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Review

Supramolecular Systems Linked to Metal-Organic Frameworks

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Abstract: Supramolecular structures with specific applications are a pillar in several areas of science. Thus, from a contemporary point of view, there are several reasons to feel inclined to cover a systematic, or historic critique of the supramolecular concept itself. First, the idea of a supramolecular material seems more secure now than it was decades ago. Second, updating the interacting of MOFs and supramolecular chemical and conversely, supramolecularity to assemble MOFs and to make efficient complex systems in multiple cutting-edge applications. Third, we should here simply confine to a consideration of how workers in this field have tried to correlate the notion of the idea of supramolecular systems linking self-assembly considerations. Thereby, this is clearly an advantage that optimized geometries obtained on the conductive bases described that undoubtedly, some of these systems have substantial applications and create a significant practical interest. The outline of this review encompasses a general introduction to MOFs and supramolecularity, the key unit of the study presented here, followed by a survey of recent advances in supramolecular chemistry in confined space, relationships of MOFs with the supramolecular chemistry, electrochemical synthesis of MOFs, and switchable MOFs. Finally, some discussion on possible future perspectives of this field is given.

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1. Introduction

The incursion into self-assembly issues to create structures with defined supramolecular architectures has given rise to strategies to obtain organometallic structures such as a homogeneous supramolecular metal-organic framework from a hexaarmed precursor based on $[Ru(bpy)_3]^{2+}$ and a cucurbit(8)uril [1]. The possible variety of these compounds has been visualized to develop a comprehensive work using the in situ heterogeneous self-assembly, and structural characterization by single-crystal X-ray diffraction (SCXRD) of mechanically bonded SCCs within a confined space of MOF channels (SCCs@MOFs). Specifically, the structures consist of Pd_8 square metal–organic polygon, a discrete Pd_{16} supramolecular cage, and a heterobimetallic Au^{III}–Pd^{II} cage [2]. Whereas cooperative effect clearly play an important role between the available void space and the distance between Pd_2 including accessibility of Pd^{II} ions in the MOF $[Pd^{II}(NH_3)_4][Pd^{II}_2(\mu\text{–}O)(NH_3)_6)(NH_4)_2]_{0.5}\{Ni^{II}_4[Cu^{II}_2(Me_3mpba)_2]_3\}\cdot 52H_2O$ with linear L_1 and bent $L_{2,3}$ ligands, it can promote the formation of self-assembled SCCs within to the con-fined space of MOFs channels, as depicted in the Figure 1 [2]. Supramolecular chemistry has broadened discussed on applications host–guest systems, for instance in the molecular recognition, drug delivery, regio–and stereoselective organic synthesis, catalysis, and bioactive materials. The feature proper to provide abundant interaction sites to form supramolecular interactions with diverse guest molecules, such as hydrogen bonding, electrostatic interactions, π–π interactions and hydrophobic effects has been commented by Liu et al. [3].

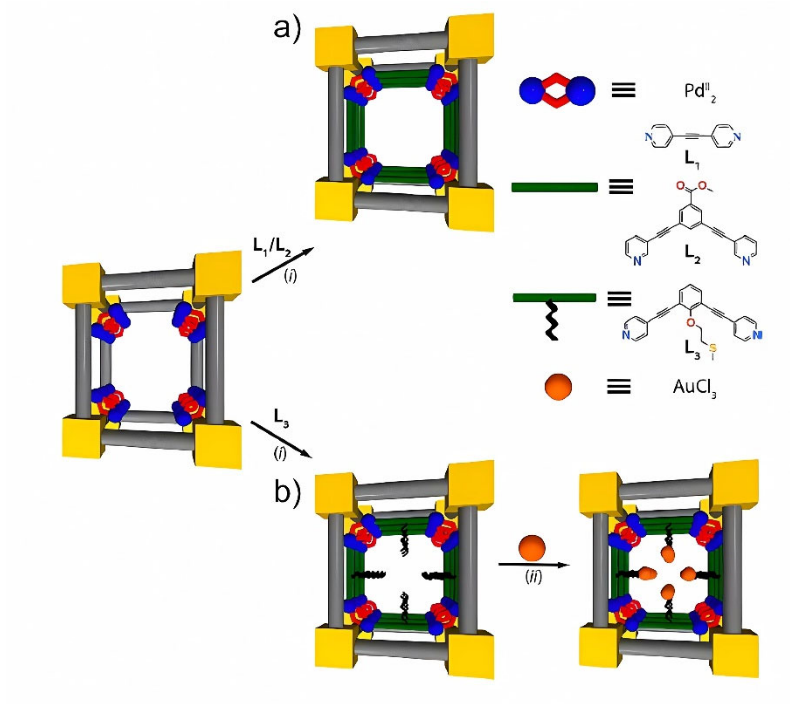


Figure 1. Methodological strategies postsynthetic for the sequential synthesis of homo- (a) and heterobimetallic (b) mechanically bonded, catalytically active SCCs within the confined space of MOF channels (SCCs@MOFs). Steps (i) Incorporation of desired organic ligand with suitable encoded structural and coordination information and step (ii) represent the post-assembly metalation of pre-formed SCCs@MOFs. Reprinted with permission from Ref. [2].

Furthermore, the underlying mechanisms were exposed in the review work by Noor. He relates the sterically bulky ligands with the chemical reactivity due to the fine tuning of electronic effect in ligand designed as an important part that can restrict the intrinsic reactivity [4]. Concerning the polynuclear transition-metal complexes show metal–metal interactions and synergistic effects among transition metal elements. This is how heteropolynuclear complexes to provide new functions and properties which are not observed in the homometallic polynuclear complexes. According to Horiuchi and Umakoshi [5], the luminescence is one of important aspects to study the metal–metal interactions in heteropolynuclear complexes, since it is sensitive to the small change of the energy differences between ground and excited states. They focused on the supramolecular chemistry and noncovalent interactions of metal complexes with coordinated NAH pyrazoles, taking advantage of the fact that pyrazoles are weak acid and act as both r-donor and p acceptor ligands. Due to the above, the authors delve into recent advances on synthetic, structural, thermodynamic, electronic and photophysical properties of Pt- and Pd-based heteropolynuclear complexes.

Wang et al. verified that MOFs/MOGs afford a broad selection of combinations between metal nodes and organic linkers and are known to produce electrocatalysts with high surface areas, variable porosity, and excellent activity after pyrolysis [6]. Some recent studies on MOFs/MOGs for oxygen electrocatalysis and their new outlooks in synthesis, and characterization, have correlations between oxygen catalyst performance with the intrinsic structure, active-site density, surface property, charge conductivity, and mass transport, essential in advancing in the development of these materials.

Several studies from the literature examine the self-assembly of MOF particles into ordered superstructures of different dimensionalities. The dynamic behavior for creating ordered MOF superstructures, including solvent evaporation, depletion-assisted assembly, electric field-assisted assembly, DNA assisted assembly, anisotropic pattern-assisted assembly, ice-templated self-assembly, and air–liquid interface assembly has been the main aimed and concern of several researchers [7].

Supramolecular gels comprise an intriguing contemporary research field owing to the challenges in defining the structure of the molecular network and the tailoring properties of the resulting gels. The potential techniques as NMR, SEM, XRD, and others have been used extensively to open new facets in the study of supramolecular gels and their properties [8].

MOF metal oxide node hydroxyl groups form during the synthesis of MOFs by hydrolysis of metal precursors, so the hydroxyl groups are incorporated into the metal oxide clusters that are nucleated in the aqueous reaction medium. These groups become structural ligands, such as the μ_3–OH groups bonded for example to Zr_6O_8 nodes and μ_2−OH groups bonded to Al−OH−Al nodes. On the other hand, MOF node hydroxyl groups can be generated by reactions of reactive node sites or ligands with water in post-synthesis treatments [9]. Similarly, Zr-based clusters with open environments around the SBUs make the metal node supported cobalt catalysts more active in the hydrogenation. Therefore, as pointed out by Lin and coworkers, advanced $Zr_8(\mu_2{-}O)_8(\mu_2{-}OH)_4$ MOF node with sterically open $Zr_2{-}\mu_2{-}OH$ ligand sites support Co-based catalysts for the hydrogenation of a broad range of unsaturated compounds such as olefins, imines, carbonyls, and heterocycles [10]. For instance, node-bound acetate ligands were stable at temperatures up to 200°C while they were eliminated substantially by evacuation at 250°C, these is consistent with observations for acetate ligands on the Zr_6O_8 nodes of UiO-66. The reactivities of the node ligands were probed with a flow of methanol vapor at 80°C and 1 bar for 24 h and then evacuated at 80°C for 12 h to remove any physisorbed species [11].

2. Supramolecular Chemistry in Confined Space

Among the molecular systems that present internal cavities typical of confined inner cavities, we can mention to crown ethers, cryptands, molecular boxes, pillararenes, cucurbiturils, and other macrocycles, and precisely display specific chemical reactivity. On the other hand, due to their structural attributes, MOFs are an excellent host for the confinement and are an outstanding heterogeneous catalyst model [12].

On the contrary, there are steric limitations in the cavities of MOFs and their walls formed by reactive structures where components are inserted that are housed despite of the unfavorable steric factors adopting conformations very specific. Despite the above, several reports have described that the steric constraints, solvent exclusion, intermediates stabilization, and conformational control of substrates provides strong impetus for chemical reactions in a confined space how an alternative for unconventional processes [13]. In this regard, significantly details established by supramolecular chemistry incorporate molecular recognition, host–guest chemistry, molecular self-assembly, folding, mechanically interlocked molecular architectures that presupposes a dynamic covalent chemistry. Depend on geometries a support not only stabilize the catalytic site but must also offer synthetic flexibility to tune the chemical environment beyond the coordination spheres based on the incorporation of molecularly defined catalytic function into MOFs [14]. In this respect, the diffusion within a MOF pore may be drastically different in homogeneous or nonconfined heterogeneous systems, and greatly affecting reaction kinetics. Molecules surrounding MOF particles only move according to the bulk molecular diffusion and the motions of the fluid to regulate the flow reactions [15].

Referring specifically to predominant with low symmetry ligand does not contain coordinating units of different denticities, Lewis and Crowley indicate an alternative mode for controlling the self-assembly process that must be incorporated into the structure. Besides, the inherent directionality of lone pair orbitals and the predictable coordination geometry of transition metal ions, geometric constraints into ligand frameworks, that in turn they avoid formation of isomeric mixtures upon self-assembly via Metallo-supramolecular self-assembly [16].

The enormous development of supramolecular and reticular chemistry converges in the encapsulation in nanoconfined spaces. This connection, having its roots also in classical host–guest chemistry, is the origin of encapsulation in the porous network of the MOFs. Encapsulation takes place when functional species are held on the walls of a MOF by either covalent bonding or van der Walls interactions in such a way that they cannot leach due to their stabilization and geometric factors. The outcome based on each nanospace of MOFs engendered by the coordination nanospace, remain better interpretable about the discrimination of guest molecules, also enables the synthesis and conversion of value-added substances by virtue of nanomodulated reactions design in the confined space [17]. For instance, representative and particularly interesting nanoreactor offers a limited confined space that imprint a key role in the chemical process by controlling the number of molecules inside and their noncovalent forces, which are predominantly guided by the supramolecular chemistry and their dynamic interactions molecular [18].

In comparison to typical covalently connected organic supramolecular hosts, met-al–organic capsules are spontaneously generated by simply mixing modular building units consistent with the general trend in preorganized ligands ability to produce symmetrically predesigned structures. In that respect, Jing et al. established strategic guidelines to build photoactive supramolecular systems through encapsulating dye molecules within the inner space of redox-active hosts. In this view, photochemistry demonstrated advantages due to the structural confinement particularity, avoiding excited state quenching caused by other chemical species concerning the radical intermediate complex by adjusting the absorption or emission of the guest through electron/energy transfer pathways [19].

In good agreement exposed by Sinha and Mukherjee, the cavity size for intake of the substrate and easy release of the product made using supramolecular architectures a better choice for catalytic transformation enzymatic. In fact, the enzymatic interactions in supramolecular molecules consolidate the conformational organization and compartmentalization by self-assembled coordination complex [20].

Lately the group of Yoshizawa has conducted a conceivable host-guest system using CH−π interactions employing a polyaromatic capsule with an atypical spheroidal cavity. The observations demonstrated a cavity efficiently bound each molecule of planar compounds through multiple CH−π interactions rather than π−π interactions. Gratifyingly, from complex mixtures of polyaromatic molecules provide twelve and ten aromatic CH groups. The authors, detail that a selective binding of planar polyaromatics and a planar metal complex utilizing multiple CH−π interactions may be the key to provide novel insight into molecular chemical interaction bonding explored using multiple polyaromatic compounds and the porphine Cu^{II} complex or bis(acetylacetonato) framework and their structural affinity diverse [21]. Rearrangement of molecular addends can easily be determined if they are accompanied by a change of the pattern of a polyaromatic cavity additionally to metallic coordination leading to spheroidal fashion characterized by multiple CH−π interactions, such as explicit in Figure 2a [21]. Rearrangement of molecular addends can easily be determined if they are accompanied by a change of the pattern of a polyaromatic cavity additionally to metallic coordination leading to spheroidal fashion characterized by multiple CH−π interactions, such as explicit in Figure 2a. For this reason, the molecules of coronene and pyrene molecules were selected to design spheroidal capsules as shown in Figure 2b,c [21]. Although the incorporation of multiple interacting groups to achieve high guest affinity has been a key principle of supramolecular chemistry for decades, it is recently that phenyl unions, the halogen bonds, and tetrahedrally shaped adamantane [(1,3,5,7-tetrakis(4-bromophenyl)adamantane] have been subject of study in the modulation of channels that can confine aromatic petrochemicals and chloroform. The supramolecular framework via van der Waals contacts confine solvents molecules be-tween them predominately using π−π interactions, which could make possible the efficient separation of toluene from benzene [22].

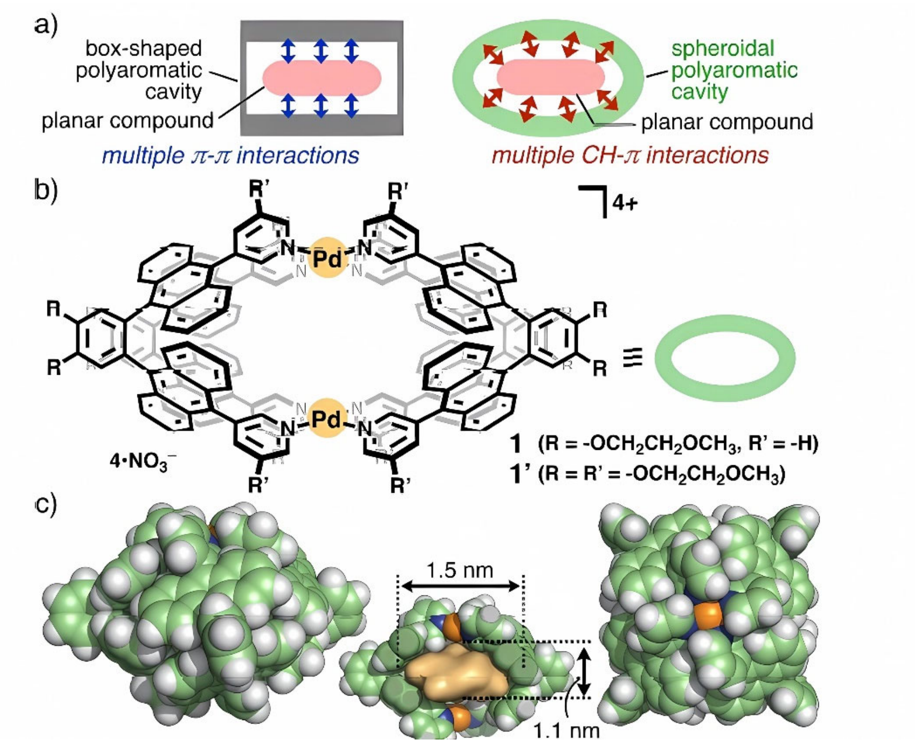


Figure 2. a) Multiple host-guest π−π and CH−π interactions in box shaped and spheroidal polyaromatic cavities respectively. b) Spheroidal polyaromatic capsules 1 and 1′. c) the crystal structure (side, sliced side, and top views; R=R′=H). The inner cavity is highlighted in yellow. Reprinted with permission from Ref. [21].

Another contribution exhibiting confined chiral microenvironment has proven very efficient in engineering such host–guest interactions and a reactive conformation exerting control over the chemo-, regio-, and stereoselectivity of asymmetric transformation is resulting in considerable activity compared with that in the bulk solution. Besides, based on noncovalent interactions, the cavities of cages could stabilize reactive and unstable species, promote the transformation of high-energy intermediates, and minimize side reactions through different transition states [23].

The assembly of superatomic crystals from several building blocks is inspired on inorganic–organic hybrid materials. It is so, to adapt certain tailor properties of a crystalline solids by controlling their structure and composition at the atomic level presents distinctive opportunities on design of new functional materials. Strategies employed have given rise to low-dimensional coordination polymers formed by linking Re_6Se_8 superatomic cores applying bipyridine bridging ligands and a carboxylic-acid-based synthetic strategy to create 2D and 3D MOFs with Co_6Se_8 superatoms [24]. It is worth mentioning at this point that the preparation of 3D mesostructures obtained by the crystallization-driven self-assembly (CDSA) of coil-crystalline block copolymers (BCPs) studied by Guerin et al. ensured strong attractive intramolecular interaction, and the nature of structural consequences from closed 3D multi-tori spherical shells to 2D toroid mesh monolayers, where the composition of the solvent is decisive. Explicitly, the self-assembly of polyferrocenyldimethylsilane-block-polystyrene (PFS_{26}-b-PS_{306}, with $M^{PS} \approx 30{,}000$) can be favored in an acetone/decane mixture containing 25 volume % of acetone. Nevertheless, it must be pointed out that the PFS_{26}-b-PS_{306} microphase separation can be predicted variation the solvent mixture [25].

3. Supramolecular Assemblies

All supramolecular structures are designed with a self-assembly technique and are feasible to have an excellent interaction with biological systems, therefore, they can be used as drug delivery systems [26]. In self-assembly, coordination systems through metal atoms can generate supramolecular materials that are too complex [27]. This also implies the principles of symmetry that provide some very insightful tools to reach an understanding of many aspects of the chemical and physical world, this characteristic be able to establish through covalent interactions, hydrogen bonds, and van der Waals forces, without excluding another inter and intramolecular interactions [28]. In an alternative approach, by Nitschke and co-workers [29], the design of metal−organic architectures is a function of directional strategies described as the directional-bonding approach, and evident symmetry-interaction approach, the molecular paneling perspective, and the weak-link viewpoint. The success of these strategies has been employed to predict metallomacrocycles based high-symmetry three-dimensional architectures.

Incorporating multiple complex systems such as mixed-metal MOFs has impeded their study because the development of complex systems, in this context, the atom probe tomography (APT) can provide useful information in characterizing mixed-metal rod MOFs [30]. Many of the applications of the MOFs have their beginnings in the APT and can be developed basically by a sequence of the metals. This illustration is the novelty of regulated targets for generating metal sequences into a mixed-metal rod MOF, this in turn involve to the thermodynamic considerations are noticeable in a random sequence, primarily, it maximizes configurational entropy that could be translated into the minimum free energy under the assumption that the enthalpy change involved in the permutation of components is negligible. Contrary, this assumption cannot be true if metals of varying sizes are mixed into an alloy [30].

The non-covalent bases of these systems are the cause of extraordinary structural change as a consequence of variations in temperature, pH, and ionic strength [31], which could not happen with systems built by covalent interactions. Supramolecular assembling systems are built by way of several reversible weak interactions to form structures with well-defined architectures. Supramolecular chemistry plays with the dynamics non-covalent interactions, including hydrogen-bonding, host-guest interactions, $\pi-\pi$ stacking, metal coordination, hydrophobic forces, and electrostatic effects [32]. The relative importance of the supramolecular assembly system is significant to develop optical materials with supramolecular tools. In view of the above, considerable effort has gone into the field of assembled luminescent materials, and this is one of the reasons for reinforcing investigations on polymeric supra amphiphiles topologies [33], as well as the photoactive supramolecular functionality for light-harvesting [34].

As it is conceivable, the design topological supramolecular network will be attractive in bioelectronics tasks, that is, for the biocompatible CPs with high conductivity, and high stretchability maintained after microfabrication as much as no crack formation under 100% strain, essential properties to maintain low-impedance and seamless biointegration [35].

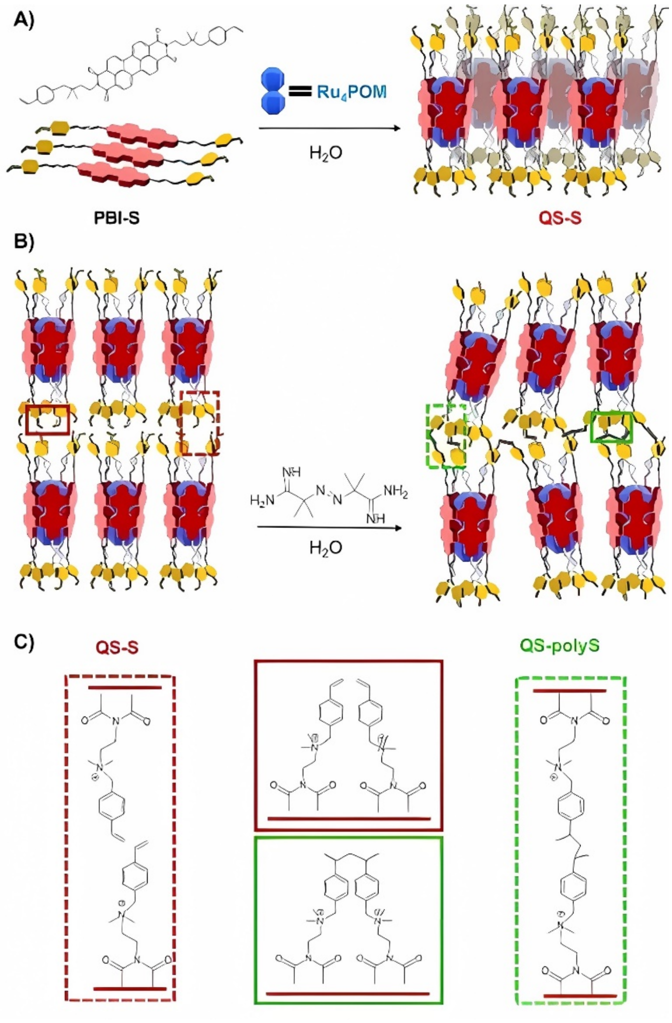
Scherman´s research team, establish an electrically conducting supramolecular polymer network (E-SPN) by an incorporation of PEDOT:PSS within a dynamic CB[8]-cross-linked poly(dimethylacrylamide) network. Hence, displaying an electrical conductivity (52 S m^{-1}) while at the same time achieving tissue mimetic supramolecular with low Young’s modulus, high compressibility, stretchability, toughness, high water content, and rapid self-recovery; consequently, the E-SPN could maintain an unmatched relationship mechanical-electronic of PEDOT:PSS hydrogels [36]. The most illustrate dominant role played by aqueous supramolecular solutions used as lubricants relies on a way that polymer and lamellar solutions at the molecular scale are in the boundary lubrication regime regarding their friction mechanisms. This correlation could be true in molecules such as polyalkylene glycol (PAG), composed of ethylene Oxide (EO) and/or propylene oxide (PO) units, used to control the sol/gel transition of aqueous solutions [37].

Seiffert and his team of collaborators carry out work classified as of high value due to their assertiveness when using transitory bonds in metal-ligand complexes. They functionalize tetraPEG precursors with 2,9-dimesityl-1,10-phenanthro- line to form networks in combination with tetraPEG precursors functionalized either with phenanthroline or terpyridine ligands at 1:1 ratio. They too, supported by reliable results, suggests that the coordination geometry preference of the utilized metal ion in comparison with the geometry requirements of the desired heteroleptic complex can be linked to defect in the composition [38].

In the constructing supramolecular materials is well documented that π stacking interaction is able to induce a narrow bandgap for instance in the MOFs and their structural design. Important observations can be drawn in this regard for tetrathiafulvalene (TTF) and MIL-140A families, where the width of the bandgap decreases as the interaction distance shortens and the interaction energy is enhanced. Faced with this, the functional groups that induce polarity in aromatic rings promote the supramolecular electrostatic coupling. And yes, it is a fact that the formation of donor–acceptor systems through the addition of functional groups is a reliable strategy to promote highly efficient π−stacking (πS) interactions, to evidence narrowest bandgaps [39].

Only a few examples there are of structural design showing the involvement of halogen bonding by using pyridine in nonaqueous media to obtain the stabilization of the phosphomolybdate, and the six terminal ligand sites within the structural vacancy between oxide and pyridyl ligands. On one hand, the structure is controlled by intramolecular spatial separation of coordinated halogenated ligands as well as intermolecular halogen−halogen interactions in the crystalline state, and on the other, it is useful tool to study the design of supramolecular materials geometrical considering halogen−halogen interactions [40].

Functionalization of perylenebisimide (PBI) with styrene moieties allowable leverage a combined supramolecularity and photopolymerization to improve the photosynthetic architecture of PBI-based artificial quantasomes in terms of lateral and orthogonal lamellar fixation. It should also be mentioned that optimized geometries obtained depend, usually in a systematic way, on basis and on the level of the formation of the quantasome assembly, and a lateral aggregation favored by the proximity of a polymerizable styrene. It is plausible additionally a yielding up to 290% compared to the styrene-free. It can thus be established a perfectly designed structural architecture of the chromophore constituted by PBI down the synthesis of a biscationic PBI scaffold with two terminal styrene groups (see Scheme 1A). This gives rise to the formation of a quantasome assembly in water (QS-S) favoring the proximity of the polymerizable styrene groups with high local density (see Scheme 1B).4. Synergistic relationships of MOFs with the supramolecular chemistry [41].



Scheme 1. (A) PBI-S and its aggregation in water and self-assembly of QS-S upon Ru_4POM intercalation. (B) Photo-polymerization of QS-S with 2,2′-Azobis(2-methylpropionamidine) as radical starter to yield QS-polyS. (C) Molecular structure of lateral and orthogonal styrene groups evolving under photo-polymerization conditions to ethylbenzene linkers between quantasome units at the intra- and inter-lamellae level. Reprinted with permission from Ref. [41].

Shortly after the knowledge the bonding patterns in supramolecular assemblies, one of the criticisms is that inherently leads to high symmetry products. It is so, there has been a concerted effort to produce low symmetry metal–organic cages using various tactics including steric, geometric complementarity, and interactions between the ligands. While model compounds do not display optimized properties, their assembly show promising perspectives toward the design of supramolecular frameworks showing good relationship with MOFs.

4. Significant Advances in MOFs Architecture and Its Analogues Assembled by Novel Strategies

Considerations of the geometric requirements for a target framework and implementation of the design are called reticular synthesis. This process requires both an under-standing of the coordination patterns of the metal and organic units which are the source of formation of ideal topologies. The reliability of the conclusions drawn of those assertions allow us to confirm what some authors have emphasized about that MOFs consisting of tetrahedral Zn^{2+} are not chemically stable, on the contrary, systems that containing Zn^{2+} in a different coordination environment, such as MOF-69 that contains both tetrahedral and octahedral Zn centers which share oxygen, have shown more stability than those essentially tetrahedral Zn^{2+} ions [42,43].

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On a fundamental level, to the extent that the geometry of each chemical constituent, size, and functionality can be modified, is possible to produce a wide variety of MOFs structures [44] with unbeatable degree of crystallinity and exceptional surface areas and pore volumes [45,46]. More tractable derivatives of the parent architecture of MOFs work similar to autonomous motors due their abilities crystalline pore organization structured by combination of metal ions and ligands. In this setting, if a ligand has several possible conformations, the framework geometry, will be hard to predict and several products can be formed. Of course, each formed complex structures are close agreement with experimental values.

Transition-metal coordination complexes are a broad class of supramolecular crosslinks used to engineer the mechanical properties of advanced structural materials. They present the ability of reform after rupture unlike conventional covalent bonds. The lability of each metal-coordinate bond can be quantified in terms of a bond dissociation rate which is inversely related to bond dissociation time. These properties, combined, have been suggested that metal-coordination bonds may be an emerging class of crosslink chemistries to tune static and dynamic mechanical properties in advanced material [47]. Grounded in the physical chemistry of metal-coordinate equilibrium dynamics, Cazzell and Holten-Andersen demonstrate that robust material cross-linking is thermodynamically favored if a minimum amount of metal is available during macromolecular self-assembly [48].

In 2012, Ikezoe et al. developed a hybrid biomimetic motor system consisting of MOF and diphenylalanine (DPA) peptide. They used the MOF $[Cu_2L_2ted]_n$ with 0.75 nm sized pore where L is 1,4-benzenedicarboxylate and ted is triethylenediamine. MOFs have the advantage of assembling small molecules into a highly ordered pores and releasing them in a more isotropic direction by breaking bonds of framework. This is because the property that MOFs is applied to is an energy-storing cell that assembles peptides inside nanoscale pores of the coordination framework. The nature of peptides enables their assemblies to be reconfigured at the water/MOF interface, and thus converted to fuel energy [49].

It should be mentioned that the biomimetic mineralization of MOFs must mainly impacts viruses. In this perspective, biotechnological encapsulation processes are increased to protect healthy cells from the biological environment. Flexibility of synergistic effects of MOFs towards cells is noteworthy [50]. Because metal-ligand bonds dissociate following a kinetics, selection of the metal ion can even change the energetic effects of the material [51]. For example, conventional wound healing loses its effectiveness because of this dissociation. The alternatives that provide greater security for more effective and faster healing such as the use of MOFs are very functionals and higher safety [52]. Very particularly, an excellent study involving MXene (a family of 2D materials with general formula of $M_{n+1}X_n$, M being an early transition metal, and X being carbon or nitrogen) and MOF-5 nanostructure were applied in co-delivery of drug and gene to increase its bioavailability and interaction with the pCRISPR. These nanomaterials were coated with alginate and chitosan to increase the surface potential. In this line of research, studies involving doxorubicin and its sustained release have made it possible to understand its cytotoxicity using HEK-293, PC12, HepG2, and HeLa cell lines, demonstrating acceptable cell viability at concentrations very low (0.1 μg mL^{-1}) and high (10 μg mL^{-1}) [53]. Under these premises, a cooperative effect optimized nanocarrier agent consisting of a combination of MOF-5 and Mxene, and chitosan and alginate, as exemplified in Figure 3, is explored in applications as drug delivery and gene delivery [53].

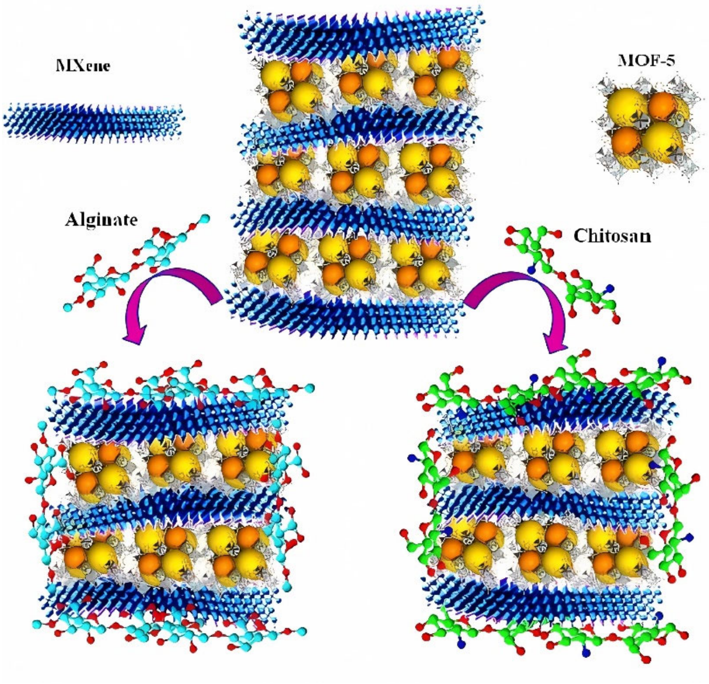

Figure 3. Illustration of MXene/MOF-5 with alginate and chitosan nanostructures. Reprinted with permission from Ref. [53].

Kashnik et al., proposed reaction sequence generating a typical supramolecular ionic framework based on a tetracationic TPE and either a dianionic octahedral molybdenum cluster complex or a tetraanionic octahedral rhenium cluster complex was synthetized at 25°C by mixing the two precursor solutions. This approach focuses on octahedral metallic cluster of general formula $A_n[M_6L^i_8L^a_6]$ (A = alkali cation, M = transition metal; L^i = inner ligand; L^a = apical ligand). The metallic scaffold M_6 is covalently bonded to face-capping ligands ($\mu3$-L^i) and is stabilized by six apical ligand L^a [54].

In the structuring of hybrid materials with unlimited functions is guaranteed by the provision of new ideas linked above all in the infinite continuum of their properties to overcome the economic and technical limitations arising in today's technology [55]. In this context, there is a great deal of space for customization on structuring MOF catalysts inherent to tailoring ability of metallic building blocks and organic ligands. This can be exploited in the structuring of MOF to be used as catalysts, by the coordination unsaturation since the most reactive sites are often located in the edges and corners. Gloag, et al., in an excellent review, lays the foundation to understand the co-catalytic metal–support interactions in single-atom catalysts (SACs), and the scaffolds and strategies on the development of improved catalytic materials. Especially in the different ways co-catalysis can influence the catalytic properties of an active site [56].

Until now, the metal-ligand coordination bonds are taking advantage extensively in organizing molecular building blocks into diverse supramolecular architectures enhancing 1D, 2D, and 3D networks, usually known as coordination polymers (CPs) or MOFs. In fact, in coordination polymers, metal ions enhance the design of desired topological structures and attractive to researchers. For instance, the strong metal–ligand (M–L) bonds, it can also be expanded to the area of crystal engineering [57]. In the context of CPs and MOFs are the aspects of the liquid and solid states. Coordination chemistry and reticular design principles offer unlimited possibilities for extending the structural diversification and properties of CPs and MOFs [58]. Furthermore, the structural role can be further complemented by an added functionality to produce of a new electronic control through non-bonding interaction. The chemistry of CPs and MOFs are intimately linked in which the inorganic nodes with metal ions or inorganic polynuclear clusters known as secondary building unit (SBU) and are linked with an organic linker through coordination bonds.

One typical example of the occurrence of carbon-based composites (M–N–C) consisting of transition metals such as Fe, Co, and Ni, and nitrogen, especially Fe–N–C, have been emerging to substitute catalyst based on platinum group metals (PGM) by virtue of their low cost, high activity, and stability. Furthermore, this can be effective catalyst for cathodic oxygen reduction reaction [59].

As anticipated, thanks to the directionality, catalyst MOFs-based may be fabricated using functional groups containing organic ligands, including active heteroatoms such as carbon, oxygen, nitrogen, boron, and sulfur [60]. As it is conceivable, MOFs are coordination compounds of crystalline of amorphous constitution formed through the self-assembly of organic ligands with metal ions that exhibit a structured and punctual porosity and surface area [61]. Obviously, the structure and topology can be designed using different chemical building units, as well as regulating synthetic parameters and post-synthetic treatments [62]. From a general view may be indicated that the topology of a molecule has a fundamental influence on its physical, chemical, and biological properties.

The consistent effect of physicochemical properties of MOFs makes them particularly interesting for a wide radius of applications such as adsorption [63], nonlinear optics [64], and others including the catalysis, gas storage and separation, air filtration, sewage treatment, sensing, and energy storage [65]. Such especial characteristics MOFs also known as porous coordination polymers (PCPs), can create stabilizing microenvironments for biomolecules to improve their performance against perturbation conditions, but also promote the separation and recovery of biomolecules from some products [66,67]. The structural richness based on metallic nodes and organic functional linkers makes them have varied structural richness with multiple and, of course, selective interactions. Several of the studies point toward strategies for improving the processability of MOFs, especially through the combination of MOFs with other materials to form macro-MOF with enhanced processability, high flexibility and mechanical properties excellent [68]. Therefore, it seems that the improved mass diffusion properties of MOFs, together with their robust single-crystalline nature, endow them with superior catalytic activity and recyclability for bulky-molecule reactions [69]. In this environment, Rosi, et al., identified the principal topological possibilities of a variety of MOFs showing that MOF-74, also called CPO-27 (coordination polymer of Oslo), is one of the most promising MOFs with stable architectures and high porosity. In fact, the authors reported the set of MOFs with polytopic carboxylates and contain Zn, Pb, Co, Cd, Mn, or Tb into its structure [70]. In another instance, detailed in depth not only the synthetic approaches and their respective advantages for mixed-metal in MOF-74 frameworks through diverse paths of ligand extensions to configure the pore size, surface area, and functionality. Thus, the inclusive role of organic bonds and their functional groups is of great relevance [71]. Following works on the biomedical field we can find reviews about the MOFs that detail specific structural requirements to have morphology to ensure biocompatibility and precise functionality in essentially all cases. For instance, 2D MOFs have been extensively studied as drug carriers for cancer applications as consequence of increased loading of chemotherapeutic drugs due MOF's high specific surface area [72]. Radical research has particularity in the underlying antimicrobial mechanisms of MOFs and comprehensive evaluation methods of antimicrobial efficiency of MOF-based materials. Thus, a focused study on a specific subject where MOFs seems to be particularly effective encompasses to next-generation MOF-based antimicrobial materials [73]. The value of the MOFs widens towards the intrinsic catalytic activity that has been well outlined over the years, in such a way that they have been the support not only of metallic nanoparticles as well as hosts for the encapsulation of enzymes [74].

As a matter fact, a convenient method for preparing mono- and bisferrocenylphosphinic acids has been developed by the group of Khrizanforov, establishing a structural reference on the coordination of phosphorus atom and reaction conditions of bisferrocenylphosphinates. These structural ligands have an impact on the coordination polymers formation and presumably their inherent properties [75].

To conclude this section, some studies are detailed on the structural complexes of carbohydrates that provides well-defined data about of the secondary structures, separated by energy barriers, has strongly suggested chemical strategies to stabilize a particular conformer. Consequently, the directed design of oligosaccharide chains is feasible to tune glycan aggregation and program supramolecular assembly [76]. In this regard, a detailed understanding of the κ-carrageenan is carried out by Mezzenga and his team of collaborators, which is very important and valuable in modulation of forms single helices when κ-carrageenan is subjected to potassium ions to build a secondary structure, further folding into single-chain supercoiled strands to form a tertiary structure and then side-by-side rigid superstrands with other chains to set up a quaternary structure. This is fundamental tool for enhancing a branched supramolecular physical network with local anisotropic orientation [77].

5. Electrochemical Synthesis of MOFs and Their Relating Specific Architecture

In the intervening 18 years since the introduction of anodic dissolution by BASF, the electrosynthesis has been polished, which has a lot to do with anodic dissolution where the oxidation of an electrode functions as a source of metal ions essential for a specific MOFs formation [78]. Anodic dissolution underlies mild reaction conditions and allows the continuous synthesis of compact homogeneous MOF thin films within short period of time. Additionally, an attempt is made to combine approaches the real time monitoring of electrodeposition allows continuous control over the synthesis and subsequent scalability [79]. Certainly, in direct electrosynthesis such as anodic dissolution and reductive electrosynthesis, the desired MOFs are formed directly on the electrode surface by an electrochemical reaction. By using indirect electrosynthesis, MOFs are generated via electrophoretic deposition, galvanic displacement, or self-templated synthesis [80]. One remarkable feature is that the MOFs-based photoelectrochemical (PEC) applications lie in alcohol oxidation, water oxidation, water splitting, CO_2 reduction, solar cells, water remediation, and sensor and biosensors, as shown in Figure 4 [81].

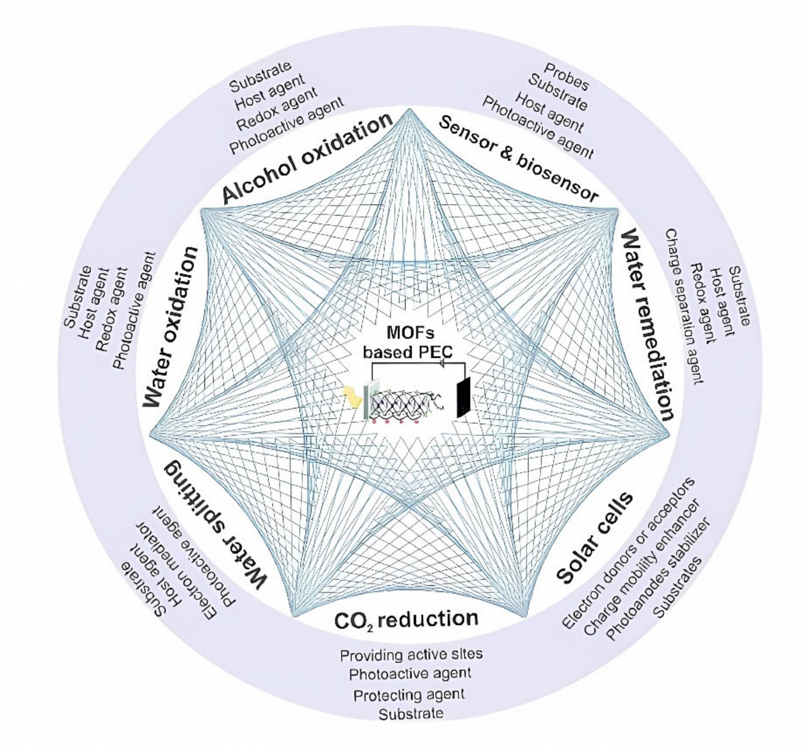

Figure 4. Specific application and role of MOFs in PEC systems. Reprinted with permission from Ref. [81].

It is noteworthy that the MOF thin films (MOFTFs) have been developed using spin-coating, seeded growth or secondary growth, electrophoretic deposition, Langmuir Blodgett, layer-by-layer

(LBL) deposition, evaporation induced crystallization (EIC), gel-layer synthesis, chemical vapor deposition (CVD), dipping layer by layer (DLBL), pump layer by layer (PLBL), hydro(solvo)thermal, spray layer by layer (SLBL), flowing layer by layer (FLBL), and electrochemical deposition (ECD) (anodic and cathodic electrodeposition) [81].

It is worth mentioning that the host–guest interactions at the single supermolecule level have influence on charge transport, achieving precise control over the conductance, this and taking advantage of supramolecular chemistry make possibly create novel techniques of supramolecular polymerization to generate a range of catalytic systems [82].

Exploreting synthetic methods to produce MOFs are increasingly tinged with innovation, however, it is feasible encompass them in hydro(solvo)thermal, microwave synthesis, electrochemical synthesis, and direct precipitation mainly. And it is goes without saying that the metallic component is of utmost importance to provide specific active sites for catalysis and adsorption [83].

It is important mention that Ni-based MOFs can form a film on nickel foam, that is, a layer of $Ni_3(BTC)_2$ can be formed by an electrochemical process at constant volage. Likewise, the effect of solvent, voltage, and reaction time, as well as the electrocatalytic efficiency of NiBTC/Ni system on the hydrogen evolution reaction (HER) is fully studied [84].

The considerable outpouring about the patterned Ni organic framework is developed by Vinesh eta al., grafting TMA with Ni(II) ions and the fractional cation replacement of Ni^{II} with Co^{II} in a paddlewheel entities of Ni MOF [85]. The bimetallic MOF carbonized at 500^{o}C generates the homogeneously spread NiO/Co_3O_4 hollow structures with hierarchical carbon architectures ($NiO/Co_3O_4/C$). The metal oxide/carbon nanocomposites loaded biodegradable corn starch bag's (BCSBs) are employed as electrochemical probes for enzyme-free glucose detection. The major impetus using $NiO/Co_3O_4/C$ as a means of diagnosing glucose came from the group of Kumar [85] in a substantial paper. In addition to using Density Functional Theory (DFT) studies and the impact on glucose electrooxidation reaction (GEOR) kinetics are commented with the diversified electrochemical characterizations.

There are continuing efforts to correlate, predict, and understand the feasibility of replacing the traditional, toxic, fossil fuel derived solvents in electrochemical MOF synthesis. Whether this is a feasible it would be a real advance in the use of cleaner alternatives. As Bhindi et al., show by making use of γ-valerolactone (GVL) and dihydrolevoglucosenone (Cyrene™) to electrochemically synthesize a wide range of MOFs with either Cu, Zn or Co as the metal component and either 1,3,5-benzenetricarboxylic acid (BTC), imidazole (IM), benzimidazole (bIM), 2-methylimidazole (mIM) or 2-ethylimidazole (eIM) as the organic linker component. However, structures a gets less stable and higher porosity indicating that the larger biosolvent molecules may also affect the synthesis of MOFs [86]. In their 2023 paper, Zhang, Fransaer and co-workers make interesting suppositions on MOF films by controlling the supersaturation of molecular building units of MOFs during anodic electrodeposition. The characteristic patterns are discussed by increasing the pH of the electrolyte to facilitate the deprotonation of linkers and thus to design a film of HKUST-1 with morphologies as varied as octahedral, cuboctahedral, and cubic. Considering electrochemical quartz crystal microbalance (EQCM) technique combined with ex-situ SEM measurements, the authors suggest that the supersaturation during crystal growth is bound to affect the crystalline morphology [87].

Another approach to the use of electrochemistry is for the synthesis of the complex CoNi-ZIFs@Ag@NF based on CoNi-ZIFs and Ag NPs. This complex is a substrate potential for SERS monitoring of tetracycline in food and environment [88].

Hiroata et al., have shown that control of crystal morphology can result in stacking of pillararene molecules with the cationic species of the electrolyte. It is possible that the host-guest complex precursor releases the guest molecules during the oxidative transformation because the obtained pillarquinone is an electron-deficient macrocycle. Moreover, manipulating the morphology by varying the solvent composition is a key factor [89].

There are clear advantages to producing MOF materials in the form of thin films with perfectly defined geometries [90]. These geometries have been finely developed over time and comprise spheres solid and hollow, prisms, rods, wires, and dendrites. Regarding the active sites in the catalyst, there have also been great advances to increase them using the electrochemical synthesis of MOFs.

6. Switchable MOFs

A MOF perfectly designed to present adaptability in its conformation and therefore modify its pore size must be constituted by chemical entities that have the property of switchability (sometimes called flexibility phenomena). Switchability implies a stepwise specific response (solid-state phase transition) at a well-defined chemical potential [91]. In fact, engineering 4D materials is equivalent to a control of activation barriers materials, a scientific field that have been moderately explored. In fact, the ON–OFF switchable function is realized by applying electrical signals [92].

It is worth highlighting the existence of a response spatiotemporal response governed by an activation barrier, reflected in the gate opening pressure (pAPHM) and one activity of a pore opening stimulating guest molecule (pstim). The ensemble-based switching can be represented by rate constant k with Δp = pstim – pAPHM [91].

Switching processes criteria lead key strategies in the adsorptive and desorptive control of materials. Compounds that perform well as switches in solution may encounter difficulties in the solid state, owing to a greater restriction of movement in the solid state. An additional encouragement of using switching processes is present in photoresponsive molecules that exhibit potential use as sensors, switches, and memory and optical data storage media. A clear example are the organometallic molecules widely investigated and used in technologies including organic light-emitting diodes (OLEDs), fluorescent probes, and laser dyes [93].

To talk about multi-photon absorption (MPA) is to detail the nonlinear optical (NLO) properties for applications as varied as telecommunications, photonics, and biomedicines. It is not surprising that, in this way, MOFs with benefits such as MPA have been designed consisting of zirconium- and hafnium-oxoclusters and featuring a chromophore linker based on the tetraphenylethene (TPE) molecule, and clearly showing a considerable two photon absorption (2PA) with cross-section values, up to 3600 unit Göppert–Mayer (GM), (1 GM= 10^{-50} $cm^4 s Photon^{-1} molecule^{-1}$) [94]. With this notion the design of MOFs for MPA applications adhere to follow several criteria for organic or organometallic NLO chromophore molecules, one is the focus of molecular dipole or multipolar structural units for an enhanced polarization of the charge distribution, another and no less relevant factor is the presence of planar structural pattern with long p-conjugation, the exaltation in fluorescence quantum yield, and clearly a narrow one photon absorption (1PA) and two-photon (2PA) absorption bands, and feature of alignment and high packing density associated to the chromophore with NLO properties[94]. The electrophilic charge polarization criterion has been generally appropriate in two series of MOFs Zr-based nodes. There are two basic approaches, in the first, an isostructural Hf-analogues is stablished; subsequently, an electron withdrawing TFA-bonded structures are modulated in order to fortunately stabilize a charge transfer, as visualized in Figure 5 [94].

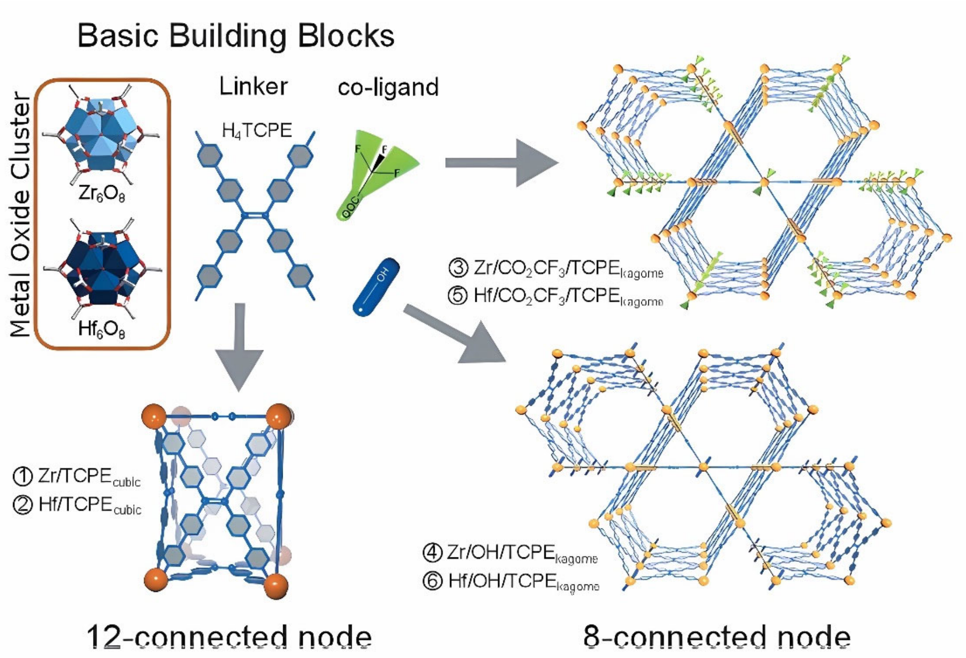

Figure 5. Top left: Views of blocks with zirconium- and hafnium- nodes {$M_6O_4(OH)_4$}, a flexible tetrakis[4-(4-carboxyphenyl)phenyl]ethylene (TCPE) linker, and the co-ligands trifluoroacetate or hydroxide. Bottom left: a schematic view of the cubic MOFs **1** (Zr/TCPE$_{cubic}$, [$Zr_6O_4(OH)_4(TCPE)_3$]) and **2** (Hf/TCPE$_{cubic}$, [$Hf_6O_4(OH)_4(TCPE)_3$]), where the nodes are formed by coordination of 12 carboxylate groups of the TCPE linkers. Right: hexagonal Kagome-type lattice MOFs 3–6 (M/X/TCPE$_{kagome}$ [$M_6O_4(OH)_6(H_2O)_4(X)_2(TCPE)_2$], M=Zr or Hf, X=OH or CO_2CF_3), where the nodes are coordinated by 8 carboxylate groups resulting in the formation of a mesoporous structure with 1D channels along the z-axis. In the case of **3**, Zr/CO_2CF_3/TCPE$_{kagome}$ and **5**, Hf/CO_2CF_3/TCPE$_{kagome}$ the nodes are also coordinated by trifluoroacetate co-ligands (top right), whereas in **4**, Zr/OH/TCPE$_{kagome}$ and **6**, Hf/OH/TCPE$_{kagome}$ the nodes are coordinated by additional OH and H_2O (bottom right). Reprinted with permission from Ref. [94].

An interesting rationalization about switchable MOFs is the exposed by Aprahamian that explains that an existing switch in the MOFs is understandable by their free volume, especially if are used side groups, but less so if they are used as part of the framework. To apply this is necessary to know the feasible corresponding to a careful crystal engineering is required to allow that the framework switching their geometrical shape freely. This is related in turn to the architecture of the types of molecules that show that the function and dynamic motion is attainable as a diversification of systems that can be used as switchable crystals [95]. It can thus be seen from Cu-MOF-SCH_3 is displays an especially switchable structure for the separation CH_4/N_2 mixture, what is assumed is due to the structural change through the equilibrium adsorption, this allows considerable separation of CH_4/N_2 specifically at 298 K and 1.0 bar [96]. Some excellent experiments have clarified and confirmed a abiding hypothesis about the metastable states upon sorption in mesoporous MOFs and the appearance of a liquid-like condensed phase within mesopores triggering a structural transition in the system DUT-49(Cu) accompanied by the called negative gas adsorption (NGA) phenomenon [97]. Recent leading works on the energy barriers that are the criterion that reveals kinetic control, emphasizes that it can arise from a stability framework coupled to the physics of the guest molecules with characteristic barriers of fluid nucleation, diffusion, and adsorption processes [91]. The progress in measuring the transformation time of a switchable MOF has consequently been a tedious task. This weight of evidence supports the cyclic variation of the applied electric potential on an electrode modified with the ZIF-8 MOF as a prototypical model labile under acidic conditions due to protonation of the Zn-Nligand bond, can reversibly activate and inhibit the payload release. In general, this is the case because the structure of ZIF-8 is characterized by having a three-dimensional

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pore network composed of larger 13.4 Å-sized sodalite cages interconnected by smaller 3.4 Å-sized apertures [92].

Negatively charged nitrogen-containing chemical entities have been exploited for the magnetic switching of a MOF structure composed of Fe Ag cyanoheterometallic [Fe(1,6-naphthyridine)$_2$(Ag(CN)$_2$)$_2$]. The presence of paramagnetic Fe^{III} either as low-spin (LS, S = 0, no unpaired d-orbital electrons) and high-spin (HS, *S* = 2, 4 unpaired d-orbital electrons) states impacts in the detectability of nitrogen vacancy (NV$^-$) in the form of optically detected magnetic resonance (ODMR) and magnetic modulation (MM) [98].

On the other hand, the replacement of silica gel and zeolite with MOFs has been carried out by Askalany and collaborators for desalination. CPO-27(Ni) MOF was used in a series of cycles of desalination, switching times, and different cooling water temperatures to identify the optimal conditions to achieve the maximum value of specific daily water production (SDWP) and Gained output ratio GOR of the cycle [99]. In another case that is not less relevant, the coordination between Cu^{+2} ions with the oxygen of the sulfonic group and the amino group of taurine have been studied. Under this premise, the PLL-fGQDs@UiO-66@NH$_2$ MOF fluorescent nanoprobe may be used as taurine biosensing in biological fluids with high specificity [100].

Another model established by the group of Youssef is linked to the volumetric magnetization of the crystalline mixture composed of poly 3-hexylthiophene- 2,5-diyl (P3HT) and the fullerene compound phenyl-C$_{61}$-butyric acid methyl ester (PCBM). P3HT:PCBM crystal blend obtained shows soft magnetic behavior with a remanent magnetization of 6.4memu/cm^3 and a magnetic field of 9.4 Oe. It is inherent that the complex P3HT:PCBM crystalline presents a trace quantity of pinning sites that stimulate the soft magnetic response improving switchable magnetics [101].

Dynamic machinery of the MOF FTR-P2 (belonging to the family of Frustrated Trigonal Rotors) has been assessed by Perego et al., these molecular dynamics may be due to a guest-stimulated flexibility, and it may well be indicated that FTR-P2 comprises a molecular dynamic of the set of BCP (synthesized by assembly bicyclo[1.1.1]pentane-1,3-dicarboxylate and azpy=4,4′-1,2-diazenediylbispyridine), metal nodes, and azo pyridyl pillars [102].

7. Summary, conclusions, and Outlook

An attempt is made through this review to bring together old and new ideas and methodologies associated with the supramolecular chemistry and its relation to MOFs covering the entire spectrum of the subject from original idea. Classical MOFs discussions have in the past and present brought together theoreticians and synthetic chemist. Also, in any attempts to understand its relationship with supramolecular structures, further interdisciplinary interaction is promoted by covering larger and larger self-assembly systems and eventually structures under strictly planned molecular design. The chemistry and physic of supramolecular has developed into science and technology of electronic materials. However, even if the reader tends to confine his view to the fundamental aspects of supramolecular structures, extended self-assembly systems create challenging problems for any discussions into MOFs and supramolecular structures and its advances in practical specificity. The other important aspect is that while being concerned with the conjugation MOFs and supramolecularity, one should not restrict the attention to intramolecular aspects. Properties such as the supramolecular chemistry in confined space, relationships of MOFs with the supramolecular chemistry, electro-chemical synthesis of MOFs, and switchable MOFs, which are regarded as being characteristic of molecules whose origin is the formation of assembly systems to obtain supramolecular MOFs cannot be understood when concentrating one´s focus on the behavior of single-molecule function, or small isolated molecules in dilute solution. Quantitative predictions and the study of marginal cases have also provided a strong challenge both to theory and experimentation. Thus, many examples still await both vigorous theoretical examination and experimental verification, and the stimulus to achieve these goals promises to continue to advance chemical knowledge.

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and editing, J.A.S.-F., visualization, J.A.S.-F., R.C.-S. and H.S.; supervision, J.A.S.-F. and R.C.-S.; project administration, J.A.S.-F; funding acquisition, J.A.S.-F. and R.C.-S. All authors have read and agreed to the published version of the manuscript.

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