



Molecular electro- and photocatalytic approach to artificial nitrogen fixation for the synthesis of green ammonia

Ottavia Bettucci^{a,1}, Giorgia Salerno^{a,b,1}, Norberto Manfredi^a, Alessandro Abbotto^{a,*}

^a Department of Materials Science and Milano-Bicocca Solar Energy Research Centre (MIB-SOLAR), Via Cozzi 55, I-20125, Milano, Italy

^b Department of Information and Electrical Engineering and Applied Mathematics (DIEM) Invariante 12/B, Via Giovanni Paolo II, 132, 84084, Fisciano, (SA), Italy

ABSTRACT

Ammonia (NH₃) stands as a cornerstone compound across industries, pivotal in agriculture, chemicals, and energy sectors. However, the conventional Haber-Bosch process demands high pressures, temperatures, and fossil fuels, calling for sustainable alternatives. Electrocatalytic Nitrogen Reduction Reactions (E-NRRs) and Photocatalytic Nitrogen Reduction Reactions (Photo-NRRs) present innovative routes, leveraging electricity and direct sunlight to convert nitrogen (N₂) to NH₃ under mild conditions, reducing emissions and softening energy requirements. Catalysts play a strategic role in these approaches, overcoming activation barriers and enhancing efficiency. However, some challenges still need to be addressed. Indeed, noble metals exhibit limits and their scarcity, geopolitical involvement, and often fluctuating costs inhibit large-scale use. Non-noble metals offer promise but require optimization and face durability concerns. Finally, carbon-based catalysts present challenges in optimization and doping. In this scenario, a molecular-based approach, comprising both specific single coordination-based molecules with transition metal centres and either metal centre coordination-based or fully organic multi-dimensional networks originating from direct molecular organic precursors, overcomes these issues while keeping the benefits of the previously mentioned classes of compounds. This mini-review explores the molecular approach to E-NRRs and Photo-NRRs from coordination compounds carrying porphyrins and phthalocyanines as organic ligands to polymeric networks based on coordination compounds between metallic centres and organic ligands (Metal-Organic Frameworks), and to networks of molecular organic units into multi-dimensional structures (Covalent Organic Frameworks). Mechanistic insights into E-NRRs and Photo-NRRs pathways elucidate N₂ conversion to NH₃. A critical comparative evaluation of reported catalysts has been carried out to highlight the limits and the possibilities of each class of compounds. Although challenges persist in terms of stability, cost and complexity of the synthesis, the use of a molecular approach in NRRs represents one of the most promising routes towards the sustainable preparation of ammonia.

1. Introduction

The versatility of NH₃ across industries and its role in agriculture, chemicals, cleaning, and its potential to be an energy carrier, makes it a crucial compound for various aspects of modern life.

Unfortunately, the traditional and widespread Haber-Bosch (H-B) process for ammonia production requires high pressures (150–300 bar), high temperatures (300–450 °C), and reliant on fossil fuels [1]. Nowadays, it is necessary to find alternatives to produce ammonia in a more sustainable way [2]. Among green approaches, the Electrocatalytic Nitrogen Reduction Reactions (E-NRRs) and Photocatalytic Nitrogen Reduction Reactions (Photo-NRRs) represent innovative routes to convert nitrogen (N₂) into NH₃ using electricity and sunlight, respectively. These approaches allow the use of very mild conditions, with low energy demand, and avoid the use of fossil fuels, thus reducing greenhouse gas emissions. In both cases the catalyst plays a significant role during the catalytic process facilitating the conversion of N₂ into NH₃ overcoming the high activation energy required for breaking the strong

N₂ triple bond, the poor water solubility of N₂, the competitive hydrogen evolution reaction (HER), and the presence of the intermediate hydrazine (N₂H₄) as a byproduct [3–5]. For this reason, the development and design of new NH₃ catalysts is critical to promote the development of alternative approaches to the H-B process. Traditional catalysts used to address this challenge are noble metals such as ruthenium (Ru) [6,7], rhodium (Rh) [8], palladium (Pd) [8], platinum (Pt) [8–10], and gold (Au) [8,11] in very fashionable nanostructures (particles, wires, crystals, rods). However, despite their good conductivity and high binding abilities to many reactants, the low natural abundance and high cost, combined with delicate geopolitical concerns, limit their use on a large scale. To overcome these issues, non-noble metals [12,13] (i.e iron (Fe) [14], copper (Cu) [15], and titanium (Ti) [16,17] have been successfully employed. However, the lower activity/efficiency requires more effort in the optimization and engineering, in addition, some non-noble metals might suffer from durability issues, such as corrosion or deactivation over time, affecting long-term performance. For all these reasons another class of materials gained attention: carbon-based catalysts

* Corresponding author.

E-mail address: alessandro.abbotto@unimib.it (A. Abbotto).

¹ These authors have contributed equally to the work.

[18–20]. However, despite their good conductivity, robust chemical stability, and high surface area, they often need precise functionalization or doping to optimize catalytic activity which can be technically challenging and might impact the material properties [18,21–23].

With the aim to combine the benefits of the previously described catalysts while overcoming their issues, in recent years a new class of catalysts gained attention: the molecular catalysts.

Molecular catalysts are chemical substances consisting of well-defined single molecules that facilitate chemical reactions without undergoing permanent chemical changes during the process. The molecular approach in the field of green energy and chemicals has been already exploited in photovoltaics [24–26], hydrogen generation [27, 28], and CO₂ use [29] with very fashionable molecular systems useful not only for catalysis but also for light harvesting and/or electron transfers such as organic dyes [30–33], and three-dimensional macromolecules [34,35].

In NRRs molecular catalysts have in common the presence of a metal centre (e.g. iron (Fe), cobalt (Co), molybdenum (Mo), or ruthenium (Ru)) which is the active site for the chemical path to ammonia. In these coordination compounds, the ligands are neutral organic molecules or atomic/molecular ions that bind the metal centre determining a coordination environment and affecting the catalyst's stability, reactivity, selectivity, and consequently the activity and selectivity of the reaction [36].

This mini-reviews collects studies on metal-porphyrins and metal-phthalocyanines, that have recently emerged as promising molecular catalysts exhibiting good performances in E-NRRs. To provide a more complete picture, we have decided to include in the review also polymeric networks based on coordination compounds between metallic centres and organic ligands (Metal-Organic Frameworks-MOFs), and networks of molecular organic units into multi-dimensional structures (Covalent Organic Frameworks-COFs). MOFs and COFs, despite being polymeric structures, are obtained from direct molecular organic precursors, therefore sharing with porphyrin and phthalocyanine-based catalysts a molecular synthetic and structural approach and therefore clearly distinct from that of other chemical structures used in this sector. Indeed, both MOFs and COFs-based catalysts are widespread in NRR applications, mostly due to their porous environments and large surface areas.

Molecular catalysts and multi-dimensional networks show several advantages over other structures, such as their highly tuneable properties. Indeed, they can be designed with specific structures, compositions, and functional groups, allowing for precise tuning to finely control and enhance catalytic activity and selectivity. In the case of Photo-NRR, they can be designed to confer light-harvesting properties allowing them to perform as photocatalytic systems using solar energy, thus, contributing to more sustainable and cheaper nitrogen reduction processes. Furthermore, these systems exhibit encouraging catalytic efficiency in NRRs, leading to improved conversion rates and potentially reduced energy requirements. Finally, research on porphyrins and phthalocyanines and their direct integration in MOFs and COF scaffolds provides insights into the NRR mechanisms, contributing to a deeper understanding of the process and facilitating improvements in catalytic design [37].

1.1. Electro- and photo-catalytic NRR mechanisms

E-NRR is a multi-step process of proton-coupled electron transfers involving six protons and six electrons in the chemical conversion from N₂ to NH₃. E-NRRs are performed in an electrocatalytic cell in which nitrogen is fluxed in continuous [38]. In the overall process water oxidation occurs at the anode (eq. (1)). The generated protons migrate to the cathode where reduction of molecular nitrogen to ammonia takes place (eq. (2)).



The electrocatalytic NRR process, which also occurs in the presence of molecular catalysts, is based on 3 steps: i) N₂ adsorption and activation on catalytic sites; ii) hydrogenation process of activated N₂ and generation of NH₃; iii) NH₃ desorption from catalytic sites. According to the hydrogenation and bond-breaking mode of N₂, two essential NRR mechanisms for molecular catalysts are proposed: dissociative and associative pathways (Fig. 1a) [38–40]. In the dissociative pathway the cleavage of N₂ precedes the hydrogenation reaction and the resulting single nitrogen atoms on the catalytic sites undergo 3 successive hydrogenation processes to generate NH₃, which are then released from the catalyst surface (Fig. 1a–i). In the associative path the N≡N cleavage takes place during the hydrogenation process with different possible N_xH_y intermediates, thus differentiating into associative distal and associative alternating routes (Fig. 1a–ii, iii) [41].

Photocatalytic ammonia synthesis via NRRs requires multiple processes (Fig. 1b). The first step is light extraction in which the semiconductor photocatalyst (the molecular catalyst) convert solar energy to electrons, which migrate to the conduction band (CB) of the material and form photogenerated holes (h⁺) in the valence band (VB). The photogenerated electrons and holes trigger the reduction and oxidation reactions. In the second steps water is oxidized to oxygen (O₂) by holes, while N₂ is reduced to NH₃ after a series of multiple proton-electron transfer steps [41].

In principle, the photocatalytic N₂ fixation reaction involves first the chemisorption of N₂ on the active site of the catalyst, followed by the cleavage of the N–N triple bond and the continuous hydrogenation occurring by protons coming from water. However, the strong bonding energy (941 kJ mol^{−1}), high ionization potential (15.85 eV), wide HOMO-LUMO gap (1.82 eV), and poor electron affinity (−1.9 eV) of N₂ make difficult electron transfer processes [42]. Therefore, the N₂ activation process is usually considered to be the rate-limiting step to determine the efficiency of the photocatalytic N₂ fixation reaction [42]. In both E-NRR and Photo-NRR processes, the pH value of the electrolyte, and consequently, the concentration of OH[−] and H₃O⁺, influences the nitrogen hydrogenation sequence and the final equilibrium conversion between ammonia and ammonium (NH₄⁺) product species [43].

1.2. Detection of ammonia

Currently, several methods are used to quantitatively determine the ammonia or ammonium content, depending on the scientific field, application, and range of concentration. Common methods for measuring ammonia generated by NRR experiments are spectrophotometry (colorimetric assays), ion chromatography (IC), and ¹H NMR spectroscopy.

The most widely adopted and cost-effective method for quantifying the generated ammonia/ammonium is through colorimetric assays. They can be carried out through indophenol blue (IB), based on the Berthelot reaction, or Nessler's reagent (NR) assay, based on the reaction between NH₃ and the Nessler's reagent [37,44,45]. Both NR and IB are easy to adapt, sensitive, and require little equipment, but are susceptible to a number of factors such as pH of the solution, metal ions, sacrificial agent, CO₂ in the air, reaction time or temperature, owing to indirect detection [46,47] These factors affects sensitivity and accuracy of the spectrophotometry methods. An essential limitation of NR assay is its toxicity, attributed to the presence of mercury. The indophenol blue method loses accuracy at higher concentrations or under acidic conditions.

Conversely, IC is highly sensitive and reproducible, enabling direct concurrent detection of ammonium and other ions but requires dedicated and more expensive instrumentation [46].

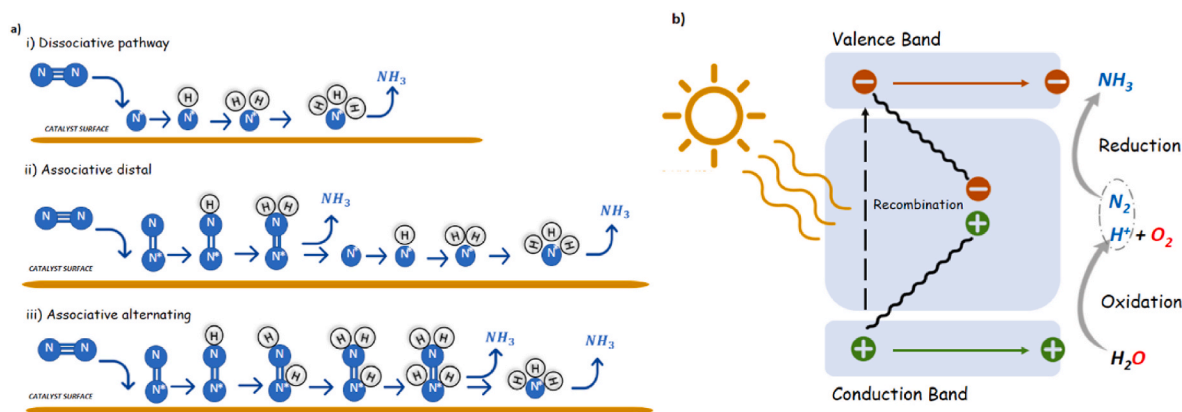


Fig. 1. a) E-NRR mechanism. i. Dissociative pathway ii. Associative distal pathway (the terminal nitrogen atom preferentially undergoes hydrogenation until release of the first molecule of NH_3 ; subsequently, the remaining nitrogen atom repeat the same hydrogenation process to produce a second NH_3 molecule). iii. Associative alternating pathway (nitrogen atoms are alternately hydrogenated in combination with proton-coupled electron transfer, and two NH_3 molecules are released sequentially at the final step of the pathway). b) Photo-NRR mechanism. The scheme shows the energy levels of the photocatalyst and the main steps: generation of charges (electrons and holes), separation of charges, and reduction/oxidation semi-reactions.

Finally, ^1H NMR is a powerful tool for the selective quantification of $^{15}\text{NH}_4^+$ vs $^{14}\text{NH}_4^+$ when employing ^{15}N isotope labelling experiments (use of $^{15}\text{N}_2$ in place of $^{14}\text{N}_2$ as the reactant) to mitigate undesired contamination or interference. This approach exploits the different heteronuclear ^{14}N - ^1H and ^{15}N - ^1H coupling patterns arising from the different spin I between ^{14}N ($I = 1$) and ^{15}N ($I = 1/2$), thus resulting in a triplet ($^1J = 52$ Hz) and a doublet ($^1J = 73$ Hz), respectively, of the NH_4^+ signal at ca. 7 ppm. Consequently, it enables the simultaneous quantification of $^{15}\text{NH}_4^+$ and $^{14}\text{NH}_4^+$ with a discernible discrimination between the two species. However, it requires expensive instrumentation and specialist knowledge [48,49].

All methods described are well-established and possibly suitable. Nevertheless, operational constraints must be considered as well as the sample matrix (pH, ions, solvents, and impurities) which can impact measurements. Although IC emerges as the best method, a combination of multiple techniques is often necessary to accurately quantify the amount of ammonia produced during NRR experiments.

1.3. Porphyrins and phthalocyanines as catalysts for NRR

Molecular catalysts are compounds designed at the molecular level and typically consist of organometallic complexes in which a transition metal is coordinated with specific ligands or organic frameworks. Among all organometallic complexes, metal-porphyrins and -phthalocyanines have been gaining attention due to their unique structural and electronic properties. Indeed, their structures can be modified and tailored by changing the central metal ions or substituents, allowing fine-tuning of their electronic and steric properties to optimize catalytic activity and selectivity for NRR. In addition, the synthesis is more affordable and cost-effective compared with other metal-based catalysts and multi-dimensional networks structures such as MOFs and COFs. Finally, from the sustainability point of view, porphyrins and phthalocyanines allow to activate and bind nitrogen molecules under relatively mild conditions compared to traditional H-B process. For all these reasons, researchers are exploring various modifications to these molecules and/or incorporating different metals to enhance their efficiency and selectivity in converting N_2 to NH_3 .

In 2021, two pioneering works reported the application of porphyrins-based catalysts in E-NRR.

In the first one, Yang and co-workers synthesized a porphyrin single iron site catalyst iron-*meso*-tetraphenyl porphyrin chloride (**FeTPPCl**) which was then studied as a model for E-NRR under ambient conditions [50]. This work proved that the electron deficiency of the Fe sites enables the strong absorption and activation of N_2 during NRR by forming

stable iron dinitride (FeN_4) coordination structures. During the NRR process, upon removing a chlorine atom from **FeTPPCl**, the Fe sites perpendicular to the Fe-porphyrin plane become the electron-deficient centres as Lewis's acid centres and can strongly coordinate a N_2 molecule. In the E-NRR tests, **FeTPPCl** showed encouraging catalytic performance reaching the highest NH_3 yield of $18.3 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ and a Faradaic Efficiency (FE) of about 17 %. No presence of hydrazine was detected, confirming a prominent selectivity of **FeTPPCl** catalyst for NH_3 formation. Additionally, remarkable stability is achieved, which can be maintained continuously for 36 h in a N_2 -saturated neutral solution (Fig. 2a.) [50].

Similarly, in a second study, Sun and co-workers demonstrated that a well-defined Co-tetraphenylporphyrin (**CoTPP**) can be suitable as a catalyst for E-NRR exhibiting good electrocatalytic nitrogen reduction activity with an NH_3 yield of $15.2 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ and a FE of ca. 11% [43]. The activity of the metal-porphyrin electrocatalyst is attributable to the full exposure of the metal-porphyrin sites, which efficiently coordinate N_2 and accelerate its activation. Moreover, the catalyst also showed satisfactory electrolytic stability and recycling test reusability [43].

Very recently, we have studied the possibility to further increase the performances of porphyrins based catalysts (**CuTPP** and **CoTPP**) introducing hydrophilic tris(ethyleneglycol)monomethyl ether (TEG) groups to increase the electrolyte-catalysts interaction and, consequently, the NH_3 yield. Encouraging results have been achieved, showing a threefold increase in NH_3 yield for hydrophilic-CoTPP (**CoTPP-TEG**) and a twofold increase for hydrophilic-CuTPP (**CuTPP-TEG**). This study suggests that the introduction of hydrophilic pendants into the porphyrin scaffold might be useful to avoid problems of low wettability of the working electrode (carbon paper) on which the catalyst is deposited. Therefore, improving the hydrophilicity of the electrocatalyst promotes interaction between the working electrode and the aqueous-based electrolyte system. Furthermore, the presence of side chains can encourage a distinct supramolecular orientation of porphyrins on the electrode substrate, thereby facilitating the N_2 fixation process.

Phthalocyanines have been also exploited as catalysts for E-NRR. In 2023, Adalder and co-workers developed a carbon-supported Mn-phthalocyanine (**MnPc/C**) with a simple and cost-effective process. The **MnPc/C** E-NRR catalyst showed excellent selectivity and specificity with a maximum NH_3 production rate of $128 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ and a FE of 35%. The electrocatalytic activity of such material can be attributed to an efficient interaction of **MnPc** with the electron cloud of carbon black, providing better electron transfer by the carbon support (Fig. 2b) [51].

On the top of our knowledge, no porphyrin or phthalocyanines have been used in Photo-NRR yet. However, the studies cited above pave the

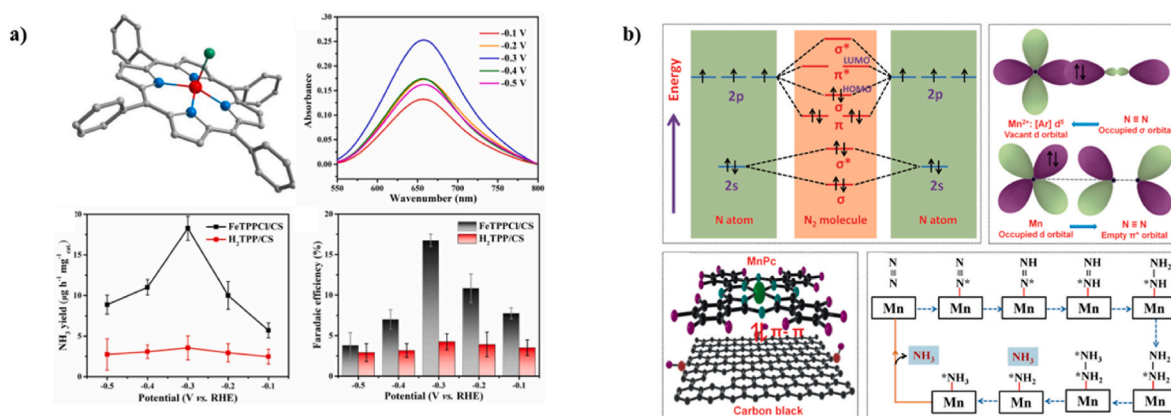


Fig. 2. a) The FeTPPCl electrocatalyst (Fe in red and Cl in green) and UV-vis absorption spectra of the electrolytes stained with indophenol blue indicator after electrolysis for 2 h in various applied potentials, average NH₃ production rate and average FE. Adapted with permission [50]. b) MnPc and carbon black interaction (the black, green, cyan, pink, and red balls are labeled C, Mn, N, H, and O, respectively) with molecular orbitals, electronic transition and probable N₂ to ammonia conversion mechanism. Adapted with permission [51]

way to scientific investigations of other transition metal-phthalocyanines/porphyrins for widespread application in NRRs. The outlook for porphyrins and phthalocyanines in NRR involves continual innovation, exploiting their unique structures and tuneable properties to engineer efficient, selective, and sustainable catalysts. This result can be achieved thanks to the possibility of varying the ligand structure by introducing functional groups, adjusting the metal centres, and creating specific active sites for N-activation and reduction, up to the exploration of the potential of nanostructured forms for improved efficiency and control in NRRs.

The performances of the above cited porphyrins and phthalocyanines-based catalysts for NRRs are summarized in Table 1.

1.4. MOFs for E-NRR

Despite the above-mentioned encouraging studies of using porphyrin and phthalocyanine-based catalysts, the research in this field is still dominated by extended networks such as MOFs [53,54].

However, the combination of MOF network and porphyrin structures has been exploited in 2021 in a work by Zang and co-workers. In the cited paper, a series of metal porphyrin-based MOFs has been successfully synthesized and used as catalysts for NRR. The Fe-based catalyst (Fe-TCPP) exhibited prominent performance with a high NH₃ yield of 44.77 μg h⁻¹ mg_{cat}⁻¹ and a FE of 16%. The superior performance was ascribed to the highly effective N₂ activation at the iron site and benefited from the overall reaction thermodynamics advantage in the key reaction step. The optimum activity of Fe-TCPP for NH₃ formation was further confirmed by DFT calculations, which verified the effective N₂ activation at the Fe site and the favorable overall reaction thermodynamics on Fe-TCPP [55].

In general, even without porphyrin pendants, MOFs have been capturing interest in E-NRRs due to the adjustable porous environments, plentiful structures, and large surface areas which confer unique advantages for electrocatalytic N₂ conversion to NH₃, such as precise construction, accessible catalytic site, good regulation, and N₂

Table 1
NRR performances of porphyrin and phthalocyanine-based catalysts.

Catalyst	NH ₃ yield rate	FE	Detection method ^a	Ref.
FeTPPCl	18.3 μg h ⁻¹ mg _{cat} ⁻¹	16.8%	IB/ ¹ H NMR	[50]
CoTPP	15.2 μg h ⁻¹ mg _{cat} ⁻¹	11.4%	IB/ ¹ H NMR	[43]
MnPc/C	127.7 μg h ⁻¹ mg _{cat} ⁻¹	35.3%	IC/ ¹ H NMR	[51]
CoTPP-TEG	1.1 μg h ⁻¹ mg _{cat} ⁻¹	37%	IC	[52]
CuTPP-TEG	1.1 μg h ⁻¹ mg _{cat} ⁻¹	28%	IC	[52]

^a IB: indophenol blue assay; IC: ion chromatography.

enrichment capacity [56–58].

The first series of E-NRR catalysts based on MOFs were reported by Zhao and co-workers in 2017, showing catalytic activity for ammonia synthesis at low temperature and ambient pressure. Among all metal ions tested the iron-based MOF (MOF(Fe)) displayed the best catalytic activity, the highest ammonia formation rate and the highest Faradaic efficiency (FE) reaching 2.1×10^{-9} mol s⁻¹ cm⁻² and 1.4%, respectively [59].

In 2020, other monometallic Fe-based MOF have been synthesized by Li and co-workers: MIL-88B-Fe and NH₂-MIL-88B-Fe [60]. They exhibit high selectivity under ambient conditions reaching the highest NH₃ yield rate of 1.2×10^{-10} mol s⁻¹ cm⁻² with a FE of 5.7% at -0.45 V and 12.4% at 0.05 V, surpassing most previous reported catalysts used under ambient conditions (Fig. 3a) [60].

Despite the promising results of Fe-based MOFs, other metals have been tested in the same period. An example is the work of Cao and co-workers where a Cu-based MOF (HKUST-1) was developed demonstrating to be a highly efficient non-precious metal catalyst for E-NRRs achieving a remarkable NH₃ yield of 46.6 μg h⁻¹ mg_{cat}⁻¹ and an FE of 2.4%, with good selectivity for N₂ to NH₃. [63] Similarly, Xiong and co-workers synthesized a conductive Co-based MOF (Co₃HHTP₂) which reached an NH₃ yield of 22.1 μg h⁻¹ mg_{cat}⁻¹ and a FE of 3.3% at -0.40 V, also providing one of the first available approaches for the ambient N₂ fixation using conductive MOFs [64].

However, one of the main issues related to E-NRR catalysts remains the inhibition of the HER competitive reaction. Recently, the main group elements, such as bismut (Bi) [65], boron (B) [66], and aluminium (Al) [67] have been corroborated as NRR catalysts with an acceptable inhibition of hydrogen evolution. Indeed, compared with the d-orbital transition metals, the p band of main-group elements is more inclined to couple with the N 2p orbital of N₂, leading to the effective inhibition of HER. [66] In this context, Fu and co-workers developed an Al-based MOF (MIL-100(Al)), which exhibited a remarkable N₂-to-NH₃ fixation ability with a yield of 10.6 μg h⁻¹ cm⁻² mg_{cat}⁻¹ and a FE of 22.6% at an ultralow overpotential (177 mV, close to the theoretical equilibrium potential) (Fig. 3b) [61].

In a similar fashion, Yan and co-workers investigated Al-based defective MOF (Al-Fum). Through a solvent-assisted linker exchange, defective Al sites have been created founding that Al-Fum enables stable and effective electrochemical NRR, in terms of the highest production rate of 53.9 μg(NH₃) h⁻¹ mg_{cat}⁻¹ and a FE of 73.8% under ambient conditions [67].

To further confirm the main group metals-based MOFs as promising electrocatalysts for NRRs, Tan and co-workers reported a post-synthetic exchange of Ti into Zr-based MOF to obtain the so-called bimetallic

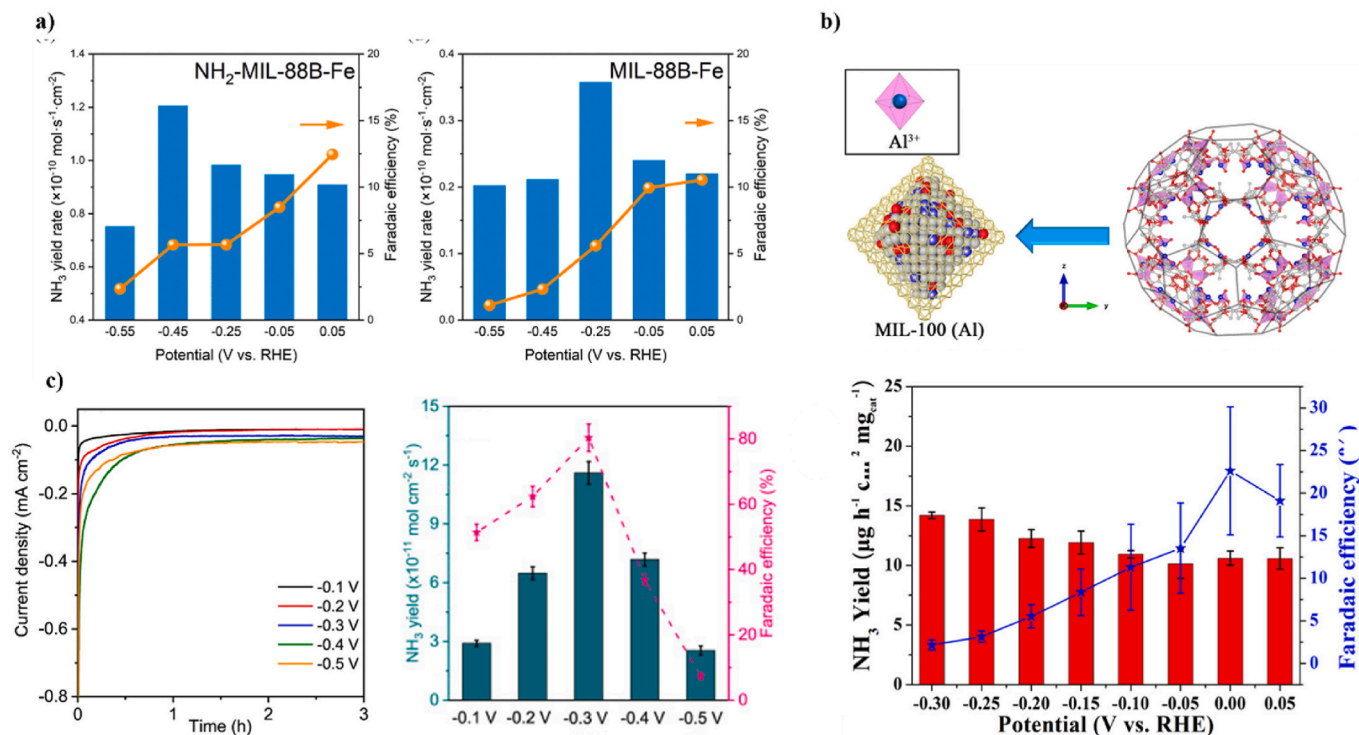


Fig. 3. Representative examples of MOF-based catalytic studies for NRR. a) NH₃ yield and FE of NH₂-MIL-88B-Fe and MIL-88B-Fe measured at different potentials. Adapted with permission [60]. b) MIL-100(Al) structure (top) and performances in NH₃ production (bottom). Adapted with permission [61]. c) Chronoamperometric curves of UiO-Zr-Ti-5d, NH₃ yield rate and FE of UiO-Zr-Ti-5d at different potentials. Adapted with permission [62].

MOF; UiO-Zr-Ti-5d. The new MOF demonstrated to efficiently catalyse N₂ electroreduction to NH₃ unfolding a NH₃ yield of 1.16×10^{-10} mol cm⁻² s⁻¹ and the highest FE of 80.36% (Fig. 3c.). [62] The incorporated Ti is found to function as active sites for NRR and benefit the improved charge-transfer efficiency, which has a positive effect on the high NH₃ yield rate. Moreover, the existence of Zr and Ti species can effectively suppress the competing HER, thus leading to high FE [62].

To further increase ammonia yields, another strategy is the combination of two metallic centres. Indeed, bimetallic MOFs often exhibit higher catalytic activity compared to their monometallic counterparts due to synergistic effects between the two metals. This synergy can lead to improved efficiency in the NRR process. Moreover, the presence of multiple metals can create unique active sites with distinct selectivity towards certain reaction pathways, enhancing the selectivity of the NRR process and reducing the formation of undesired byproducts [57]. Indeed, bimetallic MOFs retain some components of the two metal oxides which can both serve as efficient NRR exhibiting outstanding electrochemical activity and stability as well as improved structure, porosity, active site, adsorption, and selectivity [54].

In this context, CoFe- and NiFe-based MOFs emerges as efficient candidates for the electrochemical N₂ reduction to NH₃. A recent example has been reported by Duan and co-workers who synthesized a bimetallic NiFe-MOF via a feasible two-step strategy [68]. The bulk bimetallic MOFs were in-situ synthesized by mixed Ni/Fe salts and organic ligands revealing an excellent NH₃ yield ($9.3 \mu\text{g h}^{-1} \cdot \text{mg}_{\text{cat}}^{-1}$) and FE (11.5%) because of the synergy of Fe and Ni cations in the bimetallic system.

Another interesting bimetallic system is the so-called Co₃Fe-MOF developed by Li and co-workers [69]. The Fe element was incorporated into Co-MOF to generate Co₃Fe-MOF via an in-situ solvothermal synthetic method. The resultant bimetallic MOF, in the nanosheet-like form, reached a yield of $8.8 \mu\text{g h}^{-1} \cdot \text{mg}_{\text{cat}}^{-1}$ and a FE of 25.6%, further confirming that bimetallic MOFs have high intrinsic catalytic activities to promote ambient NH₃ production via sustainable electrocatalytic N₂

reduction [69].

The performances of the above cited MOF-based catalysts for E-NRR are summarized in Table 2.

1.5. MOFs for Photo-NRR

In the field of photocatalytic NH₃ generation significant studies have been carried out to develop innovative materials capable to act as catalysts, including several inorganic compounds and composites [70–72]. Nevertheless, their function as photocatalysts faces several obstacles, such as limited light capturing capabilities, short electron–hole pair

Table 2
E-NRR performances of MOF-based electrocatalysts.

Catalyst	Electrolyte	NH ₃ yield rate	FE	Detection method ^a	Ref.
Fe-TCPP.	0.1 M HCl	44.77 $\mu\text{g h}^{-1}$ $\text{mg}_{\text{cat}}^{-1}$	16.23%	IB/IC/ ¹ H NMR	[55]
MOF(Fe)	2 M KOH	2.1×10^{-9} $\text{mol s}^{-1} \text{cm}^{-2}$	1.4 %	NR	[59]
NH ₂ -MIL-88B-Fe	0.1 M Na ₂ SO ₄	1.2×10^{-10} $\text{mol s}^{-1} \text{cm}^{-2}$	12.4 %	IB	[60]
HKUST-1	0.1 M Na ₂ SO ₄	46.6 $\mu\text{g h}^{-1}$ $\text{mg}_{\text{cat}}^{-1}$	2.4 %	IB	[63]
Co ₃ HHTP ₂	0.5 M LiClO ₄	22.1 $\mu\text{g h}^{-1}$ $\text{mg}_{\text{cat}}^{-1}$	3.3 %	IB	[64]
MIL-100(Al)	0.1 M KOH	10.6 $\mu\text{g h}^{-1}$ $\text{cm}^{-2} \text{mg}_{\text{cat}}^{-1}$	22.6 %	IB	[61]
UiO-Zr-Ti-5d	0.1 M Na ₂ SO ₄	1.16×10^{-10} $\text{mol cm}^{-2} \text{s}^{-1}$	80.36%	IB	[62]
NiFe-MOF	0.1 M NaHCO ₃	9.3 $\mu\text{g h}^{-1}$ $\text{mg}_{\text{cat}}^{-1}$	11.5 %	IB/ ¹ H NMR	[68]
Co ₃ Fe-MOF	0.1 M KOH	8.8 $\mu\text{g h}^{-1}$ $\text{mg}_{\text{cat}}^{-1}$	25.6 %	IC/ ¹ H NMR	[69]

^a IB: indophenol blue assay; NR = Nessler's reagent assay; IC: ion chromatography.

lifetimes, weak electron transfer, and limited active sites [45]. To overcome these issues, a rational design of photocatalysts that satisfy all these requirements is needed. In this scenario, MOF-based catalysts become one of the most prevalent choices because of their facile synthesis, the high structural/chemical tunability, and, most importantly, the possibility to be functionalized with linkers able to improve the light-harvesting ability. To reach this purpose the combination of porphyrins with MOF scaffolds, to combine the previously mentioned benefits of molecular materials with MOF structures, has been exploited by Shang and co-workers [73]. In this work the use of porphyrins as a light harvesting ligand, allow to obtain a porphyrin-based MOF (**Al-P-MOF(Fe)**) which exhibits excellent activity toward visible light with an NH_3 production rate of $127 \mu\text{g}^{-1} \text{h}^{-1}$. Such results have been justified by the combination of the efficient light harvesting capability of the porphyrins with the highly porous structure induced by the Al presence which also acts as metal node [73].

In previous studies, the use of Fe-based MOFs without any pendants has been already exploited as a promising approach in Photo-NRRs [44]. Inspired from natural structures (i.e. nitrogenase, electron-donating Fe proteins and catalytic MoFe proteins), Li and co-workers synthesized 3 Fe-based MOFs, **MIL-88(Fe)**, **MIL-100(Fe)** and **MIL-101(Fe)**, which were employed and tested for Photo-NRRs showing NH_3 yield up to $50.3 \mu\text{mol L}^{-1} \text{h}^{-1}$ for **MIL-101(Fe)** [74]. Moreover, by comparing these catalysts with Cr-based MOF, the Fe atom emerges as a key catalytic centre having a higher electron density, and a lower reaction activation energy, increasing the generation of N-H bond (Fig. 4a). However, nowadays, to increase the light harvesting properties of MOF-based photocatalysts the side-functionalization with organic linkers is a widespread approach. Such synthetic strategy has been efficiently exploited for photocatalytic H_2 production and CO_2 reduction introducing amine functionalities in the catalyst structures [75,76]. It has also been proved that the introduction of amines as pendants in transient metal complexes can increase the selectivity of the reaction facilitating intramolecular proton movement to the metal centre, thereby promoting the formation of NH_3 rather than the undesired hydrazine [77]. In addition to the widespread amines, other types of linkers have been used

to improve the light-harvesting ability of MOFs. In 2021 Jiang and co-workers published a study in which analysed the effect of the introduction of hydroxy (OH), thiol (SH) and chloride (Cl) groups in U (**Zr-Hf**)-X MOF structure ($X = 2 \text{ SH}, 2 \text{ OH}, 2 \text{ Cl}$) [78]. Among all functional groups tested, **U(Zr-Hf)-SH** exhibited the higher NH_3 production rate reaching $116 \mu\text{mol g}^{-1} \text{h}^{-1}$ under visible light, which was associated with an optimal electron transfer pathway (Fig. 4b) [78].

Another approach to modulate the structural, optical, and chemical properties of MOF-based semiconductors is the metal-doping. A pioneering work on this field has been carried out by Zhang and co-workers who introduced Cu into **MIL-101(Fe)** to obtain a new photocatalyst (**x-Cu/MIL-101(Fe)**) capable to achieve a yield of $315 \mu\text{mol h}^{-1} \text{g}^{-1}$ of NH_3 , three times higher than that of unmodified sample [81]. Similarly, Yan and co-workers modified a series of MOF-74 with different concentration of Ru (**Ru-MOF-74**) to enhanced light-harvesting ability by narrowing the bandgap of the compound through Ru doping [79]. In this work, 2% Ru-MOF-74 showed a six times higher photocatalytic activity of N_2 fixation into NH_3 under visible irradiation, compared to the bare MOF-74 (Fig. 4c). The rationale behind this result attributed to the narrowing of the band gap induced by the introduction of Ru^{3+} ions, driven by the quantum confinement effect. In this scenario, under visible irradiation ($\lambda > 400 \text{ nm}$), more electrons and holes can be excited. The photoexcited electrons in the LUMO energy levels move to the energy levels of Ru^{3+} ions instead of recombining with the holes in the HOMO energy levels. Consequently, the rapid recombination of electrons and holes is inhibited, allowing for the separation and transfer of electrons to the surface of catalysts where they can react with N_2 and H^+ to generate NH_3 [79].

Apart from metal-doping, the introduction of defects in the MOFs structures has also been proven to be effective for Photo-NRRs [82]. Luo and co-workers discovered that ligand defects on **UiO-66** induced by UV light irradiation could significantly enhance the NRR performances which increased from $125 \mu\text{mol g}^{-1} \text{h}^{-1}$ for the pristine sample to $198 \mu\text{mol g}^{-1} \text{h}^{-1}$ for the defective sample. Such result has been justified by the formation of unsaturated metal nodes induced by the presence of defects [83]. In a similar manner, Guo and co-workers dehydrated at

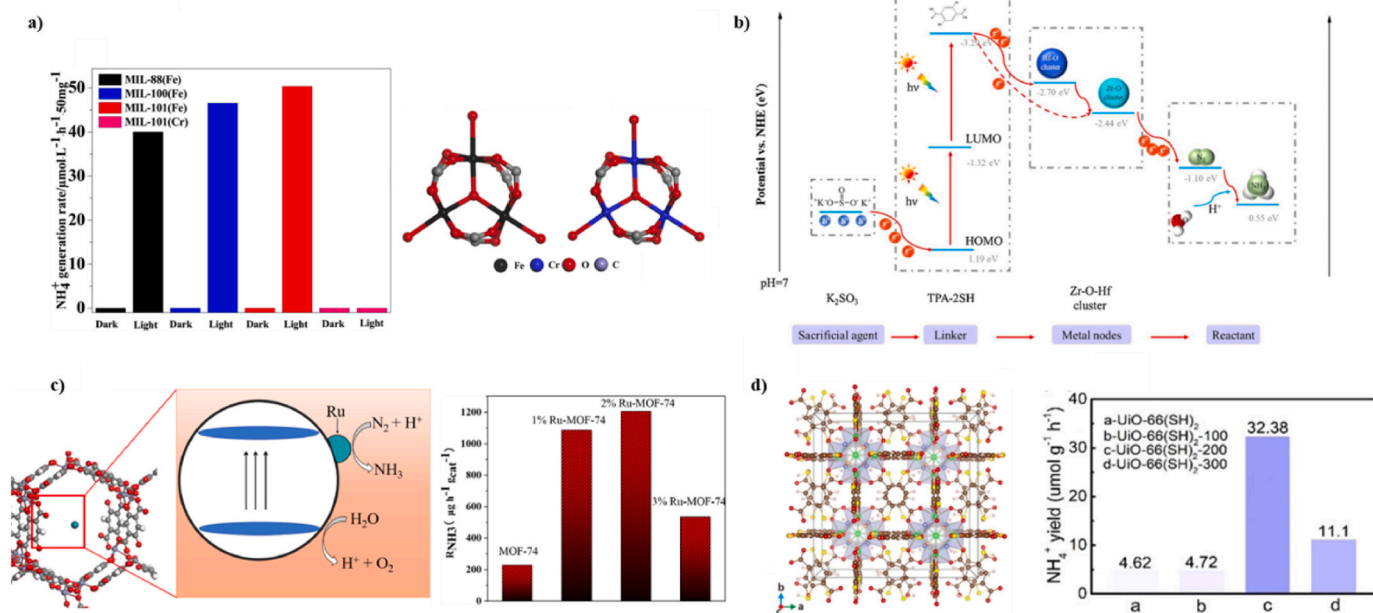


Fig. 4. Representative MOF-based catalytic studies for Photo-NRR a) Photocatalytic nitrogen fixation activities of **MIL-88(M)** samples and building unit of **MIL-101; MIL-101(Fe)** and **MIL-101(Cr)**. Adapted with permission [74]. b) Electron transfer pathway for the nitrogen reduction over **U(Zr-Hf)-SH**. Adapted with permission [78]. c) Photocatalytic mechanism of nitrogen reduction for X%**Ru-MOF-74** samples and yield rate of ammonia by Photo-NRR at different Ru concentration. Adapted with permission [79]. d) Simulated crystal structure of **UiO-66(SH)₂** and ammonia yield of various **UiO-66(SH)₂** measured within 6 h under visible light ($\lambda > 400 \text{ nm}$). Adapted with permission [80].

different temperatures (100, 200 and 300 °C) UiO-66(SH) MOF scaffold to allow to form linker defects around the metal core cluster. The experimental data show that the sample treated at 200 °C (UiO-66-(SH)₂-200) reached NH₃ yield seven times higher than the untreated sample (Fig. 4d) [80]. Indeed, the introduced linker defects were found to open a “gate” for the diffusion of N₂ into the metal cluster and the unsaturated metal nodes boost photocatalytic activity.

The performances of the above cited MOF-based catalysts for E-NRR are summarized in Table 3.

1.6. COFs for E-NRR and Photo-NRR

The layered porous structures of COFs, composed of organic building blocks that are linked together by strong covalent bonds, has been found to lead to a more precise control over their structure and properties at the molecular level. Moreover, the presence of covalent bonds also makes COFs more robust against structural changes or degradation, providing long-term stability in many environments [84]. Furthermore, the microenvironment of catalytic centres can be precisely tuned at the molecular level with predesigned building blocks. As for the previously mentioned MOFs, also in COF scaffold the combination with porphyrins and phthalocyanines has been exploited both to achieve better light harvesting in Photo-NRR and to increase the charge transfer in E-NRR. On this account, He and co-workers recently developed a series of porphyrin-based COFs loaded with Au single atoms (COFX-Au, X = 1–5) [85]. In these systems the porphyrin macrocycles act as molecular docking sites to immobilize Au species as single atoms. Interestingly, the micro-environment of Au catalytic centres is precisely tuned by changing the functional groups at the proximal and distal positions of porphyrins via a modular design strategy. All COFX-Au photocatalysts display excellent NH₃ evolution performance in photocatalytic N₂ reduction along with excellent stability. Among all catalysts, COF1-Au and COF5-Au decorated with electron-withdrawing groups, exhibited highest NH₃ production rates of 333 and 428 μmol g⁻¹ h⁻¹, respectively. The superior performances of photocatalysts decorated with electron-withdrawing groups is ascribed to the higher charge separation efficiency and lower charge transfer resistance (Fig. 5a) [85]. On the other hand, a series of pyrazine-linked metal-phthalocyanine (MPc)-based 2D c-COFs (M = Fe, Co, Ni, Mn, Zn, and Cu) has been developed by Feng and co-workers exhibiting very encouraging performances with an NH₃ yield of 33.6 μg h⁻¹ mg⁻¹ and an FE of ca. 32% for the Fe-based catalyst (FePc-pz) (Fig. 5b) [86]. The reason behind this results lies in the two-dimensional conjugated covalent organic frameworks (2D c-COFs), with high in-plane π-delocalization and weak out-of-plane π-π stacking. The resulting columnar structure with pore array and high surface area, can indeed provide a large fraction of

readily accessible active sites and sufficient mass transport, beneficial for high-efficiency electron transfer kinetics [86]. More recently, exploiting the transition metals properties, a series of fully π-conjugated phthalocyanine-rich COFs anchored with ordered N-coordinated metal centres (Ti, Cu, or Co) have been synthesized by Jiang and co-workers [87]. Benefiting from the abundant N-coordinated metal centres, the activation of inert N₂ molecules could be effectively promoted and the occurrence of the HER could be effectively suppressed. Among all M-COF tested the Ti-COF exhibited the highest catalytic activity and selectivity for the electrocatalytic NRR achieving an NH₃ yield of 26.9 μg h⁻¹ mg⁻¹ and an FE of 4.6% for E-NRR [87].

However, other approaches have been explored for the synthesis of efficient COF catalysts for NRRs. For instance, exploiting the very promising Single Atom Catalysts (SACs) research area, in 2020 a kind of COF made with Covalent Triazine Frameworks (CTF) has been found to endow the capabilities to construct SACs having metal-N_x structures suitable for Photo-NRRs. Indeed, single-atom Pt has been anchored at the N₃ sites of CTF nanosheets to obtain the so-called Pt-SACs/CTF [89]. The well-defined coordination structure of Pt-N₃ sites allows an ammonia yield of 171 μmol g⁻¹ h⁻¹ confirming that SACs have a high potential to also improve Photo-NRR due to their high specific activity while maximizing atom utilization [89].

Despite the high performances exhibited by the above-described COF structures, the ongoing economic challenges encourage the development of metal-free catalysts with extremely effective active sites since they improve output while lowering total cost. It has been found that electron deficiency, caused by boron doping in the COFs, increases their electrocatalytic activity. For this purpose, Liu and co-workers developed a boron-rich COF that exhibited a nitrogen production rate of 12.5 μg h⁻¹ mg⁻¹ with an FE of 45.4% via E-NRR [90]. To the best of our knowledge, this is the top metal-free catalyst record-breaking activity reported.

For Photo-NRRs the use of boron has been exploited as well. Dutta and co-workers, by anchoring boron atoms in a COF scaffold obtained a B@Tp-bpy-COF demonstrating that N₂ can be efficiently activated on the boron centre due to the synergistic effect of B-N. The photocatalyst exhibits 100% selectivity of NH₃ production over the HER (Fig. 5c) [88]. Moreover, the suitable band edge positions and broad visible light absorption zone resulted in acting as a promising photocatalyst. Indeed, the unique COF structure also allows the incorporation of photoactive organic species into the frameworks, thus expanding its application to a wide range of photocatalytic reactions [91]. The crystalline 2D π lattices in semiconducting COFs can act as pathways to facilitate the charge transport and separation preventing the recombination of charge carriers [92]. Finally, the photosensitizers and co-catalysts are easily assembled into a single system simultaneously due to the pre-designability and integrity of COFs as compared to conventional photocatalysts.

The performances of the above cited COF-based catalysts for NRR are summarized in Table 4.

Table 3
Photo-NRR performances of MOF-based photocatalysts.

Catalyst	Light Source	NH ₃ yield rate	FE	Detection method ^a	Ref.
MIL-101 (Fe)	full spectrum	1007 μmol h ⁻¹ g ⁻¹ cat	50%	NR	[74]
U(Zr-Hf)-SH	full spectrum	116 μmol h ⁻¹ g ⁻¹ cat	-	IB/ ¹ H NMR	[78]
Al-PMOF (Fe)	visible light (λ > 420 nm, 100 mW cm ⁻²)	127 μg h ⁻¹ g ⁻¹ cat	50%	¹ H NMR	[73]
x-Cu/MIL-101(Fe)	full spectrum	315 μmol h ⁻¹ g ⁻¹ cat	-	NR	[81]
Ru-MOF-74	λ > 400	71 μmol h ⁻¹ g ⁻¹ cat	-	NR	[79]
UiO-66 (SH) ₂ -200	λ > 400	32 μmol h ⁻¹ g ⁻¹ cat	-	¹ H NMR	[80]

^a IB: indophenol blue assay; NR = Nessler's reagent assay.

2. Conclusions

The pursuit of sustainable NH₃ production through innovative methods like E-NRR and Photo-NRR has gained significant attention in recent years. In this mini-review the molecular catalysts used in both approaches have been analysed, focusing on porphyrin and phthalocyanine-based molecular catalysts as well as more mature MOF and COF organic-based extended structures. MOFs and COFs have emerged as promising catalysts for E-NRR, with various metal centres demonstrating notable efficiency. Additionally, the incorporation of functional groups in MOF and COF structures to enhance light harvesting capability results in a good strategy for the application of these catalysts also for Photo-NRRs. From the more rigorous perspective of molecular-based catalysts, metal-porphyrins, and metal-phthalocyanines present an intriguing avenue. Studies on iron and

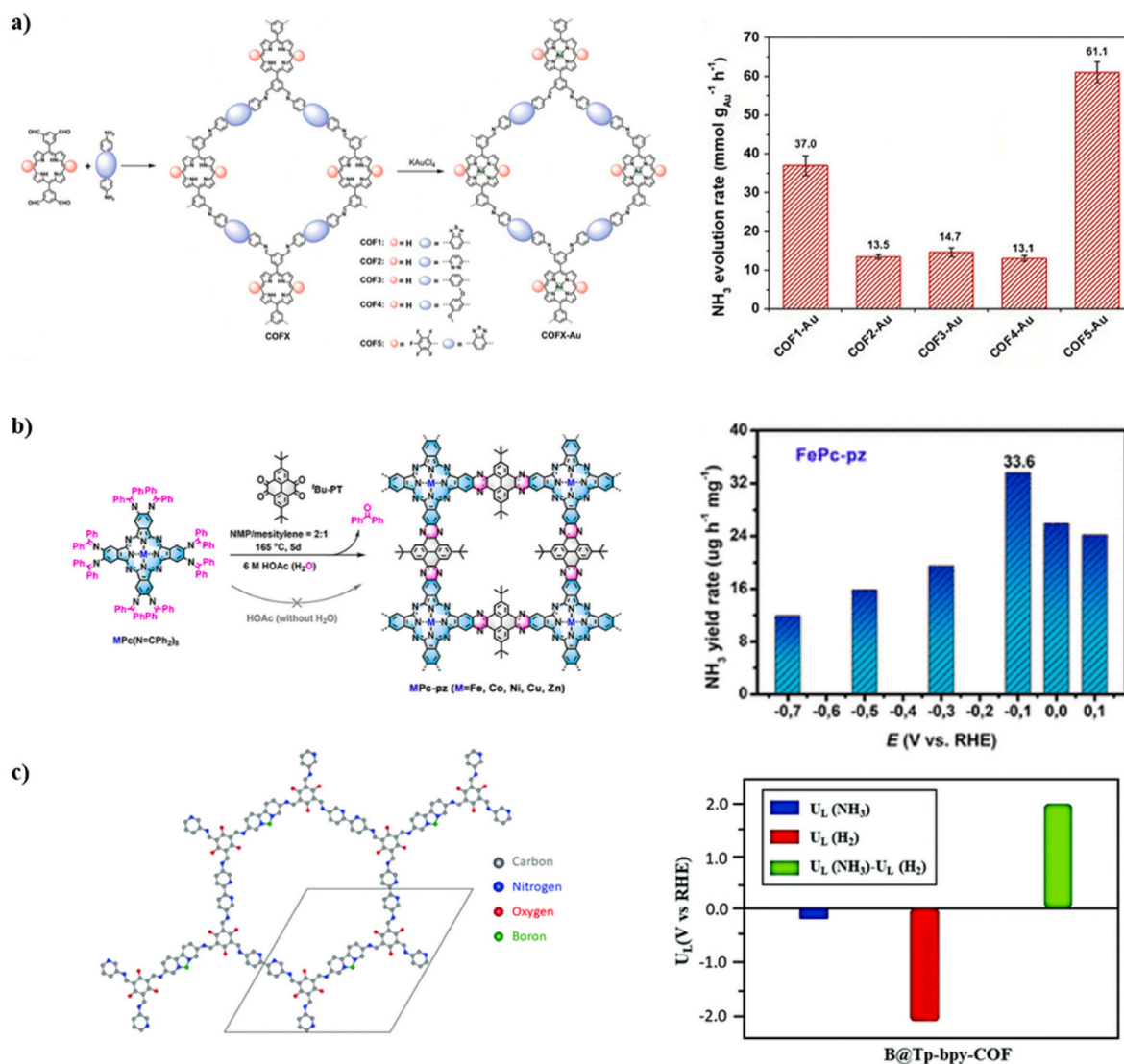


Fig. 5. Representative COF-based catalysts for Photo- and E-NRR. a) Synthetic strategy of COF-Au and their performances in Photo-NRR. Adapted with permission [85]. b) Schematic synthetic process of MPC-pz (M = Fe, Co, Ni, Cu, and Zn) and performances for FePc-pz at different potentials. Adapted with permission [86]. c) Optimized geometric structure of the B@Tp-bpy cell and comparison of the selectivity between the NRR and HER. Adapted with permission [88].

Table 4

NRR performances of COF-based photocatalysts.

Catalyst	medium	NH ₃ yield rate	FE	Detection method ^a	Type of NRR	Ref.
COF1-Au	ultrapure water	333 μmol h ⁻¹ g _{cat} ⁻¹	–	¹ H NMR	Photo	[85]
COF5-Au	ultrapure water	428 μmol h ⁻¹ g _{cat} ⁻¹	–	¹ H NMR	Photo	[85]
FePc-pz	0.01 M H ₂ SO ₄	33.6 μg h ⁻¹ mg _{cat} ⁻¹	32%	IB	Electro	[86]
Ti-COF	0.05 M HCl	26.9 μg h ⁻¹ mg _{cat} ⁻¹	4.6%	IB/IC	Electro	[87]
boron-rich COF	0.1 M KOH	12.5 μg h ⁻¹ mg _{cat} ⁻¹	45%	¹ H NMR	Electro	[90]
Pt-SACs/CTF	N ₂ -saturated water	171.40 μmol h ⁻¹ g _{cat} ⁻¹	–	NR/ ¹ H NMR	Photo	[89]

^a IB: indophenol blue assay; NR = Nessler's reagent assay; IC: ion chromatography.

cobalt-based porphyrins have shown encouraging catalytic

performances for E-NRR, while carbon-supported manganese-phthalocyanine showed high selectivity and specificity for the synthesis of ammonia. Even though molecular organometallic complexes, MOFs, and COFs still present challenges such as stability, cost, and complexity/scalability of synthesis, they exhibit distinct advantages and promising results in NRRs. Indeed, these innovative catalysts represent a significant step toward sustainable and eco-friendly production of ammonia, laying the groundwork for further advancements in the field.

CRediT authorship contribution statement

Ottavia Bettucci: Writing – review & editing, Writing – original draft, Conceptualization. **Giorgia Salerno:** Writing – original draft. **Norberto Manfredi:** Writing – review & editing. **Alessandro Abboto:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

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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