

# Current Advances in the Synthesis of CD-MOFs and Their Water Stability<sup>†</sup>

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<sup>†</sup> Presented at the 4th International Electronic Conference on Applied Sciences, 27 October–10 November 2023; Available online: <https://asec2023.sciforum.net/>.

**Abstract:** Metal–organic frameworks (MOFs) are a class of material made up of metal ions or clusters and organic linkers. Cyclodextrin-based MOFs (CD-MOFs) are gaining popularity among MOFs due to their unique features, such as high porosity, permanent porosity, and biocompatibility. This paper focuses on recent advances in synthesizing CD-MOFs and their water stability. We highlight the difficulties involved in CD-MOF synthesis and the strategies explored to increase water stability. The advances in CD-MOF synthesis and characterization open new avenues for tailoring crystal growth processes and properties, with potential applications spanning areas such as catalysis, drug delivery, and environmental remediation. The combination of innovative synthesis techniques, systematic parameter exploration, and functionalization strategies heralds a promising era for crystal growth research and applications. Finally, we discuss the current research gaps and the future outlook of CD-MOF research. Overcoming obstacles in the synthesis and water stability of CD-MOFs is crucial for their practical applications.

**Keywords:** cyclodextrin metal-organic frameworks; carbon dioxide capture; adsorption; separation



**Citation:** Lopez, E.C.R.; Perez, J.V.D. Current Advances in the Synthesis of CD-MOFs and Their Water Stability. *Eng. Proc.* **2023**, *56*, 72. <https://doi.org/10.3390/ASEC2023-15373>

Academic Editor: Manoj Gupta

Published: 26 October 2023



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## 1. Introduction

The remarkable characteristics of metal–organic frameworks (MOFs), such as their substantial surface areas, variable pore sizes, and permanent porosity, have attracted the attention of the scientific community. MOFs are composed of metal ions or clusters, organic linkers, and three-dimensional networks with open pores. MOF characteristics can be tailored by changing the metal ions, organic linkers, and synthesis conditions. Numerous applications, such as gas storage, separation, catalysis, drug delivery, and sensing, have used MOFs.

Toroidal cyclic oligosaccharides called cyclodextrins have a hydrophobic cavity comprised of glucose units. Cyclodextrins have been used as building blocks for synthesizing MOFs due to their distinctive properties, such as biocompatibility and host–guest interactions. Cyclodextrin molecules serve as organic linkers, and metal ions serve as nodes in CD-MOFs (cyclodextrin-based MOFs), a particular type of MOF.

We will examine the current state of CD-MOF synthesis research in this paper. Additionally, certain methods for enhancing the water stability of CD-MOFs are provided. For CD-MOF synthesis and applications, current research gaps and future research potential are also highlighted.

## 2. Synthesis Strategies for CD-MOFs

### 2.1. Vapor Diffusion/Slow Evaporation Method

Smaldone's group [1–3] originally created CD-MOFs by vapor diffusing methanol for 2 to 7 days while employing alkali metal building blocks and  $\gamma$ -CD in a 1:8 metal: ligand ratio.

With yields of up to more than 70% by mass, this technique produced high-quality crystals that allowed for single-crystal analysis and, eventually, crystal structure determination. The three synthesized CD-MOFs, designated as CD-MOF-1 (K-based CD-MOF), CD-MOF-2 (Rb-based CD-MOF), and CD-MOF-3 (Cs-based CD-MOF), are isostructurally linked to one another and are made of infinite body-centered frameworks of  $(\gamma\text{-CD})_6$  cubic units. In the middle of the cube is a pore with a diameter of 1.7 nm that is approximately spherical. The resulting channels connect the central pores in all three dimensions and are defined by the internal window (0.78 nm) of the  $\gamma\text{-CD}$  unit. With a calculated 54% pore vacancy, the structure has a never-before-seen topological net, *rra*, which defines a body-centered cubic network of sizable spherical pores connected via a number of channels. Each alkali metal cation is crystallographically equivalent and contributes to the formation of the  $(\gamma\text{-CD})_6$  cubes by joining two distinct tori at their primary faces as well as connecting these cubes. Eight coordinate alkali metal cations are produced as a result of this dual linking, and they coordinate to the  $\gamma\text{-CD}$  units at each glucopyranosyl residue in an alternate primary face/secondary face pattern. Although similar, the bond lengths between the coordination spheres of  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  grow longer when the ionic radii of the alkali metal cations decrease in Group IA of the Periodic Table.

Additionally, they created a number of CD-MOFs utilizing various alkali metal salts. It has been discovered that solutions of basic salts, such as hydroxides and carbonates, produce the largest, highest-quality crystals. These salts promoted crystal formation despite not producing aqueous solutions with enough basicity to deprotonate the hydroxyl groups of  $\gamma\text{-CD}$ . Except for lithium salts, almost all of the alkali metal salts studied produced a cubic shape. Using food-grade cyclodextrin and edible metal salts (potassium benzoate) as precursors and ethanol rather than methanol during the crystallization process, they also presented the synthesis of edible MOFs for the first time. Another crystal phase with a needle-shaped morphology made of  $\gamma\text{-CD}$  tori connected to one another via  $\text{Cs}^+$  ions' coordination to form channels along the crystallographic *c*-axis (CD-MOF-4) was created concurrently with the crystallization of CD-MOF-3. Later, it was discovered that CD-MOF-4 was more thermodynamically advantageous than CD-MOF-3, which is kinetically advantageous in the circumstances employed for synthesis [1–5].

The same group also reported the synthesis of the first strontium-based CD-MOF, which has a trigonal “slipped stack” configuration and results in a convoluted and non-linear channel structure that extends infinitely along the *c*-axis and is punctuated by large cavities with maximum and minimum diameters of 6.8 and 3.2, respectively.  $\text{Sr}^{2+}$  are nine-coordinate species that are triple-occupied by water and bonded to three distinct  $\gamma\text{-CD}$  units, in contrast with alkali earth metals. Additionally, they attempted to create CD-MOFs using transition metals. Because coordinative linkages between the protonated hydroxyl groups of  $\gamma\text{-CD}$  and the metal are not preferred, their attempts were ineffective. They found that the deprotonation of the CD hydroxyl groups is necessary for the formation of metal–CD bonds, joining the transition metal complexes of  $\gamma\text{-CD}$  together [1–3].

While many metal precursors have been investigated for the synthesis of CD-MOFs, it is crucial to remember that different MOF structures could result from varying the metal source. KOH and potassium benzoate were utilized as two separate sources of potassium ions in work by Al-Ghamdi et al. [1] to manufacture CD-MOF-1. The CD-MOFs made from KOH (CD-MOF-a) produced body-centered cubic crystals of space group *I*432 with a BET surface area of  $1229 \text{ m}^2 \text{ g}^{-1}$ , a total pore volume of  $0.50 \text{ cm}^3 \text{ g}^{-1}$ , and an average pore radius of 0.79 nm. The CD-MOF-1 made with potassium benzoate (CD-MOF-b), in comparison, has a trigonal crystal system that represents the space group *R*32, a BET surface area of  $417 \text{ m}^2 \text{ g}^{-1}$ , a total pore volume of  $0.22 \text{ cm}^3 \text{ g}^{-1}$ , and an average pore radius of 0.40 nm. Due to the higher basicity of KOH than potassium benzoate, CD-MOF-a has higher yields [1].

Patel et al. [6] attempted to extend the CD-MOF family using LiOH as a metal precursor, but the synthesis was unsuccessful. Instead of using pure LiOH, they co-crystallized LiOH and KOH with  $\gamma\text{-CD}$  via the vapor diffusion of methanol to produce a  $\text{Li}^+$  ion-substituted

CD-MOF (Li/K-CD-MOF), partially by replacing some of the  $K^+$  sites in CD-MOF-1 with  $Li^+$  ions without sacrificing the porous architecture of the CD-MOF. They found that the degree of  $Li^+$  substitution increased with an increasing concentration of LiOH during the co-crystallization process. The highest  $Li^+/K^+$  ratio ( $K_{1.18}Li_{0.61}$ ) was achieved from the co-crystallization of LiOH and KOH in a ratio of 1.4:0.2 for 1 mol equivalent of  $\gamma$ -CD.

Using LiOH as a metal precursor, Patel et al.'s [6] attempt to broaden the CD-MOF family proved unsuccessful. A  $Li^+$  ion-substituted CD-MOF (Li/K-CD-MOF) was created by co-crystallizing LiOH and KOH with  $\gamma$ -CD instead of using pure LiOH. This preserved the porosity architecture of the CD-MOF while partially substituting some of the  $K^+$  sites in CD-MOF-1 with  $Li^+$  ions. They discovered that when the concentration of LiOH grew throughout the co-crystallization process, the amount of  $Li^+$  substitution also increased. The highest  $Li^+/K^+$  ratio ( $K_{1.18}Li_{0.61}$ ) was obtained from the co-crystallization of LiOH and KOH in a ratio of 1.4:0.2 for 1 mol equivalent of  $\gamma$ -CD. The solid-state structure of Li/K-CD-MOF, in contrast with CD-MOF-1, occupies the trigonal space group  $R\bar{3}2$  and is made up of  $\gamma$ -CD tori bound together by  $K^+$  ions in a cubic unit cell of space group  $I432$ . When  $Li^+$  ions replace certain  $K^+$  sites in CD-MOF-1 during co-crystallization, the BET surface areas of CD-MOF-1 and Li/K-CD-MOF are practically identical, measuring at 1145 and 1205  $m^2 g^{-1}$ , respectively. They also have comparable pore maxima, with a center point of 11.7, which demonstrates the maintenance of the pore size distribution following the occupancy of the  $K^+$  sites by  $Li^+$  ions.

In an effort to create a new electrode material for lithium-ion batteries, Kruk-Berzina et al. [7] synthesized the first lithium-based CD-MOF three years later. The aforementioned Li-based CD-MOF consists of four oxygen atoms arranged in deformed tetrahedra to coordinate both  $Li^+$  ions.

By adjusting the reactant ratio, cyclodextrin concentration, temperature, reaction duration, choice of diffusing solvent, and concentration of the growth modifier, i.e., CTAB, Liu et al. [8] improved the vapor diffusion technique to manufacture  $\gamma$ -CD-MOFs. Larger cubic crystals were produced as the  $\gamma$ -CD concentration was increased, which they ascribed to the effective inhibition of the framework expansion. The  $\gamma$ -CD-MOF's particle size reduced as the reaction temperature rose because higher temperatures result in more MeOH vapor diffusing into the reactant solution, which hastens the oversaturation of the precursors. When the nucleation rate is higher than the crystal growth rate, longer synthesis times lead to smaller  $\gamma$ -CD-MOF crystals. A higher molar KOH/ $\gamma$ -CD ratio produces bigger, more polydisperse crystals of  $\gamma$ -CD-MOFs. In contrast with the nucleation rate, a quicker crystal growth rate is facilitated by an increase in the ionic concentration. The crystalline structure of  $\gamma$ -CD-MOFs is not considerably influenced by the solvent used, but the morphology that results is. Particularly, the use of EtOH results in hexagon-shaped and larger-sized crystals, whereas the use of  $Me_2CO$  results in smaller crystals. Because  $Me_2CO$  has a lower boiling point than other solvents, the vapor diffusion of  $Me_2CO$  occurs more quickly. Numerous nuclei are produced as a consequence, which is followed by the rapid development of smaller-sized crystals.

Crystal growth modifiers have also been explored for the synthesis of CD-MOFs. Cetyltrimethylammonium bromide (CTAB) was specifically employed by Furukawa et al. [9] to synthesize homogeneous, monodisperse crystals of micro- $\gamma$ -CD-MOFs (crystal size = 1–10  $\mu m$ ). Additionally, they were successful in creating nano- $\gamma$ -CD-MOFs after adding CTAB and methanol. Additionally, they created homogenous cubic gel particles for use in a variety of biomedical applications by crosslinking the cyclodextrins in the CD-MOFs using an ethanol and ethylene glycol diglycidyl ether combination. Liu et al. [8] also explored the role of CTAB as a capping agent for controlling the size and morphology of MOF crystals in aqueous systems. The crystallinity of the resulting  $\gamma$ -CD-MOF did not appear to change when the CTAB concentration was changed. However, as the concentration of CTAB was increased, the crystal size fell because CTAB coated the surface of the forming MOF crystals during crystallization, slowing the growth rate and resulting in smaller crystals. Overall, the scientists reported that by increasing the reaction temperature and

the solvent's pre-addition, the rapid and homogenous nucleation of the  $\gamma$ -CD-MOF could be accomplished. Additionally, they were able to demonstrate that essential aspects in influencing the characteristics of  $\gamma$ -CD-MOFs include nucleation and crystal growth rates, which can be changed by adjusting different synthesis parameters.

The first  $\alpha$ -CD-based MOF was synthesized in 2012 by Stoddart's team, who coordinated  $\text{Rb}^+$  and  $\alpha$ -CD in an aqueous solution to create long, hollow needles. Even with identical synthesis conditions and metal precursors, the resultant MOF structure is topologically distinct from that of  $\gamma$ -CD-MOFs. In particular, the interdigitated left-handed helical holes that are left over after the ligation of  $\text{Rb}^+$  ions to the primary and secondary faces of the CD rings can be seen running through the structure of the final crystals. This is analogous to the organizational behavior of other chiral compounds in nature, making them potentially useful for chemical sensing, energy storage, and chemical separations [10].

Sha et al. [11] added to the collection of unique CD-MOFs by synthesizing  $\alpha$ -CD-based MOF utilizing KOH as a metal precursor and methanol as the solvent. The K-based  $\alpha$ -CD-MOF, or  $\text{K}_3(\text{C}_{36}\text{H}_{60}\text{O}_{30})_2 \cdot 7\text{H}_2\text{O}$ , has indefinitely long left-handed helical chains with exceptional drug adsorption and release capabilities. In another paper by Sha et al. [12], NaOH was used as a metal precursor in the creation of a Na-based  $\alpha$ -CD-MOF. One CD molecule, one  $\text{Na}^+$  ion, and two water molecules make up the Na- $\alpha$ -CD-MOF crystal. Additionally, 5-fluorouracil, methotrexate, quercetin, and ferulic acid were all encapsulated using the Na- $\alpha$ -CD-MOF, a renewable and biocompatible drug carrier material, due to its superior drug adsorption capability [12].

Li et al. [13] expanded the use of the vapor diffusion technique to include other cyclodextrin kinds. They specifically created potassium-based CD-MOFs based on  $\alpha$ -CD,  $\beta$ -CD, and  $\gamma$ -CD. With wide holes (11 Å diameter) and tiny pores (7 Å diameter),  $\alpha$ -CD-MOF-K displayed a left-handed helical chiral layer structure;  $\beta$ -CD-MOF-K also featured bowl-like pores (6 Å) and dual channels (approximately 5 Å in size); and  $\gamma$ -CD-MOF-K contained body-centered cubic with pores (7.8 and 4.2 Å). In the CD-MOFs, the order of the hydroxyl group concentration was  $\gamma$ -CD-MOF-K >  $\beta$ -CD-MOF-K >  $\alpha$ -CD-MOF-K. According to their research, the number of hydroxyl groups increased the CD-MOFs' ability to adsorb HCHO. Furthermore, because of its porous structure and the beneficial effects of hydrogen bonding host–guest interactions,  $\gamma$ -CD-MOF-K had an adsorption capacity and rate that were approximately nine times greater than those of activated carbon.

Qiu et al. [14] created  $\gamma$ -CD-MOFs by using a seed-mediated technique to further enhance the synthesis procedure. They employed short linear-chain starch nanoparticles (SNPs), which were used as seeds in the production of  $\gamma$ -CD-MOFs via vapor diffusion. SNPs have never before been utilized as a size modifier. The crystal size of the  $\gamma$ -CD-MOFs was specifically decreased by increasing the concentration of SNP seeds. As a result, the  $\gamma$ -CD-MOF crystals developed in three phases. The first stage was the emergence of a nucleus via  $\gamma$ -CD self-assembly. The second process entailed crystal development, crystal nucleus coagulation to an appreciable size, and the aggregation of  $\gamma$ -CD-MOF.  $\gamma$ -CD may be swiftly assembled because it is adsorbed onto the surface of SNPs when they are introduced, which speeds up the nucleus' creation. Due to the steric impact of the SNP seeds, the aggregation of  $\gamma$ -CD-MOFs was also decreased following the addition of SNPs, resulting in the formation of ultra-fine  $\gamma$ -CD-MOFs. Their approach produced more crystals with good porosity and crystalline characteristics than synthesis with the conventional vapor diffusion method, decreasing the duration of synthesis of  $\gamma$ -CD-MOFs from 24 h to just 6 h.

Like other MOFs, CD-MOFs can also be functionalized to achieve improved properties for the desired applications. For instance, Hartlieb et al.'s [15] functionalization of CD-MOFs produced a framework that could permanently store carbon dioxide and provide simpler, more flexible synthetic routes to post-synthetically functionalize CD-MOFs. They specifically used a Mitsunobu reaction to replace  $\gamma$ -CD on one of its major hydroxyl groups with a phthalimide group, yielding 6<sup>A</sup>-deoxy-6<sup>A</sup>-phthalimido- $\gamma$ -CD. The functionalized CD-MOF ( $\text{NH}_2$ -CD-MOF-2) could then be made either directly by deprotecting 6<sup>A</sup>-deoxy-6<sup>A</sup>-phthalimido-CD in situ with aqueous  $\text{RbOH}$  in the presence of MeOH, EtOH, or  $\text{Me}_2\text{CO}$



vapor or indirectly by preparing 6<sup>A</sup>-deoxy-6<sup>A</sup>-amino- $\gamma$ -CD by cleaving the phthalimide with hydrazine and then crystallizing the CD-MOF. Due to phthalate anions that clog pores and are challenging to remove using an anion exchange technique, the first approach produced nonporous crystals. Both synthesized frameworks, albeit utilizing very distinct techniques, crystallized in the *I432* space group.

In order to enhance the coordination link between the CDs and the metal ions and enable structural stiffness with exposure to humid or watery environments, Xu et al. announced the creation of the first coordination polymer from transition metal ions in 2016 [16]. The organic ligand was octakis-[6-deoxy-6-(3-mercaptopropionic sodium)]- $\gamma$ -cyclodextrin (SD, also known as Sugammadex), and the transition metal ion was Cu<sup>2+</sup>. A sulfurylpropionic acid arm was replaced for each of the eight C<sub>6</sub> hydroxy groups of an octacarboxylate  $\gamma$ -CD to create SD.

A novel iron-based CD-MOF was made using the vapor diffusion approach by Abuçafy et al. [17]. By creating an ether crown in the –O– position of  $\gamma$ -cyclodextrin, this was made feasible, allowing the metals to receive electrons more easily and eventually establishing coordination bonds [1,5]. In comparison with the 70% and 72% yields achieved for  $\gamma$ -KCD and  $\gamma$ -NaCD, they obtained a 62% yield for  $\gamma$ -FeCD. After activation, the pore diameters were determined to be 24.13 for  $\gamma$ -KCD, 32.86 for  $\gamma$ -NaCD, and 30.19 for  $\gamma$ -FeCD. Both the Ca-co-2 human colon adenocarcinoma and HepG2 human hepatoma cell lines were unaffected by the produced MOFs up to a concentration of 2000 g/mL. The percentage of cell viability also did not change at any of the concentrations evaluated, supporting the notion that the synthesized CD-MOFs would be safe for medical applications. The percentages of sodium diclofenac that were successfully trapped in the  $\gamma$ -KCD,  $\gamma$ -NaCD, and  $\gamma$ -FeCD were 50%, 49%, and 55%, respectively.

Koshevoy et al. recently created CD-MOFs based on alkaline earth metals [18]. In particular, a series of coordination polymers, Ba(H<sub>2</sub>O)<sub>3</sub>( $\gamma$ -CD)]Cl<sub>2</sub>·6H<sub>2</sub>O ( $\gamma$ -CD-Ba1), [Ba(H<sub>2</sub>O)( $\gamma$ -CD)]Cl<sub>2</sub>·8H<sub>2</sub>O ( $\gamma$ -CD-Ba2), [Sr(H<sub>2</sub>O)( $\gamma$ -CD)](NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O ( $\gamma$ -CD-Sr), [Ca( $\gamma$ -CD)<sub>2</sub>]Cl<sub>2</sub>·2CH<sub>3</sub>OH·16H<sub>2</sub>O( $\gamma$ -CD-Ca), and [Pb(H<sub>2</sub>O)( $\gamma$ -CD)](NO<sub>3</sub>)<sub>2</sub>·11H<sub>2</sub>O ( $\gamma$ -CD-Pb) were obtained by reacting  $\gamma$ -cyclodextrin with alkaline earth metal ions and Pb<sup>2+</sup>, respectively. For the first time, they described the coordination polymers made from -cyclodextrin, Ca<sup>2+</sup>, and Ba<sup>2+</sup>. Divalent metal ions (Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, and Pb<sup>2+</sup>) mostly form 2D metal–organic coordination polymers as opposed to CD-MOFs based on alkali earth metals, which create 3D MOFs. Their thermal characteristics, however, are comparable to those of alkali-based CD-MOFs, which are thermally stable up to ca. 200 °C. It is interesting to note that ligand-to-metal charge transfer and metal-centered transitions cause photoluminescence in the near-UV area for the Pb- $\gamma$ -CD-MOF.

The traditional synthetic strategies for MOFs include the vapor diffusion technique. This method involves vapor diffusion contact with a more volatile solvent into an aqueous solution of reagents, which progressively reduces the solution's polarity and, as a result, the sample's solubility, causing slow crystal growth [1–3]. Compared with the solar thermal approach, it simply needs ambient temperatures and pressures and allows for the synthesis of MOF crystals with extremely high crystal yields. However, it is only widely applicable to the extent that the ligands are soluble in the selected solvent and that it takes many days, or even weeks, to complete [19]. In addition, the weak noncovalent bonding interactions between the constituents and metal centers in CD-MOFs mean that the synthetic parameters, including the solvent selection, cyclodextrin precursor selection, metal precursor /s, molar ratio of reactants, temperature, and synthesis time, among others, have a significant impact on the characteristics of the CD-MOFs [8]. Studies have rarely examined how these variables affect the structure and characteristics of the resulting MOFs.

## 2.2. Solvothermal/Hydrothermal Method

The solvothermal/hydrothermal technique, also known as the high-temperature and high-pressure synthesis of MOFs, is a traditional synthetic approach to MOF crystallization. The nucleation and development of MOFs are influenced by a number of variables,

including reaction time, temperature, pressure, reactant concentration, modifier presence, and solvent of choice.

The first study on the synthesis of chiral helices made utilizing  $\beta$ -CD molecules and metal ions was published by Lu et al. [20], who used sodium oxalate as a metal precursor to create a  $\beta$ -CD-MOF. Meanwhile, Sha et al. [11] developed left-handed chiral helical double channels coupled with four adjacent identical helical channels of an  $\alpha$ -CD-MOF that crystallize in the space group  $P2_12_12_1$  using a solvothermal method that is capable of drug loading and sustained drug re-release.

In another study, Liu et al. [21] reported two helical microporous Cs-CD-MOFs, CD-MOF-1 and CD-MOF-2, constructed with  $\beta$ -CD as building blocks as well as cesium metal salts, with the help of 1,2,3-triazole-4,5-dicarboxylic acid ( $H_3tzdc$ ), methylbenzene sulfonic acid (TsOH), or an ibuprofen molecule (IBU) as a selective template agent. The synthesis of CD-based MOFs was the first time a template-induced strategy was employed. According to their research, the solvent, temperature, and metal-salt-to- $\beta$ -CD ratio have less of an impact on the isolation and crystallization of  $\beta$ -CD-MOFs than do the presence and unit length of the chosen template agents overall.

Lead-based cyclodextrin metal-organic nanotubes (CD-MONTs) were created by Wei et al. [22] utilizing either  $\beta$ -CD or  $\gamma$ -CD with  $PbCl_2$  as the metal precursor. For the first time, a metal precursor that is not an alkali-earth mineral was employed. Both CD-MONTs crystallized in the chiral orthorhombic  $P2_12_12_1$  space group and monoclinic  $P2_1$  space group during the biphasic solvothermal synthesis.

There are not many studies on CD-MOF solvothermal synthesis in the literature. The vapor diffusion approach, which is considerably easier to use than the solvothermal procedure, was used to create the majority of CD-MOFs that have been synthesized so far. The vapor-diffusion process, however, cannot be scaled up. Given that it is easily scalable for mass manufacturing, which is required if these CD-MOFs are to be employed in large-scale applications, solvothermal synthesis has an advantage in this situation.

### 2.3. Microwave-Assisted Method

Due to the quick synthesis time required, microwave-assisted techniques have become more and more prevalent. The synthesis of CD-based MOFs was accomplished using this technique for the first time. The microwave-assisted approach was used in Liu et al.'s study [23] to create potassium-based  $\gamma$ -CD-MOFs. They altered the reaction duration, temperature, water-to-MeOH ( $v/v$ ) solvent ratio, and the addition of modulators to control the size of the  $\gamma$ -CD-MOF crystals. By adding PEG 20,000 as a surfactant, they were able to create micrometer-sized  $\gamma$ -CD-MOF crystals. To obtain crystals with a nanometer size, they employed MeOH as a size modulator. During the modulation process, MeOH and PEG 20,000 can be premixed to create much smaller crystals.

### 2.4. Ultrasound-Assisted Method

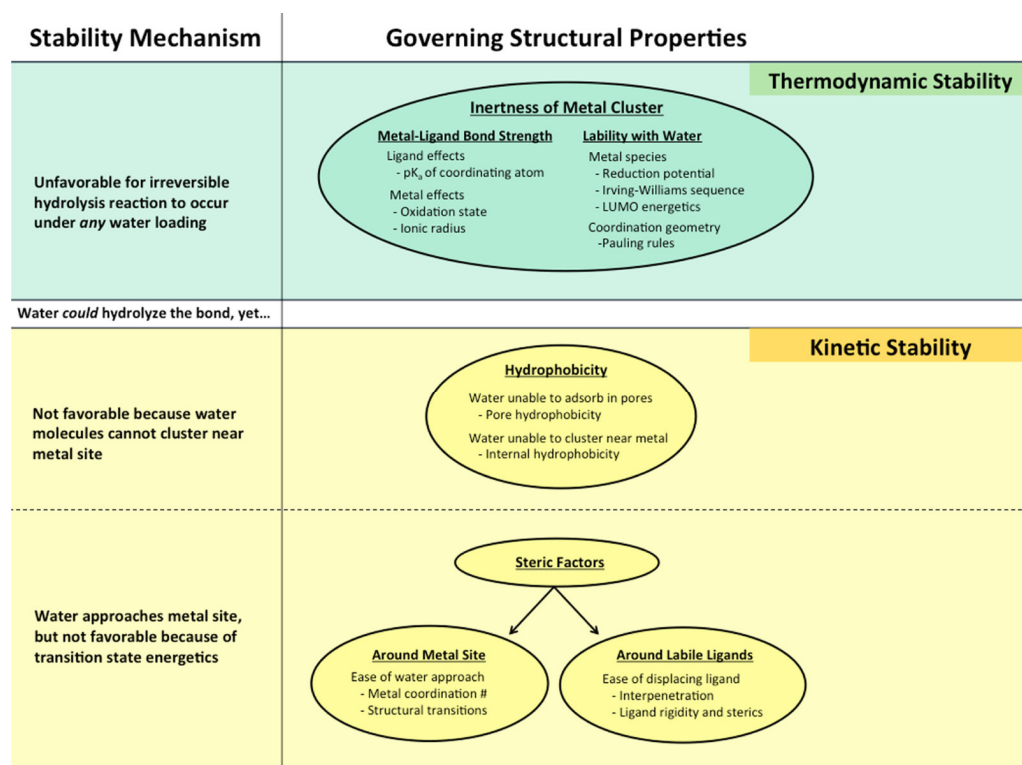
Utilizing the high energy produced by ultrasonic waves, ultrasound-assisted MOF synthesis paves the path for the rapid nucleation and development of MOF crystals. Hajra et al. [24] carried out the first demonstration of CD-MOF synthesis using ultrasound. In their experiment, cyclodextrin and sodium bicarbonate were sonicated for ten minutes before trimesic acid was added. After 24 h, the solution was sonicated once more, and DMF was used to wash the crystals. This technique was used with alpha, beta, and gamma-cyclodextrin. They discovered that the beta-CD-MOF was more stable than the alpha- and gamma-CD-MOFs and that all of the partly hydrated CD-MOFs were stable up to 200 °C under oxidative conditions.

## 3. Water Stability of Metal-Organic Frameworks

MOFs must be chemically, mechanically, and thermally stable if they are to fulfill the potential of MOFs for a variety of applications, such as but not limited to gas adsorption and separation, catalysis, sensors, drug delivery, proton conduction, and pollutant remediation.

Chemical stability refers to a substance's resistance to the effects of exposure to numerous substances in its environment, such as moisture, solvents, acids, bases, and aqueous solutions with coordinating anions. In contrast, thermal and mechanical stability refers to a MOF's capacity to maintain its structural integrity when exposed to heat, vacuum, or pressure. Unfortunately, only a few MOF families display stability, which makes it difficult to translate this technology into usable applications.

The stability of MOFs is influenced by a number of parameters, although the majority are kinetic and thermodynamic in nature. The strength of the metal–ligand coordination bond is the primary thermodynamic factor. The linker's rigidity, coordination number, surface hydrophobicity, and framework interpenetration are all kinetic factors. Figure 1 shows the stability mechanisms of MOFs and the governing structural properties for each mechanism.



**Figure 1.** Structural factors governing water stability in MOFs. Reprinted with permission from [25]. Copyright: 2014 American Chemical Society.

### 3.1. Thermodynamic Stability

Thermodynamically stable MOFs are those that do not experience structural breakdown after prolonged exposure to aqueous environments. In this context, “long-term exposure” refers to immersion in liquid water at neutral room temperature for a week or longer. It applies to a less strict time limit of only 1 day in situations where acidic/basic or high-temperature conditions are present [25].

Bio-MOF-14, MIL-101(Cr), MIL-96(Al), PCN-222(Fe), PCN-224(M), and ZIF-8 are examples of those that are known to be thermodynamically stable. Due to the inert metal cluster present in these MOFs, it is not advantageous for an irreversible hydrolysis process to take place in the presence of significant water loadings. This is because metal coordination centers in MOFs are electrophilic, whereas oxygen in water is a nucleophile. Water can coordinate with the metal cluster and cause the crystal lattice of a particular MOF to become distorted or destroyed if the metal core is not sufficiently inert. Additionally, as this bond is the weakest part of MOFs' structures, its strength can serve as a reliable predictor of the MOF's hydrolytic stability [25].

A first-order approximation of the strength of the bond between the metal and the ligand may be made using the pK<sub>a</sub> of the coordinating atom on the ligand. The characteristics of the metal species also have a significant defining influence on the strength of the metal–ligand connection, and elements such as the metal oxidation state and ionic radius must be taken into account when evaluating MOF stability. Additionally, it is important to consider the metal cluster's susceptibility to water. It was suggested that Pauling's rules and the Irving–Williams series, which are used to determine the preferred crystal structures of ionic crystals from the ratio of the cation and anion radius, could be used as guidelines to synthesize stable MOFs. The Irving–Williams series describes the relative stability of first-row transition series bivalent metal ions with a wide variety of ligands and the metals' reduction potential [25].

### 3.2. Kinetic Stability

Kinetic stability pertains to the ability of MOFs to withstand degradation upon water exposure due to the high activation energy barrier for hydrolysis reactions. Fundamentally, the hydrolysis reaction can only take place if two specific things happen: (1) water molecules must approach the metal close enough to allow interaction between the electron orbitals on the electrophilic metal and nucleophilic water, and (2) this interaction's energy must be sufficient to overcome the reaction's activation energy barrier. The product and reactant states, the particular reaction route, and the transition stages involved during hydrolysis all affect this energy barrier. Therefore, even if a particular MOF lacks thermodynamic properties that render its metal center inert, kinetic properties like hydrophobicity and the presence of steric hindrance can still raise the activation energy for hydrolysis to make the structure stable in humid environments [25].

One method to accomplish kinetic control of hydrolysis is to include hydrophobic functional groups, such as alkyl groups, or polar groups, such as fluorine, in the MOF structure. By permitting the polar groups to draw the water away from the metal center, the pore may be made hydrophobic, or the water molecules may be prevented from forming clusters around the metal centers. Utilizing metals with high coordination numbers can also prevent water molecules from forming clusters around the metal centers by creating a process known as crowding. Furthermore, because there are more bound ligands that may still sustain the structure in the event of moderate hydrolysis, a high coordination number enables framework stability. Another technique is catenation, which involves interconnecting two separate frameworks in order to prevent the labile ligand from being displaced by locking it inside the framework. This is the same as functionalizing the ligand with large groups. The MOFs MIL-100(Hf), MIL-100(Zr), DUT-67(Zr), CAU-10, MIL-125-NH<sub>2</sub>(Ti), MIL-127, MIL-53(Al), MIL-53(Cr), PCN-225(M), and the well-known UiO series of MOFs are among those that exhibit great kinetic stability [25].

### 4. Degradation Mechanism of MOFs in Water

The breakdown of the metal–ligand linkages and the emergence of molecules that are more stable than the original MOFs are generally accepted as the mechanisms by which MOFs degrade [26]. When MOFs are destroyed, coordinating competition between the organic linker and coordinating species like water molecules or hydroxide ions takes place at the metal center. In the case of metal species, the less labile a metal cation is during chemical deterioration at a given charge, the smaller it is in the framework. In contrast with their lesser-charged cousins, higher metal charges are less reactive and labile. The characteristics of the metal cation have a significant impact on the lability of a coordination bond. However, the length and rigidity of the organic linkers also have an impact on the stability of the resultant MOF. Comparatively speaking, MOFs made up of shorter linkers are more stable than those with longer linkers. Furthermore, MOFs produced from linkers with a high degree of rotational mobility are more likely to degrade in aqueous conditions compared with structures formed from stiff organic linkers.

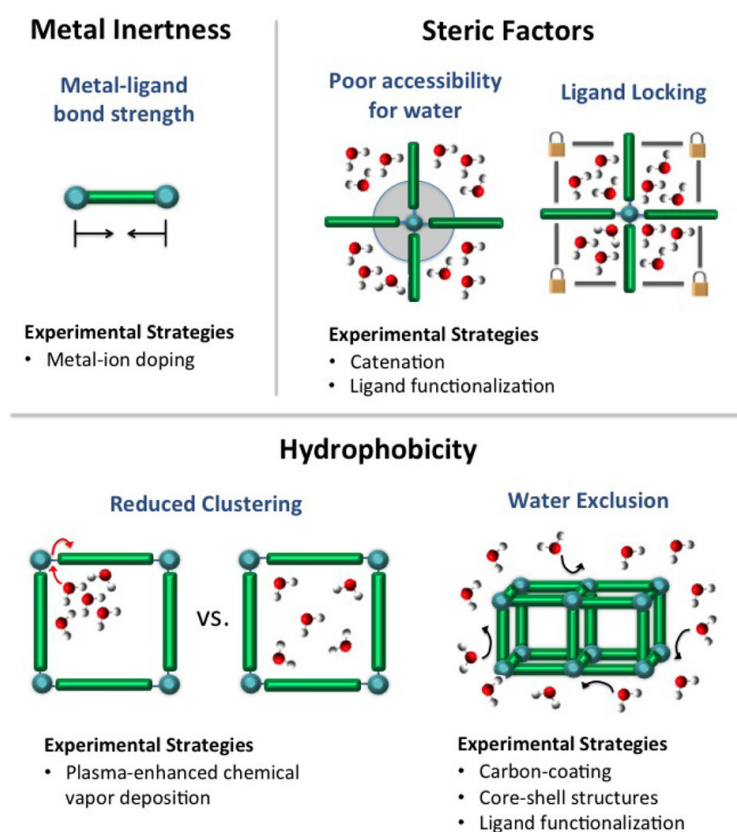


Additionally, structural deformation and pore contraction might result from an organic linker's flexibility [27].

When there is water present, MOFs normally degrade in two stages. Water molecules are first introduced into the metal–linker coordination bonds of the MOF in a process known as ligand displacement. The second stage occurs when the coordinated water molecule is deprotonated during the hydrolysis process. This completes the breakdown of the metal–linker connection and leaves a hydroxide ion attached to the metal center to preserve the charge balance. The ligand displacement process in the case of carboxylate-based MOFs causes a change from three-center, two-electron bridging carboxylates to a two-center, two-electron coordination of one atom of the carboxylate group to one metal atom. Once the entire MOF cluster has undergone hydrolysis, a MOF with the  $ML_2$  formula changes into its hydroxide form,  $M(OH)_2$ , as a consequence [27].

### 5. Current Strategies to Protect CD-MOFs from Water

The intrinsic structures of MOFs, such as the basicity, configuration, and hydrophobicity of ligands, among others, determine the chemical stability of MOFs (Figure 2). These intrinsic structures include the charge density of metal ions, connection numbers of metal ions/clusters, and basicity. By modifying these factors, we can design, theoretically speaking, stable MOFs for various applications. In general, there are two main approaches that can improve the chemical stability of MOFs. First, novel MOFs can be synthesized de novo with innate structural stability using an appropriate combination of metals and linkers. This results in a strong metal–ligand coordination bond that translates into a more stable MOF. Second, we can take advantage of the kinetics of water hydrolysis by introducing steric hindrance to water accessibility or the use of strategies to impart hydrophobicity in MOFs.



**Figure 2.** Mechanisms for improving the water stability of existing MOFs. Reprinted with permission from [25]. Copyright: 2014 American Chemical Society.

There are not many studies on improving CD-MOF stability in the literature. By crosslinking CD with crosslinkers such as diphenyl carbonate or ethylene glycol diglycidyl, it has been possible to create water-insoluble  $\gamma$ -CD-K-MOFs [9,28]. The synthesis and post-processing of this technology are difficult and time-consuming, but it is effective. Fullerene ( $C_{60}$ ) was encapsulated in  $\gamma$ -CD-K-MOF matrices in a different investigation. The outcome was that the exposed  $C_{60}$  surface gave the  $\gamma$ -CD-K-MOF increased hydrophobicity, which increased its water stability [29]. This approach, meanwhile, could lessen the ability of the CD-K-MOF to absorb carbon dioxide. A nearly identical method was utilized by Singh et al. [30], who grafted a layer of hydrophobic cholesterol onto the exterior of a  $\gamma$ -CD-K-MOF. As a result, the functionalized MOF had more water resistance than the unaltered MOF. Once more, such a method was time-consuming (lasting 24 h at 45 °C) and reduced the amount of surface area accessible for carbon dioxide loading. The treatment of a  $\gamma$ -CD-K-MOF in a hydrogen sulfide ( $H_2S$ ) atmosphere led to increased water stability.  $H_2S$  stabilized the  $\gamma$ -CD-K-MOF by coordinating with potassium metal sites and acting as new basins of attraction for the incoming water molecules, depleting the water content at the metal centers and improving its moisture resistance in contrast with other methods used to increase MOFs' moisture resistance [31].

A powerful method for adding functional groups to cyclodextrin ligands or guest molecules inside a framework to boost its water stability is post-synthesis modification (PSM). PSM may be performed in a number of ways, such as by adding chemicals that can react with the functional groups on the ligands or by adding metal ions that can more effectively coordinate with the altered ligands. It is crucial to remember that every study on stable CD-MOFs has only found ways to increase their water stability post-synthetic alterations. These methods require a lot of time, and because there is less surface area, they can lead to poorer absorption capabilities. To the best of our knowledge, no research has been conducted on synthesizing stable CD-MOFs based on the de novo strategies outlined in the previous section. Therefore, it is still urgently necessary to create stable CD-MOFs from scratch rather than via post-synthetic alteration.

It is clear that there are two methods via which we can make CD-MOFs stable: (a) using the right metals and linkers, and (b) using mixed-metal MOFs. The synthesis of more robust and stable MOFs can be accomplished by strengthening the M-O bonds using the appropriate ratio of metals and linkers. Strong coordination bonds offer stronger structural integrity and greater resistance to bond breaking owing to chemical or thermal attacks and shield the resultant MOFs from hydrolysis [26,32–37]. However, as of yet, no such technique has been discovered.

## 6. Future Research

Due to difficulties controlling stoichiometry, crystal form, and crystal size, the synthesis of CD-MOFs is complicated. Multiple hydroxyl groups found in cyclodextrins can coordinate with metal ions to form different structures with a range of characteristics. Careful regulation of the metal-to-ligand ratio, pH, temperature, and reaction time is necessary for the synthesis of CD-MOFs. The metal ions utilized and their coordination geometry can also affect the water stability of the CD-MOFs that are formed. The features of CD-MOFs, such as water stability, surface area, and pore size distribution, can be influenced by the crystal morphology of these materials. The use of templates, surfactants, or other additives during synthesis are a few methods that may be used to alter the crystal structure of CD-MOFs. By using CTAB, for instance, CD-MOFs with a consistent particle size and shape may be created.

Another critical problem in the synthesis of CD-MOFs is water stability. For practical applications, particularly in the biomedical fields where water stability is essential for long-term stability and safety, CD-MOFs with high water stability are sought. The coordination geometry of the metal ions and the functional groups on the cyclodextrin ligands govern the water stability of CD-MOFs. Better coordination with metal ions, for instance, might

be achieved by adjusting the functional groups on the cyclodextrin ligands, leading to the creation of CD-MOFs with improved water stability.

Before CD-MOFs may be employed in real applications, two significant obstacles must be removed from their synthesis and water stability. Future work should focus on developing unique synthetic methods that can produce CD-MOFs with certain features, such as high water stability and controlled crystal structure. Furthermore, the water stability and usefulness of CD-MOFs can be enhanced via the creation of novel post-synthetic modification techniques.

The development of innovative CD-MOF applications is a significant field for future research. Although CD-MOFs have shown considerable promise in a number of applications, further research is necessary to comprehend their strengths and weaknesses completely. Furthermore, the development of innovative techniques for the large-scale synthesis of CD-MOFs may make it possible to use them for commercial purposes.

In conclusion, CD-MOFs are a kind of MOF that have shown significant promise in a range of applications because of their distinctive characteristics, such as their enormous surface area, changeable pore size, and permanent porosity. Before CD-MOFs may be applied in reality, two significant obstacles must be removed: their synthesis and water stability. The development of innovative synthetic processes, post-synthetic modification methods, and the investigation of new applications for these materials should be the main foci of future study.

**Author Contributions:** Conceptualization, E.C.R.L.; writing—original draft preparation, E.C.R.L.; writing—review and editing, E.C.R.L. and J.V.D.P.; supervision, J.V.D.P.; project administration, J.V.D.P. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

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