metal-organic frameworks. Here, an attempt has been made to briefly review the photocatalytic applications of metal-organic frameworks in chemical processes such as cyclization, oxidation/reduction, cross-coupling reactions, etc. (Figure 1) [16–18].

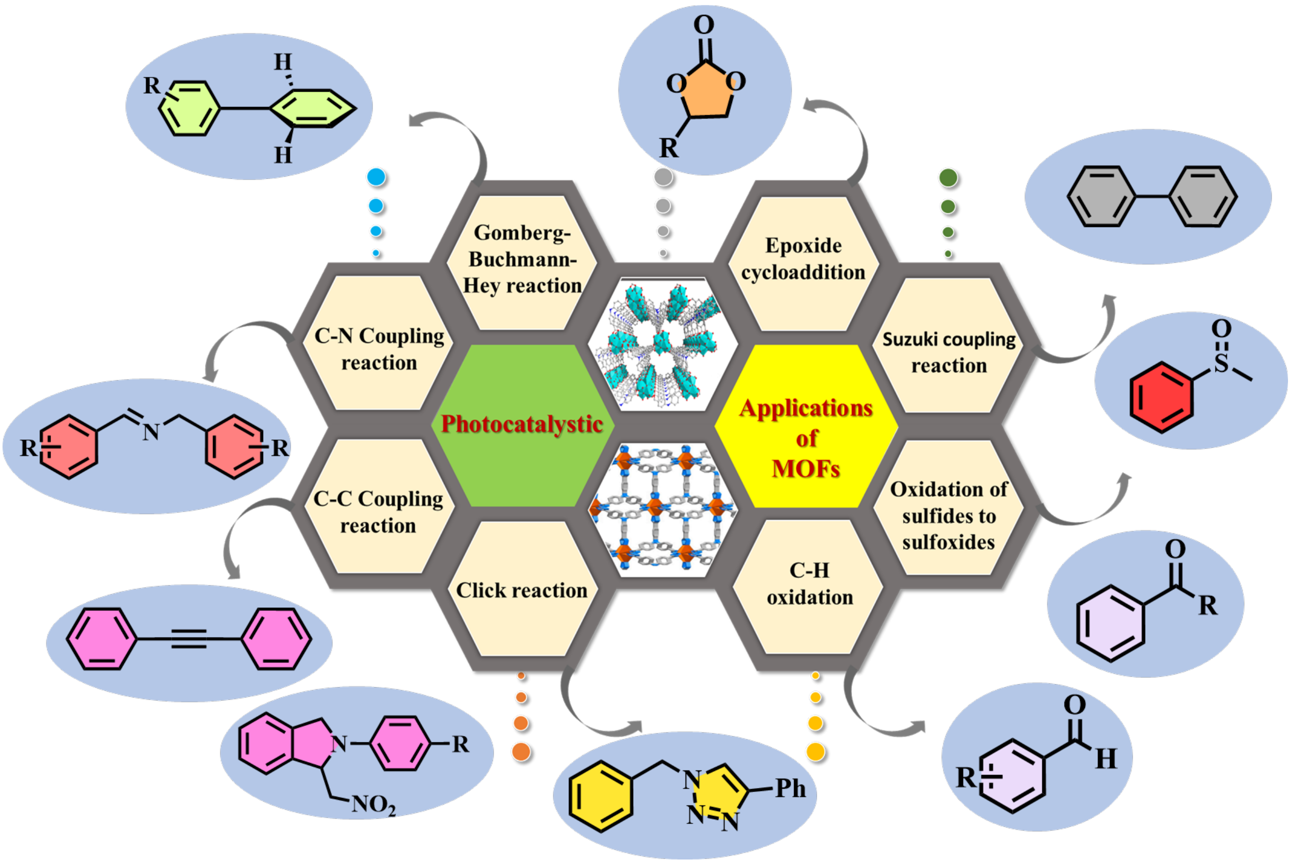
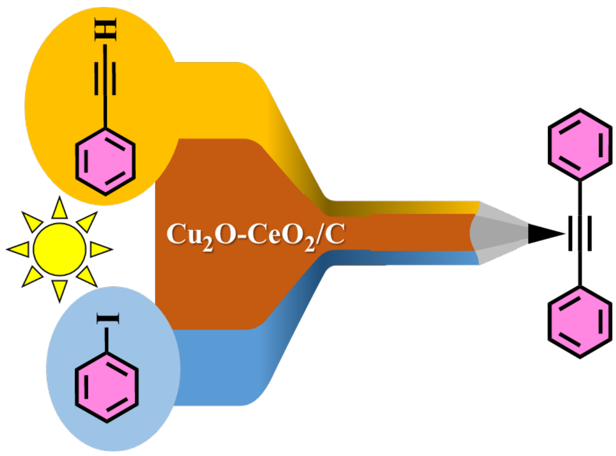


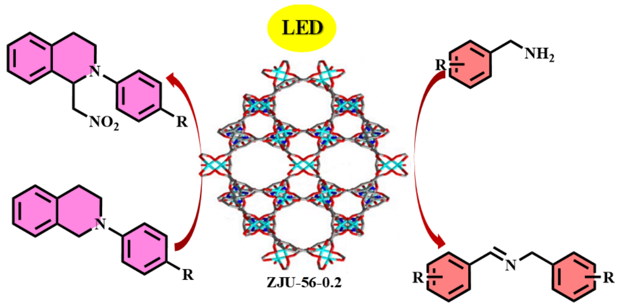
Figure 1. Various applications of metal-organic frameworks (MOFs) in photocatalytic reaction.

Abstract:

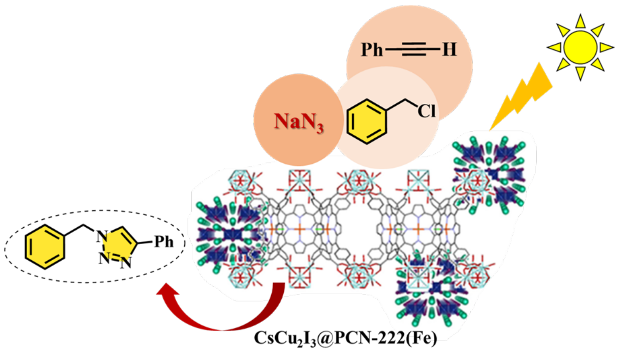
(A) Rajendra et al. successfully synthesized the visible light active catalyst Cu_2O-CeO_2/C by carbonization of CuCe-BTC bimetallic MOF. Then this photocatalyst has been used in the reaction of C–C pair with photocatalytic technique. The produced Cu_2O-CeO_2/C photocatalyst has shown good performance in the Sonogashira cross-coupling reaction. It should be noted that for the synthesis of commercial and industrial compounds with a stable catalytic process with visible light, it is essential for chemists to use a light-based catalyst such as Cu_2O-CeO_2, which is cheap and available [19].



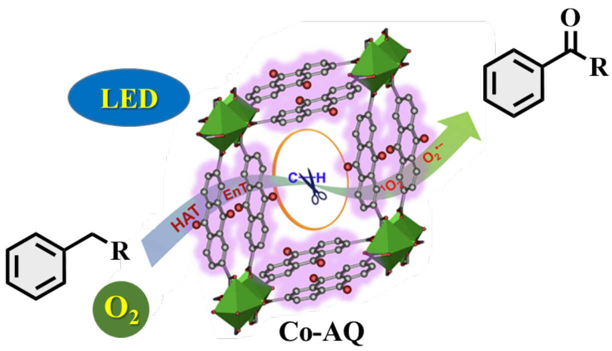
(B) Chuning Duan et al. have synthesized ZJU-56, which are heterogeneous porous catalysts with photocatalytic activity. The photocatalytic properties of this catalyst have been evaluated in the oxidative reaction of C–N benzylamine to form benzylidene-1-phenylmethanamine and the coupling of C–C N-phenyltetrahydroisoquinoline with nitromethane. Increasing the ability to absorb two photons has improved the photocatalytic efficiency under LED irradiation, which shows the importance of its synthesis [20].



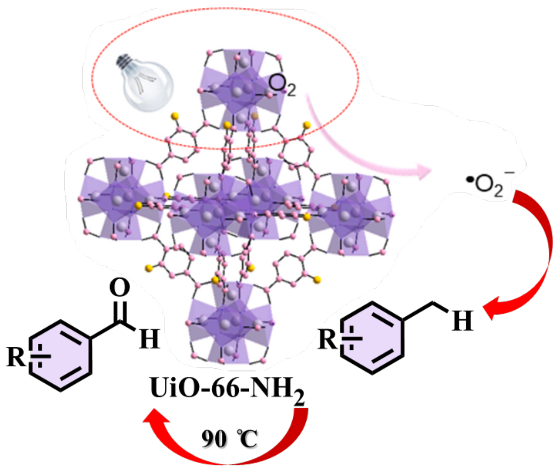
(C) Click reactions are one of the most important reactions in organic chemistry. Accordingly, Mustafa Khajeh et al. developed an innovative strategy combining iron porphyrin MOF, PCN-222(Fe), and non-toxic lead-free perovskite halide $CsCu_2I_3$, embedded in MOF channels [$CsCu_2I_3$@PCN-222(Fe)]. $CsCu_2I_3$@PCN-222(Fe) hybrid materials have been investigated as multifunctional heterogeneous catalysts for Cu(I)-catalyzed alkyne azide cycloaddition and one-pot/convonagel photoselective oxidation condensation cascade reaction. It should be noted that the $CsCu_2I_3$@PCN-222(Fe) catalyst showed higher efficiency than the individual components, including $CsCu_2I_3$ and PCN-222 (Fe), but also showed better efficiency and performance than many other catalysts, according to the results obtained. The synergistic effects of PCN-222(Fe) host and $CsCu_2I_3$ nanocrystals are attributed [21].



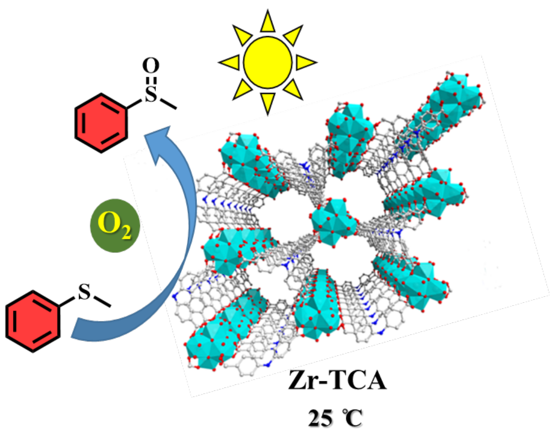
(D) Liang Zhao et al., by cleverly incorporating anthraquinone, have reported an anthraquinone-based MOF as a bifunctional heterogeneous photocatalytic platform for simultaneous activation of C(sp3)–H bonds and oxygen for C–H bond oxidation with UV-visible lights which turns into an aldehyde or aromatic ketone. Multifunctional catalytic platforms have this feature, allowing us to gain essential insights into the synergistic activation of C–H bonds and oxygen to improve oxidation. The excellent chemical stability and photocatalytic effects obtained through the immobilization of anthraquinone in a MOF have given special value to this research [22].



(E) Mi Tang et al., for the first time, reported a zirconium-based MOF (UiO-66-NH_2) as a heterogeneous catalyst with photocatalytic application for the conversion of benzyl halides to the corresponding aromatic aldehydes with high efficiency. In the presence of oxygen and DMF as solvents in this transformation, photoelectrons generated from UiO-66-NH_2 under visible light catalyzed O_2 and formed $O_2^{\bullet-}$, which was associated with high efficiency and selectivity [23].



(F) Pi-Zhu Li et al. successfully synthesized a highly porous and stable Zr-based MOF (Zr-TCA) using triphenylamine-based tricarboxylic acid as an organic ligand. The conducted research shows that the photoactive properties of MOF made of triphenylamine-based ligands are well preserved. It shows high catalytic activity in the aerobic oxidation of sulfides through the production of superoxide radical anion ($O_2^{\bullet-}$) under light irradiation. Such systems can significantly contribute to their application in transforming functional groups and generate many functional groups during the reaction [24].



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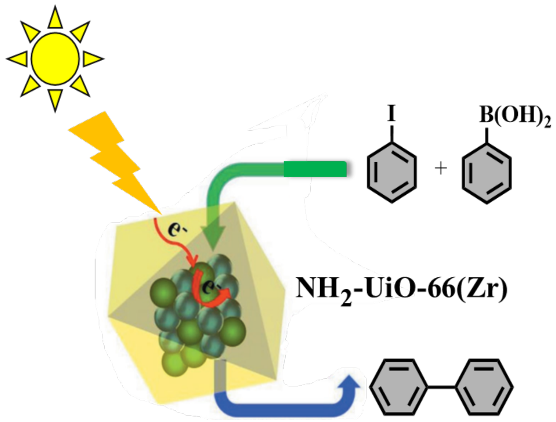
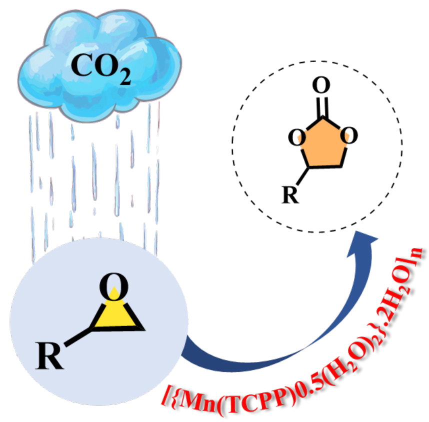
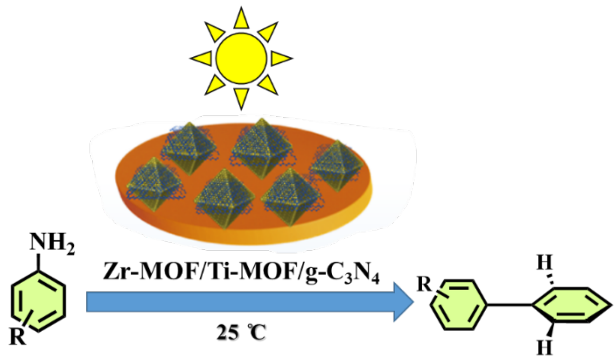
(G) Jinlin Long et al. presented the synthesis of CuPd@NH_2-UiO-66(Zr) and CuPd@NH_2-UiO-66(Zr) with small bimetallic CuPd nanoclusters encapsulated through solvent impregnation and chemical reduction with $NaBH_4$. This research highlights the potential and power of using MOFs as a smart photocatalyst for the construction of multifunctional catalysts and organic transformations under light. CuPd@NH_2-UiO-66(Zr), which is a bimetallic MOF, co-presence of palladium and copper as electron mediators to facilitate the electron transfer generated from NH_2-UiO-66(Zr) for the induced Suzuki coupling reaction with Light works very efficiently [25].



(H) Fabrication of a three-dimensional supramolecular microporous metal-organic framework of manganese (II), $[\{Mn(TCPP)0.5(H_2O)_2\} \cdot 2H_2O]_n$ (MOF) shows that an unprecedented visible light-assisted cycloaddition of CO_2 with epoxides to produce cyclic carbonates under mild reaction conditions at room temperature and 1 bar of CO_2. The catalytic conversion rate of CO_2 with visible light irradiation has been increased due to the good visible light absorption property of the porphyrin bond, which shows the importance of its synthesis. The increase in the catalytic activity of MOF1 under visible light irradiation is attributed to the in situ generation of thermal energy by the photothermal effect [26].



(I) In 2023, Zolfiegol et al. heterogeneous photocatalyst named Zr-MOF/Ti-MOF/g-C_3N_4 was synthesized by orderly growth of UiO-66(Zr) and g-C_3N_4 nanosheets on metal-organic framework MIL-125(Ti)-NH_2 with the aim of Gomberg-Buchmann-Hey reaction reaction. Visible light irradiation has a significant effect on this reaction, so the dual Z-Scheme heterojunction was used as a highly efficient photocatalyst to form C−C bonds through diazonium salts. Based on the findings, the presence of Zr and Ti metals on MOF-on-MOF and g-C_3N_4 nanosheets can significantly affect the separation of photogenerated electron-hole pairs and thus increase the photocatalytic performance [27].



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

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

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