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Porphyrin-Based Metal-Organic Frameworks as Sustainable Photocatalysts for Micropollutant Degradation: A critical review on structure, mechanism and future perspectives

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Abstract

The growing concerns due to the presence of micropollutants in the environment necessitate the development of advanced and sustainable technologies for their degradation. For this problem, Porphyrin-based Metal-Organic Frameworks (P-MOFs) are used as highly efficient photocatalysts for the degradation of micropollutants. The incorporation of metal ions into Porphyrin moieties offers a synergistic approach, combining the unique properties of P-MOFs with porosity, redox behaviour and band gap energy. This critical review provides an overview of the structures, synthesis methods, and mechanisms underlying the photocatalytic activity of P-MOFs. Recent advances and research findings are discussed, highlighting the promising outcomes and breakthroughs achieved. Performance evaluations, comparative analyses, and considerations of practical applications are explored, emphasizing the environmental impact and sustainability of P-MOFs. Moreover, current challenges, future perspectives and proposing avenues for further research to enhance the efficacy of P-MOFs in addressing environmental remediation are discussed. The review concludes with insights that P-MOFs can be used as effective and stable photocatalysts for the degradation of a wide ranges of micropollutants without losing their activity.

Keywords: Porphyrins, MOFs, micropollutants, sustainable, photocatalysis

Highlights

- Porphyrin based MOFs (P-MOFs) exhibit superior properties compared to traditional photocatalysts (e.g. TiO_2, ZnO).
- The metal nodes in the P-MOF play a crucial role in facilitating efficient charge separation.
- Porphyrin based MOFs exhibit excellent stability under photocatalytic conditions and can be easily recovered.
- A wide range of micropollutants including organic and inorganic can be degraded by using P-MOFs.
- P-MOFs act as dual function catalysts i.e. for the adsorption as well as photodegradation of micropollutants.

1. Introduction

In recent years, the growing awareness of environmental pollution, particularly the contamination of water bodies by micropollutants, has spurred extensive research into the development of innovative and sustainable remediation techniques. Micropollutants, which include a wide range of chemicals such as pharmaceuticals, personal care products, pesticides, and microplastics, pose significant risks to both aquatic ecosystems and human health, even at low concentrations. To address these challenges, a range of remediation methods have been investigated, encompassing physical, chemical, and biological approaches.[1,2] Traditional methods such as adsorption, coagulation, membrane filtration, biological degradation, and chemical treatments like chlorination, have shown varying degrees of effectiveness in the removal of micropollutants from water. However, these methods often suffer from limitations, including incomplete micropollutants removal, secondary pollution, and high operational costs.[3] Consequently, research for more efficient and sustainable alternatives continues. Among emerging technologies, advanced oxidation processes (AOPs), particularly photocatalysis, have gained significant attention as a promising solution for micropollutants degradation. Photocatalysis, which involves the generation of reactive oxygen species (ROS) under light irradiation in the presence of a photocatalyst, offers a highly efficient and environmentally benign pathway for breaking down a wide range of micropollutants into harmless by-products such as CO_2 and H_2O.[4-6] This approach is attractive due to its potential for high efficiency, environmental benignity, and compatibility with solar energy. Despite the progress made, further exploration is required to optimise photocatalytic materials, improve process efficiency, and scale up these solutions for real-world applications. A comparative table (Table 1) of Porphyrin based MOFs with traditional photocatalysts with reference to parameters i.e. band gap energy, photocatalytic activity scalability and real world application is presented below.

Table 1. A comparative study of P-MOFs with traditional photocatalyst with parameters affecting the efficiency

Parameters	**Porphyrin based MOFs (P-MOFs)**	**Traditional photocatalysts**	**References**
Band gap energy	Bandgap energy falls in visible range i.e. ,3eV due to Porphyrin ligands	Traditional photocatalysts have both UV range (i.e.TiO_2, ZnO >3eV) as well as visible range (i.e. CuO, Sb_2S_3 <3eV)	7
Photocatalytic activity	Higher photocatalytic activity due to tunable Porphyrin structure and enhanced light absorption	Due to the higher band gap energy of the some photocatalysts the photocatalytic activity is moderate	8
Charge separation	Excellent charge separation due to MOF structure	Required dopant for good charge separation	9
Stability and reusability	Excellent stability and reusability, however structural degradation over time	Good reusability with minimal loss of photocatalytic activity	10
Scalability	Limited scalability due to complex synthesis and higher cost	Traditional photocatalysts are commercially available	11
Environmental impact	Low environmental impact due to recyclability and efficiency	High environmental impact due to energy intensive production	8
Real world application	Efficient at lab scale but challenges in large-scale use	Efficient in large scale application for water treatment	12

This review focuses on the potential of Porphyrin-based metal-organic frameworks (P-MOFs) as photocatalysts for micropollutants degradation. MOFs, due to their high surface area, tuneable band gap, and structural versatility, have shown promise in addressing the limitations of conventional photocatalysts. In particular, Porphyrin-based MOFs combine the catalytic properties of Porphyrins with the structural benefits of MOFs, resulting in enhanced light absorption and charge transfer. This review will cover the synthesis, structural features, and photocatalytic mechanisms of these novel materials, with a specific focus on their application in degrading microplastics. By highlighting recent advancements and identifying key areas for future research, this review aims to contribute to the development of sustainable water treatment technologies.

2. Overview of metal-organic framework (MOFs) and Porphyrin-based MOF (P-MOFs) structures

MOFs are a class of materials formed by the coordination of metal ions or clusters with organic ligands, resulting in a three-dimensional porous structure. Their unique properties, such as high surface area, tuneable porosity, and structural versatility, make them promising candidates for various applications, including gas storage, catalysis, and environmental remediation. Several organic linkers such as corroazine, corrphycene, and phthalocyanine are used for the formation of MOFs as presented in **Figure 1**. Among these, P-MOFs are particularly notable for their photocatalytic capabilities, allowing for the efficient degradation of organic pollutants under light exposure.[13]

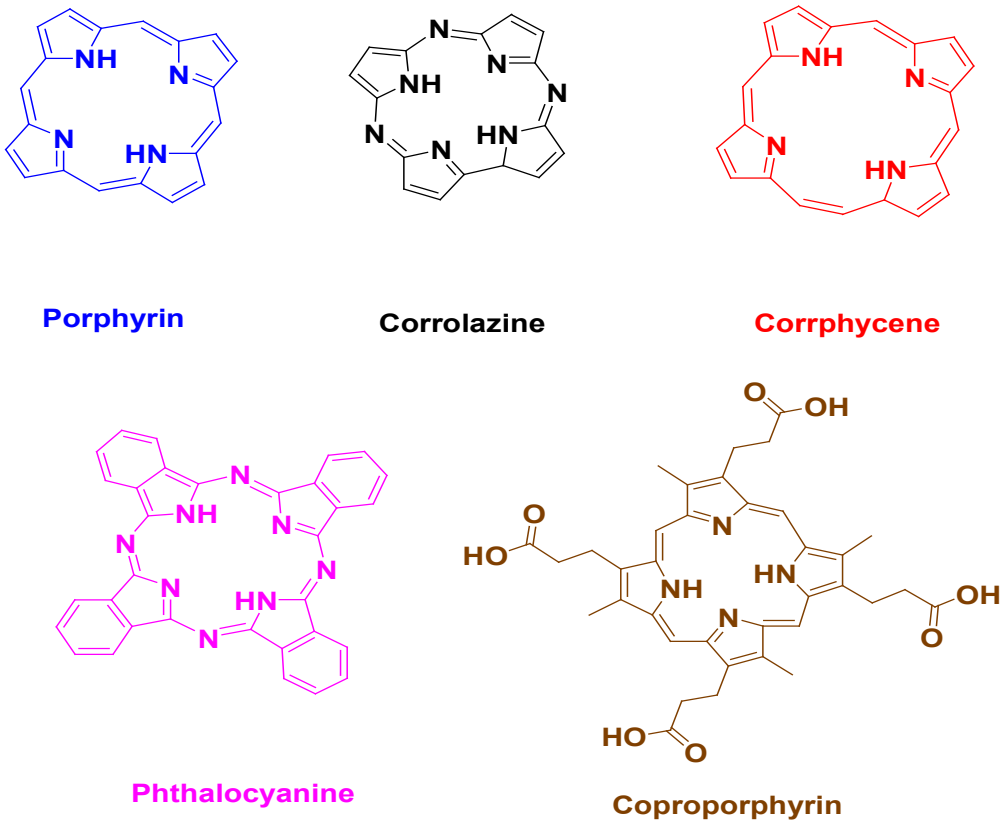

Figure 1. Overview of the organic linkers used for the formation of MOFs

The photocatalytic properties of P-MOFs arise from their ability to harness light energy, generating reactive species that can degrade contaminants into less harmful substances. This ability positions them as a potential solution to the growing concern of water pollution. Given the increasing focus on sustainable environmental practices, the development of P-MOFs for photocatalytic

applications is both timely and essential. P-MOFs have attracted significant attention due to the unique macrocyclic structure of Porphyrins, which consist of four pyrrole rings connected by methine bridges (-CH=) in one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) frameworks (**Figure 2**). The conjugated π-electron system of Porphyrins results in a highly stable and planar structure, conferring distinctive properties such as brilliant colour and photophysical activity.[14,15] These features make Porphyrins versatile, particularly in light-mediated applications like the generation of reactive oxygen species, which is crucial in catalysis and environmental remediation.[16,17]

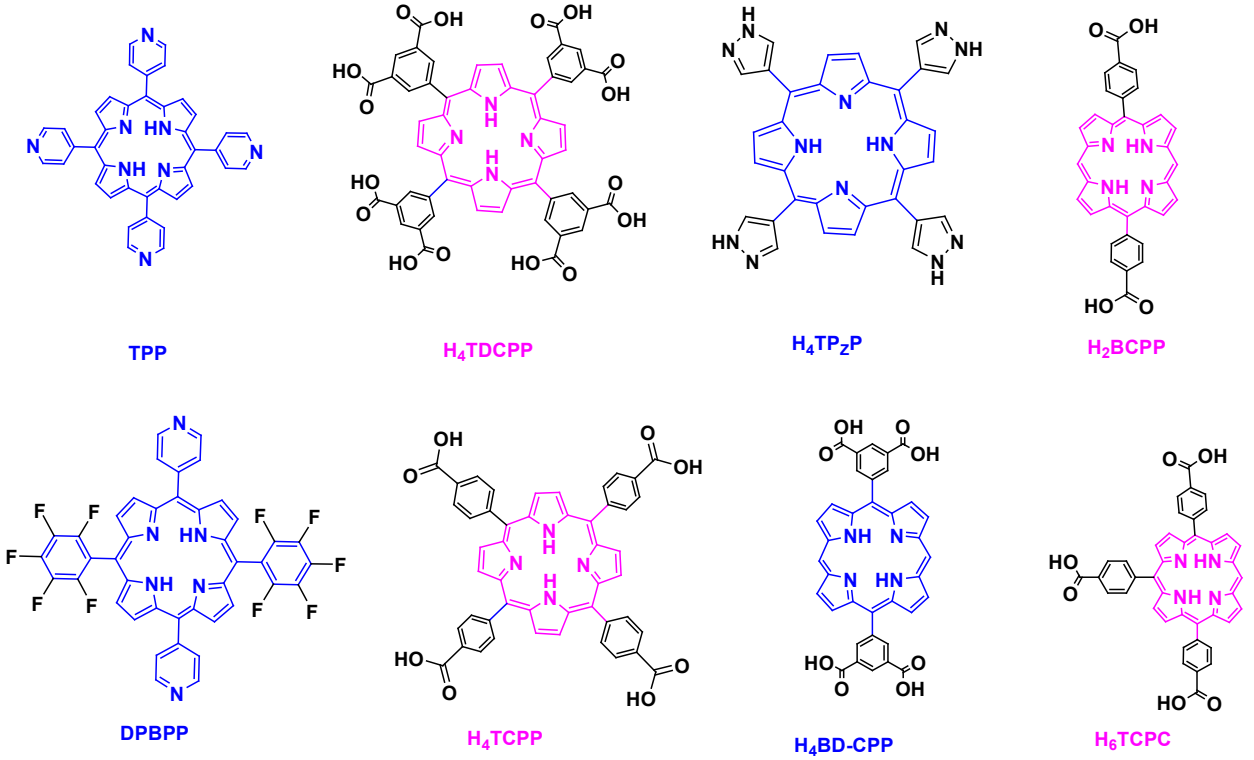

Figure 2. Molecular structure of Porphyrin linker for the synthesis of MOFs

Porphyrins, when combined with metal ions, form metallo-Porphyrins, where the central cavity of the pyrrole ring structure binds metal ions such as Fe (II), Mn (II), Co (II), Cu (II), La (II), In (II), and Zn (II). This metalation process enhances the functional versatility of Porphyrins, allowing their use in various MOF structures tailored for specific applications, such as catalysis and pollutant degradation.[18-20] Porphyrin-based MOFs have been widely employed in energy-related applications and environmental remediation, leveraging the macrocyclic structure's ability to promote efficient charge transfer and light absorption.[21,22] Studies have shown that incorporating

Porphyrins into MOF structures can significantly enhance photocatalytic performance. For instance, Hamad and his group demonstrated the tunability of Al-PMOFs doped with Fe, Cu, and Zn, enhancing their solar photocatalytic activity.[23] Guo and his team synthesized Ag@MOF-525 using a tetracarboxyphenylPorphyrin (TCPP) linker for the degradation of contaminants like Rhodamine B and tetracycline.[24] Similarly, Shi and his group used a TCPP-based La/Fe MOF for dye degradation.[25] The use of various Porphyrin linkers and metal ions, such as those found in Zn and Zr-based Porphyrinic MOFs, allows for the formation of stable 2D and 3D frameworks with diverse structural and catalytic properties.[26,27]

P-MOFs like (Porous Coordination Networks -221) PCN-221, PCN-222, PCN-223, and PCN-224 are Zr-oxoPorphyrin MOFs that exhibit tuneable catalytic activity and stability, especially when metal ions are introduced to enhance their photocatalytic efficiency.[28] Moreover, the PCN-222(Pt) complex shows significantly higher photocatalytic efficiency than its non-metalated counterpart.[29] P-MOFs have also demonstrated excellent stability and catalytic performance in other configurations, such as single oxygen-generating porous coordination networks (SO-PCNs) used for photocatalysis.[30] Overall, Porphyrin-based MOFs stand out due to their diverse structural possibilities and outstanding photophysical properties, making them ideal candidates for applications in solar cells, chemical sensors, and photo- and electrocatalysis. **Table 2** highlights key studies on P-MOFs, alongside their characteristics and the diverse photocatalytic applications.

Table 2. Overview of P-MOFs, synthesis and applications.

Porphyrin based MOF	Reaction condition	Key findings	References
Zr-Porphyrin MOF	Hydrothermal Method was used by using $ZrCl_4$ and H_2TCPP at 180°C	Zr-Porphyrin MOF (PCN-134) and its derivatives, PCN-134(Fe) and PCN-134(Cu), were used for the removal of five diverse micropollutants. The adsorption was significantly enhanced by 1.2-2.5 time in case of PCN-134(Fe) and PCN-134(Cu) as compared to (PCN-134).	31
PCN-H_2/$Pt_{x:y}$ (x:y = 4:1, 3:2, 2:3, and 0:1)	Solvothermal synthesis using of $ZrCl_4$, H_2TCPP and PtTCPP.	PMOF shown superior H_2 production (351.08μmol h^{-1} g^{-1}) under visible light	32
PCN-222 and PCN-222(M)	PCN-222 and PCN-222(M) was synthesized by ultrasonication method at 120°C for 48hr	100% reduction of Cr (VI) from water was achieved	33
Porphyrin-Based 2D Lanthanide Metal-Organic Frameworks (Ln-TCPP)	Microwave-assisted strategy between LnO_6 and TCPP	Controlled fabrication of 2D MOFs for the photo-oxidation of 1,5- dihydroxynapthalene (1,5-DHN), Yb-TCPP shows excellent activity as compared to Ce, Sm, Eu, Tb.	34
Zr(IV)-MOF	In-situ ligand substitution and Post-synthetic ligand substitution	Using post-synthetic ligand substituted MOFs showing superior photocatalytic CO_2 reduction.	35
Pt into an aluminum-based Porphyrinic MOF (Al-TCPP)	Al-TCPP MOFs was synthesized by hydrothermal reaction of $AlCl_3.6H_2O$ and H_2TCPP.	Al-TCPP exhibited an efficient electron transfer channel which significantly improve hydrogen binding energy and increase the activity of H_2 production.	36
Ir and Pt into the centre of the Porphyrin within zirconium Porphyrin MOFs (HNTM),	HNTM was synthesized by solvothermal reaction of TCPP and	HNTM-Ir/Pt shows superior activity for H_2 production (201.9 $mmolg^{-1}h^{-1}$) as compared to HTNM and HTMN-Pt.	37

	$ZrCl_4$, benzoic acid and DMF at 120°C		
Ru-TBP and Ru-TBP-Zn based MOFs	Solvothermal reaction for the synthesis of Ru-TBP and Ru-TBP-Zn between RuCl3.xH2O and H_4TBP IN DMF at 120°C.	Ru_2 secondary building blocks units shows 28 time higher activity that homogeneous control.	38
Pt@PMOF, Pt@H_2TCPP, and PMOF (Pt@H_2TCPP)	Hydrothermal method was used to synthesized PMOF between $Ti(OBu)_4$ and benzoic acid at 150 °C for 5 days.	Pt loaded PMOF shows superior activity H_2 evolution (8.52 $mmolg^{-1}h^{-1}$)	39
Ni-TCPP, Zr PMOF, Ni-Ni PMOF, and Zr-Ni PMOF	Solvothermal method was used between $ZrCl_4$, $Ni(NO_2)_3.6H_2O$ and TCPP	Zr-Ni PMOF shows higher activity as compared to Ni-TCPP, Zr PMOF, Ni-Ni PMOF	40
Porphyrin-based 2D Layered MOF- (2DZnTcpp)	Modified one-pot solvothermal method was used to synthesized ZnTCPP	ZnTCPP shows 99.99% efficiency toward the inactivation of *Escherichia coli* in wastewater	41
Py-POP MOF	Hydrothermal method was used between pyrrole and 4,4-diformyl-1,1'-biphenyl at 180°C for 72hr.	Excellent photocatalytic activity and adsorption towards MB dye in comparison to Rh B dye due to size/shape effect.	42
Zr-MOF, PCN-224	$ZrOCl_2.8H_2O$ and H2TCPP in presence of benzoic acid and DMF were mixed in round bottom flask and heated at 90°C for 6hr.	A maximum adsorption of 354.8 mg g^{-1} for TC and 207 mg g^{-1} for CIP was obtained by PCN-224.	43

MOF-525 and Ag@MOF-525	Solvothermal synthesis of 6-connect Zr_6 and TCPP to form MOF-525 and photoreduction by $AgNO_3$ to form Ag@MOF-525	91% degradation rate was achieved for Rh B in 60 min and for TC 81% degradation was achieved in 200 min.	44
Al-TCPP(H_2), Al-TCPP(Zn)	Hydrothermal method was used to synthesize PMOF between Al salt and TCPP at 180^oC	Photocatalytic reduction of Cr (VI) was increased 1.7 times for Al-TCPP(H_2), Al-TCPP(Zn) as compared to Al-TCPP.	45
Benzobisoxazole linked Porphyrin-based fully conjugated microporous polymers based on Porphyrin or metalloPorphyrin (M = Zn, Cu, Ni)	Polycondensation reaction between TCPP and 4, 6-Diaminoresorcinol dihydrochloride.	100% conversion of dye was observed in 150 min by robust oxidant free MOFs	46
MnPor-MOF	Layer by layer deposition method between Mn-TCPP and Zn_2^{4+}	Excellent photocatalytic activity (90%) for the degradation of methylene blue (MB) in 180 min.	47
(Hf)PCN-224(H_2)	Microwave-assisted synthesis between $HfOCl_2.8H_2O$, $CoCl_2$ and TCPP with DMF at 140^oC for 5 min.	Efficient in CO_2 cycloaddition and recyclable up to 8 cycles without losing its activity.	48
La@MOF-808	Solvothermal method was used between $ZrOCl_2.8H_2O$, lanthanum trioxide and trimisic acid in DMF, stirred at 100^oC and then sonicated at 40^oC.	Porous photocatalysts with high specific surface area facilitates the removal of Arsenic (As) ions from water achieving 307 mg g-1 for Total As and 325 for As (III).	49

3. Photocatalytic mechanisms of MOFs

3.1 Photocatalytic processes

The photocatalytic mechanisms of MOFs involve several key steps to degrade organic pollutants. Upon exposure to light energy exceeding their band gap energy, P-MOFs generate electron-hole pairs via electron excitation, trapping, and transfer.[50] The resulting photogenerated electrons and holes produces reactive oxygen species (ROS), such as hydroxyl radicals (°OH), superoxide radicals (°O_2^-) which are crucial in the degradation of organic contaminants.[51] An overview of this mechanism is presented in **Figure 3**.[52]

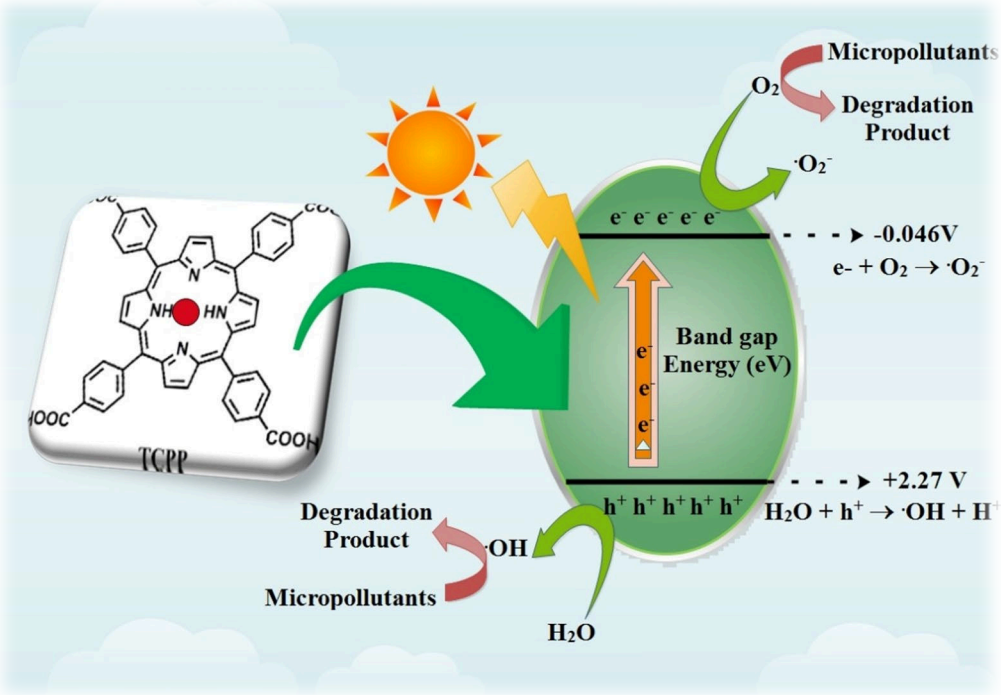

Figure 3. A photocatalytic mechanism of MOF for the degradation of micropollutants

For P-MOFs to function effectively, the generated electron-hole pairs must remain separate long enough to participate in redox reactions. Porphyrins exhibit strong light absorption in the visible and near-infrared regions, making them excellent candidates for photocatalysis. Upon absorption of photons, the Porphyrin molecules undergo an electronic transition, generating electron-hole pairs. The metal nodes in the MOF play a crucial role in facilitating efficient charge separation and the organic linker collect light from artificial or natural sources and then use the ligand to metal

cluster charge transfer (LMCT) to activate the metal sites.[53] This dual functionality of adsorption and photocatalysis makes P-MOFs particularly effective in treating water contaminants.

Further, the photo-generated electrons and holes in the conduction band (CB) and valence band (VB) are separated within the MOF structure. Electrons migrate to the metal nodes, leading to the reduction of the metal centres, while holes remain associated with the Porphyrin units. This separation of electrons and holes prevents the recombination of electron-hole pairs and enhances the overall efficiency of the photocatalytic process. The reduced metal sites and the oxidized Porphyrin act as active sites for subsequent redox reactions. The next step is the generation of Reactive Oxygen Species (ROS) which is the most important step involves n the micropollutants degradation. For the electron to reduces atmospheric oxygen (O_2), the edge band potential of the CB must be equal to or greater than -0.046 eV and the for the photogenerated holes to oxides H_2O, the edge band potential of VB should be equal or greater than 2.27eV.[54] The oxidized Porphyrin units or metal centres can react with oxygen molecules, leading to the formation of ROS such as superoxide radicals, hydroxyl radicals (•OH), and singlet oxygen which play a pivotal role in breaking down organic pollutants through oxidation reactions.[55] After the formation of the ROS, the next step is the interaction of ROS with organic contaminants. The hydroxyl radicals HO• which is generated by the reaction of h^+ with H_2O molecule in the valence band (VB) and the superoxide radicals are generated by the reaction of atmospheric oxygen by the photogenerated electron in the conduction band (CB). These processes of photocatalytic oxidation and reduction can be explained by the subsequent series of reactions as shown below in equation (1-9).[56]

$$MOF + hv \rightarrow e^- + h^+ \quad (1)$$
$$h^+ (2.27\ eV) + H_2O \rightarrow \bullet HO + H^+ \quad (2)$$
$$h^+ + 2HO^- \rightarrow HO^\bullet + HO^- \quad (3)$$
$$e^- (-0.046\ eV) + O_2 \rightarrow \bullet O_2^- \quad (4)$$
$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet \quad (5)$$
$$O_2^{\bullet-} + HO_2^\bullet + H^+ \rightarrow O_2 + H_2O_2 \quad (6)$$
$$H_2O_2 + H^+ + e^- \rightarrow HO^\bullet + H_2O \quad (7)$$
$$\text{Micropollutants} + HO^\bullet \rightarrow \text{Intermediate products} \quad (8)$$
$$\text{Intermediate products} + HO^\bullet \rightarrow CO_2 + H_2O \quad (9)$$

3.2 Role of MOFs in adsorption and degradation

By exposing the P-MOFs to light with an energy higher than its band gap energy, the equilibrium between adsorption and desorption is achieved. Electron creation, trapping, electron-hole recombination, electron transfer, reduction reactions, hole transfer, and oxidation reactions are the

processes that take place in the presence of light. For photoactive MOFs to function as photocatalysts, electron-hole pairs should be generated valence band (VB) and conduction bands (CB). P-MOFs have shown excellent adsorption with a large number of pores on their surface that could effectively adsorb target micropollutants in water by minimizing the spatial separation between micropollutants and catalytic sites. P-MOFs serve a dual purpose in environmental remediation as they facilitate the adsorption of pollutants while simultaneously catalysing their degradation under light exposure. Studies have demonstrated that PMOFs can effectively degrade a wide range of organic contaminants, including dyes and pharmaceutical compounds. For instance, Zr-TCPP loaded Ag nanoparticles was used for the efficient degradation of Cr (VI) and results indicated that the photocatalytic reduction efficiency of Cr(VI) was 57, 78 and 88 % within 120 h at 20, 40 and 60 % loading of AZT5.[57] In another study, CeO_2 or Ce-TCPP have negligible elimination action however, when Ce-TCPP and PMS are combined with visible light, the photocatalytic activity was increased significantly and Rh B is eliminated at a rate of 44% in just 60 min. Moreover, other contaminants such as MB (Methylene blue) 99%, OTC (oxytetracycline) 98%, TCL (tetracycline) 85%, and MO (methyl orange) 94% was degraded by PMS triggered Ce-TCPP.[58] In another study author examined four different Zr_6O_8-Porphyrinic MOFs (PCN-223, PCN-224, PCN-225 and MOF-525), each with distinct topologies to evaluate their effectiveness and mechanisms in the removal of contaminants form hyper saline water under visible light photocatalysis. The findings shows that variations in the molar ratio of monocarboxylates, ligands and Zr ion in these PMOF altered their porosity, pore size distribution, crystal defects and surface properties. The structural differences impacted the materials adsorption and photocatalytic performance of bisphenol A.[59] Similarly, ofloxacin was taken as a targeted pollutant for the adsorption and photocatalytic efficiency of catalysts. According to the results, UiO-66(Hf) had a clearance rate of 13.4%, with adsorption and degradation rates of 0.0109 min^{-1} and 0.0011 min^{-1}, respectively. After 60 minutes of visible light irradiation, the addition of TCPP greatly increased these effects, obtaining 24% elimination and 70% removal. Adsorption efficiency for OFL were 73% and 68% for TCPP@UiO-66(Hf)-250 and TCPP@UiO-66(Hf)-350, respectively, with photocatalytic rates rising following a 60-minute exposure to visible light. This finding suggests that the combined action of photocatalysis and adsorption enabled the quick removal of OFL from wastewater.[60] In another study Iron(III) meso-tetra(4-carboxyphenyl) porphyrin-UiO-66 (FTU), in comparison to UiO-66/Vis and Fe^{III}-TCPPCl/Vis reactions exhibits higher photocatalytic

efficiency. FTU can degrade Rh B dye 51% in 60 min which is 25% higher than UiO-66 and 27% higher than Fe^{III}-TCPPCl.[61]

In another study, two model dyes, MO (methyl orange) and MB (methylene blue), were used to investigate the photo-catalytic activity of TCPP-La and Fe-TCPP-La for 125 minutes under 200 W mercury lamp irradiation. The findings showed that, in the absence of 2% H_2O_2, the photo degrading efficiencies of TCPP-La for MO and MB were 16.7% and 23.7%, respectively, whereas the photo degrading efficiency of Fe-TCPP-La was only 4.8% for MO and 16% for MB.[25] Therefore, TCPP-La provided superior photo degradation for MO and MB in comparison to Fe-TCPP-La. Under comparable reaction conditions, most photo-catalytic tests showed that MB was easier to degrade than MO.[62,63] Shee et al. (2022) used Trans-$PdCl_2$ units coordinated with {(trans-dihydroxo)[5,10-bis(4-pyridyl)-15,20-bis(phenyl) Porphyrinato]}tin(IV) (SnP^1) to form a distinct 2D tetrameric supramolecule for the degradation of Acid Orange 7 dye.[64] The photocatalytic degradation efficiency towards AO in an aqueous solution was subsequently impacted by these structural alterations when exposed to visible light. Acid Orange 7 was fragmented in an aqueous solution when exposed to visible light in presence of photocatalysts. Within 90 minutes, these photocatalysts were able to observe Acid Orange 7 degrading efficiency values up to 91%. Meng et al. 2017 performed the visible light degradation of BPA under visible light using Zr-Porphyrin MOF PCN-222. The residual BPA concentration was effectively reduced to 0.0006 mg with great adsorption efficiency notable photodegradation was mostly detected on PCN-222 adsorbent. It was discovered that the mass of BPA in the PCN-222 channel dropped significantly between 0 and 20 min, indicating a pseudo zero-order kinetic model with a degradation rate constant of 0.004 ± 0.0002 mg min^{-1}. The maximal adsorption capacity of PCN-222 is up to 487.69 ± 8.37 mg g^{-1}, demonstrating ultrahigh removal efficiency of BPA from aqueous phase.[65] In other study, RhB and methyl orange (MO) dyes can be photocatalyzed and degraded utilizing GNPs@TCPP nanofibers as compared to GNPs and free-standing TCPP aggregates. There was a little drop in MO concentration when GNPs were utilized as the photocatalyst, despite a roughly 25% drop in RhB concentration which is most likely due to graphene's strong adsorption affinity for RhB as compared to MO.[66] The concentration of RhB and MO are reduced by 90% and 30%, respectively, after 180 minutes of irradiation under simulated sunlight, using free-standing TCPP aggregate photocatalysts. According to this finding, the free-standing TCPP aggregates exhibit good photocatalytic activity toward RhB and MO however, the use of GNPs@TCPP nanofibers

dramatically improves photocatalytic performance. After 180 minutes, MO degradation reaches 80%, while RhB degradation is 100% after 150 minutes. According to these findings, as compared to free-standing TCPP aggregates and GNPs, GNPs@TCPP nanofibers show increased photo-catalytic activity.[67] According to Zhao study, Cu-TCPP photocatalyzed the breakdown of antibiotics (NFX) and RhB dye under the influence of visible light. Cu-TCPP quickly adsorbs and lowers the concentration of RhB when exposed to visible light. The findings demonstrated that Cu-TCPP is capable of both adsorbing and degrading organic pollutants in solution environments when exposed to visible light. Furthermore, the 2D Cu-TCPP nanosheets shown remarkable photocatalytic activity in eliminating 81.2% of RhB and 86.3% of TCL in 6 hours when exposed to visible ligh.[68] Apart from these studies mentioned above several other studies have been reported so far on the Porphyrin-based MOF for the degradation of organic contaminants. A comparative table (Table 3) is presented below for the various types of Porphyrin-based MOFs.

Table 3. Metal-Porphyrin combinations and their photocatalytic efficiency in degrading various pollutants

Metal ions	Linker	Synthesis approach	Targeted pollutants	Photocatalytic efficiency (%)	References
Copper	TCPP	Microwave-assisted synthesis using copper nitrate, TCPP and pyrazine.	RhB NFX	81 86	68
Iron and Lanthanum	TCPP	Sol-gel approach was used lanthanum nitrate, iron nitrate, TCPP and DMF.	MO MB	16 24	25
Copper	TCPP	Condensation reaction using Copper nitrate, TCPP, DMF, ethanol and PVP.	RhB	88	69
Cobalt	TCPP	Solvothermal synthesis was used to synthesize 2D Co-TCPP-MOFs by copper nitrate and TCPP linker	BPA	97	70
Zirconium	TCPP	Solvothermal synthesis of 6-connect Zr_6 and TCPP to form MOF-525 and photoreduction by $AgNO_3$ to form Ag@MOF-525	RhB	94.1	44
Zinc Oxide	CuPp	New impregnation method was used to synthesis ZnO and copper (II) 5-mono-[4-(2-ethyl-p-hydroxybenzoate) ethoxyl]-10,15,20-triphenylporphyrin (CuPp) photocatalysts	RhB	63	71
Zirconium	H_2TCPP	Ultrasonically mixing of $ZrOCl_2.8H_2O$ and H_2TCPP linker followed by heating at 120°C	TC CIP	92 84	72
Hafnium	TCPP	Ultrasonically mixing of $HfCl_4$ and and H_2TCPP linker followed by heating at 120°C	NFX	94	73

Zirconium	TCPP, TBAPy	Solvothermal one pot synthesis by using $ZrOCl_2.8H_2O$, TCPP and TBAPy linker.	STZ RAN NZT TC GAT	93 96 95 87 86	74
Zirconium	H_4TCPP	Three necked-flask was used for the synthesis $ZrCl_4$ and H_4TCPP.	TC RhB	91 100	75
Aluminium	H_4TCPP (Co), TCPPCOOMe, H_6TCPP (Cu)	Condensation reaction was used to synthesis a series of Al-Based Porphyrin MOFs	MB RhB	98 96	76
Iron	H_2TCPP	Microwave synthesis of 4-rod shaped Porphyrin MOF (Fe-TCPP-1, Fe-TCPP-2, Fe-TCPP-3, Fe-TCPP-4) by using H_2TCPP and Fe^{3+} ion, benzoic acid.	CIP	73	77
Copper	H_2TCPP	Cu-TCCP was synthesized by hydroxyl double salt active intermediates on the surface of GO.	CR MB	100 95	78

4. Properties and performance of P-MOFs

4.1 Stability and water resistance

The stability of P-MOFs in aqueous environments is crucial for their practical applications in environmental remediation. Hydrolytic stability, influenced by the strength of metal-ligand bonds, is a fundamental property of coordination networks.[79] The water molecule and the organic linker both attempt to form bond with the metal node, however it is difficult for the water molecules to replace the existing link between the metal and the organic linker which shows the stability of PMOF in water.[80] The Porphyrin ligand with a carboxylic acid linker is commonly used in P-MOFs due to its adaptability in coordinating with metal cores. This adaptability is essential for developing water-stable MOFs (W-MOFs).[81] There are certain examples of PMOF that are stable in water such as Al-PMOF was the first water stable MOF used in the acid media. Later on various other MOFs such as carboxylate-coordinated MOFs i.e. Zr based Porphyrin MOFs such as MOF-525, PCN-222, and PCN224 show varying degrees of water stability. Another water stable MOF recently reported by Mouchaham on polyphenolic Porphyrin MIL-173 (Zr) using Zr^{4+} metal ion.[82] The property of the MOFs stability is dependent on the metal-ligand bonding, geometry of units and pore size. The larger pores in the MOFs structure exhibited easier water access for hydrolysis.[83] Aromatic carboxylates that coordinate with metal clusters often enhance water stability through steric hindrance, which reduces the reactivity of H^+ or OH^- ions on the surface of the MOFs. Ongoing research is focused on evaluating the effects of water on the structural characteristics and metal-ligand coordination of PMOFs, which is vital for developing W-MOFs suitable for environmental applications.

4.2 Scaling up MOF production

For P-MOFs to be viable in practical applications, scaling up their synthesis to commercial levels is essential. Recent research has focused on producing MOFs at a kilogram scale, resulting in various forms, including granules, pellets, thin films, gels, and monoliths. Several MOFs are available commercially, however P-MOF are not commercially available yet.[84, 85] One notable study produced 2.14 grams of PCN-222 in a 2L flask, highlighting the need for advancements in scalability.[86] Currently, the solvothermal method is preferred for MOF synthesis, but it poses safety risks associated with high temperatures and pressures. Alternative methods, such as sonochemical, electrochemical, and microwave synthesis, show promise for industrial-scale

production. These methods can potentially mitigate the risks associated with traditional synthesis while enabling the large-scale production of P-MOFs.

4.3 Recyclability and long-term performance

The recyclability of P-MOFs is critical for their sustainable application in environmental remediation. Several studies indicate a decrease in adsorption capacity after several cycles of use, which poses a challenge for their practical implementation.[87, 88] However, the capacity of MOFs to degrade in soil layer-by-layer could be advantageous for controlled agrochemical delivery.[89] Current literature often provides limited information on the stability and recyclability of PMOFs, typically reporting changes in adsorption efficiency in various formats, such as percentages or mg/g. The number of recycling cycles tested varies significantly, from none to 30 cycles, with varying methodologies for assessing recyclability. A standardized approach to evaluating the stability and reusability of P-MOFs is essential. Methods such as Powder X-ray Diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR), Energy-dispersive X-ray spectroscopy (EDX), and Thermogravimetric analysis (TGA) are employed, but the most rigorous assessments involve recycling P-MOFs until their performance decreases significantly. For example, the post-functionalized MOF Metalloporphyrinic Metal-Organic Framework (MMPF) was assessed for 30 cycles, with its efficiency declining from 99.2% to 86.4%. In contrast, PCN-222 demonstrated effective iodine capture (1540 mg/g), its efficiency dropped to 70% after two cycles, indicating rapid degradation. These discrepancies highlight the need for comprehensive and standardized testing methods for evaluating the long-term performance of PMOFs. Overall, assessing stability and reusability of Porphyrin-based MOFs is challenging due to the lack of standardized characterization tests. Table 4 presents the various P-MOFs stability on the basis of recycling photocatalytic experiment and percentage efficiency.

Table 4. Types of various PMOFs and their percentage efficiency after recycling experiment

etal ion	Linker	Reaction Condition	Number of cycles	Percentage efficiency	References
K_2PtCl_4	Pd-PCN-222(Hf)	PdTCPP and $HfCl_4$ inn DMF in the presence of CF_3COOH and heated 120 ^oC	3	4%	90
Hf	TCPP	$HfCl_4$, BDC and BA were sonicated in DMF and heated at 120^oC for 24 h	6	97%	73
ZnO	CuPp	New impregnation method was used to synthesis ZnO and copper (II) 5-mono-[4-(2-ethyl-p-hydroxybenzoate) ethoxyl]-10,15,20-triphenylporphyrin (CuPp) photocatalysts	5	83%	71
Cu	TCPP	Condensation reaction using Copper nitrate, TCPP, DMF, ethanol and PVP.	5	88%	69
Cu	H_4TCPP, TCPPCOOMe H_6TCPP	Condensation reaction was used to synthesis a series of Al-Based Porphyrin MOFs	7	98% MB 96% RhB	76
Zr, Fe, Mn	TCPP	Ultrasonication followed by hydrothermal reaction at 120^oC for 24hr	4	99%	91
Fe	TCPP	FeTCPP was prepared hydrothermally in DMF solution followed by reflux for 6 hrs at 120^oC	6	90%	92

5. Environmental and toxicological implications

5.1 Toxicity assessment of PMOFs

To ensure the safety of the PMOFs before environmental or biomedical application, toxicity assessment is an essential criterion. The photophysical and photo-catalytic behaviour of the PMOFs make them tuneable for the application of environmental and biomedical applications such as drug delivery and photodynamic therapy. Porphyrin ligands are considered biocompatible as they are found in heme however, the potential toxicity arises from the release of the metal ions from the MOFs skeletons, formation of ROS and the possibility of bioaccumulation of the nanosize in the ecosystem. To minimize the toxicity of the P-MOFs selection of less toxic metals such as Fe(III) and Zn (IV), are generally considered safe for both environmental and human health Research has shown that Fe (III) and Zn(IV), exhibit low or negligible toxicity.[93, 94] Studies evaluating the biocompatibility of PB-PCN-224 composites and PCN-224 with cotton fabrics confirmed their safe interaction with biological systems. Investigations into the immune response to nano-PCN-224 further support their low toxicity, highlighting their potential for safe environmental applications.[95] However, some metals ions such as Cd, Pb and Hg and Al based MOFs showed varied toxicity levels on the ecosystem therefore, future research should focus on using such type of metal ions in MOFs for the environmental applications should be analysed.[96] Another method of mitigating the toxicity is the surface functionalization with biodegradable polymers such as cellulose, chitosan and chitin which make the MOFs less toxic and can applied for the environmental applications. This multi-faceted approach ensures that while PMOFs offer significant potentials, their risks are carefully managed that leads to their safe and effective application for the environmental and biomedical applications.

5.2 Environmental impact of P-MOFs

MOFs demonstrate potential application in environmental remediation, energy generation, energy storage and gas storage and sensing application. In the context of photocatalysis, P-MOFs offer advantages for micropollutants removal such as toxic dyes, fertilizers and pharmaceutical and personal care products, leveraging non-reactive reactants like CO_2 and water. Various studies have shown the capacity of MOFs to adsorb and degrade harmful micropollutants which pose significant environmental risks. P-MOFs are excellent photocatalysts in the removal of heavy metals such as

Cr(VI), Mn (II), Fe(VI), Co(II), Cu(II), Zn(II), Mo(VI), Pd(II), Ag(I), Cd(II), Au(III), Hg(II), Pb(II) and Bi(III) form wastewater through adsorption.[97,98] The adsorption process is generally derived by the ionic interactions with MOF skeleton, coordination of metal cations, functionalization of chelating inside the MOFs.[99, 100] Apart from the environmental applications, P-MOFs can be used in energy sector facilitating photocatalytic water splitting to generate hydrogen fuel using sunlight, promoting sustainable energy solutions. Photocatalytic carbon dioxide reduction is another application of P-MOFs for generation sustainable byproducts such as aldehydes, esters methane and ether. Despite numerous applications of P-MOFs, various environmental risks are associated i.e. during photocatalytic processes, there is a possibility of release of toxic metal ions to the environment and the nanoscale size of the metal ions could raise environmental concern for bioaccumulation and biological effect. Many MOFs are non-biodegradable in nature so this is another challenge of the environment for its disposal and recycling once it is used that can results in a significant environmental concern.[101] Therefore, in order to mitigate the risks of the chemical stability of the MOFs, green synthesis route using water-based solvent and even mechanochemical processes route have been used for the synthesis of MOFs.

6. Recent advances and applications

6.1 Developments in Porphyrin nanosystems

Recent developments in Porphyrin nanosystems reveal exciting potential across diverse applications, particularly in advanced oxidation processes. One of the key advancements is the formation of PMOFs incorporated with carbon rich compounds i.e. Multi-walled Carbon Nanotubes (MWCNTs), Single-walled Carbon Nanotubes (SWCNTs), reduced graphene oxide (r-GO) which provide stability, high energy transfer capabilities and higher transfer of electrons and such type of heterojunctions exhibits promising in enhancing light-harvesting and catalytic efficiency.[102] Moreover several nanoparticles have been used for form heterojunction with Porphyrins, exhibits strong light absorption and excellent redox properties, making them suitable photocatalysts under visible light.[103,104] The Porphyrin nanosystems offer enhanced catalytic stability and recyclability, crucial for sustainable water purification technologies. Apart from the excellent photocatalytic applications for environmental remediation, P-MOFs have been used for energy generation, e.g. Zn, Fe, and Cu based P-MOFs have shown remarkable potential for the H_2

production and CO_2 reduction.[105,106] The P-MOFs design facilitates efficient charge separation which plays crucial role in promoting hydrogen and oxygen evolution reactions. These cutting-edge developments illustrate how Porphyrin nanosystems are evolving into versatile tools for environmental applications, expanding their reach into nanotechnology and sustainable energy solutions.

6.2 Future directions for research

P-MOFs hold significant potential for the degradation of micropollutants due to their exceptional properties that helps in photocatalytic application. However, these properties can be enhanced by the modification of Porphyrin ligands which minimizes the band gap energy, and the light absorption property can be enhanced. The substituent can be incorporated on the Porphyrin skeletons such as halogens, or any electron-withdrawing groups that can change the electronic property and makes them effective for photocatalytic application. This modification can improve the formation of reactive oxygen species (ROS) $^{\circ}OH/h^{+}/^{\circ}O_2^{-}$ which are critical in the degradation of persistent micropollutants. Further modification is the tuning the metal nodes or clusters within MOFs which produces the synergistic effect between metal ions and linker. For example, incorporating transition metals like Sc, Ti, V Cr, Fe, Co, and Cu which have partially filled d-orbital and have unpaired electron can facilitate good redox reactions and tune the photocatalytic efficiency.[107] For the last few years, Bimetallic or multi-metallic P-MOFs system has been introduced for the photocatalytic application which include the mixed transition-transition metal or transition-non-transition metals have been used for the formation of bimetallic MOFs.[108] This bimetallic MOFs or mixed-valence systems helps to promote enhanced electron transfer that helps in photocatalytic performance. Fabrication of biocompatible MOFs could be another solution for the efficient adsorption of micropollutants on their surface and subsequent removal form wastewater. In addition, formation of heterojunction/composites using novel nanomaterial are another strategy to improve charge separation and minimize recombination rates of photogenerated electrons and holes that enhances photocatalytic efficiency.[52] The heterojunctions are not only helps in charge separation and minimize recombination rates, but it can also provide photo stability and recycling properties. Moreover, controlling the morphology and the shape of the MOFs can also be helpful in the micropollutants removal such as controlling the morphology using a stabilizing agents could lead to the better interaction of the P-MOFs and micropollutants such as

hierarchical MOFs structure offers better micropollutants interaction with reactive sites on the surface of MOFs. Another important point is the scaling the P-MOFs synthesis using cost effective and ecofriendly could help in the practical implementation of the P-MOFs for environmental application. Mechanochemical or solvent free synthesis could reduce the environmental impact of the MOF production that can be sustainable.[109] Moreover, assessing the P-MOFs performance in the real wastewater matrices containing organic/inorganic matter, heavy metals ions, and fluctuating pH will shed light on their usefulness in real-world applications. Lastly, formation of reusable and recyclable PMOFs that can last up to 20-30 cycles can maintain the productivity. The recycling property can improve the PMOFs long term performance and affordability. Improving the development and use of PMOFs for the degradation of micropollutants would help address the expanding environmental issues and provide sustainable water purification solutions.

7. Conclusion

Overall, P-MOFs represent a ground-breaking advancement in materials science with significant potential for environmental applications, particularly in photocatalytic degradation of organic pollutants. Their unique structural properties, including high surface area, tuneable porosity, and exceptional light-harvesting capabilities, facilitate efficient adsorption and subsequent degradation of contaminants in water. Studies indicate that P-MOFs synthesized with non-toxic metals, such as Fe(III) and Zr(IV), exhibit low toxicity and biocompatibility, making them safe for both environmental and biomedical applications. The dual functionality of P-MOFs serving as both adsorbents and photocatalysts enhances their effectiveness in degrading up to 100% for a wide range of pollutants. However, challenges remain in scaling up the production of these materials, ensuring long-term stability and recyclability, and standardizing methods for evaluating their performance. While current research demonstrates promising results in small-scale applications, advancements in synthesis techniques and operational protocols are necessary to transition P-MOFs into commercially viable solutions for water treatment. Additionally, there is a need for comprehensive studies on the long-term stability and environmental impact of P-MOFs under varying conditions, particularly in complex matrices such as saline waters. The integration of P-MOFs into multi-functional platforms, such as sensors and biodegradable materials, could further expand their applicability. As the urgency to address water pollution intensifies globally, the continued investigation and innovation in P-MOF technology hold significant promise for

developing sustainable solutions that not only mitigate environmental contamination but also contribute to the broader goals of sustainability and circular economy.

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Declaration of Conflict of Interest

On the behalf of all the authors, corresponding author declare no conflicts of interest.

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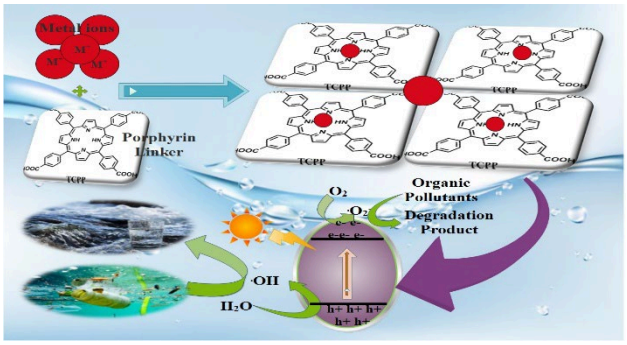
Graphical Abstract



Porphyrin-based metal–organic frameworks as sustainable photocatalysts for micropollutant degradation: a critical review on structure, mechanism and future perspectives

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