Synthesis Procedures of Porphyrin-Based Metal–Organic Frameworks

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Contributor: Arash Ebrahimi , Lukáš Krivosudský

Metal–organic frameworks (MOFs)—typically formed from metal ions/clusters bridged by multidentate ligands in an extended framework—have provided solutions to tackle challenges in areas such as catalysis. By either integrating porphyrins/metalloporphyrins inside pores freely in situ or by grafting on the surface using post-synthetic methods and/or as part of the network component, porphyrin-based MOFs could be easily constructed.

metalloporphyrins metal–organic frameworks porphyrins catalyst synthesis procedures

1. Introduction

The recently emerged porous materials, metal–organic frameworks (MOFs)—typically formed from metal ions/clusters bridged by multidentate ligands in an extended framework—have provided solutions to tackle challenges in areas such as catalysis [1][2][3], gas storge/separation [4][5], biomimetic applications [6][7][8], drug delivery [9][10][11], electrochemical applications [12][13] and biomedical chemistry [14][15]. Moreover, the structures can be tuned by replacing or incorporating specific linkers or suitable unsaturated metal ions, in addition to adjusting the pore size and/or geometry which substantially influence their catalytic behaviors toward many substances participating in the reaction [16][17]. Amongst the main categories of MOFs, porphyrin-based MOFs have demonstrated themselves as a tangible material able to provide the properties of both MOFs and metalloporphyrin complexes in one scaffold [18]. Despite being synthesized less frequently than other types of MOFs and less often explored in research, they have had considerable impact on multiple fields, particularly biomimetic and biomedical ones as catalysts, owing to their resemblance to some molecules discovered in nature [19].

Tetrapyrrole ligands such as porphyrin (or porphine in the unsubstituted form) and related macrocycles chlorin and corrin are naturally occurring in several bioinorganic metal complexes. The ability of the planar or nearly planar tetradentate ring system to stabilize kinetically labile metal centers (i.e., Mg^{II}, Ni^{II}, $Fe^{II/III}$, Co^{II}) results in the selective formation of stable metal complexes containing an extensively conjugated π system (**Figure 1**).

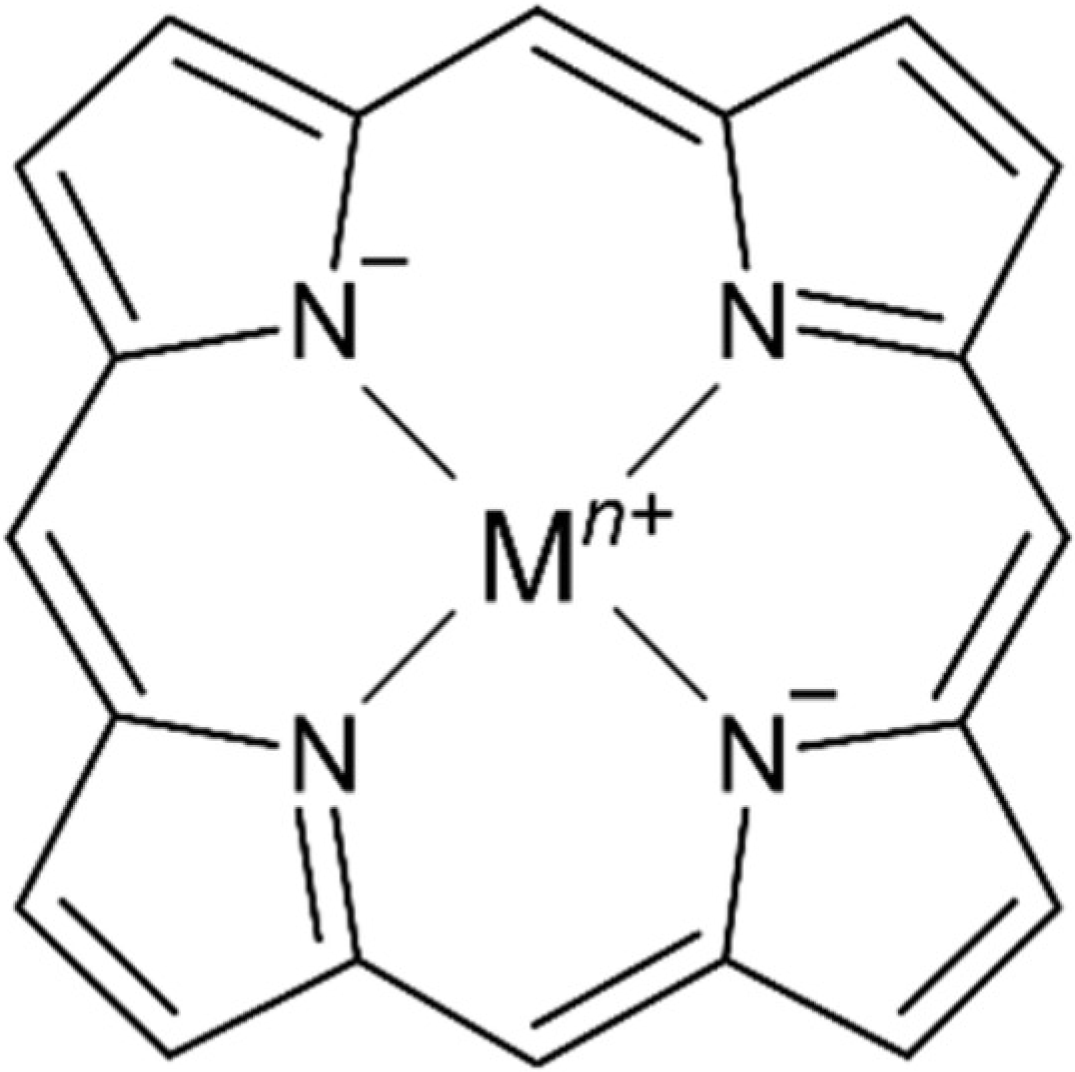


Figure 1. Representative structure of a metalloporphyrin complex with a porphine ligand core.

Thus, metalloporphyrins, due to their abundance in nature, have been explored during the last decades. The synthetic bioinspired complexes resemble in structure, central atoms, and properties the most common naturally occurring biomolecules such as hemoglobin which transports oxygen in animal bodies, chlorophyll which acts as a light-scavenging antenna in photosynthesis inside plants, or vitamin B_{12} which is important for metabolism in the cells (**Figure 2**, **Table 1**) [20]. The combination of such favorable properties makes artificial metalloporphyrins highly suited for applications in photosynthesis [21], electrochemical [22], biosensing [23], biomedical [24] applications for tumor therapy [25] and bioimaging [26].

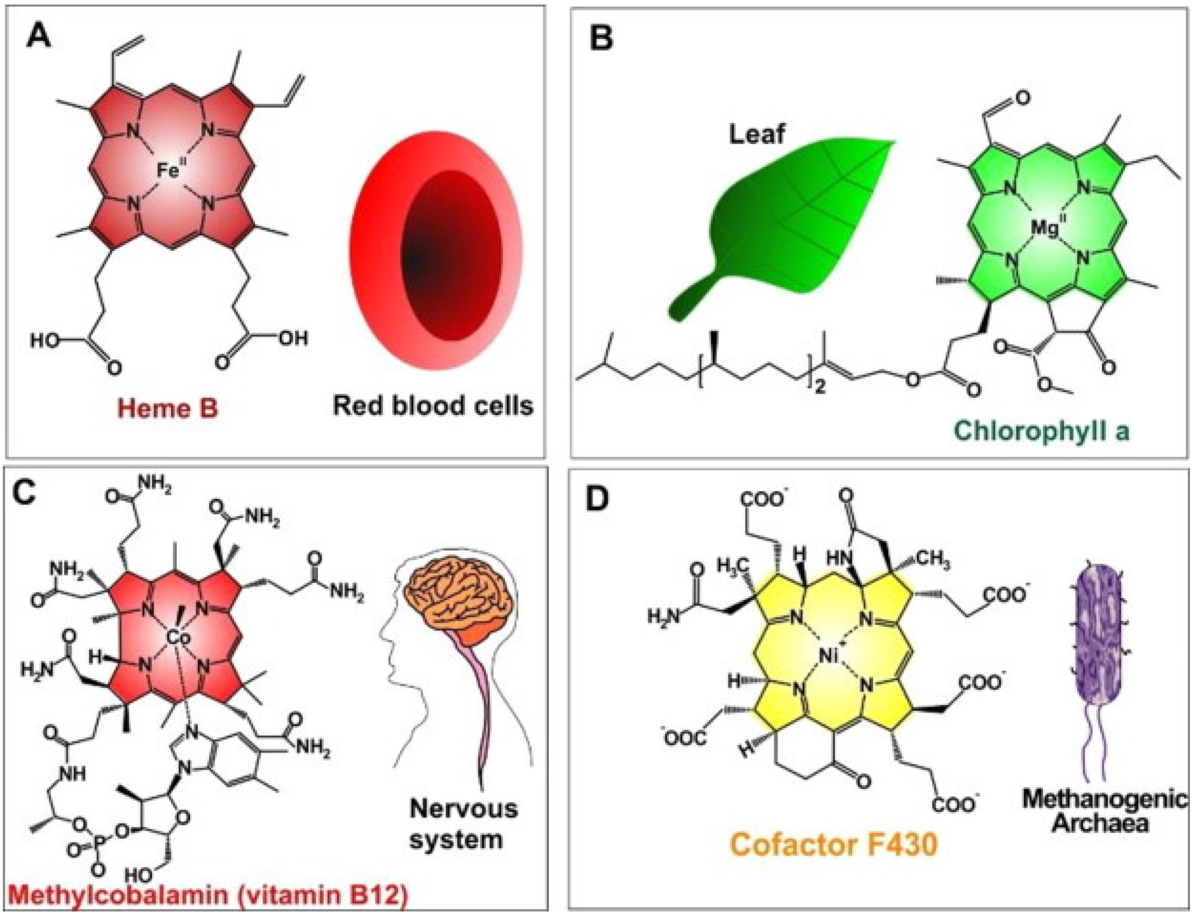


Figure 2. Naturally occurred MPs (metalloporphyrins) (**A**) iron(II)-porphyrin “Heme B in RBCs” to convey oxygen; (**B**) magnesium(II)-porphyrin “chlorophyll a” needed for plant photosynthesis; (**C**) cobalt(II)-porphyrin “methylcobalamin (as vitamin B12)” assisted to facilitate nerve system performances; (**D**) nickel(II)-porphyrin “Cofactor F430” accelerates methanogenesis in methanogenic archaea). Reprinted with permission from [20].

Table 1. Naturally occurring metalloporphyrin complexes [27].

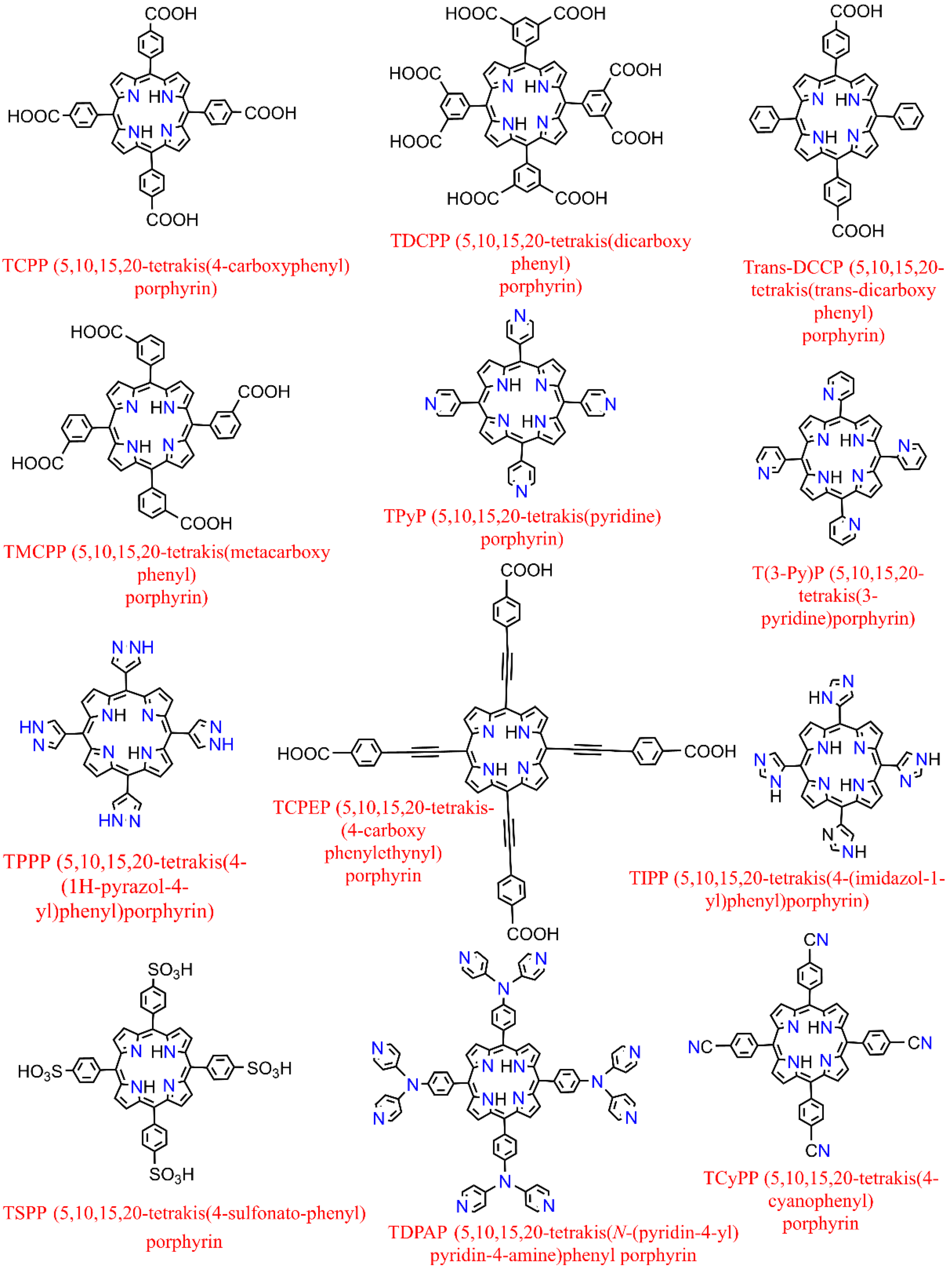
Metal Ion	Ionic Radius (ppm) *	Naturally Occurring Complex
Mg^{2+}	72	Chlorophyll
Ga^{3+}	62	Gallium(III) porphyrin complexes have been found in crude mineral oil but not in living organisms
$(V{=}O)^{2+}$	≈60	Vanadyl porphyrins are relatively abundant in certain crude oil fractions but they have not been observed in living organisms
Fe^{2+} high spin Fe^{2+} low spin Fe^{3+} high spin	78 (too large) 61 65 55 (rather small)	Fe^{n+} in various oxidation and spin systems is present in heme systems such as hemoglobin

Metal Ion	Ionic Radius (ppm) *	Naturally Occurring Complex
Fe^{3+} low spin		
Co^{2+}	65	Cobalamins (vitamin B_{12})
Ni^{2+}	73	Cofactor F_{430} (catalyzes the reaction that releases methane in the final step of methanogenesis in archaea), tunichlorin

* The ideal ionic radius for a proper *in-plane* coordination is 60–70 ppm. There have also been prepared many artificial complexes containing mostly Mn^{3+} (≈60 ppm), Cu^{2+} (73 ppm) and Zn^{2+} (74 ppm).

the early nineties [28]. The intercalation of tetrapyrrole ligands was recently recognized to be driven mostly by weak dispersive forces and either an offset or a proper π–π stacking with other components of the MOF [29][30][31][32][33]. Interestingly, there is usually a lack of a stronger specific interaction between the porphyrin sheets themselves. Therefore, the construction of a crystalline MOF depends very much on the additives and their ability to provide suitable interactions and binding with metalloporphyrin and/or other components [34][35][36][37][38].

On the other hand, further to metallization in their center [39], metalloporphyrin complexes can also be additionally peripherally functionalized at meso- or β-positions [40] (in Porphyrin, there are typically 12 positions that can be exchanged in the environs (Pyrrolic rings containing the eight β positions and the other four meso ones which are attributed to the methine substituents)) or even complexed by various (non-) transition metals providing versatile moieties which had led to their use as spacers to construct several porphyrin-based MOFs where they could serve either inside the pores (porphyrin@MOFs) [41] or as linker merged in the architecture throughout the framework (porphyrinic MOFs) [42]. The representative structures of synthetized derivatives of porphine are depicted in **Figure 3**. They benefit from the extended π conjugated system throughout the planar molecule, which moderates substitution of the metal ions and the functionalities of porphyrin itself [43]. Therefore, it illustrates exceptional electrochemical and photophysical exploitations while possessing an extraordinary chemical and physical durability. Additionally, porphyrins and their accessories normally have the strongest Soret band (400–450 nm) and a pack of steadily reduced Q-bands located somewhere in the range of 500 to 700 nm in the absorption spectrum [44]. These features have led them to be considered as one of the most significant organic chromophores with remarkable adsorption bands in the visible region.



TCPP (5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin)

TDCPP (5,10,15,20-tetrakis(dicarboxy phenyl) porphyrin)

Trans-DCCP (5,10,15,20-tetrakis(trans-dicarboxy phenyl) porphyrin)

TMCPP (5,10,15,20-tetrakis(metacarboxy phenyl) porphyrin)

TPyP (5,10,15,20-tetrakis(pyridine) porphyrin)

T(3-Py)P (5,10,15,20-tetrakis(3-pyridine)porphyrin)

TPPP (5,10,15,20-tetrakis(4-(1H-pyrazol-4-yl)phenyl)porphyrin)

TCPEP (5,10,15,20-tetrakis-(4-carboxy phenylethynyl) porphyrin

TIPP (5,10,15,20-tetrakis(4-(imidazol-1-yl)phenyl)porphyrin)

TSPP (5,10,15,20-tetrakis(4-sulfonato-phenyl) porphyrin

TDPAP (5,10,15,20-tetrakis(*N*-(pyridin-4-yl) pyridin-4-amine)phenyl porphyrin

TCyPP (5,10,15,20-tetrakis(4-cyanophenyl) porphyrin

Figure 3. Examples of some of the previously fabricated porphyrin linkers.

2. Synthesis Procedures of Porphyrin-Based MOFs

By either integrating porphyrins/metalloporphyrins inside pores freely in situ or by grafting on the surface using post-synthetic methods and/or as part of the network component, porphyrin-based MOFs could be easily constructed. However, downsizing MOFs to the nanoscale will even more profoundly develop their size-dependent properties when encapsulating or accompanying such proactive molecules for any related applications [14].

2.1. In Situ Method of Porph@MOFs Synthesis

Inspired by these facts, some promising routes to combine porphyrin derivatives into MOF frameworks emerged such as porphyrin@MOFs (porph@MOFs). These include the entrapment of (metallo-) porphyrins into the cavities or the decoration of the surface of MOFs where the former method can be performed using one-pot fabrication in situ, and the latter can be executed post-synthesis. In contrast to in situ assembly in which free porphyrin basis/metalloporphyrin are entrapped by MOF precursors (metal ion and ligand) by self-assembly simultaneously (ship-in-a-bottle) [45], the post-synthetic method which occurs by anchoring to the exterior or the inclusion of them inside the MOF pores is mainly based on weak chemical interactions such as hydrogen bonding, electrostatics, van der Waals forces and others, between the pre-obtained MOF and porphyrin base/metalloporphyrin [46]. The simplicity and straightforwardness of porphyrin entrapping by in situ formation led to this path being applied extensively by many researchers working in this field even though the post-functionalization requires the acknowledgement of some issues such as the creation of a suitable interaction between these two materials [14][20]. Parameters that should be considered before postsynthetic fabrication include the activation of MOF pores and channels by guest solvent removal inside the structure during synthesis to allow for the incorporation of porphyrin instead, the dimensions in terms of shape and size of the porphyrin encapsulated into the cavities should be appropriate, and the stimulus required to initiate bond construction between the porphyrin and MOF structure.

As described above, embedded porph@MOF can be prepared by the in situ mixing of pre-synthesized porphyrins and MOF reactants (metal ion salt and linkers). A series of metalloporphyrin-decorated Cu-based MOFs with a coral-like shape (named as M-TCPP@Cu) were obtained using a one-pot reaction strategy [47]. Accordingly, the resulting MOFs were developed through intermediate enrichment-enhanced conversion to assist the electrochemical reduction of CO_2 to C_2H_4. The respective porph@MOFs were obtained by dissolving H_3BTC and TCPP/M-TCPP in a mixture of ethanol and DMF followed by the addition of $Cu(NO_3)_2{\cdot}3H_2O$ in aqueous solution in situ to produce M-TCPP@Cu-MOF (M = Fe, Co, Ni). An ionic Mn-metalloporphyrin was reported which is presented in **Figure 4** that was encapsulated into the interior pores of ZIF-8 by a simple method through which all the precursors in DMF were sealed in a Teflon-lined autoclave and heated at 140 °C for 2 days [48]. The crystals were then used as heterogeneous catalysts for a cycloaddition reaction of CO_2 with epoxides.

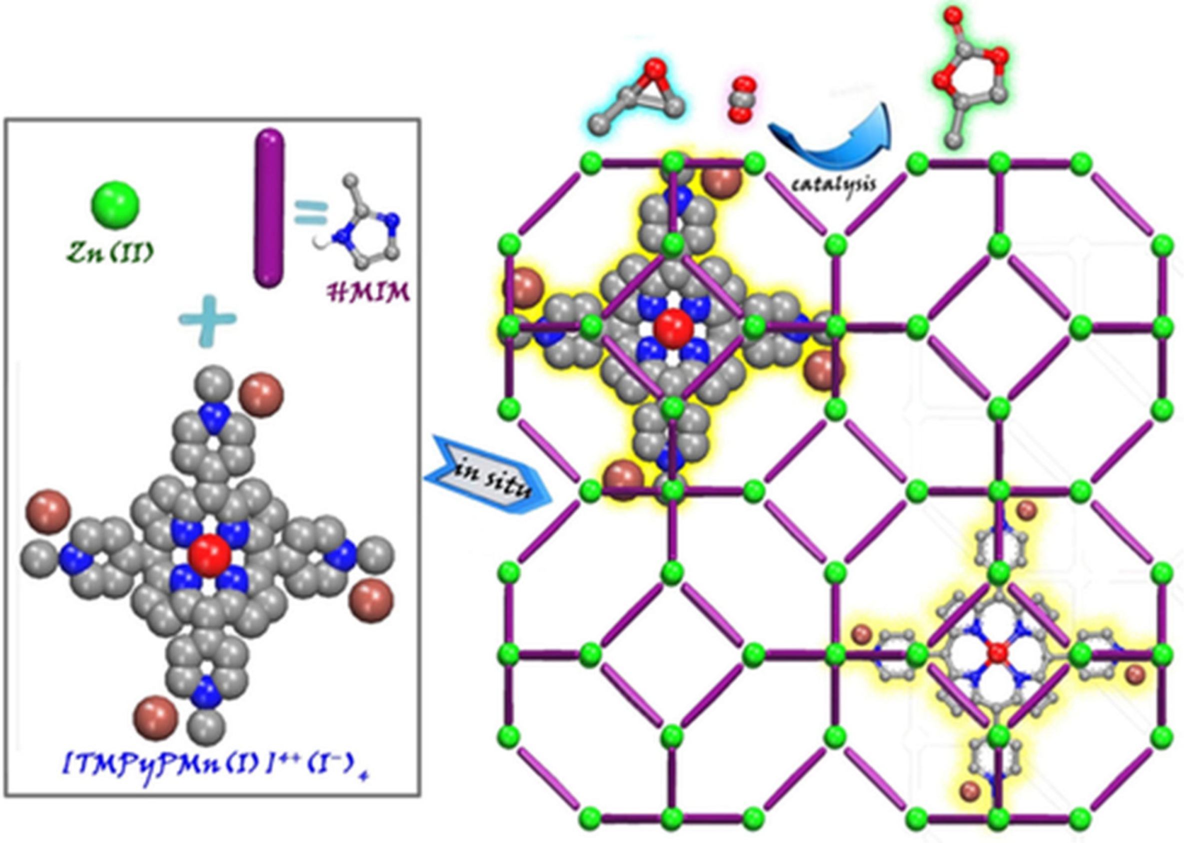


Figure 4. Illustrative demonstration of in situ enveloping of metalloporphyrin into ZIF-8 to conjoin CO_2 to epoxide. Reprinted with permission from [48].

2.2. Postsynthetic Procedure of Porph@MOFs Fabrication

For the postsynthetic fabrication of functionalized porph@MOFs, they can be either physically absorbed on the exterior or captured into the cavities, and a specific MOF must be prepared in advance; subsequently, the previously formed porphyrins are incorporated to or grafted on the MOF structure. Next, the metal can be exchanged in porphyrin via controlled-immersion of the final material in a solution of metallic salts. A post-synthetic modification (PSM) of a porphyrin-engulfed MOF to enhance the selective adsorption of CO_2 over CH_4 was reported [49]. The trapped porphyrin used as a structure-directing agent to provide a “ship-in-a-bottle” mode led to template-based Cd-porph@MOM-11 (MOM; metal–organic materials). In **Figure 5**a, the effect of the exchange of some cationic organic guests such as H_2ppz^{2+} with Li^+ on the selectivity of the adsorption of H_2 over N_2 was assessed. Remarkably, the results presented that ppz (1,1′,4′,1″,4″,1‴-quaterphenyl-3,5,3‴,5‴-tetracarboxylate) demonstrated significant kinetic trap for both the N_2 and H_2 ads-des process whilst Li displayed an increment in the pore volume size and more importantly a relatively higher H_2 isosteric adsorption heat [50]. In another case, noncatenated hydroxyl-substituted MOF were introduced and replaced by Li^+ and Mg^{2+} ions to convert pendant alcohol to metal alkoxides in order to upgrade the H_2 uptake reversibly (**Figure 5**b). Exchanging was performed via the immersion of as-fabricated MOF in THF solvent (Tetrahydrofuran) to replace the primarily occupied solvent DMF (N-N-Dimethylformamide). Afterwards, the stirring of the respective MOF in an excess of $Li^+[O(CH3)^{3-}]$ in CH_3 CN/THF solvents was performed to exchange Li^+ ions which boosted the hydrogen adsorption ability of the

MOF significantly [51]. The illustration in **Figure 5**c [52] indicates that the MOF of the formula $Zn_2(NDC)_2(diPyNI)$ (NDC = 2,6-dicarboxylate, diPyNI = *N*,*N*′-di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide) was reduced by Li^0. The interaction imposed by $H_2 - Li^+$ inside MOF pores improved its competence to adsorb H_2 which was most likely increased by the augmented ligand polarizability and framework displacement. Furthermore, the experimental work in [49] with some modifications of a combination of the first two methods mentioned in **Figure 5**d submerged single crystals of the prefabricated Cd-porph@MOM-11 into metal chloride salt solutions, with meso-tetra(*N*-methyl-4-pyridyl) porphine tetratosylate (TMPyP) in methanol serving as a template for PSM, and formed a basis for MOF formation via single-crystal-to-single-crystal ion exchange processes.

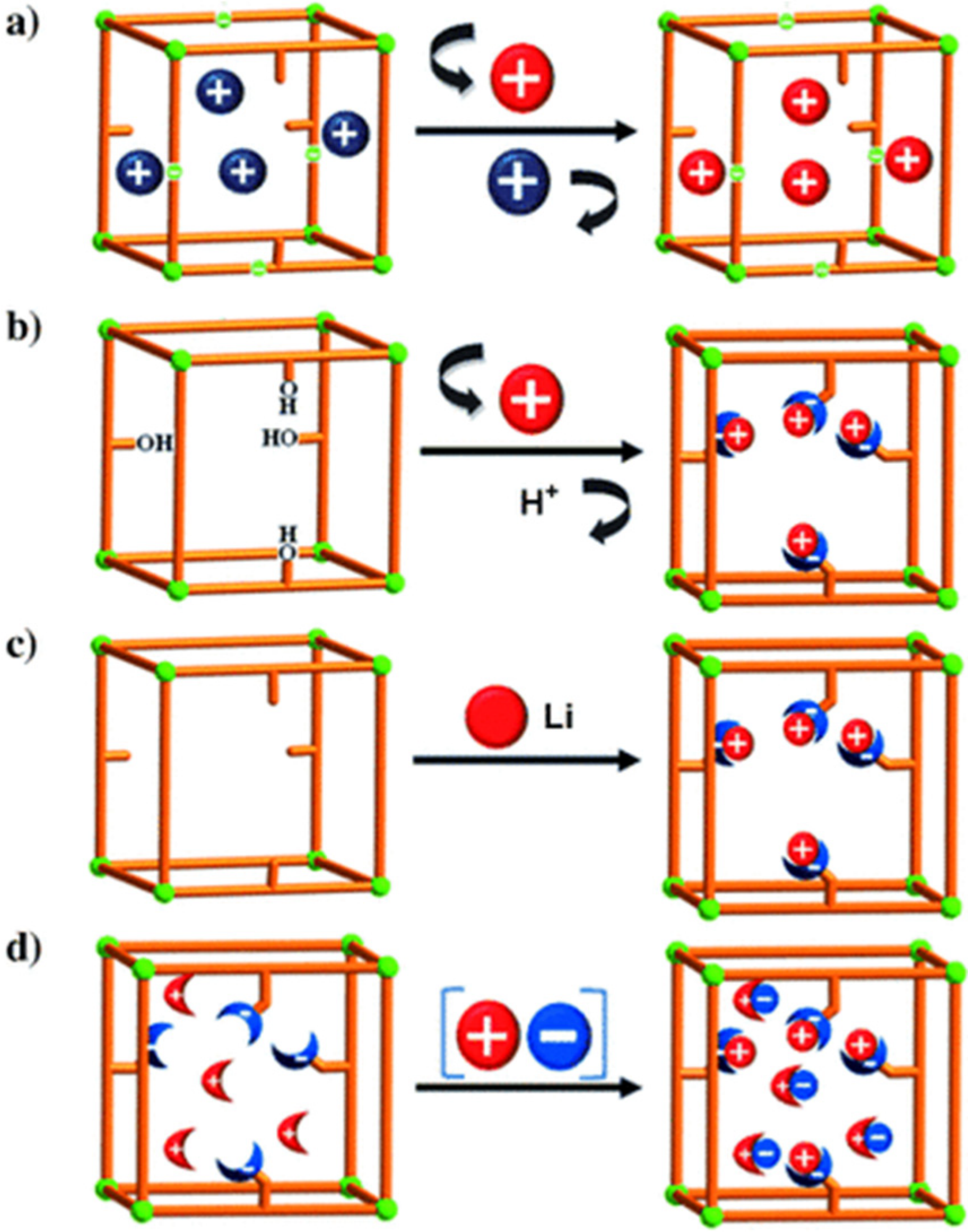


Figure 5. Three basic ways of introduction of open metal sites by PSM synthetic routes to MOFs: (**a**) cationic guests or organic cations exchange (blue balls) with metal cations (red balls); (**b**) replacement of a hydroxy protons with Li^+ and Mg^{2+} ions (red balls); (**c**) chemical reduction of MOM with Li (red balls) and (**d**) fourth method is a combination of the first two—a collaborative attachment of metal (red balls) chloride (blue ones) salts to anion and cation binding sites. Besides, the sticks and the crescent-shaped bowls attached to sticks are porphyrin-encapsulated inside MOM-11 and cation/anion binding sites. Reprinted with permission from [49].

2.3. Porphyrinic-Oriented MOFs

With regard to porphyrinic MOFs, porphyrin or metalloporphyrin functioning as an organic linker is one of the main components in the framework, which coordinates with secondary building units (SBUs). Accordingly, the choice of suitable shape, size and geometry that meet the desired pore structure to load substrate molecules and to catalyze several reactions efficiently on the surface depends entirely on the rational selection of porphyrins and SBUs. While the insertion of (metallo-) porphyrins not only equips MOFs with new functionality, they can also maintain or bring about far better stability and diversity across the building blocks. As a consequence, the catalytic performances of these types of porous coordination networks could be simply upgraded by regulating Lewis-acid metal active sites and designing well-qualified circumferential functionalities on metalloporphyrins [45]. In line with the previous statements, various parameters such as temperature, solvent, reaction time and the method as well as proper metal nodes and porphyrins chosen, could additionally determine the final product [14].

By applying peripherally functionalized porphyrin/metalloporphyrin as spacer or multidentate ligands directly with metal ions/clusters could lead to the formation of porphyrinic MOFs. Displayed clearly in **Figure 6**, the porphyrinic MOF PCN-222/MOF-545 (free base-H_4TCPP and $[Zr_6(\mu_3\text{-}O)_8(O)_8]^{8-}$ node) was used to selectively oxidize 2-chloroethyl ethyl sulfide (CEES) to a less toxic 2-chloroethyl ethyl sulfoxide (CEESO) at room temperature and neutral pH. The photooxidation of this mustard-gas simulant under mild conditions by exploiting these porous materials as photosensitizer within a half-life of up to 13 min was found to be one of the most convenient methods for the detoxification of such a poisonous compound [53].

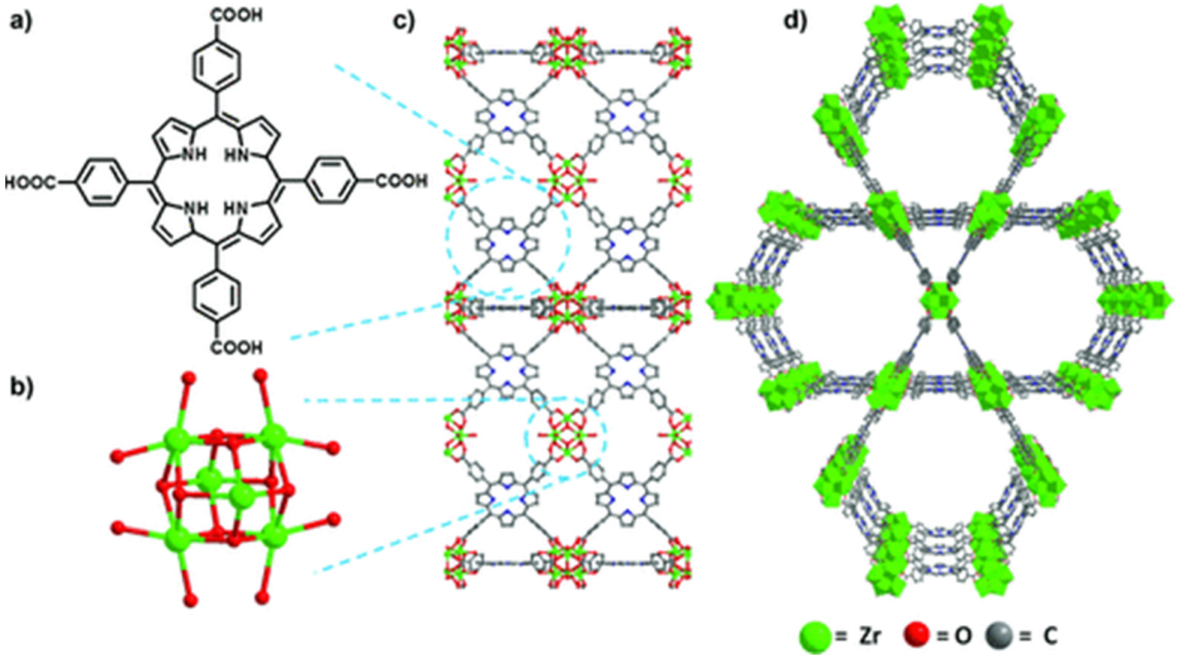


Figure 6. Comparison of free-base PCN-222/MOF-545 (fb-1). (**a**) Tetrakis(4-carboxyphenyl)porphyrin linker, H_4TCPP. (**b**) [Zr6(m3-O)8(O)8]8¢ node. (**c**) MOF fb-1, shown across the axis a (**d**) 3D structure of fb-1, depicted along the c axis. For more clarity hydrogen atoms has been omitted. Reprinted with permission from [53].

Facile insertion of $H_3PW_{12}O_{40}$ inside the solvothermally prefabricated free-base PCN-222 MOF was investigated for the photocatalytic synthesis of some bioactive N-heterocycles such as Nifedipine, Nicardipine, Nicotinic acid (Vitamin B_3), and Pyridoxine (Vitamin B_6) under visible-LED light irradiation [54]. The porphyrinic Zr-MOF scaffold was constructed by employing TFA and BA as modifiers followed by post-modification with POM to construct the POM@PCN-222 composite.

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