

Proceeding Paper

Metal-Organic Frameworks as Novel Photocatalysts: Opportunities for Catalyst Design †

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Abstract: Metal-organic frameworks (MOFs) are an evolving class of crystalline porous materials made of organic linkers and metallic nodes. The rich chemistry of MOFs allows them to have an almost infinite number of possible structures. Consequently, they have been of great interest because of their highly-tunable properties and unique features, such as their high porosity, high surface area, structural stability, structural diversity, and tailorability. These enable MOFs to be a flexible catalytic platform for photocatalytic applications. Thus, this paper discusses the opportunities of MOFs for use in catalysis. In particular, the use of metal-organic frameworks as a photocatalyst is briefly discussed. Specifically, MOFs can be used as a photocatalyst for carbon dioxide reduction (CO₂RR), nitrogen reduction reaction (NRR), and water splitting reactions (HER, ORR). However, using MOFs as catalytic platforms has some challenges that must be addressed to achieve commercialization. Therefore, this paper also discusses some prospects of designing MOFs for their specific catalytic applications to improve their catalytic properties and enhance selectivity. More importantly, an outlook is also provided on how MOF catalysts can further be developed to enable other catalytic reactions. Overall, MOFs have great potential as a photocatalytic material, provided they are uniquely designed to suit their intended applications.

Keywords: metal-organic frameworks; photocatalysis; carbon dioxide reduction; nitrogen reduction; water splitting

1. Introduction

Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), have unique physical and chemical properties, making them promising materials for various applications. Made from metal nodes and organic linkers, this class of crystalline and porous materials has an ultrahigh surface area, high porosity, high tunability of structures, and high tailorability, which made them superior over the traditional porous materials such as zeolites and activated carbons [1–5]. Specifically, MOFs, their heterostructures, and their derivatives have been extensively used for many catalytic applications owing to their large porous network that serves as catalytic sites to drive reactions including but not limited to, carbon dioxide and nitrogen reduction and catalytic water splitting. Widely-established processes such as photocatalysis [6–9], electrocatalysis [10–14], and photoelectrocatalysis [15] can be used to drive such reactions.

Using MOFs as novel catalytic materials could simplify complex organic synthesis routes toward producing hydrocarbons and other valuable chemical products. Moreover, transforming carbon dioxide from the atmosphere into more complex yet useful products could help address global warming phenomena. Furthermore, using MOFs in photocatalytic water splitting could offer a more cost-effective alternative to traditional noble metal catalysts, making the “hydrogen economy” more feasible to deploy on a larger scale. Given all these possibilities, there is no wonder that intense research is being

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done on MOFs as catalytic materials. Herein, we look at these materials as photocatalysts for the photocatalytic reduction of carbon dioxide and nitrogen. As can be seen from the detailed discussion of the mechanism of photocatalytic reduction, photocatalytic water splitting is an inevitable by-product of the reduction process. The current challenges encountered by researchers in this field based on the mechanisms presented are discussed, leading to various opportunities for designing novel MOFs as photocatalytic materials for various applications.

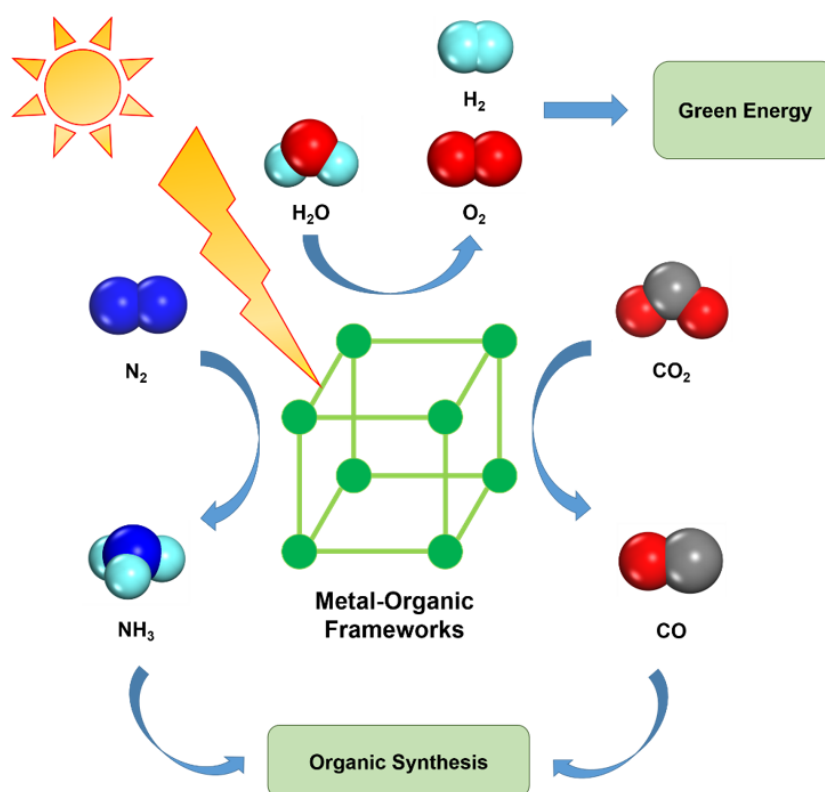


Figure 1. Metal-organic frameworks as photocatalysts. MOFs can be used to split water into hydrogen and oxygen, thus providing "green energy" in the form of hydrogen, which can be burnt without releasing carbon dioxide. MOFs can also be used to drive the reduction of carbon dioxide and nitrogen sequestered from the atmosphere to carbon monoxide and ammonia, respectively, which can be used as precursor materials for the synthesis of organic molecules. Most importantly, the MOFs can be tailored to be catalytically active in the visible light region, allowing solar energy to drive the above reactions without using electrochemical bias.

2. Metal-Organic Frameworks for Photocatalysis

Photocatalysis has been a subject of great scrutiny by many researchers for over two decades since the notable work of Honda and Fujishima [16] using semiconductor photocatalysts. Since then, various materials have been developed to find comparable alternatives to costly semiconductor materials and to improve their photocatalytic efficiencies [17–19]. In photocatalysis, a source of energetic photons is used to photo-activate the material of interest to overcome its band gap and enable its excitation. In the case of MOFs, the organic bridging ligands or linkers serve as antennas to harvest light and activate the metal nodes in the fashion of a linker to a metal cluster charge transition (LCCT) [20–24]. The photo-activated MOFs generate electrons and holes in a similar manner observed in semiconductor materials. Moreover, the transfer of the photogenerated electrons to the surface of the MOFs induces heterogeneous redox reactions, which can be tailored for carbon dioxide reduction, nitrogen reduction, water

splitting, and even in the organic synthesis where carbon dioxide can act as synthons for attaching carbon atoms in various organic compounds.

2.1. Carbon Dioxide Reduction

Carbon dioxide is a greenhouse gas that contributes to global warming. Anthropogenic sources of carbon dioxide have increased drastically since the third Industrial Revolution, leading to the increasing trend in atmospheric temperature worldwide. Current efforts to circumvent the effects of carbon dioxide are focused on reducing CO₂ production through carbon capture technologies. MOFs are one of the leading candidates for sustainable carbon capture and storage because of their high porosity and adsorption capacity [25–27]. More recently, the conversion of carbon dioxide to valuable products such as carbon monoxide, which is a key chemical intermediate in the chemical industry, and other C1 intermediates such as formic acid, methane, and methanol, among others, have emerged to be promising and feasible solution to reduce atmospheric concentrations of carbon dioxide and at the same time provide a renewable source of green energy.

Photocatalysis, being heterogeneous, has a very complex mechanism, and many reaction paths are possible, as shown in Figure The route depends on the life of charged particles. If their energy bandgap is lower, photoactivation may not be noticeable, and the electron-hole pair recombines immediately. If sufficient energy was used to activate the surface of the photocatalyst, in this case, MOFs, four possible scenarios may occur. First, the successful separation of the electron-hole pair allows the photogenerated electrons to reduce carbon dioxide in the presence of water to form various C1-C2 products (path 1). The selectivity of obtaining a particular product of interest can be fine-tuned by adequately designing the photocatalyst. Second, surface recombination (path 2) can occur when the electrons and holes recombine on the semiconductor surface. Similarly, this process is called volume or bulk recombination if the charges can recombine inside the photocatalyst volume (path 3). Lastly, just as the photogenerated electron can be used for photoreduction, the holes can be used for photo-oxidation; in this case, water is split into its constitutive elements (path 4) [28].

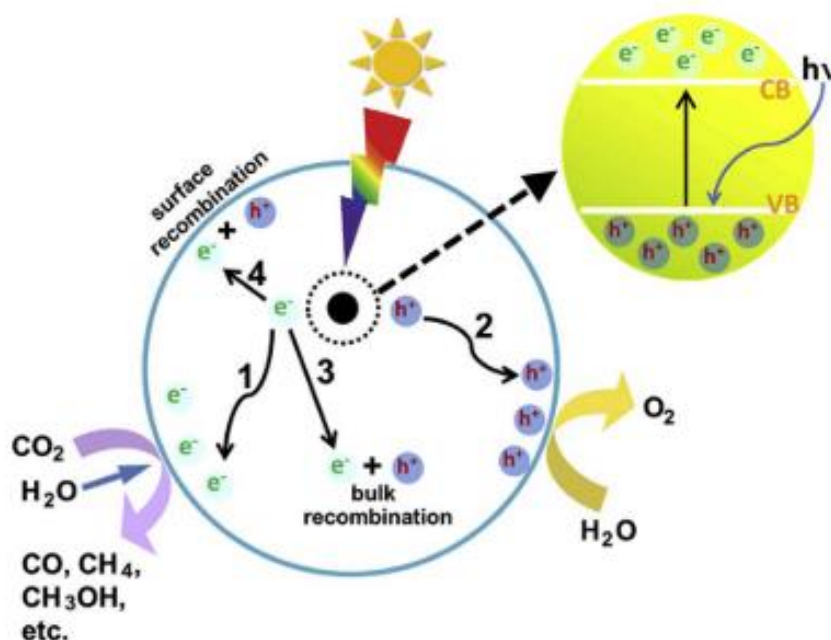


Figure 2. Schematic principle of the photocatalytic reduction of carbon dioxide. Herein, the action of an incident photon causes charge separation leading to the formation of an electron-hole pair. The photogenerated electrons can then reduce carbon dioxide mainly to carbon monoxide, but other

C1 species, such as methane and methanol, can form in more adverse conditions. Recombination processes on the surface or at the bulk of the photocatalyst are the main culprit for low efficiencies in most photocatalytic systems. Overcoming electron-hole recombination can be vital in enabling the mass adoption of this technology. Reprinted from Ref. [28], Copyright (2017), with permission from Elsevier.

MOFs for carbon dioxide reduction have gained popularity in previous years. However, it is still an active area of research across the globe because the unique structure of MOFs allows a wide variety of ligands with active functionalizing groups to be investigated for enhancing their optical properties, such as in the case of dual-linker MOFs [29] whose high activity was attributed to the co-existence of Lewis acidic and basic active sites on the catalyst derived from incompletely coordinated metal cations and uncoordinated pyridine groups. Moreover, the flexibility of MOFs to be synthesized using different metals to form multi-metallic MOFs [30,31] and the incorporation of metallic centers to form “caged” nanoparticles were reported to improve further its properties suitable for reducing carbon dioxide at wide reaction conditions [32–36]. MOFs can also be used to create composite heterostructures to have added functionalities of 2D materials such as graphene oxide [37], carbon-based materials such as carbon nanotubes and biomass [38,39], and even previously-known semiconductor photocatalysts such as titanium dioxide [40].

However, although MOFs have been successfully used for catalytic carbon dioxide reduction, many challenges continue to hound researchers. To gain acceptability for large-scale operations, the MOFs should remain catalytically active even after many cycles of operation without regeneration. Moreover, they should remain structurally stable under various operating conditions. Most importantly, since CO₂ is more thermodynamically and kinetically stable than its C1 and C2 counterparts, its reduction requires higher energy input. Therefore, solar-driven photocatalysis should be developed using visible light-active MOFs to minimize external energy use. Just like in semiconductor photocatalysis, the band gap of the MOFs can be fine-tuned to extend their catalytic activity to the visible light region; otherwise, they will only be catalytically active under UV illumination, which is energy-intensive and can potentially negate the objective of producing green fuels from carbon dioxide. Moreover, recombination processes, in which the photogenerated electrons and holes combine after photo-excitation, typically limit the photocatalytic efficiencies of photocatalysts, of which MOFs are no exception. Finally, the lifetime of the electron-hole pair is usually in the order of nanoseconds. Hence, efforts on designing MOFs that can extend the lifetime of the electron-hole pairs should be given focus.

2.2. Nitrogen Reduction Reaction (NRR)

The Haber-Bosch process, which consumes about 1% of energy worldwide, requires hydrogen produced from steam reforming of methane and atmospheric nitrogen to produce ammonia under harsh gas-phase reaction conditions, i.e., temperatures of around 500 °C and high pressures (200–300 atm), over iron- or ruthenium-based catalysts, all at the cost of a substantial carbon footprint [41]. In addition, ammonia is used as a precursor for synthesizing a wide array of essential chemicals such as urea and other synthetic amines.

Nitrogen reduction reaction (NRR), which involves the reduction of nitrogen on the surface of a catalyst and is driven either by light or electricity, has attracted worldwide research attention as a promising route for achieving green and sustainable ammonia synthesis at ambient conditions. When the NRR is successfully exploited using highly-efficient catalysts, the produced ammonia may be used in downstream chemical processes to obtain valuable chemicals. Furthermore, in tandem with photocatalytic carbon dioxide reduction and water splitting reactions, this can provide a route towards the photocatalytic synthesis of organic molecules simply from NH₃, CO₂, and H₂O. In this

regard, MOFs are seen to be promising materials to drive the nitrogen reduction reaction to fruition.

Nevertheless, although exciting advances have been made in the NRR field, the development of nitrogen-to-ammonia conversion is still very challenging because of the low ammonia yield, primarily due to the poor catalytic activity of existing catalysts. Furthermore, the photocatalytic nitrogen reduction reaction faces sluggish kinetics due to the intrinsically stable triple bond between the diatomic nitrogen molecules [42]. Therefore, the electrochemical approach seems promising but can circumvent the idea of producing ammonia in a sustainable and carbon-neutral manner. This requires high current densities to break the stable nitrogen bonds [43–47]. Hence, the rational design of photocatalysts seems to be the most effective course of action to achieve high conversion.

The nitrogen reduction reaction is well believed to proceed via two different routes, i.e., associative and dissociative mechanisms, as shown in Figure In the associative pathway, the nitrogen molecule first attaches itself to the catalyst's surface, just as in a typical catalytic reaction. The adsorbed nitrogen then undergoes catalytic hydrogenation while its two N atoms are still bound to each other, followed by the N-N bond's breakage to produce ammonia. The hydrogenation step can occur via two pathways—distal and alternating pathways. The N atom located at the furthest distance from the catalyst surface in the distal pathway is preferentially hydrogenated. This leads to releasing an NH_3 molecule, leaving an attached nitrogen atom on the catalyst surface. At a prolonged hydrogenation process, the remaining N atom is also hydrogenated.

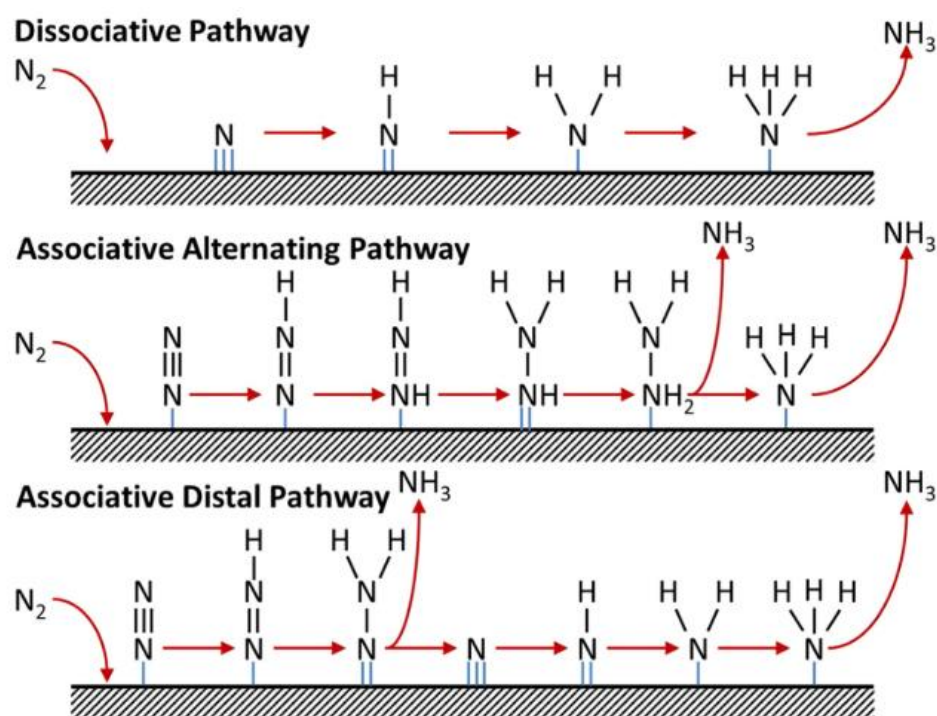


Figure 3. Schematic principle of the reduction of nitrogen on a catalyst surface to produce ammonia. There are two distinct mechanisms by which NRR can proceed: (a) associative mechanism and (b) dissociative mechanism. The associative mechanism follows nitrogen attachment, hydrogenation of nitrogen molecules either by distal or alternating pathways and then cleavage of the N-N bond. Meanwhile, the dissociative mechanism proceeds via the cleavage of the triple bond in the diatomic nitrogen molecule, followed by independent hydrogenation of each N atom. Reprinted from Ref. [47], Copyright (2017), with permission from Elsevier.

Meanwhile, in the alternating pathway, there is no preferential hydrogenation happening and, thus, releases two molecules of ammonia immediately after hydrogenation. Of course, the preferred path depends on the catalyst and the prevailing

reaction conditions. On the other hand, in the dissociative mechanism, the triple bond of the nitrogen molecule is first broken, leaving two separated nitrogen atoms attached to the catalyst surface. The adsorbed atoms then undergo hydrogenation independently before eventually converting to NH_3 molecules [47].

Like carbon dioxide reduction, photocatalytic nitrogen reduction reaction faces some challenges linked to either the effective harvesting of photons from the light source, band gap limitations, or electron-hole recombination. Although the theoretical potential required for the conversion of nitrogen to ammonia is similar to that for the hydrogen evolution reaction, the conduction band (CB) energy potential of the MOFs or any other photocatalytic material intended for NRR should be much more negative than the theoretical potential to overcome the energy barrier required for efficient NRR. Typical reasons for this are the overpotential for NRR and the energy loss of the photo-excited electrons, most probably due to recombination processes, either at the surface or at the bulk of the photocatalyst. The focus should then be made on designing MOFs through bandgap engineering and ligand engineering to tailor the band structure and enhance the efficiency of the above processes. Moreover, the crystalline structure and porous channels can be improved to enhance the porosity of existing MOFs and transport reactants and products in and out of the porous catalytic sites. Functionalities on the surface of MOFs can be added to enhance selectivity towards ammonia production and hasten the NRR by providing sites for easier accessibility toward nitrogen molecules.

2.3. Water Splitting Reaction

The water-splitting reaction consists of two significant reactions—the hydrogen evolution reaction (HER) and the oxygen reduction reaction (ORR). As shown in Figure 4, a typical process uses a photocatalyst material, such as semiconducting metal-organic frameworks, as catalysts to drive HER and ORR. Simply put, the irradiation of a photocatalyst by either ultraviolet or visible light causes the generation of electron-hole pairs which induces redox reactions, thus splitting water into hydrogen and oxygen. However, HER and ORR are usually limited by kinetic and thermodynamic constraints. For example, ORR has significantly more sluggish kinetics than HER, making it a rate-limiting step in water-splitting reactions. Thus, enhancing the ORR kinetics is the key to adopting water splitting for the hydrogen economy.

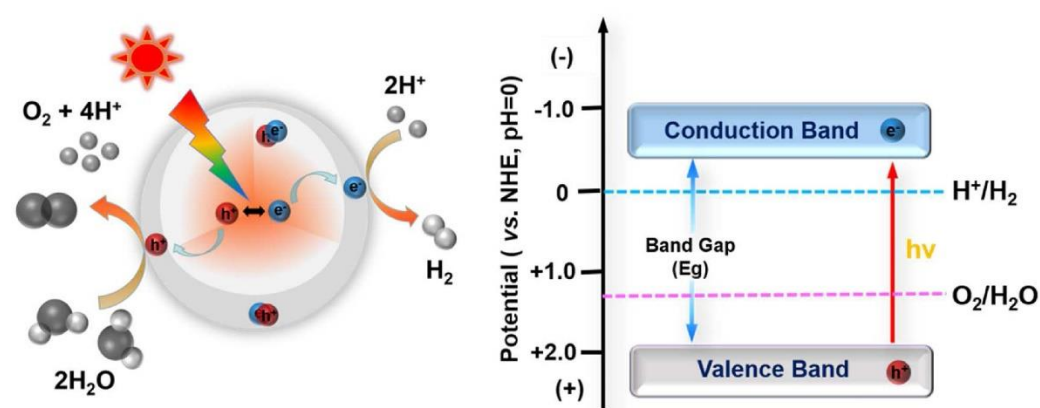


Figure 4. Schematic diagram of photocatalytic water splitting using metal-organic frameworks. Reprinted from Ref. [48], Copyright (2022), with permission from Elsevier.

Similar to typical photocatalysts, MOFs face some challenges when used for water-splitting reactions. For example, the band gap of MOFs dictates the excitation wavelength for electron-hole photogeneration. Moreover, the kinetic accessibility of the catalytic active sites is also an issue. Furthermore, the recombination of electron holes is of significant concern, for it reduces the overall efficiency of the process. Catalyst

deactivation thru sintering and poisoning is also possible, thus reducing the catalyst's performance. Most importantly, very few MOFs are stable under acidic and/or basic environments, effectively limiting the choice of MOFs.

These challenges must be overcome to use MOFs for water-splitting reactions. As such, MOFs' pores should be designed to ensure that the charge carriers travel a short distance to reduce recombination phenomena. Furthermore, functional groups may be anchored on MOFs to modify their bandgap, thus allowing them to be used for solar photocatalysis [49,50]. Metal nodes may be engineered to alter the electronic structure of the resulting MOFs [51–53]. Ligands may be chosen to serve as antennae to enhance photocatalytic water splitting. MOF construction should also consider using hydrophobic ligands to endow the resulting MOF with water stability necessary for the harsh acidic or basic conditions required during water splitting. MOFs may also be supported on hydrophobic polymers to ensure good water stability. Cocatalysts may be added to form heterojunctions with MOFs [54–56]. However, these modifications should not compromise the kinetic accessibility of the active sites.

4. Outlook on the Use of MOFs as Photocatalysts

MOFs have become potent materials in driving various catalytic reactions; the most notable to date are photocatalytic carbon dioxide, nitrogen reduction, and photocatalytic water splitting. MOFs for photocatalysis can also be extended to organic synthesis using CO₂, NH₃, and H₂O as building blocks for more complex organic compounds. Of course, this can be made possible because of the flexibility of MOFs to accommodate various modifications. Because of the tailorability of MOFs, various materials can be designed to match their intended applications. For example, an almost infinite number of MOFs can be developed by (i) varying the organic linkers to improve photon absorption, (ii) using various metal nodes, alloyed nodes, and/or using heterogeneous and multi-metallic nodes to improve the band structure and narrow its bandgap; (iii) caging metals, multi-metals, metal alloys, or nanoparticles within the porous network of MOFs to have added functionality or even achieve multi-functionalities, e.g., ORR, HER, NRR, etc.; (iv) modifying the active functional groups of organic linkers by using functionalizing agents; (v) modifying the crystal surface by creating heterostructures such as core-shell MOFs, 2D materials on MOFs, or nanoparticle-decorated MOFs; and (vi) tuning their surface morphology. Indeed, the rich coordination chemistry of MOFs allows us to design novel materials with new functionalities. As such, the role of theoretical chemists to elucidate the properties of these materials from first-principles calculations and molecular modeling coupled with machine learning to screen for the most effective recipe for ligands, metallic nodes, and metallic centers is seen to be extremely important in the coming years. Moreover, it is expected that research on MOFs and their applications to catalysis will have a bright future, especially in our quest to find sustainable, renewable, yet reliable sources of green energy and in the search for carbon-neutral industrial synthesis routes for valued chemicals.

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