**Green Metal-Organic Frameworks (GMOFs) Synthesized in Water: Synthesis, Characterization, and Applications**

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**Abstract:**

 This chapter focuses on the synthesis, characterization, and applications of Green Metal-Organic Frameworks (GMOFs) synthesized in water. The increasing demand for environmentally friendly and sustainable materials has spurred the development of GMOFs, which minimize the use of organic solvents and reduce the environmental impact associated with traditional Metal-Organic Framework (MOF) synthesis. The chapter provides an overview of the synthesis strategies for GMOFs in water, including ligand design, direct synthesis, template or structure-directing agents, coordination modulation, and the incorporation of green catalysts. Additionally, the characterization techniques employed to assess the structure, morphology, and properties of GMOFs are discussed. Finally, the chapter explores the diverse range of applications of GMOFs in areas such as gas storage, catalysis, drug delivery, and environmental remediation, highlighting their potential as sustainable materials for a greener future.

**Keywords**: Green Metal-Organic Frameworks (GMOFs), MOFs, water-based synthesis, ligand design, characterization techniques, gas storage, catalysis, drug delivery, environmental remediation.

1. **Introduction**

 Metal-organic frameworks (MOFs) are materials consisting of metal ions or clusters coordinated with organic ligands. While most MOFs are based on metal ions such as zinc, copper, or iron, green MOFs specifically refer to those that exhibit environmentally friendly characteristics, such as using sustainable and non-toxic components. Here are a few examples of green metal-organic frameworks [1] shown in (Figure-1).

 

**Figure-1. Green metal-organic frameworks**

UiO-66(Zr): UiO-66 is a well-known MOF made of zirconium (Zr) metal nodes connected by organic dicarboxylate ligands (Figure-2). The green aspect of UiO-66(Zr) lies in its stability and robustness, which allows for diverse applications such as gas storage, catalysis, and drug delivery [2].



**Figure-2. Crystal structure of UiO-66: (a) Six-center octahedral zirconium oxide unit. (b) FCC structural unit of UiO-66 (blue atom: Zr, red atom: O, white atom: C, and H atoms are omitted for clarity) Wang et al., (2015).**

 MIL-101(Cr): MIL-101 is another popular MOF constructed with chromium (Cr) nodes and organic linkers. It exhibits excellent chemical stability and high porosity. Green aspects of MIL-101(Cr) include its capability for carbon capture and storage and its potential for sustainable adsorption and separation processes [3].

ZIF-8: Zeolitic imidazolate framework-8 (ZIF-8) is a MOF comprised of zinc (Zn) metal centres coordinated with imidazole-based organic ligands (Figure-3). ZIF-8 is known for its exceptional stability, which makes it suitable for various applications, such as gas storage, sensing, and catalysis. Its green characteristics include its non-toxic components and the potential for recycling [4].

**Figure-3. Preparation of ZIF-8 using Zn2+ ions and 2-methylimidazole**

 MOF-177: MOF-177 is a MOF made from cerium (Ce) metal nodes and carboxylate-based ligands. It possesses a large surface area and high thermal stability. MOF-177 has demonstrated potential in applications like hydrogen storage, selective adsorption, and catalysis. Its green attributes include the utilization of cerium, which is abundant and less toxic than other metals [5].

 NOTT-300: NOTT-300 is a MOF composed of zinc (Zn) nodes and tetrakis (4-carboxyphenyl) porphyrin (TCPP) ligands. It exhibits high porosity and has shown promise in applications like gas storage and separation, sensing, and catalysis. Its green features include the use of zinc, a relatively abundant and environmentally friendly metal [6]

 These are just a few examples of green metal-organic frameworks; many other MOFs possess eco-friendly characteristics. The field of MOF research continues to explore new materials with improved sustainability and reduced environmental impact [7]

**1.1 Metal-Organic Frameworks (MOFs): Overview and Challenges**

 Metal-Organic Frameworks (MOFs) are a class of porous materials composed of metal ions or clusters coordinated with organic ligands [8]. They possess a highly ordered three-dimensional structure, with metal nodes or clusters interconnected by the organic ligands. This unique architecture results in MOFs having large surface areas and a well-defined pore structure, making them attractive for various applications.

MOFs offer several advantages that make them highly desirable in various fields [8]:

**1.1.1 High Porosity**: MOFs exhibit exceptional porosity, with surface areas ranging from hundreds to thousands of square meters per gram [9]. This high porosity provides ample space for gas adsorption, storage, and separation and for hosting various guest molecules.

**1.1.2 Tailorable Properties**: The choice of metal ions and organic ligands allows for precisely tuning MOF properties [10]. By selecting different components, researchers can control parameters such as pore size, pore volume, surface chemistry, and functionality, enabling the design of MOFs with specific characteristics for targeted applications.

**1.1.3 Diverse Applications**: MOFs have applications in various fields, including gas storage and separation, catalysis, drug delivery, sensing, energy storage, and environmental remediation [11]. Their tunable properties and high surface areas make them versatile materials for addressing different challenges across various industries.

However, the development and utilization of MOFs are not without challenges:

**1.1.4 Stability:** Many MOFs exhibit limited stability, especially in the presence of moisture, which can lead to the degradation of their structure and loss of porosity [8]. Enhancing the stability of MOFs under various conditions, including humid environments, is a significant challenge in their practical application.

**1.1.5 Scalability**: While MOFs can be synthesized in the laboratory on a small scale, achieving large-scale synthesis remains challenging [8]. Scaling up the synthesis while maintaining MOFs' desired properties and porosity is essential for their commercial viability and widespread use.

**1.1.6 Cost**: Some MOFs incorporate expensive metal ions or ligands, making their production costly [8]. Finding cost-effective alternatives or developing efficient synthetic methods is crucial for the practical implementation of MOFs in various industries.

**1.1.7 Selectivity and Adsorption Kinetics**: High selectivity for specific gases or molecules and fast adsorption kinetics is essential for many applications, such as gas storage, separation, and catalysis [8]. Designing MOFs with the desired selectivity and kinetics remains a challenge that requires further exploration and understanding.

**1.1.8 Characterization**: The characterization of MOFs presents challenges due to their complex structures and porosities. Advanced techniques such as X-ray diffraction, spectroscopy, electron microscopy, and gas sorption analysis are employed to study their structures, pore sizes, and properties.

**1.1.9 Integration and Practical Applications**: Incorporating MOFs into practical devices and systems can be challenging. Issues such as stability under operating conditions, compatibility with other materials, and the development of scalable fabrication methods must be addressed for successful integration into real-world applications.

Addressing these challenges requires collaborative efforts between researchers from different disciplines, including chemistry, materials science, engineering, and computational modelling. Advancements in ligand design, synthesis methods, stability enhancement strategies, characterization techniques, and scalable production methods are critical areas of focus to overcome these challenges and unlock the full potential of MOFs.

 In conclusion, MOFs are highly promising materials with unique properties and versatile applications. However, challenges related to stability, scalability, cost, selectivity, characterization, and integration into practical systems must be addressed to exploit their potential fully. By addressing these challenges, researchers canTop of Form

**1.2 Need for Green MOFs: Advantages and Importance**

 The need for green Metal-Organic Frameworks (MOFs) arises from the increasing global focus on sustainable and environmentally friendly materials. Green MOFs, also known as Green Metal-Organic Frameworks (GMOFs), are designed to minimize environmental impact throughout their lifecycle, from synthesis to application. These materials offer several advantages and hold significant importance in addressing sustainability challenges.

Advantages of Green MOFs:

**1.2.1 Reduced Environmental Footprint**: Green MOFs are synthesized using environmentally benign processes and techniques. Using water as a solvent in their synthesis, as opposed to organic solvents, minimizes the release of hazardous substances and reduces the overall environmental footprint associated with traditional MOF synthesis.

**1.2.2 Sustainable Synthesis Routes:** Green MOFs employ synthesis strategies that minimize waste generation, energy consumption, and toxic chemicals. By employing green chemistry principles, such as atom economy, renewable feedstocks, and catalytic processes, the synthesis of GMOFs aims to reduce environmental impact and promote sustainable manufacturing practices.

**1.2.3 Renewable and Biodegradable Ligands**: Green MOFs often incorporate ligands derived from renewable resources, such as biomass or waste materials. These ligands offer advantages over traditional synthetic ligands, as they can be obtained from sustainable sources and exhibit biodegradability, further contributing to the environmentally friendly nature of GMOFs.

**1.2.4 Improved Energy Efficiency:** The unique properties of MOFs, including high surface areas and tunable porosities, make them attractive for energy-related applications. Green MOFs can be designed to enhance energy efficiency by enabling processes such as gas storage, separation, and catalysis, which can contribute to sustainable energy generation and conservation.

**1.2.5 Reduced Carbon Footprint**: Green MOFs can contribute to reducing carbon emissions and mitigating climate change. They can be utilized in applications such as carbon capture and storage, where MOFs selectively adsorb and capture greenhouse gases, aiding their sequestration and preventing their release into the atmosphere.

Importance of Green MOFs:

**1.2.6 Environmental Sustainability**: Green MOFs play a vital role in addressing environmental challenges, including reducing hazardous waste, energy consumption, and carbon emissions. By adopting sustainable synthesis routes and incorporating renewable materials, GMOFs contribute to developing environmentally sustainable materials and technologies.

**1.2.7 Circular Economy:** Green MOFs align with the principles of the circular economy by utilizing renewable resources and promoting the reuse and recycling of materials. Incorporating biodegradable ligands in GMOFs supports the transition towards a more circular approach, where materials can be recovered, reused, or safely returned to nature at the end of their lifespan.

**1.2.8 Health and Safety**: Using water-based synthesis routes and avoiding toxic solvents in GMOF production promote the health and safety of researchers and workers involved in MOF synthesis. Green MOFs reduce occupational health risks and contribute to creating a safer working environment.

**1.2.9 Public Perception and Corporate Social Responsibility**: Green MOFs align with the growing demand for sustainable and socially responsible practices. Companies and institutions that adopt and promote the use of green materials, such as GMOFs, enhance their reputation, meet regulatory requirements, and appeal to environmentally conscious consumers.

 Developing and utilising Green MOFs are crucial for advancing sustainable technologies, reducing environmental impact, and promoting a greener future. Green MOFs contribute to the transition towards a more environmentally friendly and resource-efficient society by addressing the need for sustainable materials and manufacturing processes.

**1.3 Overview of GMOFs Synthesized in Water: Motivation and Scope of the Chapter**

 The synthesis of Metal-Organic Frameworks (MOFs) in water-based systems, known as Green Metal-Organic Frameworks (GMOFs), has emerged as a significant research direction driven by the increasing demand for sustainable and environmentally friendly materials [12]. The use of water as a solvent in GMOF synthesis offers numerous advantages, such as minimizing the use of organic solvents, reducing waste generation, and improving the environmental compatibility of the process [13]. This chapter provides an overview of GMOFs synthesized in water, focusing on their synthesis strategies, characterization techniques, and diverse applications (Figure- 4).

**Figure- 4 Water-Based Synthesis of a Stable Iron-BasedMetal–Organic Framework for Capturing Toxic Gases.**

 The motivation behind synthesizing GMOFs in water lies in the urgent need to develop environmentally friendly alternatives to traditional MOF synthesis methods. The excessive use of organic solvents in conventional MOF synthesis poses environmental risks and hinders the scalability and practical implementation of MOFs in real-world applications. By utilizing water as a solvent, GMOF synthesis aims to mitigate these challenges and pave the way for sustainable and greener MOF materials.

The scope of this chapter encompasses several key aspects of GMOFs synthesized in water:

**1.3.1 Synthesis Strategies:** The chapter explores various synthesis strategies employed for GMOFs in water-based systems. This includes ligand design approaches that enable the use of water-soluble ligands, direct synthesis methods that directly assemble MOFs in water, the role of template or structure-directing agents, coordination modulation strategies, and the incorporation of green catalysts in water-based GMOF synthesis.

**1.3.2 Characterization Techniques**: The chapter discusses the characterization techniques used to evaluate the structure, morphology, and properties of GMOFs synthesized in water. This includes techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal analysis (TGA, DSC), spectroscopic techniques (FTIR, NMR, Raman), and gas sorption analysis.

**1.3.3 Applications of GMOFs**: The chapter explores the diverse range of applications of GMOFs synthesized in water. This includes their potential utilization in gas storage and separation, catalysis and green chemistry, drug delivery and biomedical applications, environmental remediation and water purification, energy storage and conversion, and other emerging areas.

 By providing an overview of the synthesis strategies, characterization techniques, and applications of GMOFs synthesized in water, this chapter aims to highlight the potential and significance of these materials in promoting sustainable and environmentally friendly MOF technologies. It emphasizes the importance of water-based synthesis as a key approach to address the challenges associated with traditional MOF synthesis, opening avenues for the development of greener and more practical MOF materials.

 In conclusion, the synthesis of GMOFs in water represents a vital research direction for developing sustainable MOF materials. This chapter serves as a comprehensive resource, covering synthesis strategies, characterization techniques, and applications of GMOFs synthesized in water. By showcasing the potential of GMOFs in various fields, it aims to inspire further research and advancements in the synthesis and utilization of environmentally friendly MOF materials.

**2. Synthesis of GMOFs in Water**

 The synthesis of Metal-Organic Frameworks (MOFs) in water-based systems, commonly referred to as Green Metal-Organic Frameworks (GMOFs), has gained significant attention in recent years. GMOFs represent a sustainable approach to the production of MOFs by utilizing water as a solvent instead of traditional organic solvents, which often pose environmental and health hazards. The use of water as a medium for GMOF synthesis aligns with the growing global emphasis on green chemistry and sustainable manufacturing practices.

 The synthesis of MOFs typically involves the coordination of metal ions or clusters with organic ligands to form a porous crystalline framework. This process offers a high degree of tunability in terms of structure, porosity, and functionality. However, the use of organic solvents in MOF synthesis raises concerns about waste generation, solvent disposal, and the environmental impact of these processes. By employing water as a green alternative solvent, GMOF synthesis aims to overcome these challenges and promote the development of environmentally friendly MOF materials.

 The motivation behind the synthesis of GMOFs in water is rooted in the need for sustainable and eco-friendly materials. The use of water as a solvent offers several advantages, including reduced environmental impact, improved safety for researchers, and the potential for scalability and industrial applicability. Moreover, the integration of water as a solvent aligns with the principles of green chemistry, which emphasize the use of renewable resources, waste reduction, and the development of environmentally benign processes.

 This chapter aims to provide an overview of the synthesis of GMOFs in water, focusing on the various strategies and methodologies employed in this field. It explores the advantages and challenges associated with water-based synthesis and highlights the importance of green MOF materials in addressing sustainability challenges. Additionally, the chapter discusses the characterization techniques used to evaluate the structure and properties of GMOFs synthesized in water and provides insights into their potential applications.

 The scope of this chapter encompasses the synthesis strategies, including ligand design approaches, direct synthesis methods, and coordination modulation techniques specific to water-based GMOF synthesis. It also covers the characterization techniques used to assess the structure, morphology, and properties of GMOFs. Furthermore, the chapter explores the diverse applications of GMOFs synthesized in water, including gas storage and separation, catalysis, drug delivery, and environmental remediation.

 Overall, the synthesis of GMOFs in water represents a promising avenue for the development of sustainable MOF materials. By utilizing water as a solvent, researchers aim to address environmental concerns, enhance safety, and enable the large-scale production of MOFs. This chapter provides a comprehensive overview of the synthesis, characterization, and applications of GMOFs in water, highlighting their significance in the pursuit of sustainable and environmentally friendly materials.

**2.1 Ligand Design for Water-Compatible GMOFs**

 The design of water-compatible ligands plays a crucial role in the synthesis of Green Metal-Organic Frameworks (GMOFs) in water-based systems. The development of ligands that are soluble in water or exhibit enhanced stability in aqueous environments is essential for successful water-based GMOF synthesis [14]. This section explores various strategies and considerations in ligand design for water-compatible GMOFs.

**2.1.1 Hydrophilic Functional Groups:** One approach to enhance water compatibility is the incorporation of hydrophilic functional groups into ligand structures. Hydroxyl (-OH), carboxyl (-COOH), amino (-NH2), and sulfonate (-SO3H) groups are examples of hydrophilic moieties that promote solubility and stability in water. These groups facilitate water coordination and improve the dispersion of ligands in aqueous media, enabling successful GMOF synthesis.

**2.1.2 Ionic Ligands:** Another strategy is the design of ionic ligands that possess charged groups. Ionic ligands can form ion-pair complexes with metal ions, leading to enhanced solubility and stability in water. The use of charged ligands, such as imidazolium, pyridinium, or quaternary ammonium salts, allows for efficient GMOF synthesis in water and offers opportunities for tailored properties through the choice of counterions.

**2.1.3 Zwitterionic Ligands**: Zwitterionic ligands have both positively and negatively charged functional groups within the same molecule. These ligands exhibit high water solubility due to the balanced charge distribution and can form stable complexes with metal ions in water-based systems. Zwitterionic ligands, such as amino acids or phosphonate-based ligands, offer an effective strategy for water-compatible GMOF synthesis.

**2.1.4 Amphiphilic Ligands**: Amphiphilic ligands possess both hydrophilic and hydrophobic regions within their structures. The hydrophilic portion promotes water solubility, while the hydrophobic region facilitates interactions with metal ions and the formation of the MOF structure. Amphiphilic ligands strike a balance between water compatibility and metal coordination, enabling successful GMOF synthesis in water.

**2.1.5 Bifunctional Ligands**: Bifunctional ligands contain two distinct functional groups that serve different purposes in GMOF synthesis. One group promotes water compatibility, while the other participates in metal coordination. For example, ligands with hydrophilic groups and coordinating groups (e.g., carboxylate or amine) enable successful synthesis of GMOFs in water while facilitating metal-ligand coordination.

**2.1.6 Biomolecule-Derived Ligands**: Biomolecule-derived ligands, such as amino acids, peptides, or nucleotides, offer an intriguing approach for water-compatible GMOFs. These ligands are inherently water-soluble and can form stable complexes with metal ions. By utilizing the unique properties of biomolecules, researchers can achieve both water compatibility and functionality in GMOF synthesis.

**2.1.7 Covalent Organic Frameworks (COFs**): COFs, a subclass of MOFs, are composed of organic ligands connected through covalent bonds. The design of water-compatible COFs involves selecting ligands that possess hydrophilic groups and can form stable covalent bonds under aqueous conditions. COFs offer excellent potential for water-compatible GMOFs due to their covalent nature and high stability in water.

 In ligand design for water-compatible GMOFs, several factors should be considered, including the solubility of ligands in water, coordination ability with metal ions, stability under aqueous conditions, and compatibility with the desired MOF structure. Computational modeling and experimental studies play essential roles in guiding ligand design by predicting ligand-metal coordination and assessing ligand-water interactions.

 In conclusion, ligand design is a crucial aspect of synthesizing water-compatible GMOFs. By incorporating hydrophilic functional groups, utilizing ionic or zwitterionic ligands, designing amphiphilic or bifunctional ligands, or exploring biomolecule-derived ligands, researchers can achieve successful GMOF synthesis in water. The choice of ligand design strategy depends on the specific requirements of the target GMOF and its intended applications. Through careful ligand design, water-compatible GMOFs with tailored properties can be realized, paving the way for sustainable and environmentally friendly MOF materials.

**2.2 Direct Synthesis Approaches**

 Direct synthesis approaches for the synthesis of Green Metal-Organic Frameworks (GMOFs) in water offer a straightforward and efficient method to obtain water-compatible MOFs. These approaches eliminate the need for post-synthetic modification or ligand exchange steps, making the process more environmentally friendly and economically viable [15]. This section discusses some direct synthesis strategies employed in water-based GMOF synthesis.

**2.2.1 One-Pot Synthesis**: One-pot synthesis involves the simultaneous coordination of metal ions or clusters with ligands in a single reaction vessel. In the context of water-based GMOF synthesis, this approach allows for the direct formation of MOFs in water without the requirement for additional steps. One-pot synthesis is typically achieved by carefully selecting water-compatible ligands and coordinating them with metal ions under suitable reaction conditions, leading to the formation of GMOFs in water.

**2.2.2 Solvothermal and Hydrothermal Synthesis**: Solvothermal and hydrothermal methods involve the use of high-temperature and high-pressure conditions to facilitate the synthesis of MOFs in water. These methods promote rapid ligand-metal coordination and MOF formation by providing an environment conducive to the dissolution of reactants and the growth of MOF crystals. Solvothermal and hydrothermal synthesis can be performed in autoclaves or reaction vessels, allowing for the direct synthesis of GMOFs in water.

**2.2.3 Microwave-Assisted Synthesis**: Microwave irradiation has emerged as a promising technique for accelerating the synthesis of MOFs, including GMOFs, in water. Microwave-assisted synthesis provides rapid and efficient heating, promoting ligand-metal coordination and MOF formation. The use of microwaves can significantly reduce reaction times and enhance the yield and purity of GMOFs synthesized in water.

**2.2.4 Ultrasonic-Assisted Synthesis**: Ultrasonic irradiation, or sonication, has been employed as a means to facilitate the direct synthesis of GMOFs in water. Ultrasonic energy promotes the dispersion and mixing of reactants, enhances mass transfer, and increases the reactivity of the system, leading to the rapid formation of MOFs. Ultrasonic-assisted synthesis offers advantages such as shorter reaction times, improved product uniformity, and the ability to operate at lower temperatures.

**2.2.5 Mechanochemical Synthesis:** Mechanochemical synthesis involves the use of mechanical force, such as grinding or milling, to facilitate MOF formation. In the context of water-based GMOF synthesis, mechanochemical methods offer a direct and solvent-free approach to obtain water-compatible MOFs. By grinding the reactants in the presence of water, MOFs can be formed through the mechanical activation of the ligand-metal coordination process.

**2.2.6 Ionic Liquid-Assisted Synthesis**: Ionic liquids are molten salts composed entirely of ions and have been utilized as solvents or additives in GMOF synthesis. Ionic liquid-assisted synthesis in water involves the incorporation of water-miscible ionic liquids, which can enhance the solubility of ligands and metal precursors, promote ligand-metal coordination, and facilitate MOF formation in water.

 Direct synthesis approaches offer several advantages in the synthesis of GMOFs in water. They eliminate the need for additional purification steps, reduce waste generation, and streamline the synthesis process. These methods allow for the direct formation of MOFs in water, enabling the production of water-compatible GMOFs with enhanced sustainability and practicality.

 In conclusion, direct synthesis approaches for GMOFs in water provide efficient and environmentally friendly methods for obtaining water-compatible MOFs. One-pot synthesis, solvothermal/hydrothermal synthesis, microwave-assisted synthesis, ultrasonic-assisted synthesis, mechanochemical synthesis, and ionic liquid-assisted synthesis are some of the strategies employed in this regard. These methods offer advantages such as simplicity, reduced reaction times, and enhanced control over MOF synthesis. By employing direct synthesis approaches, researchers can contribute to the development of sustainable and water-compatible MOF materials.

**2.3 Template or Structure-Directing Agents in Water-Based Synthesis**

 In the synthesis of Green Metal-Organic Frameworks (GMOFs) in water, template or structure-directing agents play a crucial role in guiding the formation of desired MOF structures. These agents provide a template or framework around which the metal ions and ligands can assemble, leading to the formation of well-defined and controlled GMOFs [16]. This section explores the use of template or structure-directing agents in water-based GMOF synthesis.

**2.3.1 Surfactants**: Surfactants are widely employed as template agents in water-based GMOF synthesis. Surfactants consist of hydrophilic and hydrophobic moieties, allowing them to self-assemble into organized structures, such as micelles or vesicles, in aqueous solutions. These organized structures can serve as templates for MOF growth, influencing the size, shape, and crystallographic orientation of the resulting GMOFs.

**2.3.2 Biomolecules:** Biomolecules, such as proteins, peptides, DNA, or polysaccharides, have been utilized as structure-directing agents in water-based GMOF synthesis. These biomolecules possess unique structural motifs and functional groups that can interact with metal ions and ligands, guiding the formation of specific MOF structures. Biomolecules offer advantages such as biocompatibility, water solubility, and the potential for incorporating bioactive components into GMOFs.

**2.3.3 Coordination Modulators**: Coordination modulators are small molecules that can influence the coordination environment around metal ions, affecting the formation of MOF structures. In water-based GMOF synthesis, coordination modulators can promote or inhibit specific metal-ligand interactions, leading to the desired MOF architectures. By adjusting the concentration or type of coordination modulator, researchers can control the structure and properties of GMOFs synthesized in water.

**2.3.4 Inorganic Salts**: Inorganic salts, such as alkali metal salts or ammonium salts, are frequently employed as structure-directing agents in water-based GMOF synthesis. These salts can influence the solubility, nucleation, and crystal growth of MOFs by altering the ionic strength or pH of the reaction medium. The presence of inorganic salts can affect the formation kinetics and crystal morphology of GMOFs, allowing for control over their structure and properties.

**2.3.5 Organic Additives**: Organic additives, such as organic acids, amines, or alcohols, can act as structure-directing agents in water-based GMOF synthesis. These additives can interact with metal ions and ligands, influencing their coordination behavior and promoting the formation of specific MOF structures. Organic additives can also provide steric hindrance or act as hydrogen bond donors/acceptors, influencing the packing and connectivity of MOF components.

 The choice of template or structure-directing agent depends on the desired GMOF structure, the characteristics of the metal ions and ligands used, and the reaction conditions. The proper selection and optimization of these agents are crucial to achieving the desired MOF morphology, porosity, and functionality in water-based synthesis.

 In conclusion, template or structure-directing agents play a vital role in guiding the synthesis of GMOFs in water. Surfactants, biomolecules, coordination modulators, inorganic salts, and organic additives offer diverse strategies for controlling the structure and properties of water-based GMOFs. By incorporating these agents, researchers can achieve precise control over the synthesis process, leading to the development of functional and tailored GMOF materials.

**2.4 Coordination Modulation Strategies for Water-Soluble MOFs**

 The development of water-soluble Metal-Organic Frameworks (MOFs) has gained significant attention due to their potential applications in various fields, including catalysis, drug delivery, and sensing. Coordination modulation strategies play a key role in achieving water solubility while maintaining the structural integrity and functionality of MOFs. This section explores some coordination modulation strategies employed for the synthesis of water-soluble MOFs.

**2.4.1 Ligand Functionalization**: One approach to enhance water solubility is the functionalization of ligands with hydrophilic groups. Hydroxyl (-OH), carboxylate (-COO-), amino (-NH2), or sulfonate (-SO3-) functional groups can be incorporated into ligand structures to improve their water solubility. These hydrophilic groups facilitate water coordination and promote the dispersion of MOFs in aqueous solutions, resulting in water-soluble MOFs.

**2.4.2 pH-Responsive Ligands**: pH-responsive ligands offer a unique strategy for achieving water solubility in MOFs. These ligands possess functional groups that can undergo protonation or deprotonation in response to changes in pH. At low pH, the ligands are protonated, enhancing their water solubility. As the pH increases, the ligands deprotonate, leading to the formation of insoluble MOFs. This pH-dependent solubility behavior enables the controlled dissolution and precipitation of MOFs in water.

**2.4.3 Hydrolytically Stable Linkers**: Hydrolytically stable linkers are crucial for the synthesis of water-soluble MOFs. These linkers are resistant to degradation in aqueous environments, ensuring the structural integrity of the MOFs. Hydrolytically stable linkers can be designed by incorporating robust functional groups, such as fluorine atoms or bulky substituents, into the linker structure. The presence of these groups hinders water penetration and protects the MOF structure from hydrolytic degradation.

**2.4.4 Metal Ion Selection**: The choice of metal ions in MOF synthesis can impact the water solubility of the resulting MOFs. Some metal ions exhibit higher solubility in water due to their coordination chemistry and hydration properties. These metal ions can form stable metal-aqua complexes that promote water solubility. By selecting metal ions with higher aqueous solubility, researchers can enhance the water solubility of MOFs.

**2.4.5 Counterion Exchange**: Counterion exchange is a technique that can be employed to impart water solubility to MOFs. The counterions associated with the MOF structure can be exchanged with more hydrophilic ions, such as alkali metal ions or ammonium ions. This ion exchange process increases the water solubility of MOFs by enhancing the electrostatic repulsion between the MOF particles and promoting their dispersion in water.

**2.4.6 Surface Modification**: Surface modification of MOFs involves coating the MOF particles with hydrophilic materials or polymers. This modification enhances the water solubility of MOFs by providing a hydrophilic shell around the MOF particles, preventing aggregation and facilitating their dispersion in water. Surface modification can be achieved through techniques such as ligand exchange, encapsulation, or post-synthetic surface functionalization.

 The selection and combination of coordination modulation strategies depend on the specific requirements of the water-soluble MOF and its intended applications. Computational modeling and experimental characterization techniques play crucial roles in guiding the design and optimization of coordination modulation strategies for water-soluble MOFs.

 In conclusion, coordination modulation strategies are essential for achieving water solubility in MOFs while preserving their structural integrity

**2.5 Incorporation of Green Catalysts in GMOFs**

 The incorporation of green catalysts in Green Metal-Organic Frameworks (GMOFs) has emerged as an important strategy to develop sustainable and efficient catalytic systems. Green catalysts are characterized by their high catalytic activity, selectivity, and environmentally friendly nature. This section explores the incorporation of various types of green catalysts into GMOFs and their potential applications.

**2.5.1 Enzymes**: Enzymes are highly efficient and selective catalysts that play a crucial role in many biological processes. Incorporating enzymes into GMOFs offers several advantages, including enhanced stability, recyclability, and improved catalytic performance. The porous structure of GMOFs provides a suitable environment for immobilizing enzymes, preserving their activity, and facilitating substrate access. Enzyme-GMOF hybrid catalysts have shown great potential in diverse applications, such as biocatalysis, enzymatic reactions, and biosensing.

**2.5.2 Metal Nanoparticles**: Metal nanoparticles (NPs) are widely utilized as catalysts due to their unique size-dependent properties and high surface area. The incorporation of metal NPs into GMOFs allows for the precise control of their size, dispersion, and coordination environment, leading to enhanced catalytic activity and stability. Green metals, such as gold (Au), silver (Ag), and palladium (Pd), are commonly used in GMOF-based catalysts due to their low toxicity and high catalytic performance in various reactions, including hydrogenation, oxidation, and carbon-carbon bond formation.

**2.5.3 Organocatalysts:** Organocatalysts derived from organic molecules have gained significant attention in green catalysis. Incorporating organocatalysts into GMOFs can provide a heterogeneous catalytic system with improved reusability and stability. The porous structure of GMOFs allows for the effective immobilization of organocatalysts, enabling their easy separation from reaction mixtures and reducing the need for additional purification steps. Organocatalyst-GMOF hybrids have been successfully employed in various transformations, including asymmetric reactions, C-C bond formation, and polymerization reactions.

**2.5.4 Heterogeneous Catalysts**: Heterogeneous catalysts based on earth-abundant and environmentally friendly materials are highly desirable for sustainable catalysis. Incorporating these heterogeneous catalysts into GMOFs can enhance their stability, catalytic activity, and recyclability. Examples of green heterogeneous catalysts include metal-organic frameworks (MOFs) containing earth-abundant metals, porous carbon-based materials, and non-toxic metal oxides. The combination of GMOFs and green heterogeneous catalysts has been explored in various reactions, such as catalytic hydrogenation, oxidation, and carbon dioxide capture and conversion.

**2.5.5 Photocatalysts:** Photocatalysis offers a promising approach for sustainable and energy-efficient catalysis. Incorporating photocatalysts into GMOFs allows for the harnessing of solar energy to drive catalytic reactions. GMOFs can provide a favorable environment for the immobilization of photocatalytic species, enhancing their stability and light-harvesting efficiency. Photocatalyst-GMOF composites have been employed in various photocatalytic reactions, including water splitting, pollutant degradation, and organic synthesis under mild conditions.

 The incorporation of green catalysts in GMOFs offers several advantages, including improved catalytic performance, recyclability, and sustainability. These catalysts enable the design of efficient and environmentally friendly catalytic systems with potential applications in diverse areas, including fine chemical synthesis, energy conversion, and environmental remediation.

 In conclusion, the incorporation of green catalysts in GMOFs provides a powerful platform for sustainable and efficient catalysis. Enzymes, metal nanoparticles, organocatalysts, heterogeneous catalysts, and photocatalysts can be successfully integrated into GMOFs, offering enhanced catalytic performance and enabling the development of environmentally friendly chemical processes. Continued research in this field holds great potential for the advancement of green chemistry and sustainable catalysis.

**3. Characterization Techniques for GMOFs**

 Characterization techniques play a crucial role in understanding the structure, properties, and performance of Green Metal-Organic Frameworks (GMOFs). These techniques provide valuable insights into the morphology, crystallinity, surface area, porosity, and chemical composition of GMOFs, enabling researchers to optimize their synthesis, assess their stability, and evaluate their suitability for specific applications [17]. This chapter focuses on the various characterization techniques employed for GMOFs and their significance in advancing the field of sustainable materials.

 The characterization of GMOFs requires a multidisciplinary approach that combines techniques from materials science, chemistry, and physics. Researchers utilize a range of analytical tools to gain a comprehensive understanding of the structure and properties of GMOFs at different length scales, from the atomic and molecular level to the macroscopic scale. These techniques enable the investigation of GMOFs' crystal structure, pore size distribution, thermal stability, surface chemistry, and catalytic activity.

This chapter will discuss a variety of characterization techniques commonly used for GMOFs, including:

***X-ray Diffraction (XRD***): XRD is a powerful technique for determining the crystal structure, phase purity, and crystallinity of GMOFs. By analyzing the diffraction patterns obtained from X-ray scattering, researchers can identify the crystallographic phases present in GMOFs and quantify their crystalline domains. XRD provides information about the unit cell parameters, crystal symmetry, and orientation of GMOF crystals.

***Scanning Electron Microscopy (SEM):*** SEM allows for the visualization of GMOF morphology and surface features at high resolution. By bombarding GMOF samples with electrons and detecting the emitted signals, SEM provides detailed information about the particle size, shape, surface morphology, and distribution of GMOFs. It is particularly useful for examining GMOF films, coatings, or composite materials.

***Transmission Electron Microscopy (TEM):*** TEM provides a more detailed view of GMOFs at the nanoscale. By transmitting a beam of electrons through ultra-thin GMOF samples, TEM enables the visualization of individual nanoparticles, their crystal structure, and interparticle interactions. It is instrumental in studying GMOF growth mechanisms, defects, and particle size distributions.

***Fourier Transform Infrared Spectroscopy (FTIR):*** FTIR spectroscopy allows for the characterization of the chemical bonding and functional groups present in GMOFs. By measuring the absorption of infrared radiation by GMOF samples, FTIR provides information about the types of chemical bonds, coordination modes, and ligand-metal interactions in GMOFs. It is valuable for studying the ligand coordination, guest-host interactions, and surface functionalization of GMOFs.

***Gas Adsorption and Porosimetry:*** Gas adsorption techniques, such as nitrogen or carbon dioxide adsorption, provide information about the porosity, surface area, and pore size distribution of GMOFs. By measuring the adsorption and desorption isotherms, researchers can determine the specific surface area, pore volume, and pore size distribution of GMOFs, which are crucial for applications involving gas storage, separation, or catalysis.

***Thermal Analysis:*** Thermal analysis techniques, including thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), are employed to assess the thermal stability, decomposition behavior, and phase transitions of GMOFs. These techniques provide information about the stability, decomposition temperatures, and gas release patterns of GMOFs under different thermal conditions.

 These are just a few examples of the characterization techniques commonly used for GMOFs. Other techniques, such as nuclear magnetic resonance (NMR) spectroscopy, dynamic light scattering (DLS), and surface area analysis (BET), are also employed depending on the specific properties and applications of GMOFs.

 In summary, characterization techniques are essential tools for understanding the structure, properties, and performance

**3.1 Structural Characterization**: X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM)

 Structural characterization techniques are vital for understanding the atomic and molecular arrangement, crystal structure, and morphology of Green Metal-Organic Frameworks (GMOFs). This section focuses on three key techniques used for structural characterization: X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM).

**3.1.1 X-ray Diffraction (XRD):**X-ray Diffraction (XRD) is a widely used technique for determining the crystal structure, phase purity, and crystallinity of GMOFs. XRD involves irradiating GMOF samples with X-rays and analyzing the resulting diffraction pattern. The interaction of X-rays with the crystal lattice leads to constructive interference, resulting in diffraction peaks that can be measured and analyzed.XRD provides valuable information about the unit cell parameters, crystal symmetry, and orientation of GMOF crystals. By comparing the observed diffraction pattern with known reference patterns, researchers can identify the crystallographic phases present in GMOFs. XRD also allows for the determination of lattice parameters, crystallographic indices, and the presence of structural defects in GMOFs.

**3.1.2 Scanning Electron Microscopy (SEM):** Scanning Electron Microscopy (SEM) is a powerful technique for visualizing the surface morphology and topography of GMOFs. SEM uses a focused electron beam to scan the surface of a GMOF sample, and the interactions between the electrons and the sample generate signals that are detected and used to create an image.SEM provides high-resolution images of GMOF samples, allowing researchers to observe the particle size, shape, and surface features. It enables the examination of GMOF films, coatings, or composite materials, providing insights into the arrangement and distribution of GMOF particles. Additionally, SEM can be coupled with energy-dispersive X-ray spectroscopy (EDS) to obtain elemental composition information of GMOFs.

**3.1.3 Transmission Electron Microscopy (TEM):**

 Transmission Electron Microscopy (TEM) is a technique that provides detailed information about the atomic-scale structure and morphology of GMOFs. TEM involves transmitting a beam of electrons through an ultra-thin GMOF sample and analyzing the resulting transmitted and scattered electrons.

 TEM allows for the visualization of individual GMOF nanoparticles, their crystal structure, and interparticle interactions. It provides high-resolution images that reveal the atomic arrangement, lattice fringes, and defects in GMOFs. Furthermore, TEM techniques such as selected area electron diffraction (SAED) can be employed to determine the crystal orientation and phase distribution in GMOFs.

 The combination of X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM) offers comprehensive structural characterization of GMOFs. XRD provides information about the crystal structure and phase identification, while SEM and TEM provide detailed imaging of the GMOF morphology and atomic arrangement. Together, these techniques contribute to a better understanding of the structure-property relationships in GMOFs and aid in the optimization of their synthesis and performance

**3.2 Morphological Analysis: Atomic Force Microscopy (AFM) and Scanning Probe Microscopy (SPM)**

 Morphological analysis techniques are crucial for studying the surface characteristics, nanoscale features, and morphology of Green Metal-Organic Frameworks (GMOFs). In this section, we will explore two widely used techniques for morphological analysis: Atomic Force Microscopy (AFM) and Scanning Probe Microscopy (SPM).

**3.2.1 Atomic Force Microscopy (AFM):**

 Atomic Force Microscopy (AFM) is a high-resolution imaging technique that provides detailed information about the surface topography and physical properties of GMOFs. AFM works by scanning a sharp probe (cantilever) across the surface of the GMOF sample, measuring the forces between the probe tip and the surface.

 AFM enables the visualization of GMOF surfaces with exceptional resolution, allowing researchers to observe surface features, such as pores, aggregates, and defects. It provides three-dimensional topographic images, revealing nanoscale details of the GMOF morphology. Additionally, AFM can measure other properties, including surface roughness, mechanical properties, and surface charge distribution, providing valuable insights into the surface characteristics of GMOFs.

**3.2.2 Scanning Probe Microscopy (SPM):**

 Scanning Probe Microscopy (SPM) encompasses a family of techniques that include AFM and other related methods, such as Scanning Tunneling Microscopy (STM) and Electrostatic Force Microscopy (EFM). SPM techniques employ a sharp probe that interacts with the GMOF surface, allowing for the mapping of various surface properties.

 STM, in particular, is a powerful technique for investigating the electronic and atomic structure of GMOFs. It operates based on the principle of quantum tunneling, measuring the current flowing between the tip and the GMOF surface to create atomic-scale images. STM provides information about the arrangement of atoms and molecules on the GMOF surface, enabling the visualization of individual atoms and the identification of surface defects.

 EFM, on the other hand, measures the electrostatic forces between the probe tip and the GMOF surface. It can provide information about surface charge distribution, local dielectric properties, and the presence of electrically active sites on the GMOF surface.

 SPM techniques offer valuable insights into the nanoscale morphology and surface properties of GMOFs. They provide high-resolution imaging capabilities, allowing for the visualization of individual nanoparticles, surface roughness, and defects. Moreover, these techniques can probe local physical and chemical properties, aiding in the understanding of surface interactions, adsorption phenomena, and surface reactivity of GMOFs.

 In summary, Atomic Force Microscopy (AFM) and Scanning Probe Microscopy (SPM) techniques provide powerful tools for morphological analysis of GMOFs. AFM enables the visualization of surface topography and physical properties, while SPM techniques, such as STM and EFM, offer atomic-scale imaging and characterization of GMOF surfaces. The combination of these techniques aids in the understanding of GMOF morphology and surface-related phenomena, contributing to the development and optimization of GMOFs for various applications

**3.3 Thermal Analysis**: Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

 Thermal analysis techniques are essential for investigating the thermal stability, decomposition behavior, and phase transitions of Green Metal-Organic Frameworks (GMOFs). Two widely used techniques for thermal analysis are Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

**3.3.1 Thermogravimetric Analysis (TGA):**

 Thermogravimetric Analysis (TGA) is a technique used to measure the weight changes of GMOFs as a function of temperature. During TGA, a GMOF sample is subjected to a programmed temperature increase while its weight is continuously monitored. The weight changes are recorded as a function of temperature or time.

 TGA provides information about the thermal stability and decomposition behavior of GMOFs. It can identify the temperature at which weight loss occurs, indicating the onset of thermal degradation or decomposition. TGA curves can reveal multiple weight loss steps, indicating the presence of different components or decomposition stages within the GMOF structure. Additionally, TGA can provide insights into the thermal stability of GMOFs under various atmospheres, such as air, inert gas, or reactive environments.

**3.3.2 Differential Scanning Calorimetry (DSC):**

 Differential Scanning Calorimetry (DSC) is a thermal analysis technique used to measure the heat flow associated with physical and chemical changes in GMOFs as a function of temperature. DSC involves comparing the heat flow to a reference material as the GMOF sample is heated or cooled.

 DSC provides information about phase transitions, such as melting, crystallization, and glass transitions, occurring in GMOFs. It can determine the enthalpy change associated with these transitions, allowing for the calculation of parameters like heat capacity and degree of crystallinity. DSC can also identify exothermic or endothermic reactions taking place in GMOFs, providing insights into thermal decomposition, gas release, or guest-host interactions.

 By combining TGA and DSC, researchers can gain comprehensive information about the thermal behavior of GMOFs. TGA reveals weight loss and decomposition patterns, while DSC provides insights into phase transitions and associated heat flow. These techniques are particularly valuable for assessing the stability and thermal performance of GMOFs, which is crucial for their applications in gas storage, catalysis, and sensing.

 In summary, Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) are essential thermal analysis techniques for characterizing GMOFs. TGA allows for the determination of weight loss and thermal stability, while DSC provides information about phase transitions and associated heat flow. These techniques contribute to the understanding of the thermal behavior of GMOFs and aid in the optimization of their synthesis and application conditions.

**3.4 Spectroscopic Techniques: Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR), and Raman Spectroscopy**

 Spectroscopic techniques play a vital role in the characterization of Green Metal-Organic Frameworks (GMOFs) by providing valuable information about their chemical bonding, functional groups, and molecular structure. In this section, we will explore three important spectroscopic techniques used for GMOF analysis: Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR), and Raman Spectroscopy [18].

**3.4.1 Fourier Transform Infrared Spectroscopy (FTIR):**

 Fourier Transform Infrared Spectroscopy (FTIR) is a widely used technique for analyzing the chemical bonding and functional groups present in GMOFs. FTIR works by measuring the absorption of infrared radiation by GMOF samples. Different chemical bonds and functional groups absorb specific wavelengths of infrared light, resulting in characteristic absorption bands in the FTIR spectrum.

 FTIR provides information about the types of chemical bonds, coordination modes, and ligand-metal interactions in GMOFs. By comparing the FTIR spectrum of a GMOF with reference spectra, researchers can identify the functional groups and ligands present in the framework. FTIR is particularly useful for studying the ligand coordination, guest-host interactions, and surface functionalization of GMOFs.

**3.4.2 Nuclear Magnetic Resonance (NMR):**

 Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful technique for investigating the molecular structure, chemical environment, and dynamics of GMOFs. NMR exploits the magnetic properties of atomic nuclei, such as hydrogen (1H), carbon-13 (13C), or other nuclei present in GMOFs. By subjecting the GMOF sample to a strong magnetic field and applying radiofrequency pulses, NMR spectroscopy detects the resonant frequencies associated with nuclear spin transitions.

 NMR provides detailed information about the connectivity of atoms in the GMOF structure, as well as the chemical shifts, coupling constants, and relaxation times of nuclei. It can determine the connectivity between metal ions and ligands, identify different molecular species within the GMOF, and investigate the dynamics and motion of molecules within the framework. Solid-state NMR techniques are particularly relevant for studying GMOFs, as they can provide insights into the structure and properties of these materials under real-world conditions.

**3.4.3 Raman Spectroscopy:**

 Raman Spectroscopy is a technique that provides information about the vibrational modes and molecular structure of GMOFs. Raman spectroscopy involves irradiating the GMOF sample with monochromatic light and analyzing the scattered light that is shifted in frequency due to molecular vibrations.

 Raman spectroscopy allows for the identification of vibrational modes and the determination of bond lengths, bond angles, and crystal symmetry in GMOFs. It can provide insights into the coordination environments of metal ions, the presence of functional groups, and the arrangement of ligands within the framework. Raman spectroscopy is also valuable for studying the chemical stability, phase transitions, and structural changes of GMOFs under different environmental conditions.

 By utilizing Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR), and Raman Spectroscopy, researchers can gain comprehensive information about the chemical structure, bonding, and molecular dynamics of GMOFs. These spectroscopic techniques enable the characterization and understanding of GMOF properties, facilitating the optimization of synthesis methods and the development of tailored applications for these materials.

**3.5 Gas Sorption Analysis: Gas Adsorption Isotherms and Surface Area Measurement**

 Gas sorption analysis is a crucial characterization technique for evaluating the gas storage capacity, surface area, and porosity of Green Metal-Organic Frameworks (GMOFs). Gas sorption analysis provides insights into the adsorption behavior of GMOFs and is important for applications such as gas storage, separation, and catalysis. This section focuses on two key aspects of gas sorption analysis: gas adsorption isotherms and surface area measurement.

**3.5.1 Gas Adsorption Isotherms:**

 Gas adsorption isotherms describe the relationship between the amount of gas adsorbed by a GMOF sample and the equilibrium pressure at a given temperature. By measuring the amount of gas adsorbed at various pressures, researchers can obtain information about the adsorption capacity, adsorption kinetics, and gas selectivity of GMOFs.

 The most commonly used gas for adsorption analysis is nitrogen (N2), although other gases such as carbon dioxide (CO2) or hydrogen (H2) may also be employed depending on the specific application. Gas adsorption isotherms can be measured using various techniques, including volumetric methods (such as the BET method) and gravimetric methods (such as the Sievert's method).

 Gas adsorption isotherms provide valuable information about the porosity, surface area, and pore size distribution of GMOFs. Different isotherm shapes, such as Type I (characteristic of microporous materials), Type II (mesoporous materials), or Type IV (indicating hierarchical porosity), can indicate the nature and accessibility of the pores within the GMOF structure. The analysis of gas adsorption isotherms allows for the calculation of parameters like specific surface area, pore volume, and pore size distribution using various models and theories, such as the BET (Brunauer-Emmett-Teller) model.

**3.5.2 Surface Area Measurement**:

 Surface area measurement is an important aspect of gas sorption analysis and provides information about the total accessible surface area of GMOFs. A higher surface area generally corresponds to a greater number of active sites for gas adsorption and higher gas storage capacity. Several techniques are employed for surface area measurement, including the Brunauer-Emmett-Teller (BET) method, the Langmuir method, and the single-point BET method.

 The BET method is widely used for determining the specific surface area of GMOFs. It involves measuring the gas adsorption isotherm at low relative pressures and fitting the data to the BET equation. The specific surface area is calculated based on the monolayer adsorption capacity and the gas properties.

 Surface area measurement provides valuable information for understanding the porosity and gas adsorption properties of GMOFs. It aids in the evaluation of their potential for gas storage, separation, and catalytic applications. The surface area data, along with other characterization techniques, contribute to the understanding of the structure-property relationships in GMOFs.

 In summary, gas sorption analysis, including gas adsorption isotherms and surface area measurement, is essential for characterizing the gas storage capacity, porosity, and surface properties of GMOFs. Gas adsorption isotherms provide insights into the adsorption behavior and porosity characteristics, while surface area measurement quantifies the total accessible surface area. These techniques are crucial for evaluating the potential applications of GMOFs in gas storage, separation, and catalysis.

**4. Applications of GMOFs**

**4.1 Gas Storage and Separation**

 Gas storage and separation is a significant application area for Green Metal-Organic Frameworks (GMOFs) due to their exceptional porosity, large surface area, and tunable adsorption properties. GMOFs have shown great potential in storing and separating gases such as hydrogen, methane, carbon dioxide, and other greenhouse gases [19]. This section highlights the application of GMOFs in gas storage and separation and explores their impact on addressing energy and environmental challenges.

**4.1.1 Hydrogen Storage:**

 Hydrogen is a promising clean energy carrier with the potential to replace fossil fuels. However, efficient and safe storage of hydrogen remains a significant challenge. GMOFs offer a solution by providing high surface area and porosity for hydrogen adsorption. The tailored design of GMOFs allows for the optimization of hydrogen adsorption capacity, surface interactions, and stability. By carefully selecting ligands and metal centers, GMOFs can achieve high hydrogen storage densities and overcome limitations associated with traditional storage methods.

**4.1.2 Methane Storage and Natural Gas Purification**:

 GMOFs have shown promise in the storage and purification of methane, the main component of natural gas. The abundant porosity and adsorption sites of GMOFs enable high-capacity methane storage at moderate pressures and temperatures. This can facilitate the efficient storage and transportation of natural gas, enhancing its accessibility as a clean energy source. Additionally, GMOFs can selectively adsorb impurities, such as carbon dioxide and water, from natural gas, contributing to its purification and quality enhancement.

**4.1.3 Carbon Dioxide Capture and Storage:**

 The capture and storage of carbon dioxide (CO2) play a vital role in mitigating greenhouse gas emissions and combating climate change. GMOFs offer a promising approach for CO2 capture due to their high surface area and tailored adsorption properties. By designing GMOFs with specific pore sizes, functional groups, and metal centers, selective and efficient CO2 capture can be achieved. GMOFs can be used in post-combustion capture processes in power plants, industrial processes, and carbon capture from the atmosphere. Moreover, GMOFs can facilitate the controlled release of captured CO2, contributing to its storage and utilization.

**4.1.4 Gas Separation and Selective Adsorption:**

 GMOFs possess the capability to selectively adsorb and separate different gases based on their size, polarity, and interactions with the framework. This property opens avenues for various gas separation applications. For example, GMOFs can be employed in the separation of carbon dioxide from flue gas emissions, allowing for its capture and subsequent utilization or storage. GMOFs can also enable the separation of gas mixtures, such as the separation of hydrogen from other gases for clean energy applications. The ability to tailor GMOFs' pore sizes, functionalities, and metal centers provides control over selectivity, enabling efficient gas separation processes.

 The application of GMOFs in gas storage and separation has the potential to significantly impact the energy sector, environmental sustainability, and climate change mitigation. By offering efficient, selective, and sustainable solutions for gas storage and separation, GMOFs contribute to the development of clean energy systems, reduced greenhouse gas emissions, and the efficient utilization of natural resources. Ongoing research and development in this field aim to optimize GMOF materials, enhance their stability, and improve their performance for real-world applications.

**4.2 Catalysis and Green Chemistry**

 Catalysis plays a crucial role in numerous chemical processes, and the development of sustainable and environmentally friendly catalytic systems is a key objective in the field of green chemistry. Green Metal-Organic Frameworks (GMOFs) have gained significant attention as catalysts due to their unique properties and tunable nature. In this section, we explore the applications of GMOFs in catalysis and their contributions to green chemistry.

**4.2.1 Efficient Catalytic Reactions:**

 GMOFs offer a platform for designing efficient catalytic systems. The incorporation of metal centers within the framework provides active sites for catalytic reactions. The tunability of GMOFs allows for the selection of specific metals and ligands, enabling control over the catalytic activity, selectivity, and stability. GMOFs have been employed as catalysts in various reactions, including organic transformations, C-H activation, cross-coupling reactions, and biomass conversions. Their high surface area and porosity enhance the accessibility of reactants to the catalytic sites, leading to improved reaction rates and selectivity.

**4.2.2 Selective and Sustainable Catalysis:**

 GMOFs can exhibit selective catalytic properties by incorporating ligands and metal centers with specific functionalities. This selectivity enables the transformation of specific chemical bonds or the selective production of desired products. Furthermore, GMOFs can contribute to sustainability in catalysis by using abundant and environmentally benign metals, reducing the need for rare and expensive catalysts. The design of GMOFs can also promote recyclability and reusability, minimizing waste generation and reducing the environmental impact of catalytic processes.

**4.2.3 Photocatalysis:**

 GMOFs have shown promise in the field of photocatalysis, where light energy is utilized to drive chemical reactions. The unique structure of GMOFs, with their metal centers and ligands, allows for the generation and utilization of photoexcited states. GMOFs can serve as photocatalysts for various reactions, including water splitting for hydrogen production, organic synthesis under mild conditions, and degradation of organic pollutants. Their porosity and surface area facilitate efficient light absorption and enhanced photocatalytic performance.

**4.2.4 Enzyme-Mimicking Catalysis:**

 GMOFs can mimic the functions of enzymes, known as artificial enzymes or metal-organic frameworks with enzyme-like activity (MOFzymes). These MOFzymes exhibit catalytic properties similar to natural enzymes, such as high selectivity, substrate specificity, and enzyme-like reaction mechanisms. MOFzymes have been developed for a range of enzymatic reactions, including oxidation, reduction, and hydrolysis. The advantage of MOFzymes over natural enzymes lies in their stability under a wider range of conditions and the ability to be synthesized and tuned for specific applications.

 The applications of GMOFs in catalysis and green chemistry hold great potential for advancing sustainable and efficient chemical processes. By providing selective, recyclable, and environmentally friendly catalytic systems, GMOFs contribute to the development of greener and more sustainable chemical industries. Ongoing research and exploration in this field aim to further optimize GMOF catalytic properties and expand their applications in various industrial and environmental processes.

**4.3 Drug Delivery and Biomedical Applications**

 Green Metal-Organic Frameworks (GMOFs) have emerged as promising materials for drug delivery and various biomedical applications. Their unique properties, such as high surface area, tunable pore size, and the ability to incorporate functional molecules, make them attractive candidates for improving therapeutic efficacy, targeted drug delivery, and diagnostic imaging. This section highlights the applications of GMOFs in drug delivery systems and their potential in biomedical research.

**4.3.1 Controlled Drug Release**:

 GMOFs offer a controlled and sustained release of therapeutic agents, addressing the limitations of conventional drug delivery systems. The porous structure of GMOFs allows for the encapsulation and protection of drug molecules, preventing their premature degradation and release. By tailoring the pore size and surface chemistry of GMOFs, the release rate and duration of drug molecules can be precisely controlled, resulting in improved therapeutic outcomes and reduced side effects.

**4.3.2 Targeted Drug Delivery:**

 GMOFs can be functionalized with targeting ligands, such as antibodies, peptides, or aptamers, to specifically deliver drugs to desired sites in the body. The functionalization of GMOFs enables active targeting of specific cells, tissues, or organs, increasing the drug's accumulation at the target site while minimizing its distribution to healthy tissues. This targeted drug delivery approach enhances drug efficacy, reduces systemic toxicity, and improves patient compliance.

**4.3.3 Theranostics:**

 GMOFs have gained attention in theranostic applications, which combine therapy and diagnostics. By incorporating both therapeutic agents and imaging probes into the GMOF structure, theranostic platforms can be developed. These platforms enable simultaneous imaging and therapy, allowing for real-time monitoring of drug release, biodistribution, and therapeutic response. Theranostic GMOFs offer a personalized and precise approach to medicine, enabling tailored treatments and individualized patient care.

**4.3.4 Bioimaging:**

 The unique optical and magnetic properties of GMOFs make them promising candidates for bioimaging applications. GMOFs can be functionalized with fluorescent dyes, quantum dots, or magnetic nanoparticles, allowing for enhanced imaging contrast and visualization of specific targets. Additionally, the large surface area of GMOFs provides ample space for loading imaging agents, facilitating multimodal imaging approaches that combine different imaging modalities for comprehensive and accurate diagnosis.

**4.3.5 Tissue Engineering and Regenerative Medicine:**

 GMOFs have shown potential in tissue engineering and regenerative medicine applications. The porous structure of GMOFs can serve as a scaffold for cell growth, providing a supportive environment for tissue regeneration. By incorporating bioactive molecules and growth factors, GMOFs can promote cell adhesion, proliferation, and differentiation. GMOFs can also be engineered to release bioactive molecules in a controlled manner, facilitating tissue regeneration and wound healing processes.

**4.3.6 Biosensing and Detection:**

 GMOFs have been explored in biosensing and detection applications. By incorporating specific ligands or metal centers, GMOFs can exhibit selective and sensitive responses to target analytes, such as biomarkers, proteins, or small molecules. The interactions between the analyte and the GMOF structure can induce changes in fluorescence, electrical conductivity, or optical properties, enabling the detection and quantification of the analyte. GMOFs offer potential in areas such as disease diagnosis, environmental monitoring, and food safety.

 The applications of GMOFs in drug delivery and biomedical research are promising and hold potential for transforming the field of medicine. With further advancements in GMOF design, functionalization, and understanding of their interactions with biological systems, these materials are expected to contribute significantly to the development of more effective and targeted therapies, improved diagnostics, and regenerative medicine approaches.

**4.4 Environmental Remediation and Water Purification**

 Green Metal-Organic Frameworks (GMOFs) have emerged as promising materials for environmental remediation and water purification applications. Their unique properties, such as high surface area, tunable porosity, and selective adsorption capabilities, make them well-suited for the removal of pollutants and contaminants from water and air. This section explores the applications of GMOFs in environmental remediation and water purification.

**4.4.1 Heavy Metal Removal:**

 GMOFs have demonstrated excellent capabilities for the removal of heavy metals from contaminated water sources. The high surface area and specific metal-ligand interactions of GMOFs enable the selective adsorption of heavy metal ions, including lead, mercury, cadmium, and arsenic. The tunability of GMOFs allows for the design of materials with tailored affinities for specific heavy metal contaminants, facilitating efficient and selective removal. GMOFs offer a promising solution for the remediation of heavy metal-contaminated water sources, contributing to environmental sustainability and human health.

**4.4.2 Organic Pollutant Removal:**

 GMOFs can effectively remove organic pollutants from water, including dyes, pesticides, pharmaceuticals, and other organic contaminants. The porous structure and functionalization of GMOFs provide adsorption sites for the organic molecules, allowing for their effective capture and removal. The tailored design of GMOFs can enhance their adsorption capacity and selectivity towards specific organic pollutants. Furthermore, GMOFs can be regenerated and reused, making them a sustainable and cost-effective solution for organic pollutant removal.

**4.4.3 Water Purification and Desalination:**

 GMOFs have shown promise in water purification and desalination processes. The tunable porosity and selective adsorption properties of GMOFs enable the removal of impurities, such as ions, organic compounds, and microorganisms, from water sources. Additionally, GMOFs can be functionalized to selectively adsorb specific contaminants or target emerging pollutants, ensuring the production of clean and safe drinking water. In desalination processes, GMOFs can assist in the removal of salt ions from seawater, contributing to the development of efficient and sustainable desalination technologies.

**4.4.4 Air Purification:**

 GMOFs have the potential to be utilized in air purification systems for the removal of volatile organic compounds (VOCs), toxic gases, and air pollutants. The high adsorption capacity and selectivity of GMOFs make them effective in capturing and removing harmful compounds from indoor and outdoor air. GMOFs can be incorporated into air filters or packed beds to efficiently remove pollutants and improve air quality. Their tunability allows for the design of materials that target specific pollutants, offering tailored solutions for air purification.

**4.4.5 Waste Water Treatment:**

 GMOFs can play a significant role in waste water treatment processes. They can be employed for the removal of various contaminants, such as heavy metals, organic pollutants, and nutrients, from industrial and municipal waste water. The selective adsorption properties and large surface area of GMOFs facilitate the efficient removal of contaminants, contributing to the purification and treatment of waste water before discharge. GMOFs offer a promising solution for sustainable waste water treatment, addressing environmental concerns and ensuring the protection of water resources.

 The applications of GMOFs in environmental remediation and water purification demonstrate their potential in addressing pollution and sustainability challenges. By providing efficient and selective removal of pollutants from water and air, GMOFs contribute to the development of sustainable and environmentally friendly solutions for environmental remediation and the provision of clean water resources. Ongoing research and development in this field aim to optimize GMOF materials, enhance their stability, and improve their performance for real-world environmental applications.

**4.5 Energy Storage and Conversion**

 Green Metal-Organic Frameworks (GMOFs) have shown promise in energy storage and conversion applications, contributing to the development of sustainable and efficient energy systems. The unique properties of GMOFs, such as their high surface area, tunable porosity, and diverse functionalities, make them suitable for various energy-related processes. This section explores the applications of GMOFs in energy storage and conversion.

**4.5.1 Energy Storage:**

 GMOFs have been investigated for energy storage applications, particularly in the fields of batteries and supercapacitors. The high surface area and porosity of GMOFs provide ample space for the storage and transport of ions and molecules, enabling efficient energy storage. GMOFs can be utilized as electrode materials or as components of composite electrode structures, enhancing the performance of energy storage devices. Their tunability allows for the optimization of charge storage capacity, cycling stability, and energy density, contributing to the development of advanced and sustainable energy storage systems.

**4.5.2 Gas Storage:**

 GMOFs exhibit significant potential for gas storage applications, particularly in the storage of clean and renewable gases, such as hydrogen and methane. The porous structure of GMOFs enables high gas adsorption capacities, providing a means to store and transport gases for various energy applications. GMOFs can be tailored to enhance their gas adsorption selectivity, improving the efficiency and safety of gas storage systems. Additionally, GMOFs can contribute to the development of efficient gas separation processes, facilitating the purification and utilization of gases in energy production.

**4.5.3 Photovoltaics:**

 GMOFs have been explored in photovoltaic applications, such as solar cells and light-harvesting devices. Their unique structures and the incorporation of light-absorbing chromophores allow for the generation and transport of photoexcited electrons. GMOFs can be utilized as photoactive layers or as components of hybrid photovoltaic systems, contributing to efficient light absorption, charge separation, and electron transport. By optimizing the design and properties of GMOFs, their photovoltaic performance can be enhanced, promoting the development of sustainable and low-cost solar energy technologies.

**4.5.4 Catalytic Energy Conversion**:

 GMOFs have shown promise in catalytic energy conversion processes, including electrocatalysis and photocatalysis. The presence of metal centers and organic ligands in GMOFs allows for the design of active catalytic sites. GMOFs can be utilized as catalysts for various energy conversion reactions, such as water splitting for hydrogen production, carbon dioxide reduction, and oxygen evolution reactions. The tunability of GMOFs enables the optimization of catalytic activity, selectivity, and stability, facilitating efficient energy conversion processes.

**4.5.5 Energy Harvesting and Storage:**

 GMOFs can be incorporated into energy harvesting and storage devices, such as thermoelectric generators and hybrid energy systems. The thermal and electrical conductivity properties of GMOFs, combined with their tunable structures, allow for the efficient conversion and storage of energy from different sources. GMOFs can contribute to the development of lightweight, flexible, and scalable energy harvesting and storage technologies, enabling the utilization of waste heat, ambient vibrations, and other energy sources for sustainable power generation.

 The applications of GMOFs in energy storage and conversion highlight their potential in advancing sustainable energy systems. By providing efficient energy storage, gas storage, and catalytic conversion capabilities, GMOFs contribute to the development of clean and renewable energy technologies. Ongoing research and development aim to optimize GMOF materials, explore new functionalities, and integrate them into practical energy devices for real-world applications.

**4.6 Other Emerging Applications**

 In addition to the applications discussed earlier, Green Metal-Organic Frameworks (GMOFs) have shown promise in various emerging fields and applications. This section explores some of the emerging applications of GMOFs that are currently being explored and hold significant potential.

**4.6.1 Sensing and Detection**:

 GMOFs have been investigated for sensing and detection applications due to their unique structural and optical properties. The incorporation of specific ligands or metal centers in GMOFs allows for selective and sensitive detection of target analytes, such as gases, biomarkers, and pollutants. GMOFs can serve as sensing platforms for applications in environmental monitoring, healthcare diagnostics, food safety, and security. Their tunable properties and high surface area facilitate the development of highly sensitive and selective sensors for rapid and accurate detection.

**4.6.2 Energy-efficient Separation Processes:**

 GMOFs offer potential in energy-efficient separation processes, such as membrane separations and adsorption-based separations. The tunable porosity and selective adsorption capabilities of GMOFs enable the efficient separation of mixtures, including gases, liquids, and solutes. GMOFs can be utilized as membrane materials, adsorbents, or catalysts in separation processes, offering advantages such as high selectivity, enhanced separation efficiency, and reduced energy consumption. The development of GMOF-based separation technologies holds promise for applications in gas separation, water purification, and industrial separations.

**4.6.3 Gas Sensing and Capture:**

 GMOFs have been explored for gas sensing and capture applications. The high surface area and selective adsorption properties of GMOFs enable the capture and removal of harmful gases, such as carbon dioxide (CO2) and volatile organic compounds (VOCs), from air or gas streams. GMOFs can also be utilized for the detection and monitoring of gas emissions in environmental and industrial settings. The incorporation of functional molecules or metal centers in GMOFs allows for selective gas capture and real-time monitoring of gas concentrations.

**4.6.4 Supramolecular Chemistry and Self-Assembly:**

 GMOFs offer a platform for supramolecular chemistry and self-assembly, enabling the design and construction of complex architectures and functional materials. The precise control over ligand design and metal coordination in GMOFs allows for the formation of supramolecular structures with tailored properties. GMOFs can serve as templates or building blocks for the fabrication of hierarchical materials, nanocomposites, and functional devices. The exploration of GMOFs in supramolecular chemistry and self-assembly opens avenues for the development of advanced materials with tunable properties and novel functionalities.

**4.6.5 Electronic and Optoelectronic Devices:**

 GMOFs have shown potential in electronic and optoelectronic applications. The incorporation of conductive ligands or metal centers in GMOFs allows for the development of materials with semiconducting or conducting properties. GMOFs can be utilized as active layers or components in electronic devices, such as sensors, transistors, light-emitting diodes (LEDs), and photodetectors. The tunability of GMOFs enables the optimization of their electronic and optoelectronic properties, facilitating the development of sustainable and energy-efficient electronic devices.

**4.6.6 Gas Storage for Vehicle Applications:**

 GMOFs have garnered interest in the field of gas storage for vehicle applications, particularly for the storage of clean and renewable fuels, such as hydrogen and natural gas. GMOFs offer advantages such as high storage capacity, low weight, and improved safety compared to traditional storage methods. The development of GMOFs for on-board fuel storage in vehicles can contribute to the advancement of fuel cell technologies, reducing greenhouse gas emissions and promoting sustainable transportation systems.

 The emerging applications of GMOFs demonstrate the versatility and potential of these materials in various fields. Ongoing research and development efforts aim to further explore and optimize GMOFs for these applications, focusing on enhancing their performance, stability, and scalability. As the understanding of GMOFs deepens and new ligand designs and synthetic strategies emerge, their applications in emerging fields are expected to expand, opening up new avenues for sustainable technologies and innovative solutions.

**5. Challenges and Future Perspectives**

 While Green Metal-Organic Frameworks (GMOFs) hold great promise in various applications, there are several challenges that need to be addressed for their widespread implementation. Overcoming these challenges will pave the way for the future development and utilization of GMOFs in a more efficient and sustainable manner. This section discusses the challenges and provides future perspectives for GMOFs [20].

**Stability and Scalability:**

 One of the major challenges in the field of GMOFs is ensuring their stability under different environmental conditions. GMOFs can be sensitive to moisture, temperature, and chemical exposure, leading to structural degradation and loss of functionality. Future research should focus on developing GMOFs with enhanced stability, allowing for their long-term use in practical applications. Additionally, scaling up the synthesis of GMOFs while maintaining their properties and performance is crucial for their industrial adoption.

**Water Compatibility:**

 While the synthesis of GMOFs in water has been achieved, the challenge lies in developing water-compatible GMOFs with sufficient stability and porosity. Water can often disrupt the framework structure or inhibit the desired properties of GMOFs. Future research should aim to design ligands and metal clusters that are compatible with water-based synthesis methods while maintaining the desired properties and performance of GMOFs.

**Cost-effectiveness:**

 The synthesis and production of GMOFs can be costly, limiting their large-scale utilization. Future research efforts should focus on developing cost-effective synthesis methods and scalable production techniques for GMOFs. This includes exploring alternative ligands, metal sources, and synthesis approaches that can reduce the overall cost of GMOF production without compromising their quality and performance.

**Selectivity and Functionality:**

 GMOFs need to exhibit high selectivity and functionality for specific applications. Future research should focus on designing ligands that can effectively bind and interact with target molecules or ions, allowing for enhanced selectivity and performance. The development of multifunctional GMOFs that can exhibit multiple properties and perform multiple tasks simultaneously would further expand their applications.

**Characterization and Standardization:**

 Accurate characterization techniques and standardized protocols for GMOFs are essential for reliable and reproducible results. Future research should aim to develop comprehensive and standardized characterization methods that can effectively determine the structural, morphological, and functional properties of GMOFs. This will enable better understanding of GMOFs and facilitate their comparison and integration into various applications.

**Integration and Practical Implementation:**

 To realize the full potential of GMOFs, it is essential to integrate them into practical devices and systems. Future research should focus on developing methodologies for incorporating GMOFs into devices and optimizing their performance in real-world conditions. Collaboration between researchers, industry partners, and policymakers is crucial for the successful implementation of GMOFs in commercial applications.

**Environmental Impact:**

 While GMOFs offer numerous advantages, their environmental impact throughout their lifecycle should be carefully considered. This includes the sustainability of raw materials, energy consumption during synthesis, and potential for waste generation. Future research should aim to develop environmentally friendly synthesis routes, optimize resource utilization, and explore recycling or reusability of GMOFs to minimize their environmental footprint.

 In conclusion, GMOFs have immense potential in various applications, but addressing the challenges outlined above is crucial for their successful implementation. Future research should focus on enhancing stability, scalability, water compatibility, cost-effectiveness, selectivity, characterization, integration, and considering the environmental impact of GMOFs. With continued efforts, GMOFs can become key components in sustainable technologies, enabling advancements in fields such as energy storage, catalysis, environmental remediation, and beyond.

**5.1 Synthesis Strategies and Scalability**

 The synthesis of Green Metal-Organic Frameworks (GMOFs) and their scalability are essential factors in realizing their practical applications. This section discusses synthesis strategies and scalability considerations for GMOFs.

**5.1.1 Synthesis Strategies:**

 Various synthesis strategies have been developed for GMOFs, aiming to achieve controlled and efficient formation of the framework structures. Some commonly employed strategies include:

**a) Solvothermal/Hydrothermal Synthesis**: This method involves the reaction of metal ions with organic ligands in a high-temperature and high-pressure solvent. Solvothermal or hydrothermal conditions facilitate the formation of well-defined GMOF crystals with controlled sizes and morphologies.

**b) Microwave-Assisted Synthesis**: Microwave irradiation can accelerate the synthesis of GMOFs by promoting rapid heating and efficient energy transfer. This technique offers advantages such as reduced reaction time and enhanced yield.

**c) Ionothermal Synthesis**: Ionothermal synthesis utilizes ionic liquids as solvents or reaction media for GMOF formation. This strategy allows for the incorporation of specific ions from the ionic liquid into the framework structure, leading to unique properties and enhanced stability.

**d) Mechanochemical Synthesis:** Mechanochemical methods involve the use of mechanical force, such as grinding or milling, to induce the formation of GMOFs. This approach offers the advantage of solvent-free synthesis and can be scaled up for large-scale production.

**e) Green Synthesis:** Green synthesis approaches aim to minimize the use of hazardous solvents, reduce energy consumption, and employ sustainable raw materials. These methods often utilize water as a solvent and bio-based ligands for GMOF synthesis, making the process more environmentally friendly.

**5.1.2 Scalability Considerations:**

 To achieve the practical implementation of GMOFs, their synthesis methods must be scalable to enable large-scale production. Several considerations should be taken into account for the scalability of GMOF synthesis:

**a) Raw Materials:** Availability and cost-effectiveness of raw materials are crucial for scalability. Researchers should explore alternative and sustainable sources of metal ions and ligands that can be obtained in large quantities at reasonable costs.

**b) Reaction Conditions**: Optimizing the reaction conditions, such as temperature, pressure, and reaction time, is essential to ensure reproducibility and scalability. The synthesis parameters should be carefully controlled to achieve consistent product quality and high yields.

**c) Process Automation**: Developing automated synthesis systems can enhance the scalability of GMOF production. Automation reduces human error, improves process control, and allows for continuous and efficient synthesis on a larger scale.

**d) Continuous Flow Synthesis:** Continuous flow synthesis methods enable the continuous production of GMOFs, eliminating batch-to-batch variations and improving efficiency. This approach offers advantages in terms of reaction control, scalability, and productivity.

**e) Upscaling Techniques**: Researchers should explore upscaling techniques to translate laboratory-scale synthesis methods to industrial-scale production. This includes optimizing reactor designs, reactor configurations, and reactor materials to accommodate larger volumes and ensure efficient mass and heat transfer.

**f) Process Optimization**: Continuous improvement and optimization of the synthesis process are necessary for scalability. This involves identifying critical reaction parameters, optimizing ligand-metal ratios, and developing efficient purification and separation techniques.

 By considering these synthesis strategies and scalability considerations, researchers can advance the development of large-scale production methods for GMOFs. Collaboration between academia, industry, and policymakers is essential to overcome the technical and economic challenges associated with GMOF synthesis and scale them up for practical applications.

**5.2 Stability and Water Compatibility of GMOFs**

 The stability and water compatibility of Green Metal-Organic Frameworks (GMOFs) are critical factors in their practical applications, especially in aqueous environments. This section discusses the challenges associated with the stability of GMOFs and strategies to enhance their water compatibility.

**5.2.1 Stability of GMOFs:**

 GMOFs can exhibit varying degrees of stability depending on their composition, structure, and the surrounding environment. Some challenges associated with the stability of GMOFs include:

**a) Moisture Sensitivity**: Many GMOFs are prone to structural degradation and loss of porosity in the presence of moisture. Water molecules can coordinate with metal sites or disrupt the intermolecular interactions, leading to framework collapse. Strategies to address moisture sensitivity include incorporating hydrophobic ligands, introducing moisture-resistant coatings, or developing post-synthetic modification methods.

**b) Thermal Stability**: GMOFs may exhibit thermal instability, especially at elevated temperatures. The organic ligands can undergo thermal decomposition, resulting in the collapse of the framework structure. Enhancing the thermal stability of GMOFs can be achieved through ligand engineering, metal coordination modulation, or the introduction of metal oxide nodes.

**c) Chemical Stability**: GMOFs can be susceptible to chemical degradation in the presence of aggressive chemicals or certain solvents. The choice of ligands and metal nodes can influence the chemical stability of GMOFs. Rational ligand design, selection of appropriate metal nodes, and post-synthetic treatments can enhance their chemical stability.

**d) Structural Collapse:** External stimuli such as temperature, pressure, or chemical exposure can induce structural collapse in GMOFs. The framework's flexibility, intermolecular interactions, and guest molecules play crucial roles in determining the stability of GMOFs. Strategies to mitigate structural collapse include designing rigid frameworks, introducing cross-linking agents, or utilizing post-synthetic stabilization techniques.

**5.2.2 Water Compatibility of GMOFs:**

 The water compatibility of GMOFs is essential for their practical applications, especially in aqueous environments. Challenges in achieving water compatibility include:

**a) Hydrophilicity:** Many GMOFs are hydrophobic, making them incompatible with water-based systems. Modifying the ligand structure to introduce hydrophilic functional groups can enhance the water compatibility of GMOFs. Hydrophilic ligands can facilitate water molecule coordination and improve the stability of GMOFs in aqueous environments.

**b) Water Stability**: GMOFs synthesized in water may suffer from rapid framework decomposition or loss of porosity upon prolonged exposure to water. Designing ligands that can form stable coordination bonds with metal nodes in the presence of water is crucial for achieving water stability. Post-synthetic treatments such as solvent exchange or encapsulation of water-sensitive GMOFs can also enhance their water stability.

**c) Ion Exchange:** GMOFs synthesized in water may undergo ion exchange reactions with ions present in the aqueous solution. This can lead to changes in the framework structure or properties. Careful selection of metal nodes and ligands can minimize ion exchange effects and maintain the integrity of GMOFs in water.

**d) Surface Modifications**: Surface modifications can be employed to enhance the water compatibility of GMOFs. Coating the GMOF surface with hydrophilic polymers or introducing hydrophilic functional groups through surface functionalization can improve their dispersibility and stability in aqueous environments.

 To overcome these challenges, future research should focus on developing ligand designs that exhibit both water compatibility and stability. Exploring post-synthetic modification techniques, surface modifications, and encapsulation strategies can further enhance the water compatibility of GMOFs. Comprehensive characterization techniques and standardized protocols for evaluating the stability and water compatibility of GMOFs are also crucial for reliable assessment and comparison of different materials.

 Overall, addressing the stability and water compatibility challenges of GMOFs will contribute to their practical implementation in diverse applications such as catalysis, gas storage, drug delivery, and environmental remediation.

**5.3 Further Characterization Techniques for GMOFs**

 In addition to the characterization techniques discussed earlier, there are several other important techniques that can provide valuable insights into the properties and behavior of Green Metal-Organic Frameworks (GMOFs). This section introduces some of these techniques for further characterization of GMOFs.

**Solid-State NMR (Nuclear Magnetic Resonance):**

 Solid-state NMR spectroscopy is a powerful technique for studying the atomic-level structure and dynamics of GMOFs. It can provide information about the connectivity between metal nodes and organic ligands, guest-host interactions, and the presence of defects or disorder within the framework. Solid-state NMR techniques such as magic-angle spinning (MAS) NMR and high-resolution 2D/3D NMR experiments can be employed to probe the local environments and chemical shifts of nuclei within the GMOF structure.

**Powder X-ray Diffraction (PXRD):**

 PXRD is a widely used technique for determining the crystal structure of GMOFs. It provides information about the unit cell parameters, crystal symmetry, and arrangement of atoms within the framework. By analyzing the diffraction patterns of GMOFs, researchers can determine the phase purity, crystallinity, and any structural changes induced by external stimuli or guest molecule adsorption.

**In situ Characterization Techniques**:

 In situ characterization techniques allow for the real-time monitoring of the structural and chemical changes in GMOFs under specific conditions. These techniques include in situ X-ray diffraction (XRD), in situ spectroscopy (e.g., FTIR, Raman), and in situ gas sorption analysis. In situ studies provide valuable insights into the structural transformations, guest molecule interactions, and dynamic behavior of GMOFs, which are crucial for understanding their properties and performance under working conditions.

**Electron Paramagnetic Resonance (EPR) Spectroscopy:**

 EPR spectroscopy is a technique used to study the electronic and magnetic properties of paramagnetic species within GMOFs. It can provide information about the presence of unpaired electrons, their local environment, and their interaction with neighboring species. EPR spectroscopy is particularly useful for investigating the behavior of metal ions and radicals incorporated into GMOFs, as well as their catalytic or magnetic properties.

**Photoluminescence Spectroscopy:**

 Photoluminescence spectroscopy is employed to study the optical properties and luminescent behavior of GMOFs. By exciting GMOFs with light of different wavelengths, researchers can analyze the emission spectra and study the nature of the electronic transitions within the framework. Photoluminescence spectroscopy is useful for evaluating the photophysical properties, energy transfer processes, and potential applications of luminescent GMOFs in areas such as sensing and optoelectronics.

**Electrochemical Characterization:**

 Electrochemical techniques, such as cyclic voltammetry and impedance spectroscopy, are employed to investigate the electrochemical properties and behavior of GMOFs. These techniques provide insights into the redox behavior, charge storage capacity, and electrocatalytic activity of GMOFs for applications in energy storage and conversion devices.

**Computational Modeling:**

 Computational modeling techniques, such as density functional theory (DFT) calculations and molecular dynamics simulations, can complement experimental characterization by providing atomic-level insights into the structure, stability, and properties of GMOFs. Computational modeling allows for the prediction and understanding of the behavior of GMOFs under different conditions, guiding the design and optimization of new materials [21].

 By employing these additional characterization techniques, researchers can gain a comprehensive understanding of the structural, electronic, optical, electrochemical, and dynamic properties of GMOFs. These insights are crucial for optimizing GMOFs for specific applications and for advancing the fundamental understanding of their behavior and potential in various fields.

**5.4 Advancements in Applications and Industrial Scale-Up**

 Green Metal-Organic Frameworks (GMOFs) have shown great potential in various applications, and recent advancements have contributed to their practical implementation. This section discusses the advancements in GMOF applications and the challenges associated with industrial scale-up.

**5.4.1 Advancements in GMOF Applications**:

**a) Gas Storage and Separation**: GMOFs have been extensively studied for gas storage and separation applications. Advancements in ligand design and framework engineering have led to improved gas adsorption capacities, selectivities, and storage densities. GMOFs have demonstrated promising performance in storing gases such as hydrogen, methane, carbon dioxide, and volatile organic compounds. Furthermore, their tunable pore sizes and chemical affinities enable efficient gas separation processes.

**b) Catalysis and Green Chemistry**: GMOFs have emerged as efficient catalysts for various chemical transformations. Advancements in incorporating catalytic active sites within the framework structure have led to enhanced catalytic activities, selectivities, and stability. GMOFs have been employed in diverse catalytic reactions, including organic transformations, oxidation, hydrogenation, and photocatalysis. Their high surface area, tuneable pore environment, and molecular sieving properties contribute to their catalytic efficacy.

**c) Drug Delivery and Biomedical Applications:** GMOFs offer unique opportunities for drug delivery systems due to their high surface area, porosity, and ability to encapsulate and release therapeutic agents. Advancements in surface modifications and functionalization have enabled improved drug loading capacities, controlled release kinetics, and targeted delivery. GMOFs have shown potential in applications such as cancer therapy, imaging, and regenerative medicine.

**d) Environmental Remediation and Water Purification**: GMOFs have attracted attention for their applications in environmental remediation and water purification. Advancements in GMOF design have led to the development of materials with high adsorption capacities for pollutants, heavy metals, and organic contaminants. Their chemical tunability and affinity for specific contaminants allow for efficient removal and remediation processes. GMOFs have shown promise in wastewater treatment, air purification, and groundwater remediation.

**e) Energy Storage and Conversion**: GMOFs have demonstrated potential in energy storage and conversion devices. Advancements in the design of GMOFs with redox-active metal centers and conductive frameworks have enabled their use in supercapacitors, batteries, and fuel cells. Their high surface area, pore accessibility, and electronic conductivity contribute to enhanced energy storage and conversion performance.

**5.4.2 Industrial Scale-Up Challenges**:

 While GMOFs have shown promise in various applications, their industrial-scale production and implementation face several challenges:

**a) Cost and Availability of Raw Materials**: Scaling up the synthesis of GMOFs requires a consistent and cost-effective supply of raw materials, including metal ions and organic ligands. The availability and cost of these materials can impact the feasibility of large-scale production.

**b) Reproducibility and Batch-to-Batch Variations**: Achieving reproducibility and minimizing batch-to-batch variations are crucial for industrial-scale production. Standardizing synthesis protocols, controlling reaction parameters, and ensuring consistent product quality are essential challenges in scaling up GMOF synthesis.

**c) Process Efficiency and Throughput**: Developing efficient and high-throughput synthesis processes is essential for industrial-scale production. Optimization of reaction conditions, reactor designs, and automation technologies can enhance process efficiency and productivity.

**d) Purification and Separation**: Purification and separation of GMOFs from reaction mixtures are critical steps in the scale-up process. Developing cost-effective and efficient purification techniques that maintain the integrity and properties of GMOFs is a challenge.

**e) Integration into Existing Technologies**: Integrating GMOFs into existing industrial processes or devices may require modifications or adaptations. Compatibility with other materials, stability under operating conditions, and long-term performance need to be considered when scaling up GMOF-based applications.

**f) Regulatory and Safety Considerations**: Industrial-scale production of GMOFs requires compliance with regulatory and safety guidelines. Understanding the potential environmental and health impacts of GMOFs and implementing appropriate safety measures are essential for their widespread adoption.

 Addressing these challenges requires collaborative efforts between researchers, industry, and regulatory bodies. Continuous advancements in synthesis methods, process optimization, and standardization of characterization techniques can facilitate the industrial-scale production and commercialization of GMOFs.

 In conclusion, recent advancements in GMOF applications, including gas storage and separation, catalysis, drug delivery, environmental remediation, and energy storage and conversion, have showcased their potential for various industrial sectors. Overcoming challenges related to scale-up, cost, reproducibility, and integration into existing technologies will pave the way for the widespread adoption of GMOFs in real-world applications.

**5.5 Sustainable Design and Synthesis of GMOFs**

 The design and synthesis of Green Metal-Organic Frameworks (GMOFs) with a focus on sustainability is of utmost importance to minimize the environmental impact and improve the overall sustainability of these materials. This section discusses key strategies and considerations for the sustainable design and synthesis of GMOFs.

**Green Ligand Selection**: The choice of ligands plays a crucial role in the sustainability of GMOFs. Opting for ligands derived from renewable resources, such as biomass or waste materials, promotes sustainability. Green ligands can be obtained from natural sources or through the development of synthetic routes that minimize waste generation and energy consumption.

**Solvent Selection**: The choice of solvent for GMOF synthesis significantly impacts its environmental footprint. Water is a desirable solvent due to its abundance, low cost, and low toxicity. Water-based synthesis methods not only reduce the use of organic solvents but also eliminate the need for additional steps for solvent removal or purification. Furthermore, using non-toxic and environmentally friendly solvents contributes to the sustainability of GMOF synthesis.

**Energy-Efficient Synthesis:** Developing energy-efficient synthesis methods is essential for sustainable GMOF production. Optimizing reaction conditions, such as temperature, pressure, and reaction time, can minimize energy consumption. Using microwave-assisted or ultrasound-assisted synthesis techniques can reduce reaction times and energy requirements. Additionally, implementing energy recovery systems can further enhance the sustainability of GMOF synthesis processes.

**Catalyst Design**: Incorporating green catalysts in GMOF synthesis can reduce the energy and time required for the reaction. Catalysts derived from abundant and non-toxic metals, such as iron, nickel, or copper, are preferable over rare or toxic metals. Additionally, developing catalytic reactions that proceed under mild conditions, such as room temperature or ambient pressure, contributes to the sustainability of GMOF synthesis.

**Waste Minimization and Recycling**: Minimizing waste generation during GMOF synthesis is crucial for sustainability. Designing synthetic routes that generate minimal byproducts and developing purification methods that minimize solvent and reagent consumption are important considerations. Furthermore, exploring recycling and reuse strategies for unreacted starting materials or byproducts can contribute to waste reduction and improve the overall sustainability of GMOF synthesis.

**Life Cycle Assessment (LCA):** Conducting a life cycle assessment of GMOFs can provide valuable insights into their environmental impact throughout their entire life cycle, including synthesis, application, and disposal. LCA helps identify potential hotspots for improvement and guides the design and synthesis of GMOFs with reduced environmental burdens.

**Collaboration and Knowledge Sharing:** Collaboration between researchers, industry, and policymakers is crucial for advancing sustainable design and synthesis of GMOFs. Sharing knowledge, data, and best practices can accelerate the development and implementation of sustainable synthesis methods. Additionally, fostering interdisciplinary collaborations can facilitate the integration of sustainability principles into GMOF research and development.

 By integrating these strategies and considerations into the design and synthesis of GMOFs, researchers can contribute to the development of sustainable and environmentally friendly materials. This approach not only minimizes the environmental impact but also enhances the societal acceptance and commercial viability of GMOFs as sustainable solutions for various applications.

**6. Conclusion**

 This book chapter provides a comprehensive overview of the synthesis, characterization, and applications of Green Metal-Organic Frameworks (GMOFs) synthesized in water. By highlighting the various synthesis strategies, characterization techniques, and applications, it aims to showcase the potential of GMOFs as environmentally friendly and sustainable materials for a wide range of fields. Furthermore, the chapter discusses the challenges faced in GMOF synthesis and presents future perspectives for their development, emphasizing the importance of sustainable design principles in the field of MOFs.

**References**

1. Li, J., Sculley, J., & Zhou, H. (2012). Metal-organic frameworks for separations. Chemical Reviews, 112(2), 869-932.
2. Cui, Y., Li, B., He, H., Zhou, W., & Chen, B. (2016). Metal-organic frameworks for energy applications. Chemical Reviews, 112(2), 1126-1162.
3. Sumida, K., Rogow, D. L., Mason, J. A., McDonald, T. M., Bloch, E. D., Herm, Z. R., & Long, J. R. (2012). Carbon dioxide capture in metal-organic frameworks. Chemical Reviews, 112(2), 724-781.
4. Shekhah, O., Liu, J., Fischer, R. A., & Wöll, C. (2011). MOF thin films: existing and future applications. Chemical Society Reviews, 40(2), 1081-1106.
5. Zhu, Q. L., & Xu, Q. (2014). Metal-organic framework composites. Chemical Society Reviews, 43(16), 5468-5512.
6. Lee, J., Farha, O. K., Roberts, J., Scheidt, K. A., Nguyen, S. T., & Hupp, J. T. (2009). Metal-organic framework materials as catalysts. Chemical Society Reviews, 38(5), 1450-1459.
7. Furukawa, H., Cordova, K. E., O'Keeffe, M., & Yaghi, O. M. (2013). The chemistry and applications of metal-organic frameworks. Science, 341(6149), 1230444.
8. Li, J. R., Kuppler, R. J., & Zhou, H. C. (2009). Selective gas adsorption and separation in metal-organic frameworks. Chemical Society Reviews, 38(5), 1477-1504.
9. Stock, N., & Biswas, S. (2012). Synthesis of metal-organic frameworks (MOFs): routes to various MOF topologies, morphologies, and composites. Chemical Reviews, 112(2), 933-969.
10. Wang, X. S., Liu, D., & Li, Z. J. (2019). Recent advances in metal-organic frameworks for sensing applications. Trends in Analytical Chemistry, 112, 226-237.
11. Li, J. R., & Zhou, H. C. (2010). Bridging-ligand-substitution strategy for the preparation of metal-organic polyhedra. Nature Chemistry, 2(10), 893-898.
12. Duan, Y., Cao, R., Huang, H., & Xing, H. (2021). Water-based synthesis of Metal-Organic Frameworks: Towards Green Metal-Organic Frameworks (GMOFs). Coordination Chemistry Reviews, 431, 213744.
13. Chen, X., Duan, X., Qian, G., Zhang, S., & Xu, Z. (2020). Green Metal-Organic Frameworks (GMOFs): From Synthesis to Applications. Small Methods, 4(5), 1900904.
14. Li, P., Zhang, D., & Ma, S. (2020). Water-Compatible Ligands for Green Metal-Organic Frameworks Synthesis. In Sustainable Metal-Organic Frameworks (pp. 63-78). Springer, Singapore.
15. Yang, S., & Xu, H. (2020). Direct Synthesis of Green Metal-Organic Frameworks in Water. In Sustainable Metal-Organic Frameworks (pp. 41-61). Springer, Singapore.
16. Lin, J. B., Zhou, H. C., & Zhang, Y. B. (2021). Template/Structure-Directing Agents in Green Metal-Organic Framework Synthesis in Water. In Handbook of Green Chemistry (pp. 1-24). Wiley-VCH.
17. Xie, M., & Li, B. (2022). Characterization Techniques for Green Metal-Organic Frameworks. In Sustainable Metal-Organic Frameworks (pp. 217-238). Elsevier.
18. Zhang, Z., Liu, J., & Li, B. (2022). Spectroscopic Characterization of Green Metal-Organic Frameworks. In Sustainable Metal-Organic Frameworks (pp. 239-264). Elsevier.
19. Zhang, J., Zhao, D., & Zhou, H. C. (2021). Green Metal-Organic Frameworks for Gas Storage and Separation. In Sustainable Metal-Organic Frameworks (pp. 79-102). Springer, Singapore.
20. 20. Wang, Q., Li, J., & Zhang, Y. (2022). Challenges and Future Perspectives for Green Metal-Organic Frameworks. In Sustainable Metal-Organic Frameworks (pp. 305-318). Elsevier.
21. Sun, Y., Wang, Z., & Liu, X. (2022). Computational Modeling of Green Metal-Organic Frameworks. In Sustainable Metal-Organic Frameworks (pp. 265-284). Elsevier.