Porous framework materials for capture and storage

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Porous Framework Materials for Capture and Storage

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Porous Framework Materials for Capture and Storage

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ABSTRACT

Porous framework materials have been widely studied, due to their numerous attracted intrinsic properties. With the extensive development of this field, incorporating exotic functional anchors have become a new theme to enrich and develop the usage of such materials, which inspires much interest of fabricating hierarchical materials. The implantation of multiple functional anchors to host framework materials not only brings attracting structural backbone and physical properties but also opens new routes for the extensive development of such materials in chemistry, material science and engineering. The primary focus of this thesis has been made to compare the recent advancements of porous framework materials in structure and post-functionalization, and analyse their advantages and disadvantages in structural design and application performance so that some critical challenges can be summarized and research motivation can be thus inspired. Next, our three-works related to the porous framework materials design based on the above analysis were introduced and discussed in details, ranging from the decoration of structure, to external polymer incorporation, and to improve its conductivity via conjugated bonding. Subsequently, summary and outlook in this rapidly developing area are finally discussed. Clearly, such unique porous framework materials will continue to attract the increasing attention, and the display stage will be offered to them in future, owing to their superior application potential.

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Chapter 1: Advancement of Porous Framework Materials in Structure and Application

Abstract

Porous framework materials, main in metal-organic frameworks and covalent-organic frameworks, which are constructed via linking the inorganic metal sites and organic ligands to make an extended and ordered network, is currently gaining tremendous research interest. The intrinsic design renders the porous materials various structural characters, such as the building unit from the selected metal site and organic linkers, the defined nanospace, and the uniform porosity. In such context, more functions are expected to integrate with pore for fabrication of more smart and useful materials. As a result, the field has bloomed in the past decade, such as efforts in physical encapsulation and chemical bonding, and they have been widely applied, like protecting cover, trace detection and energy storage. In this chapter, the recent developments of porous framework materials and their outstanding performance in the abovementioned aspects will be described. In addition, the fabrication strategies and the extensive development of such materials in previously mentioned applications will also be reviewed. Finally, my research motivation from these progresses and my scientific contribution for the whole thesis will be demonstrated.

1.1 Introduction

Porous framework materials, particularly metal-organic frameworks (MOF) and covalent-organic frameworks (COF), have been a burgeoning class of porous materials, ranking closely behind the porous carbon and silica. Since its discovery by Yaghi and co-workers in 1995^{1,2} it continues to be a hot topic with thousands of publications annually, owing to their outstanding structural characters and physicochemical properties.³ Its chemistry is quite different from the conventional chemistry, whereby the framework is assembled by first linking the specific metal sites and the molecular units or linking the organic linkages with well-defined shape before forming a periodic network.^{4,5} Such assembling strategy allows the construction of permanently microporous materials with amazing internal surface areas, well-defined and uniform pore as well as easy-tunable cavity space.⁶⁻⁸ Undoubtedly, more in-depth investigation into better utilization of the internal structure is highly desirable. In addition, the integration of smart functions has become an interesting area to explore when functionalizing such materials over the past few years.^{9,10} There are various approaches to achieve these smart functions. Some researchers choose to target the design of functional organic linkers and selection of metal sites¹¹⁻¹³ while others focus on the post-functionalization of the assembled framework materials.¹⁴⁻¹⁶ On top of them, another approach is to utilize the remaining space in the frameworks to upload versatile materials for the implantation of smart functions.¹⁷⁻¹⁹

As a well-known leading figure in the field, Omar M. Yaghi's group has contributed a lot to the science and applications of such framework materials for the past years, ranging from the designing of building blocks, to the selection of transition metal site and organic linkages, and to the integration of multiple functions.^{5,11,20,21} Since the first report on porous

framework material in 1995, more than 2500 robust regular structures have been developed around the world and this number even exceeds the amount of porous zeolites or carbon materials. In terms of physical property, this kind of materials exhibit ultrahigh surface areas (the highest one reported to date has managed to attain up to $\sim 7,000 \text{ m}^2/\text{g}$),²² which is unquestionably superior to the conventional porous materials. Moreover, the exceptional characteristic of physical stability in air and at the temperatures up to 500°C has attracted increasing interest as it demonstrates their promising potential for industrial applications.²³⁻²⁵ In terms of material preparation, simple, easy-to-handle and high-yielding synthetic strategies have been developed in recent years^{26,27} to replace the challenges of time-consuming and complicated syntheses as well as stringent reaction conditions, thereby simplifying the introduction of variations in combinations of the inorganic metal clusters and the organic linkers, required for optimizing their performance in practical usage.

With such superior structural characteristics and physical properties, such framework materials have triggered much research interest and many scientists in various fields continue their pursuit to explore its potential. Unfortunately, the required rigorous assembly conditions adversely hinder the development of integrating multiple functions on frameworks. In order to explore the use of such materials in different fields, various solutions have been recently developed, as such the easy-to-handle assembling strategy, and post-functionalization to strengthen the properties of materials, as well as the diverse performance exploration in difference fields. It is worthy to be noted that the implantation of external functions, regardless in structure decoration or in hybrid fabrication, has gained attention rapidly as it allows the self-assembly of any expected unit involving inorganic nanoparticles, organic materials and biological macromolecules. For example, MOF acts as a protection cover to

enhance the overall stability. Besides that, its superior structural characteristics, like uniform porosity and ultrahigh surface area, do not have any adverse effect on the properties of the encapsulated object, even if it is in contact with the exterior surface. In addition, its tunable pore sizes ranging from sub-nanometer level to micrometer level, the high surface area up to 7000 m²/g, and relatively low tap density less than 0.13 g/cm³ have far exceeded general porous materials.²² Thus, a smart combination of framework materials and other functional materials should allow efficient harnessing of their strengths, maximizing their potential and diversifying their applications, like guest molecule absorption, heterogeneous catalysis, chemical sensing and molecule recognition (Scheme 1.1).

This chapter first presents the recent progression of post-functionalizing framework materials in their fabrication, function integration and performance in different areas, where we will selectively focus on their applications in lithium ion storage, stimuli-response and molecule recognition. In addition, the roles and performances of framework materials will be evaluated objectively. Following which, my research interest and motivation in the niche will be introduced for subsequent understanding of my research progress.

Scheme 1.1 Graphic illustration of function implantation and pore engineering design to further develop framework-based hybrids. Reproduced with permission from ref. 28. Copyright 2015 American Chemical Society.

1.2 Post-functionalizing porous framework materials with inorganic nanoparticles

The development of hybrids of MOF incorporating with inorganic nanoparticles dated back a decade. Notably, their intrinsic particular properties are different from those of bulk analogues. The reasonable incorporation effectively solved the problems of easy aggregation and challenge of fusion of inorganic nanoparticles during long-range lodgment, handling and performing. Also, the robust thermal stability and available pore nanospace from MOF improve the overall resistance while the encapsulated material continues to be in contact with the exterior. Hence, the utilization of MOFs as support platform to improve the current problem of easy-aggregation and dispersion in practical applications is an absolutely smart choice. In this section, I have categorized several notable advancements of MOF-based hybrids based on their synthetic strategies, morphology tuning and performance optimization, in which the discussion on their performance will be mainly centered on catalysis, optoelectronic and stimuli-response.

Scheme 1.2 Representative structures of the composites consisted of metal nanoparticles and a MOF. Reproduced with permission from ref. 29. Copyright 2016 American Chemical Society.

Conventional synthetic techniques have been summarized in Scheme 1.2, such as directly upload upon surface energy defect, bonding *via* the interaction with the secondary building unit (SBU) and growing isorecticular porous materials to cover the inorganic

nanoparticle seed. Direct deposition of nanoparticles on the MOF surface generally relies on the assistance of physical surface energy balance, thermal evaporation, and sputtering method.^{30,31} These techniques incorporate both inorganic nanoparticles and MOF well to form an integrate. The method of physical surface energy balance makes use of the vacancy defect to drive the combination of nanoparticle and porous MOF, as in the case of conventional porous silica nanoparticles. As for thermal evaporation, it undergoes vapor deposition, which often requires a vacuum chamber to carry out this process. The third method enables the coverage of nanoparticles on the surface of MOF by sputtering. By using these strategies, the inorganic nanoparticles can be successfully uploaded to the porous MOF while the uniform porosity and stable structure of MOF remain, resulting in a smart integrate with advantages of the individual constructs.

Scheme 1.3 Schematic illustration of conventional synthetic techniques for the hybrids of MOF decorating inorganic nanoparticles: (a) upon surface energy defect to decorate nanoparticles on the surface of MOF; (b) chemical post-synthesis for combining inorganic nanoparticle and MOF;

Copyright 2014 Nature. (c) Shaped nanoparticles wrapped by MOF. Copyright 2016 Royal Society of Chemistry and 2014 Nature Publishing Group and 2016 Wiley-VCH.

Alternatively, some chemical strategies have been developed as shown in Scheme 1.3b. One classic representative is the introduction of specific functional group on the ligand to allow bonding with the inorganic components, like charged matter, metal nanoparticles and biological macromolecules, as shown in Figure 1.1. Many works by Yaghi and co-workers showcased the benefits of this strategy. In 2009, his student, Li Qiaowei grafted molecule recognition units to MOFs for selective entrapping of other objects depending on their interactions (Figure 1.1a), whereby an erect organic linker was implanted with a macrocyclic crown-ether as a recognition site that is capable of binding to various matters.¹² Subsequently, this work was developed by his group, in which a variety of functionalities were incorporated on linkages with varying ratios in a way that combines the linker,¹⁶ rather than forming independent blocks as shown in Figure 1.2. Our group also explored its ability of binding to metal ions. In 2012, we reported our work on two rigid MOFs functionalized with the small crown-ether macrocycle as recognition site.¹³ Although they showed the unexpected interpenetrated structures, its capability of binding to metal ions inspired our further exploration. Later, we designed a shorter linker to improve the interpenetrated structure.³² As predicted, the separated strut showed a high surface area and selective gas absorption. In addition, we studied its ability of storing lithium ions. To our delight, the designed MOF could undergo a large amount of Li^+ storage without destroying the framework, which was calculated to be an average of 0.7 Li^+ ion to one crown-ether macrocycle for the whole crystal structure, due to the rich specific sites in MOF.

Figure 1.1 (a) Illustration of polyether units are implanted into organic linker and the MOF formation using them, where $[\text{Zn}_4\text{O}(\text{CO}_2)_6]$ is used as metal site (green building blocks) and organic linker is exhibited in grey rods and the recognition unit is highlighted in red rings; (b) Crystal superstructures of two crown ether-based MOFs that have an interpenetrated structure; (c) Single crystal structure of a crown ether unit grafted on a short linkage to construct the building block, where metal joints are still using $[\text{Zn}_4\text{O}(\text{CO}_2)_6]$ colored with blue and crown ether units is colored with yellow contrasting to the gray organic linker. Reproduced with permission from ref. 13,32,33. Copyright 2009 Science, 2013 and 2016 Royal Society of Chemistry.

With continuous development and much effort, multivariate functions have been grafted on the MOF, enabling the direct interaction of MOF with inorganic nanoparticles. However, key challenges for the abovementioned strategies are the complicated syntheses and the required post-processing efforts, retarding its further exploitation. To overcome this challenge, we turned to other techniques. Self-assembly is a well-known method that has been widely used in supramolecular chemistry, nano-chemistry and biological chemistry. One advantage is its simple procedures and some can even be prepared under ambient conditions. Therefore, it is not surprising that this methodology of making MOF incorporating nanoparticles is gaining interest increasingly. Such composites can be synthesized by either directly uploading nanoparticles using the cavity space of MOF such

that small nanoparticles or clusters can be embedded inside, or by using MOF to encapsulate pre-synthesized nanoparticles, in which the nanoparticles are usually pretreated with some surfactants or phase-transfer agents. However, for the two mentioned methods, there is a possibility that the size of nanoparticle exceeds the pore space of MOF, resulting in its growth on the surface of MOF instead of immobilization inside, or staying inside MOF but breaking its structure.

Figure 1.2. Illustration of a wide variety of combination of functional linkers to fabricate MOF. Reproduced with permission from ref. 16. Copyright 2010 Science.

Apart from the mentioned undesired possibility, there are additional drawbacks that could be further improved. For example, it is hard to fully harness the benefits of the nanoparticles if the desired nanoparticles are totally confined in the cavity space of MOF. Next, the control of the morphology and composition of the incorporated nanoparticles is mandatory as it will definitely influence relevant properties of the particles but still remains a challenge. In addition, the aggregation of nanoparticles is a common problem because they are very sensitive to the surrounding environment. Up to date, the integration of multivariate nanoparticles within one MOF matrix possessing a reasonable spatial distribution has not been realized yet.

In order to address the problems, Huo and co-workers reported a smart and tunable encapsulation method that activates the various hybrid combinations of inorganic objects and MOF as shown in Figure 1.3, in which the nanoparticles are pretreated with a specific surfactant to improve the dispersion and enable the growth of MOF crystals by surrounding them. In this way, the continuous incorporation of nanoparticles on the successively generated surfaces of the growing MOF effectively controls the amount of encapsulated nanoparticles and the distribution these nanoparticles in the MOF cavities can be modulated by adjusting the ratio of the pretreated nanoparticle with surfactant and the reagents forming MOF crystal, as well as the addition time during the formation of MOF crystal.

Figure 1.3. Schematic graphic of the controllable incorporation of nanoparticles in the cavities of MOF. Reproduced with permission from ref. 34. Copyright 2012 Nature Publishing Group.

Figure 1.4 (a) Graphic illustration of the deposition of shaped metal nanoparticles on the MOF upon the assistance of reductant; SPM characterizations of the nanostructured hybrids consist of metal and

MIL-101: (b) Pt, (c, d) Pd, and (e) Pt-Pd alloy. Reproduced with permission from ref. 35. Copyright 2013 American Chemical Society.

In a recent review on the progress of MOF hybrids by Xu and co-workers, a significant work on immobilizing metal nanoparticles with polyhedral shape by simple wetting and subsequent reduction was reported and the methodology proved to be applicable for both monometallic and bimetallic nanocrystals. In the presence of a reductant, several metal nanoparticles, including Pd, Pt and their alloys, could be successfully reduced and deposited on the surface of MOF. Besides that, their morphologies were also controllable with various sizes and polyhedral shapes (Figure 2). In this method, the reducing agents, i.e. CO and H₂, were firstly bonded on the MOF surface, enabling these metals to be directly reduced and deposited on MOF facets. Even in Pt-Pd alloy crystal, it showed the same reducing effect as the monometallic nanoparticles and it was proven to be capable of fabricating the core-shell structure.

Figure 1.5 (a) Graphic illustration of the implantation of Au-Ni alloy both in the MOF surface and cavity upon the concentration-dependent reduction method. (b-d) TEM images of alloy@MOF hybrid achieved when the concentration of reductant at 0.6, 0.4 and 0.2 M, respectively. Reproduced with permission from ref. 36. Copyright 2013 American Chemical Society.

Although the strategy of using MOFs to confine the growth of nanoparticles looks simple and effective, the resultant nanoparticles unfortunately faced the problem of aggregating on the deposition surface, resulting in an adverse effect on the performance. To address the mentioned drawback, a novel method using hydrophilic-hydrophobic solvent helped improve the aggregation,^{35,36} whereby metal nanoparticle precursors were absorbed in the hydrophilic solvent, followed by suspending them in the hydrophobic medium with large amount. The larger inner surface area of MOF effectively minimized the deposition of metal nanoparticles outside the MOF, regardless whether the metal precursor enters the hydrophilic channel or not. By applying such strategy with the assistance of a reductant, various metal nanoparticles could be successfully reduced and dispersed inside the cavity of MOF without aggregation. Moreover, the amount of metal nanoparticles immobilized in the cavity of MOF could be controlled *via* tuning the density of the metal precursor. In the experiment, it is found that non-noble metal nanoparticles are hard to be reduced even in the presence of strong reducing agent, owing to the instability at high reaction temperatures and poor physical stability. To address the critical issue, a new and more powerful reduction strategy using NaBH_4 in double liquid mediums was introduced. It could reduce non-noble metal nanoparticle *in situ* at the solid-liquid surface and immobilized them into the cavity of MOF, assuming that an excess of NaBH_4 was added so that the metal presomas deposited on the inner surface of MOF were completely reduced in the channel of MOF with its addition and followed by fixation onto the cavity by capillary force. Based on the experimental observation, no aggregated nanoparticle on the surface of MOF was observed (Figure 1.5), as opposed to some metal nanoparticles remaining outside the MOF if the reduction of metal precursor was not completed. Indeed, the aggregated nanoparticles have not been found in

the analysis of electron microscopy images and only well-dispersed metal nanoparticles with uniform size and confined shape was observed to be immobilized in the pore of MOF.

1.3 Post-functionalizing porous framework materials with organic objects

Inspired by the success in the area of inorganic nanoparticle/MOF composites, scientists turn to looking into the integration of organic particles and MOF materials to form structures that could be precisely controlled. Till date, many MOF-organic material hybrids have been reported, including small molecules, shaped organic nanoparticles polymers and biological macromolecules, owing to their functional diversity and ease of structural tuning. A careful examination of reported works pinpointed the following crucial key factors for success: (a) organic particles should be kept stable in organic solvents, such as DMF and methanol; and (b) the large interfacial energy between organic particles and MOFs should be minimized. With these factors in mind, the importance and potential of organic nanoparticle@MOF core-shell structures could then be investigated, especially for sensor and biological detection. Notably, a number of artificial MOF cells storing organic molecules have been designed over the past few years (Figure 1.6), in which synergistic effect has been exhibited whereby the organic object as functional core responds to external stimulation while MOF with high surface area and porosity provides platform for separation and reactor space. In addition, scientists have utilized the porous character of MOF to construct the two dimensions (2D) or three dimensions (3D) organic materials. This strategy avoids the difficult self-assembling and enables the growing step to be directly performed, hence simplifying the micro-nano fabrication. This kind of hybrid will be discussed in detail,

through showcasing several representative works on the smart design, optimized performance and their potential applications.

In 2012, a bio-inspired dynamic system based on a hybrid of MOF and peptide was developed by Kitagawa's group (Figure 1.6a),³⁷ in which guest molecules staying in a state of uniform alignment can be freely released which the highly-ordered structure remains intact in the process. In this system, the complex framework of MOF was assembled by covering the peptide as the storage unit, while the peptide stayed inside the cavities of MOF to supply energy. This design is able to overcome the low energy transfer efficiency caused by the random organic molecules discharging. Furthermore, the platform with certain surface-tension getting in the re-assembling of hydrophobic peptides can successively supply power to its dynamic movement. As a consequence, the ca. speed dependent on the volume for the hybrid nanoparticle is enhanced and the generated energy for the whole system exceeds twice that of the previous conventional solid-liquid systems.

Next, the incorporation of organic shaped particles with MOF has been gradually developed to include emissive chromophore, bio-macromolecules and polymeric molecules. There were two notable works combining chromophores with MOF to achieve emissive composites. Lan and co-workers constructed an emissive chromophore-MOF hybrid with white emission that consisted of stable mesoporous MOF with blue emission serving as the host and a complex of aluminum and quinoxaline with yellow-green emission as the guest (Figure 1.6b).³⁸ The composite possesses excellent stability and tunable luminescent emission. While the tunable fluorescent characteristics of luminescent MOFs have been previously reported by using chemically functionalized organic ligands or adjusting specific metal clusters, the low luminous efficacy is a major drawback which restricts their usage

even though they have superior stability. Hence, the uploading of guest chromophores is a novel solution to avoid the problem. This strategy has attracted much attention especially since white-light emission can be achieved.

Figure 1.6 Schematic illustration of several encapsulation strategies for MOF-based hybrids: (a) Structure of hybrid peptide–MOF motor. Reproduced with permission from ref. 37. (b) Encapsulating apposite chromophores into MOF for tunable luminescence emission; Reproduced with permission from ref. 38. (c) Synthesis of DNA–MOF hybrid for biological application; (d) The fabrication of polymer–MOF hybrid for ion exchanging. Reproduced with permission from ref. 39. Copyright 2012 Nature Publishing Group, 2015 Royal Society of Chemistry, 2014 Nature Publishing Group and 2014 American Chemical Society.

Following which, Wong et al. also developed a serial of luminescent particle/MOF composites by employing polyvinylpyrrolidone-modified organic crystals as seeds, which is inspired by luminescent metal–organic complexes and the composition of ZIF-8. Amorphous Znq_2 powder was chosen as the candidate, due to the fact that it is generally insoluble in most organic solvents except DMSO, to ensure its stability in organic solvents. Next, a similar approach as Huo was adopted, in which an amphiphilic surfactant of PVP was used to improve the surface energy of organic polyhedron for further encapsulation, which allowed

the crystal of ZIF-8 to grow on the Znq_2 seeds. Notably, the rational selection of appropriate organic species enables more functional organic particle/MOF composites with specific structures to be realized.

In 2014, Xia and co-workers incorporated the biomolecule, DNA, to MOF *via* simple self-assembly of electrostatic attraction and the hydrophilicity-hydrophobicity interaction (Figure 1.6c).⁴⁰ Significantly, the addition of MOF for the whole hybrid not only enhanced the physical stability of nanostructured biomolecule in aqueous medium, it also enriched the library of bio-molecule-based hybrids. In this work, a tetrahedral nano-assembly was firstly constructed by several separate oligonucleotides, followed by encapsulation by MOF. The difference from Wong's works is that no surfactant is required and a metal complex, water-insoluble $\text{Pd}_{12}\text{L}_{24}$ sphere framework was chosen to bind with DNA instead. The pyridine group in ligand coordinated with Pd^{2+} and the built polyhedron could be used for accommodating the nanostructured biomolecules in its center space. Finally, a composite material (Pd_6L_4 -3D DNA) promoting the stability of DNA in water was achieved and this provided the platform for extensive research.

In 2014, the hybrid of polymer threaded in MOF was developed by Chan et al. (Figure 1.6d),³⁹ in which the ion-exchange behavior was studied, through the confined space in the MOF threaded by polymer. This was the first report of selective ion-exchange in porous MOF integrating the porosity and breathing effect. It addressed some existing shortcomings of ion-exchange molecules, such as amorphous porosity and inaccessible reacting sites. In addition, a desired synergistic effect was observed in this hybrid, in which the interlocked polymer could stay in aqueous medium under the protection of MOF, while the high porosity and thin thickness of MOF covering did not have any adverse effect on the

polymer in contact with external environment. This study inspired much research interest and some related works have been reported later. We will also disclose our work of using a MOF with large porosity as host and thread an emissive polymer as functional core to respond to external stimulation later in Chapter 4.

Figure 1.7 Graphic illustration of polymer growing in the cavity of MOF: (A-B): the set-up of electrode using MOF/polymer/Pt electrode and then covering with aniline; (C-D): the electrochemical reaction; (E-F): the preparation for the followed polymerization of aniline; (K-L): the structure of MOF and the simulated structure of MOF after polymerization; M: the 3D cross-linked nano-polymer. Reproduced with permission from ref. 41. Copyright 2014 Wiley-VCH.

Upon the threaded growing of polymer in porous MOF, Qiu and co-workers constructed a 3D microporous conductive polymer (Figure 1.7).⁴¹ As we know, both linear extensive structure and small surface area are two key properties for conventional polymers.

With the development of covalent-organic framework, the polymers have been upgraded

from linear backbone to platform framework. Although the common redox, deposition, and the opto-electronic conversion could similarly activate the polymers, the conductivity could not meet the demand, which is possibly caused by the insufficient π - π stacking style and the relatively low charge flow. Hence, scientists look into bridging the linear-backbone structure into a 3D architecture while providing both pore-riched and high electricity. In this work, polyaniline was chosen due to its promising opto-electrical properties. The MOFs were employed as the sacrifice templates to induce the growth of polymer. The achieved polymer in this way showed a well-defined spatial structure. Moreover, its porosity and surface area have been significantly enhanced. It also exhibited a conductance of 0.125 S cm^{-1} upon the addition of I_2 . Its excellent conductivity as compared to the classic porous materials makes it a key candidate for future development.

Kitagawa et al. also contributed much to the polymer-assisted MOF. The first milestone of ordered alignment of polymer chains was developed by his group, in which they utilized a method called “well-organized crosslinks” to induce the polymer growth in highly uniform crystalline, where a cross-linker was embedded in a coordination polymer with porous structure and followed by a polymerization of styrene in the channels of the host polymer (Figure 1.8).⁴² Notably, the methodology can be generalized for other vinyl monomers. Prior to this discovery, the chain alignment is only applicable in semi-crystalline polymeric materials growing extensively in lamellar direction, despite the fact that the study of introducing the disordered chain to the polymeric materials has been ongoing for some time. Furthermore, the complicated condition of crystallinity in polymers definitely limits its extensive exploration, such as high microstructural regularity, particular polymeric sites for extensive growth and the requirement of catalysts. The reported strategy activated the high

crystallinity in polymeric materials by inducing crosslinking during the crystalline formation process and ensuring the polymer chains were in well-defined states, where the anisotropic property of polymer could be amplified by coherent macromolecular alignment. The highly ordered polymer chain also offers the possibility of controlling the growth of polymeric chains at multiple dimensions and provides opportunity for the space to be extensively functionalized.

Figure 1.8 Schematic illustration of MOF deposition on the hybrid electrospun fibrous substrate. Reproduced with permission from ref. 42. Copyright 2013 Nature Publishing Group.

1.4 Multivariate applications for smart porous framework materials

Based on those above-discussed advantages of MOF-based hybrids, it is highly desirable to introduce multivariate functions to make them superior materials. In particular, some nanoparticles with attractive intrinsic properties, like high surface area, large volume and outstanding catalysis activity upon interaction with MOFs, are expected to improve the performance in gas selective capture, asymmetry catalysis and stimuli-response by relying on

the confinement effect of MOF for controlling the growth of nanoparticle and the selectivity from the porosity and channel of MOFs. Next, we will discuss some recent works on using MOF-based composites in protective coatings, sensing and energy storage.

1.4.1 Role as protective coatings

Recently, Wu et al. disclosed the deposition of several MOFs on ternary PVA/PAA/SiO₂ nanofibrous substrate in precursor solutions at high temperatures, including ZIF-8, HKUST-1 and MIL-53(Al), which were mainly prepared *via* solvothermal method (Figure 1.9).⁴³ The morphology, crystal structure and pore properties obtained during the deposition was systematically studied, as well as the thermal stability, which indicated that the hybrid electrospun fibrous mats were ideal adaptive substrates as guest MOF particles. The obtained MOF composites were flexible and the structure of support materials was intact after the deposition at high temperature. The fibrous substrate exhibited great potential for MOF crystal deposition and could be used directly without further modification or seeding procedure. MOF composite materials combined the advantages of highly porous structure and free-standing property, exhibiting improved chemical and physical performances as a new type of sorbents.

Figure 1.9 Schematic illustration of MOF deposition on the hybrid electrospun fibrous substrate. Reproduced with permission from ref. 43. Copyright 2016 American Chemical Society.

The sensitivity of bio-macromolecules towards the external environment is still a critical issue that scientists are facing. One solution is to optimize the practical performance in chemical assembling, processing and application, hence making it more robust. In 2015, Falcaro et al. reported a biomineralization method,⁴⁴ in which the biomacromolecules were completely encapsulated by porous MOF as protection cover. There are different strategies of inducing diverse biomacromolecules for this kind of coating formation. For bio-enzymes, peptide and DNA, the protective MOF were rapidly induced to form the coatings and the crystallization of MOF surrounding the bio-molecules was homogeneous and ordered. With the assistance of MOF coating, the final hybrid was ultra-stable and could withstand harsh conditions. Notably, the bioactivity of some bio-enzymes could be retained despite being subjected to strong heating conditions due to the protection of MOF shell while they usually undergo decomposition at high temperatures in their native form. In summary, the biomineralization strategy allows the potential utilization of more biomolecules.

Figure 1.10 Graphic representative of biomolecule-functionalized MOF hybrid, including peptide, bio-enzyme and genes, encapsulated within the pore cavity of MOF. Copyright 2015 Nature Publishing Group.

The synergistic assembly of MOF and biological units is the most attractive part in this work, in which MOF units were growing in a crystalline structure under the induction of biomacromolecules while surrounding the biomacromolecule as the protective coating at the same time. During this assembly, the growth of MOF have to accommodate the biomacromolecules, resulting in slight modification of the physical properties, like crystal shape, size and robustness, upon the induction of biomacromolecules to form new pore to encapsulate the bio-objects. The assembly of MOF encapsulating bio-enzyme showed that the protecting effect of MOF cover is superior to common porous materials, like silica nanoparticle and CaCO_3 , as the bioactivity of enzyme could be retained even under extreme conditions. In addition, encapsulation by MOF does not have any adverse effect on the delivery of the bio-object inside and its release could be realized easily *via* simple etching. With this strategy, the problem of poor stability for numerous bio-materials could be overcome and their practical usage could be realized. It addresses the major constraint of requiring anti-solvent macromolecules for the orientated growth of MOF for

biomacromolecules. Otherwise, it would adversely affect the encapsulation and subsequent post-synthetic infiltration. Notably, the method sufficiently showed the promising potential of biomimetic mineralization and effectively improved the current situation, including the assembling of bio-hybrids, the synergistic effect and their final performance in practical applications. Its generalization in applications would no doubt inspire further development of bio-mineralization.

Apart from these, the combination of MOF and polymeric material is also attracting increasing attention over the past years, of which blending is a common way for fabricating such hybrid. In particular, the direct deposition of MOF powder on the polymer membranes has been the most preferable way, using various polymeric materials and incorporation methods. However, there are some critical issues impairing in the direct deposition, like particle dispersion and the interaction of particle and membrane at the surface. Inspired by common gelation *via* the specific ion-exchange, Zhu and co-workers reported an interesting *in-situ* uploading method for directly incorporating MOF with a polymeric hydrogel substrate,⁴⁵ which addressed the limited processing of MOF deposit on the designed substrate.

Figure 1.11 Schematic illustration of the set-up of the hydrogel-MOF hybrid and the images of cross-linking of hydrogel with metal ions. Reproduced with permission from ref. 45. Copyright 2016 American Chemical Society.

The hydrogel-MOF hybrids were built by cross-linking metal ion exchange during the formation of MOF on the membrane substrate. In this *in-situ* growth, the MOG particles were distributed well on the surface of membrane then incorporated into the membrane instead of aggregating together. Moreover, the morphology of the hybrid is tunable among bulk, wires and sheet, depending on the morphology of gelation. Furthermore, such method has wide applications, ranging from HKUST analogue to other MOF analogues, like MIL and ZIF.

In order to investigate deeper on the interaction of hydrogel and MOF, such as the reason for integrating together, how MOF will grow on it and whether the ion exchange process will break MOF crystalline, the authors utilized the EDX technique to map elemental of the hydrogel-MOF hybrids, in which the distribution of each contained element was clearly shown (Figure 1.12). Notably, the difference between two kinds of MOFs was very distinct in the mapping of the constituent elements with the exception of carbon. The mapping of cobalt and nitrogen showed that they were the missing pieces to the other two kinds of elements mapping as shown in Figure 1.12B, which was beneficial to the analysis of the hydrogel-MOF formation and the process of ion exchanging.

Figure 1.12 Cross-section backscattered graphs of different MOF-based hybrid: (A) HKUST analogue and (B) ZIF analogue (the scale bar inset represents 60 μm) and the element analysis from EDX mapping. (C) The corresponding structures of chemicals using in this work. (D-E) Graphic illustration of the fabrication of MOF-based hybrids and their assembling process. Reproduced with permission from ref. 45. Copyright 2016 American Chemical Society.

In the assembling of hydrogel-MOF hybrid, the polymeric salt played an important role in the formation of hydrogel, which not only offered the binding sites for ions but also supplied the metal sources for the followed MOF integration. The selective ion-exchange process could be realized by the different degree of binding affinity between metal ions and complex sites. For example, copper ions were able to exchange with sodium but cobalt could not do so. It resulted in the formation of hydrogel-HKUST analogue and no hydrogel-ZIF analogue as seen in their chemical structures (Figure 1.12C-F). The resultant interactions between the copper ions and the hydrogel presoma ligands led to a complex effect which bound them together. In comparison to ZIF analogue formation, there was no binding

between the cobalt ions and the polymeric ligands, due to the weak interaction ability, hence the followed MOF growth failed.

Besides that, the issue of moisture sensitivity of MOFs has been addressed. In 2014, Jiang and co-workers reported an effective solution by converting the characteristics of the surface of MOFs from hydrophilic to hydrophobic.⁴⁶ A hydrophobic polydimethylsiloxane (PDMS) has been implanted on the MOF substrate to improve the hydrophilic-hydrophobic property by a facile vapor deposition technique significantly. As compared to conventional methods, this strategy could overcome drawbacks, such as reduced porosity, tedious procedure and complex instrumentation. Furthermore, it could be generalized to other weaker MOFs, including MOF-5, HKUST-1, and ZnBT. These coated samples could then inherit their original crystalline nature and pore characteristics. Strikingly, the surface areas of these MOFs were nearly 100% retained after PDMS-coating. Such a coating process might render MOFs applicable in the presence of water or humidity in areas such as gas sorption and catalysis.

Figure 1.13 Schematic illustration of PDMS-Coating on the Surface of MOFs and the Improvement of Moisture/Water Resistance of MOFs. Reproduced with permission from ref. 46. Copyright 2014 American Chemical Society.

Upon the facile polydimethylsiloxane (PDMS)-coating treatment to form a protective hydrophobic layer on the surface of MOFs for improving their moisture/water stability, these PDMS-coated MOFs significantly exhibited highly hydrophobic behavior and excellent moisture/water tolerance while retaining their inherent porosity. As compared to the pristine MOFs, all PDMS-coated samples exhibited water contact angles $130 \pm 2^\circ$, revealing their hydrophobic character (Figure 1.14a–f). To further study the performance of the polymeric membrane as covering layer, element distribution using a composition line-scan profile was conducted for coated MOF-5 (Figure 1.14g–h). The results indicated that a small amount of Si element uniformly existed on the crystal and the Si/Zn atom ratio was $\sim 4.1\%$, proving that the PDMS was successfully coated on the MOF surface. It is important to note that MOFs with total coating showed nearly intact porosity and unaltered surface area, which are crucial to many applications of MOFs, possibly due to the good permeability nature of the thin PDMS layer and/or incomplete MOF surface coating, which will open a new avenue to moisture/water stable MOFs.

Figure 1.14 Schematic illustration of Illustration of PDMS-Coating on the Surface of MOFs and the Improvement of Moisture/Water Resistance of MOFs. Reproduced with permission from ref. 46. Copyright 2015 Nature Publishing Group.

1.4.2 Porous framework materials support for sensing

In the past few years, MOF-based composites have also been applied to solid-state emissive materials *via* specific metal ion complex, chemical functionalization and uploading chromophore depending on their intrinsic structural characters. To date, lighting display using mercury (Hg) vapor as the main excitation source to achieve the photoluminescence from the corresponding semiconductor has been widely used in our daily life, such as the white-light luminescence. With this target in mind, scientists looked into porous MOFs as an option for luminescence since they could have multivariate metal sites and organic linkers. Besides that, their porosity would enable the incorporation of light-emissive building blocks

via physical encapsulation as uploading strategy as the naked MOFs could not have good performance.

In 2011, Kitagawa et al. reported a structure-dependent guest molecule detection fabricated by a fluorescent chromophore treaded in a porous network,⁴⁷ where a transformation of host structure to a new conformation was achieved by the introduction of guest molecules, resulting in a recognizable fluorescent signal. (Figure 1.15). Notably, the output luminescent signal was directly captured by the naked eyes, simplifying the requirement of recognition and activating immediate processing for well adapting to perspective complicated work conditions. The designed hybrid is particularly sensitive to acetylene, CO₂ and their analogues. This unprecedented example of detection using conformational alternation without any assistance of charge transfer or physical interaction is an attractive option for quantification of adsorption *via* the conformational change.

In comparison to the conventional detection strategies using energy transfer between host and guest molecules, its advantage lies in its versatility. Previously, gases used to induce luminescence are mainly limited to O₂ and NO₂ which could produce recognizable fluorescence signal. Furthermore, the quenching mechanism for energy transfer was also hard to accurately feedback the external threat. Although they offered some advantages like switchable and reversible properties for gas detection, they are lacking in areas such as the general responsiveness for multivariate gases, accurate and rapid response as well as recycling performance, hence limiting their performance. This work well addressed these critical issues by utilizing a smart conformation change caused by the incursion of guest molecules. The structural transformation of porous networks for the invaded guests led to a dynamic breadth by adapting to the addition of guests and causing the corresponding host-

guest recognition. This adjustment successfully resulted in the corresponding recognition information, which is according to the morphology and location of guest molecule.

Figure 1.15 Schematic illustration of MOF deposition on the hybrid electrospun fibrous substrate. Reproduced with permission from ref. 47. Copyright 2011 Nature Publishing Group.

Recently, there was a report on functionalizing ZnO with porous ZIF as guest separator to promote the response sensitivity and applied in vapor sensing. This study showcased the improved selectivity of metal oxide gas sensor which had previously been a huge challenge. Although there were many studies on promoting the sensing parameters, novel enhancement ways in simplifying the material fabrication, enhancing the response selectivity and sensitivity as well as overcoming the interference of environment and noise have yet to be achieved. In this work, Fan *et al.* successfully synthesized ZIF-8-protected

ZnO hybrids, in which ZnO nanorods were used as the self-template to provide Zn^{2+} sources for the subsequent crystallization of ZIF-8 and ZIF-8 was coated on the outside of ZnO nanorods as shell.⁴⁸ Zheng was the first to fabricate the well-defined ZnO@ZIF-8 nanorod with core-shell heterostructure, by utilizing the synthetic strategy with ZnO nanorods as self-sacrificial templates for the ZIF-8 shell.⁴⁹ It also triggered much research interest, such as Fan's work which explored the promising potential of ZnO@ZIF-8 in gas sensors with the assistance of porous ZIF. The solid performance of ZnO@ZIF-8 in gas sensing showed the significance of ZIF covering and its excellent selectivity for formaldehyde gas over ammonia, acetone, toluene, methanol and ethanol. Such performance was ascribed to the limited pore space of ZIF-8, hence rejecting the large guest objects and only permitting molecules with suitable sizes to enter and interact.

Figure 1.16 (a) Schematic diagram and (b) TEM image of the ZIF-8-protected ZnO hybrids synthesized with ZnO nanorods as a template in the mixed solvent at 70 °C for 24 h; (c) Two aperture sizes of ZIF-8 structure. (d) Graphic representation of the ZIF-8-protected ZnO hybrids sensor with selectivity for different vapor molecule. Reproduced with permission from ref. 48. Copyright 2015, American Chemical Society.

The sorption properties and structural versatility of metal–organic frameworks (MOFs) make them superior chemical sensing materials with high sensitivity and selectivity, where their high porosity for sorption offers the entry channel to screen out the proper guest molecules and activates the interaction of guest and the core material with higher sensitivity. Moreover, the thermal stabilities of many MOFs, typically exceeding 200 °C, are also beneficial for sensing application. As a result, MOFs have the potential to be utilized as future chemoselective sensing materials with wide range of chemical tunability. Comparing with commercialized sensor materials, MOFs could address the potential to meet the challenges of selectivity and reusability that impede the advancing of sensor devices.

For the implementation of MOF sensors, Li and co-workers proposed a simple yet powerful optical sensing motif based on ultrathin MOF-coated monolayer colloidal crystals (MCCs),⁵⁰ which provided high efficiency in vapor sensing through changes in their effective refractive index (RI). Two optical modes exist in this sensor, namely, photonic eigen modes and Fabry–Pérot oscillations, both of which could be used as the signal transducer. Selective response to a series of alcohols, water and acetonitrile was observed, reflecting the characteristic sorption properties of the integrated MOF, in which colorimetric reporting was readily achieved as shown in Figure 1.17. Linear response to a broad dynamic range of vapor concentration was realized too. The sensitivity was found to be closely dependent on the thickness of the MOF coating and could be further optimized accordingly. Ultrafast response time (<5 s) and excellent recyclability were also demonstrated. These substantial improvements in performance are attributed to the efficacy of signal transduction and the enhanced pore accessibility and diffusion efficiency, which are intrinsically endowed by the

optical motif design. Our findings should provide new insights into the design and fabrication of MOF sensors toward real-world applications.

Figure 1.17 Schematic diagram of fabricating the ultrathin MOF-coated monolayer colloidal crystals for optical sensing (above); Optical micrographs illustrating the variations in the color of the ultrathin MOF-coated MCCs supported by silicon wafers for an increasing PS sphere diameter (D) and number of ZIF-8 growth cycles (N). Each frame represents an actual area of $0.3 \times 0.3 \text{ mm}^2$ (below). Reproduced with permission from ref. 50. Copyright 2015, American Chemical Society.

Figure 1.18 (i) Graphic Illustration of fabricating the ultrathin MOF-coated monolayer colloidal crystals; (ii) SEM images with different magnifications illustrating the different morphologies of ultrathin MOF-

coated monolayer colloidal crystals for one (a, e), two (b, f), three (c, g), and four cycles (d, h) of ZIF-8 growth. Reproduced with permission from ref. 50. Copyright 2015, American Chemical Society.

During the signal transduction mentioned above, monolayer colloidal crystals were employed as the scaffold for deposition of ultrathin MOF films, resulting in ultrathin-MOF-coated crystals that could effectively convert molecular sorption into readable optical signals. These crystals have multiple merits in terms of lower needs in analyte quantity and compatibility with standard film processing techniques. The sensing performance in the aspects of sensitivity, selectivity, response and reusability could be altered by the choice of MOFs, in which size exclusion and chemically specific interactions could effectively enhance the strength of analyte binding. Response rate depends on the sorption kinetics, which is governed by the dynamics of analyte transport within MOFs. Structurally, the varying pore sizes of the frameworks activate the controlled diffusion, which reduces the mass transport resistance. The ability of enlarged pores to adsorb gas or vapor analytes is poorer as compared to small ones, thereby affecting the sensitivity. As a result, the sensor exhibits selective responses toward a series of vapors, a broad dynamic range, the capability of colorimetric reporting, ultrafast response rates, as well as an excellent stability and reusability. Therefore, this work should offer new insights into the design and fabrication of optical MOF sensors with optimized performance.

Besides that, there is one work developed by Li *et al.* allowing tracing of explosives using MOP and surface-enhanced Raman scattering (SERS),⁵¹ in which the cage of MOP was assembled by metal sites and organic linkers provided the space to temporarily accommodate guest molecules and permitted the interactions in the nanoreactor. In this case, the size of cage offers a platform of selectivity for screening out and binding with the invaded guest molecules, where the explosive molecules were the target guests. With the

assistance of SERS, the integrate exhibited enhanced detecting sensitivity, enabling the ultratrace monitor for trapping the existence of explosive.

Figure 1.19 Graphic representation of (a) the MOP assembly and its trapping capability of explosives, and b) the practical application of sensing explosives using the as-designed MOP with the assistance of plasmon. Reproduced with permission from ref. 51. Copyright 2015, WILEY-VCH.

Figure 1.20 The response behavior for the stimuli of explosives: (a) absorbance spectrum of monitoring the incursion of explosives using the as-designed MOP (from below to top: naked MOP, with the addition of TNT, and after the treatment of RDX); (b-c) concentration calibration of the

invaded explosive molecules at room temperature. Reproduced with permission from ref. 51. Copyright 2015, WILEY-VCH.

The above discussed method was then applied to some common explosives, like HMX, TNT, and RDX. This method utilized the pore space of MOP and the specific interaction between the MOP and explosives, in which the -NH_2 group on the organic linkers donates electrons and interacts with the invaded electron-poor explosives. It may involve acid-base neutralization, energy-transfer between electron donor and acceptor, thus facilitating the interaction of host-guest. The resultant synergistic effect effectively overcomes the exclusion from MOP for the incursion of exotic guest while the available pore space builds up a platform of selective response for screening of the incursion of explosives. It offers the advantage of a high detection sensitivity that is lower than nano-molar for the three mentioned explosives, making it significant for ultratrace detection. The proposed mechanism is also well-supported by the comparison of practical experimental result and theoretical calculation study. In summary, it inspires more interest and motivation for the further development due to its reversibility and recycling performance, making it suitable for potential large-scale application.

1.4.3 Porous framework materials support for energy storage

In the aspect of energy storage, MOF-based hybrids are gaining research interest increasingly. In particular, their superior performance in the electrochemical process triggers scientist' interest in their application to electrochemical energy storage, which includes surface uploading, encapsulation and exchange. Apart from that, there is also much research into their applications in the energy harvesting, energy conversion and energy storage process. In the past years, this promising potential of MOFs have been proven in lithium ion storage, solar energy conversion and carrier transportation in electronic equipments.

Figure 1.21 The applications of metal–organic frameworks in electric energy storage. Reproduced with permission from ref. 52. Copyright 2016 Elsevier.

In 2013, photosensitizer-functionalized MOFs were developed to address their limited absorption bands for solar photochemistry applications. Hupp and co-workers not only implanted the photosensitizer, i.e. porphyrin, to MOFs to enhance the photon-harvest but also introduced quantum dots to facilitate the energy transfer and thus optimizing its optical applications.⁵³ The introduction of quantum dots made up for the limited light-harvest ability of the MOFs and even facilitated the energy transfer with transferring efficiencies up to ~85%. As a result, more than 50% enhancement in light-harvest could be achieved based on such hybrid strategy. This is a great contribution to the area of fabricating hybrids of quantum dots and MOFs.

The integration of MOFs and quantum dots is due to the chemical binding between CdSe/ZnS core/shell quantum dots and MOFs. As we know, quantum dots semiconductor is different from these molecular building blocks, which have broad absorption spectra, desirable quantum yields and high efficiency of extinction. In the aspect of broad absorption, the coverage of whole optical spectrum had also been realized previously through the alternation of the size of quantum dots to complement the characteristics of MOFs to form a

hybrid with better photon-harvest ability. The matching energy levels between quantum dots and MOF enable the excitons from quantum dots to be easily delivered to the MOFs through the conventional PRET mechanism, i.e. photon resonance energy transfer, achieving transferring efficiency of up to ~85%. As such, the utilization of quantum dots to broaden the initial limited light-harvesting provides a valuable experience as reference for subsequent extensive research and opens up new route for improving the current challenges of MOF in photon energy harvesting.

Figure 1.12 Schematic illustration of the set-up of photosensitizer-functionalized MOFs and the implantation of quantum dots to MOFs promoting the photo-harvesting. Reproduced with permission from ref. 53. Copyright 2013, American Chemical Society.

In 2015, Zou and co-workers fabricated a cobalt sulfide (CoS_2)-doped porous polyhedron for enhancing the energy storage capacity. In their work, the cobalt not only binds to ionic sulfur but also acts as the metal site for the in-situ growth of MOF, in which ZIF-67 consisting of ionic Co and N-rich methylimidazole was chosen. As a result, ZIF-67 grew finely based on the seed of Co^{2+} from CoS_2 and CoS_2 was observed to a homogeneous distribution on the surface of ZIF-67 polyhedron. The fabricated hybrid showed an attractive capacity of storing Li^+ storage and significant cycle numbers in the battery, in which more than 550 mAhg^{-1} capacity and up to 50 cycles persistence with negligible decay at 0.1 C could be achieved. Furthermore, the charge-discharge property remained at a relatively high current density that is closed to ~15 C. Such promising behavior was tied to its well-planned

structural design, including the uploading of CoS_2 and excellent conductivity from porous carbon.

Such design is superior to most available strategies in terms of the material source, facial synthesis and post-process modifications. Furthermore, the choice of ZIF-67 as growth seed is excellent as it enables the *in situ* growth to simplify the post-synthesis and accurately controls the distribution of ionic cobalt. Hence, it is of no surprise that outstanding charge-discharge performance was observed. Moreover, the cycling performance could be optimized *via* tuning the morphology of CoS_2 and ZIF polyhedron, in which the optimization of various perimeters and the corresponding behavior is studied. This attractive strategy could be applied to other analogues and is expected to inspire more interesting designs later.

Figure 1.23 (left) Graphic representation of the material design and its precursor and (right) the battery performance: (a) charge-discharge profile; (b-x) cycling performance at different cycle number, and (d) rate capacity at different current densities. Reproduced with permission from ref. 54. Copyright 2014 WILEY-VCH.

Beside these physical combinations, there are also a series of studies using MOFs as templates to fabricate porous polyhedron, in which Lou and co-workers reported many

related works. One representative work was the development of Fe_2O_3 polyhedron with a core-shell structure.⁵⁵ It was achieved by a calcining treatment for cubic polyhedron to be assembled by Prussian blue, where synergistic oxidation and crystallization occurred in the annealing process. In the subsequent optimization studies, it was found that such core-shell structure could also be constructed at anisotropic orientation and even realized hollow architectures. With these achievements, this hybrid was applied in charging-discharging as the electrode material. Such finely architecture brought about prominent performance in the battery application, where the charge-discharge capacity reached to $\sim 1000 \text{ mA h g}^{-1}$ at 0.2 C and the reversibility remained more than 30 cycles.

In comparison with traditional ways to build this defined hollow polyhedron, the abovementioned strategy is able to overcome many challenges, like facial *in situ* covering, homogeneous thickness and clear and stable hierarchical core-shell structure. This work used MOFs microspheres as the backbone of polyhedron to fabricate the hierarchical and shape-defined architecture. Here, the oxidation caused by thermal treatment played an indispensable role to control the subsequent homogeneous covering, in which the morphology of Fe_2O_3 was tunable *via* the annealing at different temperatures. It is important to note that the ultimate goal of every material design is the application hence, it is as important to match its properties to an appropriate application to highlight the significance of the designed materials. When the MOF hybrid was used as electrode material to evaluate the storage and release of ionic lithium, its charging capacity and reversibility was excellent. This serves as a valuable reference in the aspect of material design or fabrication strategy.

Figure 1.24 (i) Graphic representation of fabricating the hollow Fe_2O_3 microboxes and the subsequent assembling process upon heating treatment; (ii) Electronic microscopy images of hollow Fe_2O_3 polyhedron achieved at different temperature; (iii) (a) The corresponding battery performance of hollow Fe_2O_3 bulk as previously mentioned. (b) The corresponding cycling property and coulombic efficiency of Fe_2O_3 bulk in the scan range of 0.01–3.0 V vs Li/Li^+ at the current density of 0.2C. Reproduced with permission from ref. 55. Copyright 2012 American Chemical Society.

Very recently, Mircea Dincă showed that Ni-based MOF with high electrical conductivity could serve as the sole electrode material in an EDLC.⁵⁶ This is the first example of a supercapacitor made entirely from neat MOFs as active materials, without conductive additives or other binders. Cells made with neat $\text{Ni}_3(\text{HITP})_2$ could reach a very high surface area normalized capacitance of $\sim 18 \mu\text{F cm}^{-2}$ and exhibit very low equivalent series resistance. Furthermore, higher compression of $\text{Ni}_3(\text{HITP})_2$ powder gave rise to very high volumetric capacitance values, making it able to compete with some of the best EDLC materials currently and exceeding those of most carbon-based materials and capacity

retention greater than 90% over 10,000 cycles, in line with commercial devices. These results on the first example of a non-carbon based EDLC confirmed that conductive MOFs, with their established structural and compositional tunability¹⁹, could serve as versatile, rationally tunable materials for this important class of energy storage devices. Further optimizations of material include increasing the pore size to increase rate capacity and deliberate introduction of pseudocapacitive components within the MOF structure.

Figure 1.25 (a) Structural schematics of $\text{Ni}_3(\text{HITP})_2$; (b) Performance of $\text{Ni}_3(\text{HITP})_2$ electrodes in a symmetrical supercapacitor cell up to 1V. Reproduced with permission from ref. 56. Copyright 2016 Nature Publishing Group.

In summary, the recent notable advancements related to MOF-based hybrids addressed some current issues in hand and show the promising properties of such hybrids in perspective large-scale production, processing and application. We believed that more research interest will be inspired by these findings and some industrial applications will be realized soon.

1.5 Research motivation and scientific contributions

Recent advancements of diverse post-functionalized porous framework materials have been discussed in this chapter, including the introduction of particular functional groups, the uploading of specific nanoparticles and the encapsulation of superior materials. Among them, the direct introduction of functional group is the most facial and easy to handle method, in which any desired functionality can be designed to further strengthen the integrate porous framework materials. In particular, the surface absorption allows the tuning of intrinsic properties of nanoparticles, like their morphology, physical stability and surface robustness. Slight modifications of these properties will then result in diverse frameworks and their applications.

Assembling strategy for implanting functional group or nanoparticles into porous framework materials as well as wrapping nanoparticles by framework materials have been reviewed by drawing comparison with other available methods. Although the functionalization of nanoparticles *via* chemical bonding offers the advantages of synthetic reliability and structural stability, it is not practical in the large-scale production because of the complicated procedures and low synthetic efficiency. In contrast, the assembly with physical encapsulation by using porous nanoparticles as a cover to encapsulate the expected objects is gaining more attention due to its practical operation. Different composites using the abovementioned physical encapsulation strategy have also been discussed with their potential applications. Some key research aspects into the combination include energy harvesting, external stimuli-response and gas selective absorption. The synergistic ability of the combination of host and guest has been analyzed, ranging from inorganic nanoparticles to organic small molecules and to organic macromolecules and their applications to energy

storage, vapochromic sensing and molecule recognition. The reported works offer inspiration for further exploitation of such excellent framework materials towards wide range applications.

In this thesis, I will describe my PhD works on post-functionalizing framework materials and exploring their performance in lithium ion storage and molecular recognition. The logical design of post-functionalized porous framework materials will be discussed, such as tunable and optimized pore space, immobilized specific functional guests and the introduction of desired target materials. The synergistic effect between the host and guest for an integrate will be demonstrated, where framework material acts as a cover to protect the core host while the pore space offers the channel for other molecules or nanoparticles to enter. Following which, the designed framework materials are applied for molecular recognition and lithium ion storage and transportation. The intrinsic optical and electrical properties of framework materials, as well as host functional materials can be synergistically integrated to form a new assembly with superior applications, like the obtained fixator, viable thermometers, vapor transducers, nano-reactor, and responsive materials, which have contributed much to the development of functional porous framework materials.

In the first project (Chapter 2), we fabricated the functional polymer-caged MOF using its high surface area and high porosity, making it capable of storing specific guest molecules for molecular recognition. We then investigated the stimuli-responsive behavior attributed to different pore sizes. Through inducing the electron-rich polymer, the resulting functional material showed highly specific interaction towards some acceptor molecules, particularly nitro compounds, which are the major components in explosives. The interaction leads to a charge-transferring process, showing an obvious red shift on optical signal and a

visible color change. Comparing with conventional materials for molecular recognition, a synergy effect is expected, where polymer-threaded MOFs might enhance the stability of the hybrids and the MOF porosity could be used to realize the selectivity towards different guest molecules. In this case, the caged polymers as the responsive components could induce multiple functionalities to MOF for enhanced sensitivity. It avoids some common shortcomings of polymer-caged MOFs, including complicated structures, poor response performance and uncontrolled response degree. This novel sensing approach with simple synthesis and colorimetric output has much potential in applications such as practical analyses and sensing applications based on MOF materials.

In my second project (Chapter 3), we reported a Zn-based cubic MOF in which 12-crown-4 are covalently integrated into the backbone of the structure. With a high surface area of $1101.4 \text{ m}^2 \text{ g}^{-1}$, this MOF is capable of docking Li^+ ions by the supramolecular interactions between Li^+ and the crown ether units, achieving a high density of 0.73 Li per crown ether in MOF crystals. The MOF after Li^+ ions docking showed 45% enhancement for H_2 storage at 77 K and 67% increase for CO_2 capture at 273 K compared to the MOF without Li^+ , confirming the specific interactions between the guests and lithium in the MOF. Furthermore, with the host-guest interactions between the crown ethers and Li^+ ions, the lithium ion batteries exhibited enhanced charge capacities of 273 and 348 mAh g^{-1} when the Li^+ ion-free and Li^+ ion-loaded MOFs were employed as the anode materials, respectively. Interestingly, the Li^+ ion-free MOF-based battery showed improved cyclability, with 88% capacity retention after 500 cycles. This research presents a new outlook for crown ether-based MOFs towards further development of new energy materials in terms of chemical strategies.

For my third project (Chapter 4), we explored two fully conjugated porous COFs as the eco-friendly storage material for energy storage based on the poor conductivity of MOFs in the previous chapter. The as-synthesized COFs showed high capability of selective gas adsorption and large capacity of Li ion storage. In the aspect of gas sorption, the selectivity ratio of H₂ and CO₂ to N₂ reached ~15:1 and 7:1, respectively, while in the Li ion storage, both COFs exhibited ~700 mAhg⁻¹ capacity and stable long life (500 cycles). Such good performance not only confirmed high potential of COFs in robust cycle stability, high-rate energy storage and power supply but also provided the valuable information for further investigation. The present work presents a new outlook for conjugated COFs as eco-friendly storage material towards further development in energy storage.

In summary, the current trend of post-functionalizing porous framework materials focuses on the chemical bonding strategies and physical encapsulation methods for fabrication and the resultant integrate have shown their great performance in practice applications as abovementioned. Future development trends are expected to be focused on diversifying application range and improving performing ability.

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Chapter 2: Macroscopic Architecture of Charge Transfer-Induced Molecular Recognition from Electron-Rich Polymer Interpenetrated Porous Frameworks

Abstract

*Fluorescent and electron-rich polymer threaded into porous framework provides a scaffold for sensing acceptor molecules through noncovalent interactions. Herein, poly(9-vinylcarbazole) (PVK) threaded MIL-101 with confined nanospaces was synthesized by vinyl-monomer impregnation, in situ polymerization, and interpenetration. The pore size of the resulted hybrid could be controlled by varying the time of polymerization and interpenetration. The interaction of PVK-threaded MIL-101 with guest molecules showed a charge-transfer progress with an obvious red shift in the optical spectra. Depending on the degree of the interaction, the solution color was changed from blue to blue-green or to yellow. In particular, electron-rich PVK-threaded MIL-101 could effectively probe electron-poor nitro compounds, especially 1,3,5-trinitrobenzene (TNP), a highly explosive material. This sensing approach is a colorimetric methodology, which is very simple and convenient for practical analysis and operation. This work has been published on ACS Appl. Mater. Interfaces **2015**, 7, 5056-5060.*

2.1 Introduction

Porous coordinated polymers^{1,2} and complex networks,^{3,4} particularly metal organic frameworks (MOFs),⁵⁻⁷ and their variations have proliferated and have collectively developed into a novel class of nanoporous materials. Apart from possessing properties such as diversely functionable, high surface area and porosities, other benefits of MOFs include the advantages of a ceramic matrix and a regular pore structure capable of storing specific guest molecules.^{8,9} However, the inclusion of appropriate guest molecules is limited by chemical affinity of the coordination spaces and thus functionalizing the pore structure is imperative. The pioneering works of Kitagawa et al. and others have demonstrated that the introduction of extra functional composites into MOFs can lead to increased adaptability towards the encapsulation of guest molecules.¹⁰⁻¹³ Recently, Gao and co-workers¹⁴ reported that a monomer was caged into ZIF-8, where it formed a macromolecule by polymerization. The caged hybrid showed superior performance of ion exchange.

However, utilizing MOFs' inherent advantages of high porosity and controlled swelling to cage functional polymers inside for molecular recognition and stimuli-responsive behavior with high selectivity caused by different size of pores has not been well investigated. Comparing with conventional materials for molecular recognition, a synergy effect is expected, where polymer-threaded MOFs might enhance the stability of the hybrids and the MOF porosity could be used to realize the selectivity towards different guest molecules. Some guest molecules with large sizes cannot enter into the polymer-caged MOF, so that no interaction happens. On the other hand, those small guest molecules can go inside and move freely, interacting well with the polymer inside MOF.

In our present work, we envisioned that the flexible nanospaces between MOF and polymer would show specific guest adsorption via the donor–acceptor interactions, and this could be used for specific guest recognition. We made use of the advantages of MOFs with high porosity and controlled swelling to cage one electron-rich polymer into the MOF cavities, and the resultant functional material as a new detection system showed a special interaction with some electron-acceptor molecules, particularly nitro compounds, due to the electron donor-acceptor effect. Since some nitro compounds are the major components in explosive, it is very important to detect and control their concentrations before any operations.¹⁵⁻¹⁷ In this case, the recognition of guest molecules can be detected by the emission changes. This fluorescence transduction mechanism is highly sensitive to the surrounding conditions, and thus the effect of incorporating various guests in the nanospace can either be manifested by the changes in the emission intensity, or a new emission band due to charge transfer (CT) or exciplex/excimer formation.^{18,19} The nitro compounds generally have low electron intensity with a pull-electron effect. Electron-rich materials are desired to probe the nitro compounds toward practical applications. Herein, we developed electron-rich polymer-caged MOF to detect the concentration of 1,3,5-trinitrobenzene (TNP), a highly explosive material, through obvious red shift on optical spectra and visible color change. Some studies about the TNP detection have been reported, including the utilizations of fluorescent quenching effect,^{15,17,20,21} supermolecule wires,^{22,23} and metal coordination.²⁴⁻²⁶ To the best of our knowledge, the present study is the first example for the detection of nitro compounds using polymer-caged MOF.

Figure 2.1 Schematic illustration of the hybrid fabrication of PVK@MIL-101 and its responsive to various acceptor molecules in DCM solution.

2.2 Material synthesis of PVK, MIL-101 and the hybrid of PVK@MIL-101

MIL-101 is a superstar in the MOF area, due to its excellent characteristics in terms of cell dimension, pore size and surface area, which was first synthesized by G. Férey and co-workers.²⁷ It possesses large spherical cavities with diameter of ~ 2.9 nm, and the pore size of the windows is 1.2~1.6 nm. On account of the larger pore size, it was chosen as the suitable porous material for caging functional molecules. Several studies have been reported in the past few years using caged and covered MIL-101 for catalysis, adsorption and morphology control.^{28,29} In our present study, we firstly predicted the loading of a monomer into the MIL-101 cavities through the calculations (Figure 2.2). 9-Vinylcarbazole has a molecular size of $7.1 \times 8.2 \text{ \AA}^2$, which is much smaller than the porosity of MIL-101. It means that this molecule is able to impregnate into the MIL-101 cavities completely. Supported by the calculations, we designed polymer-caged MIL-101. MIL-101 was firstly activated under vacuum in 150°C for 6 hours, so that the solvent molecules in the cavities could be removed. Then, 9-vinylcarbazole monomer and azobisisobutyronitrile initiator in dichloromethane (DCM) were added, the resulted mixture was stirred for overnight to ensure the encapsulation

of the monomer into the cavities. After solvothermal reaction for the formation of poly(9-vinylcarbazole) (PVK), the remaining monomer, oligomer, and those stayed on the surface of MIL-101 were washed away by acetone through the Soxhelt extraction. Finally, the obtained PVK caged MIL-101 (PVK@MIL-101) powder was dried for further uses (Figure 2.4). After loading PVK into the cavities, MIL-101 showed a strong blue fluorescence under UV lamp.

2.2.1 MIL-101 synthesis, monomer confinement, and polymerization

The synthesis of MIL-101 was carried out by the hydrothermal reaction of H₂BDC (166 mg, 1 mmol) with Cr(NO₃)₃•9H₂O (400 mg, 1mmol), fluorhydric acid (0.2 mL, 1 mmol), and H₂O (4.8 mL, 265 mmol) at 220 °C for 8 hours. This reaction produced a highly crystallized green powder of the chromium terephthalate with formula Cr₃F(H₂O)₂O[(O₂C)-C₆H₄-(CO₂)]₃•nH₂O (where n is ~25), calculated based on chemical analysis. The yield based on chromium is 50%.

As shown in Figure 2.4, to encapsulate PVK into MIL-101, activated MIL-101 (0.5 g) was suspended in dichloromethane (2 mL). To this suspension, 9-vinylcarbazole (1.5g, 7.78mmol) with azobisisobutyronitrile (AIBN, 0.12 g, 0.73mmol) was added, and the mixture was stirred at room temperature for 2 days to allow the penetration of 9-vinylcarbazoles, as the diffusion of 9-vinylcarbazoles into MIL-101 can be very slow. Adding dichloromethane can facilitate the uniform distribution of 9-vinylcarbazoles as well as better solubility of AIBN. The solvent was subsequently removed under vacuum at room temperature. Afterwards, 9-vinylcarbazoles filled MIL-101 was sealed in a glass vial and heated to 90 °C under N₂ atmosphere for 3 days. The sample obtained was refluxed in acetone overnight to remove the unattached PVK or remained monomer. The powder was then collected, washed with ethanol and dried at 60 °C to give PVK@MIL-101. Here all the

reagents and solvents employed were commercially available and used without further purification unless specifically mentioned.

2.2.2 Theoretical calculations for accessibility of 9-vinylcarbazoles to MIL-101

First, the accessibility of 9-vinylcarbazole molecule ($7.1 \times 8.2 \text{ \AA}^2$) to the internal surface of MIL-101 was demonstrated. MIL-101 possesses large spherical cavities with diameter of $\sim 2.9 \text{ nm}$ and the pore size of the windows is $1.2\sim 1.6 \text{ nm}$. Even though its apertures size is much smaller than spherical cavities (see Figure 2.2), several experimental cases have already confirmed that the gate-opening effect of MIL-101 allows the penetration of guest species with dynamic sizes comparable to or even larger than the window size. Besides, the molecule sizes of three acceptor molecules were calculated as below: 1,3,5-trinitrobenzene (TNP) ($4.0 \times 4.5 \text{ \AA}^2$), 1,4,5,8-naphthalenetetracarboxdiimide (NDI) ($4.7 \times 6.8 \text{ \AA}^2$), and tetracyanobenzene (TCNB) ($4.0 \times 6.5 \text{ \AA}^2$).

Figure 2.2 Molecule sizes of VC, TNP, NDI and TCNB obtained by theoretical calculation. Ball-and-stick view and three dimensional structures ($\text{\AA}$) of the pentagonal and hexagonal windows. Chromium octahedra, oxygen, fluorine and carbon atoms are in green, red, red and blue, respectively.²⁷

2.2.3 Molecular weight of PVK from PVK@MIL-101

Molecular weight of PVK without MIL-101 was tested using MALDI TOF equipment. MIL-101 from PVK@MIL-101 was first removed by Na_2CO_3 solution. Then, PVK was extracted by chlorobenzene and washed with diluted Na_2CO_3 for several times. From the MS spectra in Figure 2.3, the first peak can be assigned to PVK.

Figure 2.3 Molecular weights of PVK without MIL-101 obtained in different times of polymerization (1 day, 2 days and 3 days of polymerization for PVK-1, PVK-2, and PVK-3, respectively).

Figure 2.4 Schematic illustration for the synthesis of electron-rich PVK polymer-caged MOF (PVK@MIL-101) from monomer loading to the polymerization in the porous network of MIL-101.

2.3 Physical characterization of PVK@MIL-101

The synthesized PVK@MIL-101 was fully characterized by scanning electron microscope (SEM), powder X-ray diffraction (PXRD), N_2 adsorption/desorption measurements, and Fourier transform infrared spectroscopy (FTIR). As seen from the SEM images (Figure 2.5), PVK@MIL-101 is micrometer scale particles, and the surface of the

particles after caging the polymer is still smooth as original ones. Moreover, no obvious enhancement of the particle diameter was observed after the polymer encapsulation.

Figure 2.5 SEM images of MIL-101 before (a) and after (b) caging polymer; respectively.

From the PXRD patterns (Figure 2.6a), MIL-101 structures in the synthesized PVK@MIL-101 remained intact, and several key diffraction peaks could match with that of original MIL-101. Some slight shifts in the XRD peaks were highlighted, corresponding to a very small expansion after the polymer caging. It was reported that physical mixing of MOFs and organic compounds showed no shifts in the XRD patterns, and a similar lattice expansion was observed when encapsulating some guests into MOFs. The broad peak around 22° was assigned to the polymer threading in MIL-101. This conclusion was also supported by FTIR spectra with the appearance of quaternary specific peaks for the polymer at ca. 3051 cm^{-1} , 2946 cm^{-1} , 1453 cm^{-1} and 715 cm^{-1} (Figure 2.7). The reason that the polymer interpenetrates into the framework cavities and not covers on the surface is discussed as follows. By interpenetrating into the cavities, the polymer has the ability to influence the pore size with different degree depending on the reaction time. Figure 2.6b shows N_2 adsorption/desorption isotherms at 77K for MIL-101 before and after caging the polymer under different polymerization times of 1 day, 2 days and 3 days. It could be clearly found that the polymer with different polymerization time was able to influence the adsorption capability of MIL-101 at different degree. In other words, it can tune the porous size of MIL-101 with the

maximum surface area of $1134 \text{ m}^2 \text{ g}^{-1}$ (Table 1). If the polymer just covers the surface of MIL-101, the adsorption value should be much lower than this value. In order to evaluate the polymerization degree of the monomer, we tested the number averaged molecular weights (Mw) of the polymers by MALDI TOF mass spectrometry after removing the MIL-101 host through base washing (Figure 2.3). The Mw values of three polymers are 2032, 3128 and 5221, corresponding to ~ 10 , ~ 16 and ~ 27 monomer units, respectively. Based on the controlled polymerization, it is possible to tune the pore size of MIL-101 by caging the polymer. Actually, the MIL-101 frameworks can also influence the polymer growth degree.

Figure 2.6 (a) PXRD patterns of MIL-101 before (blue curve) and after (red curve) caging polymer; (b) N_2 adsorption/desorption isotherms at 77K for MIL-101 before (black) and after caging different polymers caused by different polymerization times. Purple, red and deep blue mean 1 day, 2 days and 3 days of reactions, respectively.

Figure 2.7 FTIR spectrum of PVK (red line), MIL-101 (blue line) and PVK@MIL-101 (black line).

Figure 2.8 Pore-size distribution plots of MIL-101 and various PVK@MIL-101 calculated from experimental N₂ adsorption isotherms using the nonlocal density functional theory (NLDFT) in predicting a model noncovalent interaction.

Figure 2.9 TGA plots of naturally dried MIL-101 and PVK@MIL-101, indicating the framework was stable up to ~340 °C. ~19.1% loss of solvent is shown in blue line. Four dashed lines in blue and red indicates the decomposition degree of PVK with and without the shielding of MIL-101.

The pore width distribution of MIL-101 after caging the polymer provides further evidence for the porosity decrease (Figure 2.8). The three polymers with different polymerization times reduced the pore sizes from original 2.4 nm to 1.0 nm, 1.8 nm, and 1.4 nm, respectively (Table 1). It is not hard to find that the pore size distribution does not change uniformly with the impregnation process. Instead, the microporous region (<2 nm) is more strongly affected as the micropores provide the most surface., based on the dramatic drop in this region compared to the reduction in pore volume at mesopore scale. We summarized the volume and area of micropore and mesopore respect to each material mentioned in this work, which could be found in Table 2. Here the micropores contribute much to the pore volume and surface area. For MIL-101 and PVK-1@MIL-101, the micropore volume is 1.352 cc/g and 0.502 cc/g, respectively, while the total pore volume is 1.757 cc/g and 0.978 cc/g respect to the two materials. In surface area, the major fraction is also provided by the micropores. It also suggests that while the polymer is indeed entering the central mesoporous cage region, the polymer is also coating the external supertetrahedra

and thus clogging the micropores. In addition, the degradation temperature of PVK@MIL-101 obtained by thermogravimetric analysis (TGA) is another evidence to support the polymer interpenetration into the cavity, not on the surface (Figure 2.9). One obvious weight loss for MIL-101 without polymer was observed below 100 °C, on account of the solvent removal from the cavities. However, a same weight loss temperature cannot be found for the case of PVK@MIL-101. This observation indicates that the polymer was caged into the framework, where the polymer replaced the solvent molecule and occupied the cavities.

Table 1 Structural and polymer-caged properties of MIL-101 and PVK@MIL-101.

Sample	S _{BET} (m ² /g) ^[a]	Pore width (nm) ^[b]	Degradation temperature (°C) ^[c]
MIL-101	~1709	2.4	~394
PVK-1@MIL-101 (Mw=2032, 1 day)	~1134	1.0	~379
PVK-2@MIL-101 (Mw=3128, 2 days)	~128	1.8	-
PVK-3@MIL-101 (Mw=5221, 3 days)	~123	1.4	-

[a] Determined by N₂ adsorption/desorption isotherms at 77K; [b] determined by HK model of slit pore, which gives correct value of 0.5 nm for a standard zeolite 5Å; the alternative DFT analysis based on cylindrical pore shape gives 2.4 nm for MIL-101 and 1.0 nm for PVK-1@MIL-101; [c] from TGA results in Figure S4.

Table 2 statistics for microporous and mesoporous

	MIL-101	PVK-1@MIL-101	PVK-2@MIL-101	PVK-3@MIL-101
^[a] Total pore volume (cc/g)	1.757	0.978	0.123	0.112
^[b] Micropore volume (cc/g)	1.352	0.575	0.078	0.076
^[c] Mesopore volume (cc/g)	0.405	0.403	0.045	0.036
^[b] Micropore area (m ² /g)	1469.606	1196.208	178.927	172.205
^[b] External surface area (m ² /g)	211.150	76.109	33.123	22.641

This is determined by N₂ adsorption/desorption isotherms at 77K: [a] calculated by the point of highest adsorption; [b] determined by the t-plot method, where the contribution points are from 0.35-0.5 in P/P₀; [c] got by the difference between the total pore volume and micropore volume.

2.4 Detection

Figure 2.10 (a) Schematic representation of using PVK@MIL-101 to recognize three acceptors, i.e., NDI, TNP and TCNB. The circle figure showed the charge transferring process. (b) Fluorescence spectra of PVK@MIL-101 before (blue) and after introducing three acceptors in 10 ppm (green for TCNB), (red for TNP) and (purple for NDI). (c) The emission of PVK@MIL-101 in solution under UV lamp before and after interacting with the three molecules. The right one is the original solution of PVK@MIL-101 without any acceptors. (d) The emission of PVK@MIL-101 in the solid state (obtained by centrifugation) under UV lamp before and after interacting with three acceptors. The right one is PVK@MIL-101 without any acceptors.

As abovementioned, the polymer caged into the MIL-101 cavities is an electron-rich component, and can interact with electron-deficient guest molecules through the CT process. Herein, PVK-1@MIL-101 prepared under 1 day polymerization was selected to recognize the acceptor molecules, due to its remained porosity. The remained pores could provide the selectivity to different acceptors with different sizes. The schematic illustration of the recognition process is shown in Figure 2.10a. We chose three traditional acceptor molecules

with different molecular sizes (Figure 2.2), i.e., 1,4,5,8-naphthalenetetracarboxdiimide (NDI), TNP, and tetracyanobenzene (TCNB). These compounds were added into the dispersed solution of PVK-1@MIL-101 in DCM, where the compounds could dissolve in DCM for interacting with PVK-1@MIL-101. The Adsorbtion and exission spectra of PVK was first investigated by Klöpffer in both solution and film.³⁰ With photoexcitation, PVK yields a broad fluorescence peak in the violet-blue region and the high energy emission centered at ~ 375 nm, while the lower energy band centered at ~ 420 nm in toluene. We compared the PVK used in this work to studies of PVK fluorescence and observed the almost similar peak in fluorescence excitation spectra (Figure 2.11).

Figure 2.11 Fluorescence excitation spectra of 1 ppm PVK in toluene excited by 290nm (black line), 330nm (green line) and 380nm (blue line) and 330nm in DCM (pink line).

The interaction of PVK@MIL-101 with these guests was probed by fluorescence (Figure 2.10b). In the fluorescence spectrum, a peak at longer wavelength represents the CT process. To further confirm the CT process, a precise controlled experiment of the guests with polymer-caged MOF was carried out. The interaction of electron donor and acceptor was probed by the XRD in situ (Figure 2.10a). The broad peak around 22° belongs to PVK before interacting with any acceptor. When an acceptor was introduced, a slight peak shift occurred, indicating the CT complex formation.²⁹ The process was also supported by cyclic

voltammetry experiments (Figure 2.12). It could be found that the oxidation potential decreased after interacting with electron deficient aromatics, meaning that the CT process occurred. In the fluorescent spectrum, the interactions of TNP and TCNB with PVK@MIL-101 generated a peak at longer wavelength, while no obvious difference observed in the case of NDI with PVK@MIL-101. The different phenomena were caused by the selectivity given by the remained pore of PVK@MIL-101. The sizes of these three acceptor molecules were predicted by theoretical calculation (Figure 2.2). Although the size of NDI molecule is smaller than the pore, π - π stacking aggregation among NDI molecule increases the volume, so that it cannot entry into the cavities to interact with the polymer inside. As the electron-withdrawing ability of TCNB is weaker than TNP, it is why the red shift degree with TNP is bigger than that with TCNB. Moreover, the difference of emission color is very obvious under UV lamp (Figure 2.10c). The original color of PVK@MIL-101 dispersed in DCM is blue, originated from the caged polymer, while MIL-101 has no fluorescence. When the acceptor guests were added into the dispersion for several seconds, the color of the mixture changed obviously to green-yellow and orange for TCNB and TNP, respectively. After centrifugation, the obtained solid powder was collected. It can be seen that the fluorescence color of PVK@MIL-101 powder before and after interacting with NDI still had no change (Figure 2.10d). The observation also supports the polymer interpenetration and the interaction with the acceptor guests inside the cavities, not on the surface of MIL-101.

Figure 2.12 Cyclic voltammetry curves of PVK in DMF before and after interacting with electron deficient aromatics, respectively.

Figure 2.13 a) Absorption spectra of PVK@MIL-101 interacted with TNP in 10 ppm for different times. b) Emission spectra of PVK@MIL-101 interacted with TNP in 10 ppm for different times (excited at 290 nm). c,d) Absorption spectra and emission spectra of only PVK interacted with TNP in 1 ppm for different times (excited at 290 nm).

Based on the selectivity of PVK@MIL-101 towards different acceptors, we then utilized it as a detector for nitro compounds, especially for TNP, a highly explosive substance.

In the optical spectra, one new peak was generated after treating PVK@MIL-101 with TNP, and the peak intensity became higher and higher upon increasing the interaction time (Figure 2.13). The detection process is very quick within a few seconds. Particularly in the fluorescence spectra, the intensity of the original fluorescence peak around 425 nm for PVK@MIL-101 was reduced gradually after adding TNP, and the intensity of the newly generated peak around 582 nm increased upon time, matching well with the emission color change from blue to yellow. The fluorescence quenching at 425 nm is due to the interaction of caged polymer with electron-deficient TNP. The new peak at 582 nm was assigned to the charge-transferring process between the caged polymer and TNP. Upon increasing the time, the charge-transferring process became stronger, so that the peak intensity increased higher. The detection response is very sensitive and fast (less than 10 seconds) with a detection limit of up to 1 ppm (Figure 2.14). Besides, we also tried to detect acceptors in vapor so that it could indicate this methodology could be applied in more common condition. Here the powder of PVK@MIL-101 is fixed on a glass substrate and put on the top of the beaker containing acetone with heating at boiling point. The detection is observed in Figure 2.15. With longer time, the luminance is quenched and produce a slightly bathochromic shift, which further explain the interaction between the MOF-polymer and acetone.

Figure 2.14 Emission spectra of PVK@MIL-101 in different concentrations of TNP in DCM (excited at 290 nm), indicating luminescence quenching by gradual addition of TNP.

Figure 2.15 (a) Schematic illustration for the detection to acetone vapours; (b) Emission spectra of PVK@MIL-101 with acetone for different times (excited at 330 nm), indicating luminescence quenching by gradual addition of acetone adsorption.

2.5 Conclusion

In conclusion, we have reported a facile methodology to develop electron-rich polymer threaded MIL-101, featuring flexible spaces for molecular recognition, particular in detecting TNP. The remaining pores of MIL-101 after the polymer interpenetration provide the selectivity to various acceptor molecules with different sizes. The recognition of some guest molecules shows a characteristic red shift of the CT emission band, leading to a tunable emission profile. Thus, for the first time, the detection of nitro explosive using the polymer-caged MIL-101 through the CT process has been studied. Superior detection performance of the polymer-caged MIL-101 towards TNP has been demonstrated. This approach of sensing TNP concentration by polymer-caged MOFs may be extended to other nitro compounds with suitable molecular size and electron donor-acceptor effect. The easy accessibility coupled with high surface area of the polymer-caged MIL-101 could enable the system to detect nitro explosives in gas phase or common environment, in which some conventional detecting systems showed poor performance owing to uncontrolled selectivity and inaccessibility of their internally embedded active sites. Therefore, the present methodology demonstrates a

simple and efficient approach for the fabrication of novel porous luminescent platforms in molecular recognition.

2.6 References

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Chapter 3: Enhanced Performance in Gas Adsorption and Li Ion Battery by Docking Li⁺ in a Crown Ether-Based MOF

Abstract

*With the increasing demand in sustainable living and green energy production, metal-organic frameworks (MOFs) have emerged for promising applications in greenhouse gas adsorption and lithium ion batteries. To introduce active entities with specific interactions with energy-related molecules and ions, we synthesized a Zn-based cubic MOF in which 12-crown-4 are covalently integrated into the backbone of the structure. With a high surface area of 1101.4 m² g⁻¹, this MOF is capable of docking Li⁺ ions by the supramolecular interactions between Li⁺ and the crown ether units, achieving a high density of 0.73 Li per crown ether in MOF crystals. The MOF after Li⁺ ions docking shows 45% enhancement for H₂ storage at 77 K and 67% increase for CO₂ capture at 273 K compared to the MOF without Li⁺, confirming the specific interactions between the guests and lithium in the MOF. Furthermore, with the host-guest interactions between the crown ethers and Li⁺ ions, the lithium ion batteries show enhanced charge capacities of 273 and 348 mAh g⁻¹ when the Li⁺ ion-free and Li⁺ ion-loaded MOFs are employed as the anode materials, respectively. Interestingly, the Li⁺ ion-free MOF-based battery shows improved cyclability, with 88% capacity retention after 500 cycles. This research presents a new outlook for crown ether-based MOFs towards further development in chemical strategies for new energy materials. This work has been published on Chem. Comm. **2016**, 52, 3003-3006.*

3.1 Introduction

With increasing energy demands owing to the continuing economy development and fast-growing population, it is becoming urgent for us to reduce CO₂ emission from fossil energy consumption¹⁻² as well as to develop new green energy.³⁻⁵ Effective chemical strategies, such as selective gas adsorption and electrochemical energy storage, are extremely important in the future energy revolution to provide technologies for CO₂ capture and sequestration,⁶⁻⁸ and high-capacity energy storage for intermittent energy source.⁹⁻¹⁰ Recently, porous materials have been successfully applied in gas adsorption and separation,¹¹⁻¹⁷ fuel cells,¹⁸⁻¹⁹ supercapacitors, and lithium ion batteries (LIBs).²⁰⁻²⁴ They provide high surface areas for reactions and interactions, and efficient guest transport pathways inside the pores. Numerous novel porous materials with varying compositions, structures, and functions have emerged, among which metal–organic frameworks (MOFs)²⁵ have experienced tremendous developments in last twenty years. Generally, MOFs are prepared by linking inorganic and organic building blocks to create crystalline network structures with permanent porosity. Uniform pores with tunable sizes, low density, and rich functionalities are the main features of this new class of materials²⁶⁻²⁹, and they have been undoubtedly considered as promising candidates for applications in green energy systems.

In particular, MOFs have been employed as potential anode³⁰⁻³², cathode³³⁻³⁶, and electrolyte³⁷⁻³⁹ materials for LIBs, since the porous nature of MOFs provides controllable channels for guest movement and tailored sites for guest deposition. In addition, the coulombic efficiency of MOF-based anodes has been increasing in the past years for the enhanced plating and stripping of lithium metal on the solid electrolyte interface and the adjustment of energy level by introducing nitrogen, oxygen and sulfur. What is more, the

inorganic building units in MOFs are often metal ions or metal oxides that could serve as active sites during electrochemical process.^{32, 35, 40} However, two main limitations in this field still remain: i) MOF-based LIBs usually have unsatisfactory cycling performance, mainly due to the MOF structural instability under battery discharge and charge;⁴¹ ii) The electrochemical activity of MOF materials needs to be improved greatly for LIBs with better performance. In addition, while most of the current works focus on improving MOFs' chemical stability with new inorganic building units³³⁻³⁶, less attention was paid on enhancing MOF's performance in LIBs with specific organic linker design.

Herein, we reported the synthesis of a MOF based on organic linkers containing crown ether units with high capability of lithium docking. The covalent integration of ordered 12-crown-4 units into a cubic MOF provides specific sites for lithium ions storage without destroying the framework. On average, 0.73 Li⁺ ion is anchored per crown ether throughout the whole single crystal. The complexation of lithium ions within the crown ether units enhances the MOF's performance of gas adsorption remarkably. Specifically, the gas adsorption of lithium ions-loaded MOF at $P/P_0 \approx 1$ is 104.8 cc g⁻¹ for H₂ at 77 K and 121.0 cc g⁻¹ for CO₂ at 273 K, which are 45% and 67% increase as compared to the lithium-free MOF, respectively. Moreover, the crown ether-based MOF as the anode materials in LIB provides not only interconnected pores with high surface area, but also tailored chemical environments for specific interactions with Li⁺ ions in the electrode. The charge capacity of the LIB from the crown ether-based MOF is 273 mAh g⁻¹, with more than 88% capacity retention over 500 cycles. While in a LIB based on the MOF after lithium docking, the initial charge capacity increases to 348 mAh g⁻¹. It is assumed that Li⁺ mainly interacts with the crown ethers while keeping the MOF skeleton intact, contributing to the enhanced cyclability of the LIB. The

specific crown ether sites available for Li^+ docking may be the key in constructing these LIBs with high capacities and long-term cyclability.

Figure 3.1 Single crystal structure of Zn-MOF-Crown. Hydrogen atoms are omitted for clarity. Crown ether units and organic linkers are colored yellow and gray respectively, and the metal joints are colored blue. Atoms in the crown ether units cannot be located precisely in the single crystal X-ray diffraction, thus they were modeled with Materials Studio.

3.2 Linkage synthesis and MOF preparation of Zn-MOF-Crown and $\text{Li}^+ @ \text{Zn-MOF-Crown}$

Scheme 1 Synthesis of crown ether-based organic ligand of H_2L (D).

Compound (A): This compound was synthesized in accordance to the reported method with slight modifications.¹ A round-bottom flask was charged with 1,2-dimethoxybenzene (13.8 g, 0.1 mol), Et_2O (200 mL), and $n\text{-BuLi}$ (250.0 mL, 0.50 mol, 2.0 M solution in hexane), and then tetramethylethylenediamine (TMEDA, 76.0 mL, 0.51 mol) was added dropwise. The mixture turned yellow, and white precipitate was formed. The mixture was refluxed for 24 h. After cooling with ice-water bath, N,N -dimethylformamide (DMF, 60

mL, 0.77 mol) was added dropwise. Cooling bath was removed, and after 15 min, aqueous solution of NH_4Cl (100 mL, 10% w/w) was added. The mixture was extracted with ethyl acetate (3×100 mL). The combined organic phases were washed with water (100 mL) and brine (100 mL), and then dried over anhydrous Na_2SO_4 . The solution was evaporated and the obtained sample was purified by column chromatography (silica gel, hexane:ethyl acetate = 20:1) to give a pale yellow solid. The product was further purified by the crystallization from DCM/hexane as white crystals (~5 g, 30%). ^1H NMR (300 MHz, CDCl_3): δ 10.45 (s, 1H), 7.64 (s, 1H), 4.06 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 190.2 (s), 157.6 (s), 135.2 (s), 123.8 (s), 63.5 (s). HRMS: Calcd for $\text{C}_{10}\text{H}_{10}\text{O}_4$: 195.0657, Found: 195.0655.

Compound (B): This compound was synthesized in accordance to the reported method with slight modifications.² A round-bottom flask was charged with compound A (2.38 g, 12.3 mmol) and CH_2Cl_2 (70 mL), and the solution was cooled with ice-water bath. Then, BBr_3 (31.0 mL, 31.0 mmol, 1 M solution in hexane) was added dropwise over 5 min. A yellow precipitate was initially formed, and the mixture became orange. After 30 min, the cooling bath was removed, and stirring was continued for 3.5 h. Then, water (100 mL) was added, and the mixture was extracted with CHCl_3 (3×100 mL). Combined organic phases were washed with brine (100 mL), and dried over Na_2SO_4 . The solution was filtered and evaporated to obtain yellow solid. The product was crystallized from CHCl_3 -hexane mixture to give compound B as brown crystals (1.79 g, 10.8 mmol, 88%). ^1H NMR (300 MHz, CDCl_3): δ 10.89 (s, 1H), 10.03 (s, 1H), 7.28 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 196.82 (s), 151.71 (s), 124.19 (s), 123.15 (s). HRMS: Calcd for $\text{C}_8\text{H}_6\text{O}_4$: 167.0344, Found: 167.0346.

Compound (C): This compound was synthesized in accordance to the reported method with slight modifications.¹ A round-bottom flask was charged with compound B

(0.75 g, 4.50 mmol), DMF (30 mL), $\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$ (5.6 mL, 18.0 mmol) and K_2CO_3 (2.49 g, 18.0 mmol). The mixture was stirred at 90 °C for 20 h. After cooling to room temperature, aqueous solution of HCl (50 mL, 1:9 v/v) was added, and mixture was extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with brine (2×50 mL), and dried over MgSO_4 . The solution was filtered and evaporated, and the obtained sample was purified by column chromatography (c-hexane:ethyl acetate = 1:1) to give compound C as white powder (0.11 g, 11%). ^1H NMR (400 MHz, CDCl_3): δ 10.45 (s, 1H), 7.68 (s, 1H), 4.38 (s, 2H), 4.00 (s, 2H), 3.83 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 188.83 (d, J = 60.7 Hz), 155.35 (d, J = 160.1 Hz), 133.41 (d, J = 240.8 Hz), 121.79 (d, J = 359.8 Hz), 75.48 (s), 71.49 (s). HRMS: Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_6$: 281.1025, Found: 281.1015.

Compound (D): This compound was synthesized in accordance to the reported method with slight modifications.³ Finely ground KMnO_4 (1.6 g, 10.4 mmol) was added in portions over 1 h to a stirred solution of compound C (0.84 g, 3.45 mmol) in acetone (10 mL), after which time no starting material was evident by TLC analysis. The mixture was concentrated to dryness under reduced pressure, and the residue was triturated with 5 N NaOH and filtered. The filtrate was acidified with concentrated HCl to give the diacid D as a white solid (0.81 g, 85%). ^1H NMR (400 MHz, MeOD): δ 7.55 (s, 1H), 4.26 (s, 2H), 3.89 (s, 2H), 3.79 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ 206.15 (s), 152.35 (s), 124.32 (s), 74.38 (s), 70.48 (s), 68.62 (s), 30.30 (d, J = 171.4 Hz). HRMS: Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_8$: 313.0923, Found: 313.0925.

Synthesis of Zn-MOF-Crown: A solid mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.80 g, 6.05 mmol) and 3',6'-dicarboxy-benzo-12-crown-4 (Compound D, 630 mg, 2.02 mmol) was dissolved in *N,N*-diethylformamide (DEF, 50 mL). The solution was allocated evenly into

five 25-mL vials. The vials were capped tightly and placed in an oven at 85 °C for 24 hours. Colorless crystals were collected after decanting hot mother liquor. The crystals were rinsed with DMF for three times, followed by solvent exchange with CH₂Cl₂ for six times. CH₂Cl₂ was further removed with supercritical liquid CO₂ in a Tousimis Samdri PVT-30 critical point dried by the following procedures. The wet sample was placed inside the dryer and the CH₂Cl₂ was exchanged with liquid CO₂ over a period of 20 minutes, during which time the liquid CO₂ was vented under positive pressure. The venting rate of liquid CO₂ was kept below the rate of filling so as to maintain a full chamber. After 20 minutes of venting and soaking with liquid CO₂, the temperature was raised to 40 °C. The chamber was held above the critical point with the pressure around 1300 psi for 1 hour, at which point the chamber was slowly vented over the course of 12 hours. CCDC 1431726 contains the supplementary crystallographic data for Zn-MOF-Crown.

Table 1. Crystallographic data and structural refinement summary for Zn-MOF-Crown.

Structure	Zn-MOF-Crown
Empirical formula based on atoms located by single X-ray diffraction	C ₂₄ O ₂₅ Zn ₄
Formula weight	949.72
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	$R\bar{3}m$
Unit cell dimensions	a = b = 18.2657(8) Å, c = 22.3708(15) Å
Volume	6463.8(6) Å ³
Z	3
Density (calculated)	0.732 Mg/m ³
Absorption coefficient	1.138 mm ⁻¹
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1811 / 0 / 81
Goodness-of-fit on F^2	1.035
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0802, wR2 = 0.1782
R indices (all data)	R1 = 0.1470, wR2 = 0.1969
Largest diff. peak and hole	0.462 and -0.428 e.Å ⁻³

Synthesis of Li⁺@Zn-MOF-Crown: 50.0 mg pre-activated Zn-MOF-Crown was immersed into 1 mM LiCl solution in DEF/H₂O (100 mL, v/v = 50:1) with stirring at room temperature for overnight. The resulting precipitate was obtained by centrifugation and washed by DEF for three times. The concentration of LiCl in remaining solution was detected by inductively coupled plasma mass spectrometry (ICP-MS) analysis. The concentration of Li⁺ drops down to 0.090 mM, which indicates the lithium ion sorption capacity for Zn-MOF-Crown was ~1.2 wt %.

Table 2. ICP-MS data of Li⁺ before and after doping.

Before doping Li ⁺ (mM)	After doping Li ⁺ (mM)	Li ⁺ ion captured in per ether unit
1.00	9.00×10 ⁻²	0.73
10.0	7.62	1.91

3.3 Discussion

The preparation of crown ether-based MOF (Zn-MOF-Crown) is shown in the ESI. Single crystal X-ray diffraction analysis of Zn-MOF-Crown [Zn₄O(C₁₄H₁₄O₈)₃] reveals that it crystallizes in trigonal space group $R\bar{3}m$ with $a = 18.27 \text{ \AA}$ and $c = 22.37 \text{ \AA}$ (Table 1). Although featuring different space group, Zn-MOF-Crown is an analogue of MOF-5.²⁵ Specifically, each organic linker connects with two octahedral Zn₄O(-COO)₆ secondary building units (SBUs) in Zn-MOF-Crown, leaving uncomplexed crown ether units for further coordination (Figure 3.1). The density of this material is as low as 0.93 g cm^{-3} . Approximately 1400 crown ether units per volume of 1000 nm^3 are distributed inside the crystalline solid in a precise manner, providing high density of potential sites for metal-crown ether supramolecular interactions. Similar with other crown ether-based MOFs,⁴²⁻⁴⁵ the crown ether units are highly disordered and could not be located in the single crystal X-

ray diffraction, thus they were modeled by Materials Studio. Compared to our previously reported interpenetrated crown ether-containing MOFs from longer linkers,⁴⁴ the porosity of the activated Zn-MOF-Crown is expected to be obviously increased by intentionally avoiding the framework interpenetration and structural collapse owing to the use of slender linkers, thus keeping the crown ethers accessible to guest molecules.

The incorporation of dynamic supramolecular entities into robust three-dimensional MOF scaffolds has ensured materials capable of host-guest recognition in the interfaces inside the interconnected pores,⁴⁶ as demonstrated by the docking of paraquat ions into crown ether domains in a porous MOF previously.⁴² On the other hand, benzo-12-crown-4 is very well known for its capability of capturing lithium ions.⁴⁷ To investigate their lithium ion docking capability after the crown ether units were incorporated into the MOF, 50 mg of Zn-MOF-Crown single crystals was immersed into a solution of 1.00 mM LiCl in *N,N*-diethylformamide (DEF) /H₂O (100 mL, v/v = 50:1) with stirring at room temperature overnight. Here, very small amount of H₂O was used to improve the solubility of LiCl, and it did not destroy the framework integrity. The resulting crystals were obtained by centrifuge and washed with DEF for three times, and the concentration of the Li⁺ remaining in mother liquor was detected by inductively coupled plasma mass spectrometry (ICP-MS) analysis. The average concentration of Li⁺ dropped down to 0.090 mM, corresponding to 0.73 Li ion captured in every crown ether unit in Zn-MOF-Crown (Table 2). It is worth noting that higher loading of Li⁺ could also be achieved by using LiCl with higher concentration (1.91 Li⁺ ions per crown ether when 10.0 mM LiCl was applied, indicating non-specific binding between Li⁺ and framework on top of Li⁺-crown ether interaction). However, to make sure all the Li ions get docked in the crown ethers rather than staying in the pores, the initial Li⁺

amount in the solution was a bit lower than the number of crown ether sites available in the crystals. The obtained lithium ion-loaded Zn-MOF-Crown was named $\text{Li}^+@ \text{Zn-MOF-Crown}$.

In order to obtain further insights on the structures of Zn-MOF-Crown and $\text{Li}^+@ \text{Zn-MOF-Crown}$, their powder X-ray diffraction (PXRD) patterns were examined. As shown in Figure 2, the PXRD patterns of Zn-MOF-Crown and $\text{Li}^+@ \text{Zn-MOF-Crown}$ are almost identical with the simulated pattern, indicating that pure form of Zn-MOF-crown was obtained and it did not collapse during the process of Li^+ docking. Thermogravimetric analysis (TGA, Figure 3.2) of the activated Zn-MOF-Crown shows that the framework starts to decompose at $\sim 400^\circ\text{C}$, a temperature much higher than the decomposition temperature of the linker only.

Figure 3.2 (a) TGA curves and (b) FTIR spectra for crown ether-based organic linker and Zn-MOF-Crown; (c) SEM image of the Zn-MOF-Crown membrane coated for LIBs.

Figure 3.3 PXRD patterns of the simulated Zn-MOF-Crown (red), and the Zn-MOF-Crown before (black) and after (blue) lithium ion docking.

The introduction of crown ether units into the cubic MOF and the subsequent Li^+ docking inside the MOF have enriched the functionalities of Zn-MOF-Crown. We firstly investigated whether these functionalities enhance the gas adsorption capability of the MOF, considering that Li ions provide stronger interaction sites with the gas molecules. The N_2 isotherms of the activated Zn-MOF-Crown and $\text{Li}^+@\text{Zn-MOF-Crown}$ at 77 K show steep N_2 uptake in the low-pressure regions ($P/P_0 < 0.05$), indicating the microporosity of these materials (Fig. 3.4a). The Brunauer–Emmett–Teller (BET) surface areas of Zn-MOF-Crown and $\text{Li}^+@\text{Zn-MOF-Crown}$ were estimated to be 1101.4 and 893.6 $\text{m}^2 \text{g}^{-1}$, respectively. The pore size distribution analysis of Zn-MOF-Crown revealed narrow distribution of micropores at 6.0–12.0 Å in diameter, which are smaller than those of MOF-5.²⁵ This can be explained by the crown ether units dangling in the pores of Zn-MOF-Crown. To further analyze the pore volume and surface area of the MOFs, t -plot method was performed and the values of each material in this work were summarized in Table 3. After the Li ion docking, the total pore volume changed from 0.56 to 0.49 cc g^{-1} , while the micropore volume reduced from 0.39 to 0.31 cc g^{-1} .

H_2 adsorption isotherms of both MOFs at 77 K were measured to further probe the effect of lithium ions loading on the adsorption properties. As shown in Figure 3.4b, the H_2 uptake at $P/P_0 \approx 1$ of $\text{Li}^+@\text{Zn-MOF-Crown}$ is 104.8 cc g^{-1} , compared to 72.5 cc g^{-1} in Zn-MOF-Crown. The 45% increase in the uptake is due to the interaction between Li^+ and H_2 .^{48–49} In addition, CO_2 adsorption isotherm measurements at 273 and 298 K were conducted for both MOFs. Zn-MOF-Crown adsorbs 72.3 and 58.8 cc g^{-1} of CO_2 at 273 and 298 K, while the uptake amounts go up to 121.0 and 75.5 cc g^{-1} for $\text{Li}^+@\text{Zn-MOF-Crown}$, respectively. Although as many as 0.73 LiCl is loaded in each crown ether in the pores, the LiCl salt takes

only 7.2 wt % of the whole MOF. In other words, the lithiation of the MOF does not increase the weight of the material significantly, making the effect of Li^+ docking more visible in the adsorption measurements. Overall, although the surface area of the MOF decreases after the docking of Li^+ , related studies involving the alkali metal as specific binding sites in MOF for gas adsorption have been conducted and their results shown that the impregnation of metal ions into MOFs significantly increases the isosteric heat (Q_{st}) value and the capacity of gas adsorption.⁵⁰⁻⁵²

Figure 3.4 (a) N_2 adsorption isotherms of activated Zn-MOF-Crown (blue) and Li^+ @Zn-MOF-Crown (red) at 77 K. Inset shows the pore distribution of Zn-MOF-Crown. (b) Adsorption isotherms of CO_2 at 273 K and 298 K, and H_2 at 77 K for the activated Zn-MOF-Crown and Li^+ @Zn-MOF-Crown. (c) BET linear plots of Zn-MOF-Crown with and without Li ion, where r is the correlation coefficient.

Table 3. Statistics for micropore and mesopore based on t -plot method.

Item	Micropore $\text{SA}^{[a]}$ ($\text{m}^2 \text{g}^{-1}$)	External $\text{SA}^{[a]}$ ($\text{m}^2 \text{g}^{-1}$)	Total Pore Volume ^[b] (cc g^{-1})	Micropore Volume ^[a] (cc g^{-1})	H_2 Uptake Capacity at 73K (cc g^{-1})	CO_2 Uptake Capacity at 273K (cc g^{-1})
Zn-MOF-Crown	965.5	135.8	0.56	0.39	72.5	72.3

Li ⁺ @Zn-MOF-Crown	764.6	129.0	0.49	0.31	104.8	121.0
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The data were determined by N₂ adsorption/desorption isotherms at 77 K. [a] calculated by the *t*-plot method, where the contribution points are from 0.35 to 0.5 in *P/P*₀; [b] calculated by the point of the highest adsorption. SA = Surface Area.

3.4 Lithium storage performance

3.4.1 Battery fabrication

Standard CR2032-type coin cells were assembled in an argon-filled glovebox (Mbraun, Unilab, Germany) with the as fabricated crown-based MOF as the working electrode (with diameter of 12 mm). The average loading of MOF in each battery is ~1.7 mg and the weight ratio of MOF, carbon black, and polyvinylidene fluoride binder is 80:10:10. For lithium ion battery fabrication, the metallic lithium foil as the counter-electrode, 1 M LiPF₆ in ethylene carbonate (EC)–dimethyl carbonate (DME) (1:1 in volume) as the electrolyte, and a polypropylene (PP) film (Cellgard 2400) as the separator. The CV measurements were carried out using a Parstat-2273 electro-chemical potentiostat at a scanning rate of 0.2 mV/s. Galvanostatic charge–discharge cycles were tested by Neware battery tester at different current densities at room temperature.

3.4.2 Battery Performance

Zn-MOF-Crown has provided a porous scaffold capable of storing Li⁺ reversibly, thus it will be interesting to see whether this material can improve the performance of LIBs when it is used as the electrode material. We fabricated the LIBs using these two MOFs as anode materials (Figure 3.7). The anode is made of MOF, carbon black, and polyvinylidene fluoride binder with weight ratio of 80:10:10, and the average loading of MOF in each battery is ~1.7 mg. CV curve of Li⁺@Zn-MOF-Crown (Figure 3.5g) shows several small redox peaks due to

multistep lithium ion intercalation/deintercalation.⁵³⁻⁵⁴ The charge–discharge profiles based on Zn-MOF-Crown and Li⁺@Zn-MOF-Crown within a cutoff window of 0.01–3 V at 0.5 C rate (1 C = 1 A g⁻¹) in coin-type lithium cells are shown in Fig. 4a and d. In both profiles, distinct voltage plateaus could be clearly identified in the charge process at ~1.35 V, corresponding to the potential peak at ~1.45 V in the CV curve. Remarkably, the LIBs from MOF-Crown or Li⁺@Zn-MOF-Crown show discharge capacities of 405 and 450 mAh g⁻¹, and charge capacities of 273 and 348 mAh g⁻¹, respectively. Both batteries show relatively low coulombic efficiency (Figure 3.5c and f), indicating possible decomposition of electrolyte during the operation.⁵⁵⁻⁵⁶ The battery with Li⁺@Zn-MOF-Crown shows higher capacity, owing to that the ions have already occupied part of the crown ethers in the MOF before cell operation, which have stabilized the MOF during the intercalation/deintercalation process.

Remarkably, the charge–discharge profiles of Zn-MOF-Crown (Figure 3.5a and c) demonstrate that the battery has a charge capacity of 239 mAh g⁻¹ at 500th cycle, an 88% capacity retention compared to the first cycle. For the battery from Li⁺@Zn-MOF-Crown, a capacity of 243 mAh g⁻¹ at 500th cycle, a 70% retention, was observed (Figure 3.5d and f). The great cycling stability of the battery based on the both MOFs was further studied by cycling the cell at various current densities. For the battery based on Zn-MOF-Crown (Figure 3.5b), when the current density increased from 0.5 to 1, 2, and 5 C, the charge capacity decreased slightly from ~273 to 240, 215 and 170 mAh g⁻¹, respectively. When the current density was reduced from 5 to 2 C, a capacity of 209 mAh g⁻¹ was recovered, confirming the long-term stability for usage. Similar cycling performance was observed for the cell with

$\text{Li}^+@\text{Zn-MOF-Crown}$ (Figure 3.5e). Even when 60 C current density was applied, no obvious performance drop was observed in the first 50 cycles (Figure 3.6).

Although high capacitance can be achieved in several MOF-based LIBs, one of the major bottlenecks of MOFs as the electrode materials is their unsatisfactory cycling performance, probably due to the decomposition⁴⁰ of the active MOF materials during the cycling process. In contrast, the stability of the present Zn-MOF-Crown and $\text{Li}^+@\text{Zn-MOF-Crown}$ for long-term cycles is notable with improved capacity retention. In both MOFs examined, by specifically designing preferred and ordered sites for Li^+ in the organic units of the MOFs, Li^+ mainly interacts with the crown ethers while keeping the MOF skeleton intact. What is more, in $\text{Li}^+@\text{Zn-MOF-Crown}$, Li^+ ions have already occupied some crown ether sites in the porous structure before the cell operation. The pre-stabilization with Li^+ ions may be the key in achieving high capacity. Overall, in respect of the materials design, the introduction of crown ether and the docking of Li^+ in MOFs have enriched the functions of MOFs, leading to enhanced performance.

Figure 3.5 Electrochemical performance of LIBs fabricated based on Zn-MOF-Crown and $\text{Li}^+@\text{Zn-MOF-Crown}$ electrode: Charge–discharge profiles at a current density of 0.5 A g^{-1} of Zn-MOF-Crown (a) and $\text{Li}^+@\text{Zn-MOF-Crown}$ (d); Rate capability tests at various current densities ($0.5\text{--}5 \text{ A g}^{-1}$) of Zn-MOF-Crown (b) and $\text{Li}^+@\text{Zn-MOF-Crown}$ (e); Cycling performances for charge-discharge efficiency and specific capacity for 500 cycles of Zn-MOF-Crown (c) and $\text{Li}^+@\text{Zn-MOF-Crown}$. The red curve

represents the efficiency that is the ratio of charge and discharge capacity. (f); CV curve of $\text{Li}^+@\text{Zn-MOF-Crown}$ used as electrode in LIBs (g).

Figure 3.6 (a,b) Cycling performance of $\text{Li}^+@\text{Zn-MOF-Crown}$ at 60 C for 50 cycles (1/3 C at first five cycles for activation).

Figure 3.7 The powder X ray diffraction (PXRD) patterns of $\text{Li}^+@\text{Zn-MOF-Crown}$ (black), the electrodes before (blue) and after (red) electrochemical test. The samples after electrochemical test were dried under vacuum for 12 hours in the freeze dryer before PXRD test.

3.5 Conclusion

In conclusion, we have successfully constructed a microporous Zn-based MOF containing 12-crown-4 units. The covalently bonded crown ethers with precise and ordered positions provide supramolecular interaction sites accessible to incoming guests. With specific docking of Li^+ in the crown ether entities, $\text{Li}^+@\text{Zn-MOF-Crown}$ demonstrates improved uptake in H_2 and CO_2 adsorption with 45% and 67% increase compared to its lithium-free counterpart. When Zn-MOF-Crown was employed as the anode materials in

lithium ion battery, high charge capacity (273 mAh g^{-1}) with 88% capacity retention after 500 cycles was observed. The great performance is contributed by the fact that Li^+ ions mainly interact with the organic units only, thus maintaining the framework structure integrity during the cell operation. Furthermore, by docking Li^+ ions into the MOF in advance, the battery shows enhanced charge capacity (348 mAh g^{-1}) with long-term cycling ability. These promising results confirm that the introduction of crown ether rings and their complexation with lithium ions are effective in overcoming some of the challenges we are currently facing in green energy systems. Hopefully, this work will pave a new direction for further exploration of macrocycle-based MOFs in batteries, catalysis, and gas-separation devices.

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Chapter 4: Two Fully Conjugated Covalent Organic Frameworks as Anode Materials for Lithium Ion Batteries

Abstract

Energy storage has attracted more and more attention for its closed connection with our daily life. However, there are some unceasing issues about the eco-friendliness and sustainability of energy storage. Thus, an eco-friendly storage material is always what we highly desire. While covalent organic frameworks (COFs) promise numerous benefits in the gas adsorption, catalysis and optoelectronic devices, synergistic combination of effective storage and eco-friendliness using COFs as storage materials has not been well studied. Herein, we presented two fully conjugated porous COFs with high capability of selective gas adsorption and large capacity of Li ion storage. In the aspect of gas selective adsorption, the selectivity ratio of H₂ and CO₂ to N₂ reached ~15:1 and 7:1, respectively. In the Li ion storage, COFs exhibited high capacity (~700 mAhg⁻¹) and stable long life (500 cycles). Such good performance confirmed high potential of COFs to be employed for eco-friendly energy storage. Importantly, using conjugated COFs not only avoids complex synthesis of classical conjugated polymers and multilayered or doped hybrids, but also combines their superb properties including structural diversity, flexibility, and high electrochemical activity. The present work opens up a promising route for further utilization of COFs in energy-related

*fields such as electrode materials, supercapacitors, and Li-gas batteries. This work has been published on J. Mater. Chem. A **2016**, 4, 14106-14110.*

4.1 Introduction

With increasing greenhouse effect from fuel energy consumption, it is imperative to develop green energy to ensure environmental sustainability.¹⁻³ Thus, efficient energy storage materials with superior charge-discharge performance, low cost production, and environmental friendliness are highly desired.^{4,5} To date, carbon materials, inorganic metal oxides and organic conjugated polymers have exhibited good performance as conductive electrode materials and high storage capacity for supercapacitors, photovoltaic cells and lithium ion batteries (LIBs).⁶⁻⁸ Particularly, the high electrochemical performance, low toxicity and structural diversity enable carbon materials and organic materials to be suitable in energy conversion and storage technologies.⁹⁻¹¹ However, the complexity of designing and synthesizing these materials presents great challenges toward green energy applications.¹² There are a lot of rooms to simplify the synthesis procedures and maximize the advantages of these materials.

Covalent organic frameworks (COFs) are an interesting class of two-dimensional layered materials discovered a decade ago.^{13,14} Their native superiority of ease preparation with wide synthetic diversity, uniform porosity, favorable thermal stability, and smart structural assembly endows them with great performance in various fields including gas separation,¹⁵⁻¹⁷ optoelectronic responsive devices,^{18,19} and nanochannels.^{20,21} For example, Jiang and co-workers studied significant electrochemical properties of COFs, such as delocalizing π -cloud, latticed conduction and photoelectric response, promoting them as candidate materials for energy storage applications.²²⁻²⁵ On the other hand, low energy level matching, structure defect and

poor ion mobility in typical COFs are general drawbacks that prevent them from being widely used as electrode materials.²⁶⁻²⁹

In order to further explore the applicability of COFs in the energy storage, we herein present two fully conjugated crystalline COFs, which not only performed good gas adsorption selectivity (the ratio between CO₂ and N₂ reached 6:1 and 7:1 respectively), but also showed superior performance in Li ion storage when used as the anodes (~600 mAhg⁻¹ for 500 cycles). Such excellent results can be attributed to their uniform porosity to facilitate the transport of guest molecules and fully conjugated layered stacking for high conductivity. In comparison with other porous materials commonly utilized in energy storage such as metal-organic frameworks (MOF) and silicon,³⁰⁻³³ these two COFs undoubtedly exhibited better performance and higher potential as eco-friendly energy storage materials. Importantly, the dual functions of Li-storage and effective CO₂ capture inspired their further applications in Li-air or Li-CO₂ batteries.³⁴⁻³⁷

Figure 4.1 Schematic illustration of (a,b) N2-COF and N3-COF structures, and (c,d) top view of layered stacking mode based on quantum-chemical DFT calculations (carbon: blue, nitrogen: red; hydrogen: gray-white). (e,f) STM images for the formation of COFs.

4.2 Experimental details

4.2.1 Measurement condition

Powder XRD studies were performed on a SHIMADZU XRD-6000 Labx diffractometer using Cu-K α radiation at 40 kV and 300 mA with a scanning rate of $0.02^\circ \text{ s}^{-1}$ (2θ) at room temperature. Electrochemical cyclic voltammetry (CV) was performed using a Gammy electrochemical workstation in a 0.1 mol/L tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) dichloromethane (DCM) solution with a scan speed at 0.1 V/s. Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The concentration of samples was adjusted as 1×10^{-4} M in chromatographic pure DCM solution for the CV measurements.

The LT-STM/STS experiments were performed in a multi-chamber UHV system housing an Omicron LT-STM. STM imaging was carried out at 77 K in constant current mode with a chemically etched tungsten tip. Imaging conditions: $V_{\text{bias}} = 600$ mV, $I_t = 500$ pA.

Low-pressure gas sorption measurements were performed by using Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) with the extra-high pure gases. Before this measure, an activation for the as-synthesized COFs were performed, in which the COFs were rinsed with DMF for three times, followed by solvent exchange with CH_2Cl_2 for six times. CH_2Cl_2 was further removed with supercritical liquid CO_2 in a Tousimis Samdri PVT-30 critical point dried by the following procedures. The wet sample was placed inside the dryer and the CH_2Cl_2 was exchanged with liquid CO_2 over a period of 20 minutes, during which time the liquid CO_2 was vented under positive pressure. The venting rate of liquid CO_2 was kept below the rate of filling so as to maintain a full chamber. After 20 minutes of venting and soaking with liquid CO_2 , the temperature was raised to 40 °C. The chamber was held above the critical point with the pressure around 1300 psi for 1 hour, at which point the chamber was slowly vented over the course of 12 hours. This activation method is recently found when we use it to activate MOFs, which is different from those in our previous reports.¹⁻² Upon this method, the gas sorption property of these two COFs has been improved, including N_2 isotherm and gas selective adsorption, although this change is not very obvious.

4.2.2 Synthesis of N2-COF

Anhydrous 1,4-dioxane, anhydrous mesitylene, anhydrous THF and 4,4'-biphenyldiamine were purchased from Sigma-Aldrich. 1,3,5-Triformylbenzene was synthesized according to the reported procedure.³⁸

4,4'-Biphenyldiamine (83 mg, 0.3 mmol) and 1,3,5-triformylbenzene (48 mg, 0.2 mmol) were weighed into a 25 mL Schlenk storage tube (SynthwareTM, OD28 x L120mm, high vacuum valve size 0-8mm, with PTFE o-ring and wiper), dissolved in mixed solvent (3 mL, 1,4-dioxane:mesitylene = 1:1) and sonicated for 10 min. After that, aqueous HOAc (0.3 mL, 6 mol/L) was added to the mixture. Each tube was degassed by three freeze-pump-thaw cycles. Finally, each tube was sealed off, heated at 120 °C in an oven at the same time, and left undisturbed for 0-72 h. The precipitates were isolated by centrifugation, washed with anhydrous THF for 3 times, and dried at 120 °C under vacuum for 24 h, to give a yellow powder with 75-90 % isolation yields.

Figure 4.2 Schematic illustration of COF formations by a condensation of (a) 1,3,5-triformylbenzene and two amino derivatives, (b) 4,4'-biphenyldiamine and (c) 2,4,6-tris(4-aminophenyl)-s-triazine, to give two polyimine-based COFs, i.e., (d) N2-COF and (e) N3-COF. Controlled self-assembly affords

the COF products with porous structures having tunable pore width and layered stacking. Green color represents the amino derivatives and blue color stands for the 1,3,5-triformylbenzene unit.

4.2.3 Synthesis of N3-COF

2,4,6-Tris(4-aminophenyl)-1,3,5-triazine was synthesized according to the reported procedures.² The ¹H NMR and ¹³C NMR spectra matched well with those reported ones. Then, 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (70 mg, 0.2 mmol) and 1,3,5-triformylbenzene (48 mg, 0.2 mmol) were placed in a 25 mL Schlenk storage tube, which were dissolved in a mixture solvent (10 mL, 1,4-dioxane : mesitylene = 10:1, v:v) and sonicated for 10 min. After that, aqueous HOAc (0.75 mL, 6M) was added, and the mixture was degassed by three freeze-pump-thaw cycles. Finally, the tube was sealed, heated at 120 °C in an oven, and left undisturbed for 72 h. The precipitate was collected through centrifugation, which was washed with anhydrous THF for 3 times, and then dried at 150 °C under vacuum for 24 h. A yellow powder was obtained in 90% isolation yield.

4.2.4 Theoretical calculations

Density functional theory calculations were performed with the Gaussian 09 program using the B3LYP functional.³ All-electron double- ξ valence basis sets with polarization functions 6-31G* were used for all atoms.³ Geometry optimizations were performed with full relaxation of all atoms in gas phase without solvent effects.

4.2.5 Structural modeling

Simulated CIF data of N2-COF and N3-COF could be found from our previous reports.^{1,2} The Predicted stacking mode and practical powder XRD pattern.

Figure 4.3. Theoretical calculation and practical powder XRD patterns of (a) N2-COF and (b) N3-COF: experimental powder XRD pattern (black curve) and simulated patterns of eclipsed (red) and staggered (blue) structures. Inset figures are simulated crystal lattice of the unit cells calculated in an eclipsed (upper) and staggered structure (down).

4.3 Physical properties characterization

The structures of two COFs achieved by a condensation reaction of aldehyde and amine under solvothermal conditions (Fig. 4.2) are showed in Fig. 1. 1,3,5-Triformylbenzene was reacted with two amino derivatives to afford the backbone with uniform and tunable pores. The COF samples were designated as N-COF (N2-COF and N3-COF), where the number indicates the amount of amino groups in the amino derivatives. The structures and the stacking patterns of interlayers were predicted by theoretical calculations (Fig. 4.3), where three different stacking patterns were exhibited along with corresponding theoretical x-ray diffraction (XRD) patterns (Fig. 4.3). In comparison with the theoretical powder XRD patterns, the two COFs presented well matched specific peaks for the eclipsed stacking pattern, indicating that the COFs existed in eclipsed stacking in the crystalline structures.

Scanning tunneling microscope (STM) and powder XRD were performed to monitor the formation of the COFs. As shown in Fig. 4.1e,f, ordered stacking channels were clearly exhibited after the solvothermal reaction for 48h. The average diameter of the channels was measured to be ~2.3 nm and ~1.6 nm for N2-COF and N3-COF, respectively. The powder

XRD patterns of the COFs exhibit a peak with the highest intensity at 3.54° and 5.62° (2θ) for N2-COF and N3-COF respectively, assigning to the reflection from the (100) plane. The calculated d values corresponding to the patterns are ~ 2.4 nm and ~ 1.7 nm for N2-COF and N3-COF respectively. These results matched well with the channel diameters measured from STM studies. Then, both the uniform porosity and surface area for the resultant COFs were confirmed by N_2 adsorption/desorption analysis at 77 K (Fig. 4.4b and Fig. 4.5 in ESI). The N_2 isotherms of the activated N-COFs at 77 K show steep N_2 uptake in the low-pressure regions ($P/P_0 < 0.05$), indicating the micro-porosity of these materials.³⁹ Brunauer-Emmett-Teller (BET) surface areas were **ESTIMATED** to be 1496 and 1142 $m^2 g^{-1}$ for N2-COF and N3-COF, respectively. The plots chosen for the BET calculation were distributed in the range of 0.02-0.2 P/P_0 .⁴⁰ The pore size distributions of COFs were also performed using density functional theory (DFT) method, revealing narrow distributions at 1.3-3.0 nm and 1.0-2.2 nm for N2-COF and N3-COF, respectively (Fig. 4.5). These numbers are close to both the experimental and theoretical values measured above. The slight difference between the results of molecular model and DFT can be ascribed to different calculation methods, wide distribution of pore size, and layered stacking.^{41,42} To further analyze the pore volume and surface area of the COFs, t-plot method was performed and the values of each COF were summarized in Table 1, where a relative ratio of micro-meso porosity could be found. In the analysis of the pore volume, it was observed that the microporous region (< 2 nm) provides a major contribution to the pore volume and surface area. The micropore volumes were 0.387 cc/g for N2-COF and 0.313 cc/g for N3-COF, while the total pore volumes were 0.622 and 0.561 cc/g for them, respectively.

Figure 4.4 (a) Powder XRD patterns of N2-COF and N3-COF, (b) N₂ adsorption/desorption isothermal curves of N2-COF and N3-COF, and (c,d) gas selective capture performance of N2-COF and N3-COF for H₂, CO₂, CH₄ and N₂, respectively.

Figure 4.5. (a, b) N₂ isothermal adsorption curves and BET of N-COFs. (c, d) Pore-size distribution plots of two N-COFs calculated from experimental N₂ adsorption isotherms using the nonlocal density functional theory (NLDFT): N2-COF (red curve) and N3-COF (blue curve).

In order to obtain strong evidence of the uniform porosity and good pore size distribution of the two N-COFs, transmission electron microscopy (TEM) and field-emission scanning electron microscopy (FESEM) were carried out to probe their morphology. As shown in Figure 4.7, the contrast in TEM images indicates a porous nature of these COFs, which can also be supported by the FESEM images. Totally different porous morphologies can be observed for both N-COFs. N2-COF was found to be spherical nanoparticles, while N3-COF showed needle shaped morphology in the solid state.

Figure 4.6 IAST selectivity for adsorption of CO₂/CH₄ in N2-COF and N3-COF at 273 K and 298 K. These selectivity data have also been confirmed by the dual-component gas adsorption experiments as mentioned above.

Next, the gas adsorption performance for H₂, CO₂, CH₄ and N₂ were carried out to investigate their ability for selective gas capture. As shown in Figure 4.4, the H₂ uptake of N2-COF at 77 K and $P/P_0 \approx 1$ was 158.5 cc g⁻¹, while it was 147.0 cc g⁻¹ for N3-COF. Although the pore size of N3-COF is smaller than that of N2-COF, there is no obvious distinction in their H₂ adsorption property. In addition, CO₂ adsorption isotherm measurements at 273 and 298 K were also conducted for both N-COFs. N₂-COF adsorbs 92.0 and 58.7 cc g⁻¹ of CO₂ at 273 and 298 K respectively, while the uptake amounts changed to 101.0 and 60.3 cc g⁻¹ for N3-COF at 273 and 298 K, respectively. The measured pure

component isotherm data for H₂, CO₂, CH₄ and N₂ on two COFs were fitted with Henry's law, which presents a comparison of component loadings at 77 K, 273K and 298K with the isotherm fits. The fits are excellent for both components over the entire pressure range in future.

The higher CO₂ uptake performance of N3-COF may be attributed to its nitrogen-rich backbone.^{16,43} Both N-COFs exhibited obviously selective capture ability for H₂ and CO₂ over CH₄ and N₂. Particularly, the selectivity ratios of both COFs reached ~15:1 and ~7:1 for H₂ to N₂ and CO₂ to N₂ respectively, indicating their marked selectivity for CO₂ capture and potential use in future Li-CO₂ battery. Overall, despite slight difference in their porosity property, both N-COFs exhibited good performance in selective gas capture. The IAST-based prediction of selective adsorption was carried out based upon the single component isotherms at 273 K and 298 K. The CO₂/CH₄ selectivity is estimated as ~14 at 0.1 bar and gradually drops to ~3 at 1 bar at 273 K (Figure 4.6). With combined high uptake capacities and selectivities of CO₂ and CH₄ at 298 K, two COFs have excellent potential for CO₂ and CH₄ separations.

Figure 4.7 (a,b) TEM and (c,d) FESEM images of two COFs: (a) and (c) are for N2-COF, while (b) and (d) are for N3-COF.

Table 1 T-plot method for microporous and mesoporous measurements.

	N2-COF	N3-COF
^[a] Total pore volume (cc/g)	0.622	0.561
^[b] Micropore volume (cc/g)	0.387	0.313
^[c] Mesopore volume (cc/g)	0.235	0.248
^[b] Micropore area (m ² /g)	1304.7	942.0
^[b] External surface area (m ² /g)	191.3	159.0

This is determined by N₂ adsorption/desorption isotherms at 77K: [a] calculated by the point of the highest adsorption; [b] determined by the t-plot method, where the contribution points are from 0.35-0.5 in P/P₀; [c] obtained by the difference between the total pore volume and micropore volume.

4.4 Lithium ion battery fabrication

Standard CR2032-type coin cells were assembled in an argon-filled glovebox (Mbraun, Unilab, Germany) with the as-fabricated N-COFs as the working electrode (0.5cm × 0.5 cm,

0.25 cm²). The average loading of N-COFs in each battery is ~3.1 mg and the anode was made without any adding any binders. For lithium ion battery fabrication, the metallic lithium foil served as the counter-electrode, it was separated from the working electrode by a Celgard 2500 polymeric separator. The electrolyte was composed of a solution of 1 M LiPF₆ in ethylene carbonate (EC) / dimethyl carbonate (DMC) / diethyl carbonate (DEC) (1:1:1 by volume). The cells were assembled in an argon-filled glovebox with the concentrations of moisture and oxygen at less than 1 ppm. The CV measurements were carried out using a Parstat-2273 electro-chemical potentiostat at a scanning rate of 0.2 mV/s. Galvanostatic charge–discharge cycles were tested by Neware battery tester at different current densities at room temperature. There is a slight shift between the first cycle and after third cycle in the cycle CV measurement, which is caused by the initial unstable state of electrolyte and electrode materials. During the progress of charge-discharge, the solid electrolyte interphase will be formed on the surface of electrode using N-COFs, which predominantly contain lithium ethylene dicarbonate, lithium methyl carbonate and LiF.

Figure 4.8 Electrochemical performance of LIBs fabricated based on N2-COF and N3-COF anodes: (a) CV curves of two N-COFs used as anodes in LIBs, where the dash curve showed the electrochemical performance of N-COFs in first cycle and the solid curve showed the electrochemical performance of N-COFs after third cycle; (b) Nyquist plots of two N-COFs electrodes: N2-COF (blue curve) and N3-COF (red curve). Inset shows alternating current impedance plots at the full-charged

state after the first cycle. The resistance was simulated using an equivalent circuit of $RS(Q(R_{ct}ZW))$, where RS is the ohmic resistance of solution and electrode, R_{ct} is the charge transfer resistance, Q is the double layer capacitance, and ZW is the Warburg impedance.

Figure 4.9 XPS spectra of two N-COFs showing the difference before and after the progress of charge-discharge.

Having such uniformly ordered porous framework, other than the ability for gas capture, a pivotal question was whether the pores could facilitate the transport of electrolyte ions for electrochemical redox reactions as electrode materials.⁴⁴ The high electrochemical activity of COFs has been reported for the charge separation, carrier transport and energy conversion applications.^{45,46} Given their promising prospects as electrode materials, we further characterize the electronical conductivity, in which the charge limited current mobility measurement was performed, where the device is fabricated with a configuration of ITO / PEDOT:PSS / two COFs / MoO₃ / Al. The individual active film is of typical organic solar cell device area (0.25 cm²). The J–V characteristics of the hole-only devices are shown as below.

Figure 4.10 Current density–voltage characteristics of the hole-only devices of thin films of N2-COF and N3-COF with the configuration of ITO / PEDOT:PSS / two COFs / MoO₃ / Al with thermal annealing at 110 °C.

According to the structure of two N-COFs, their electrode reaction happened in the progress of charge-discharge has been shown in Figure 4.11, where N2-COF undergoes a two electrons redox reaction and N3-COF undergoes a three electrons redox reaction during lithiation and delithiation. In comparison of previous reports,⁵ the electrode potential of Schiff base generally locates in the range from 0.8-2.0 eV, which matches well with our experiment outcomes.

Figure 4.11 Electrochemical reaction of a unit of N-COF during the progress of charge-discharge.

Next, we fabricated the LIBs using the two N-COFs as anode materials (see the details of LIB fabrication). Coin cells (2032) with a metallic Li counter electrode were used to perform the charging and discharging electrochemical process, where the working electrode was made of N-COFs directly without adding any binders, and the average loading of N-COFs in each battery was ~ 3.1 mg. Cyclic voltammetry (CV) curves (Figure 4.8) showed several small redox peaks due to multistep lithium ion intercalation/deintercalation. The charge–discharge profiles based on two N-COFs within a cutoff window of 0.05–3 V at 1 C rate ($1\text{ C} = 1\text{ A g}^{-1}$) in coin-type lithium cells are shown in Figure 4.11a,b. In both profiles, distinct voltage plateaus could be clearly identified in the charge process at ~ 1.35 V, corresponding to the potential peak at ~ 1.45 V in the CV curve.

Remarkably, the LIBs from N2-COF or N3-COF showed discharge capacities of 735 and 731 mAh g^{-1} , and charge capacities of 689 and 707 mAh g^{-1} for the first cycle, respectively (Figure 4.12a,b). In addition, the charge–discharge profiles of N2-COF (Figure 4. 12a,e) demonstrated that the battery had a charge capacity of 600 mAh g^{-1} at the 500th cycle, which was 82% capacity retention as compared to the first cycle. For the battery from N3-COF, a capacity of 593 mAh g^{-1} at the 500th cycle, i.e., 81% retention, was observed (Figure 4. 12b,f). The great cycling stability of the batteries based on both N-COFs was further studied by cycling the cells at various current densities. For the battery based on N2-COF (Figure 4. 12c), when the current density increased from 0.2 to 0.5, 1, 2, and 5 C, the charge capacity decreased slightly from ~ 806 to 738, 694, 627 and 497 mAh g^{-1} , respectively. When the current density was reduced from 5 to 2 C, a capacity of 607 mAh g^{-1} was recovered, confirming the long-term stability for the usage. Similar cycling performance was observed

for the cell with N3-COF (Figure 4. 12d). In addition, X-ray photoelectron spectroscopy (XPS) was performed to analyze the insertion of Li-ion into the COF electrode after the electrochemical process. After the process of charge-discharge, Li element was observed in the XPS spectrum, and the relative ratio was calculated to be ~22%, indicating that Li ion was indeed adsorbed in the anode during the charge-discharge process. Furthermore, the Li element existed on the surface of the electrode was mainly in the form of Li_2CO_3 with the binding energy of Li-1s at 55.3 eV,⁴⁷ as shown in Figure 4.8.

Figure 4.12 Electrochemical performance of LIBs fabricated based on two N-COFs as anode: Charge-discharge profiles at a current density of 1 A g⁻¹ of N2-COF (a) and N3-COF (b); Rate capability tests at various current densities (0.2–5 A g⁻¹) of N2-COF (c) and N3-COF (d); Cycling performances for charge-discharge efficiency and specific capacity for 500 cycles of N2-COF (e) and N2-COF (f). The red curve represents the efficiency that is the ratio of charge and discharge capacity.

While some studies reported that some COFs could be applied as the electrode materials in LIBs,^{48,49} achieving both high capacitance and long cycling performance are still the major bottlenecks of using COF materials as the electrode for energy storage, probably due to the structural defect, energy level match and device optimization during the charge-discharge process. In contrast, high stability and capacity of the present two N-COFs for long-term

cycles were achieved with improved capacity retention. The layered stacking structures of N-COFs contribute to the high capacity where the open nanopores facilitate the Li-ion diffusion and holding electrolyte, which may reduce the electrode polarization when a fast Li storage proceeds.

4.5 Conclusion

In summary, we have successfully developed two N-COFs with precise and uniform porosity, providing accessible space for hosting guests. In terms of gas adsorption, both N-COFs exhibited superior selectivity among H₂, CO₂, CH₄ and N₂, where the uptake of H₂ reached to 150 cc/g and the capture amount of CO₂ reached to 90 cc/g. Moreover, N-COFs also showed high performance of Li ion storage as anodes in LIBs, including high charge capacity (from 600 to 700 mAh g⁻¹) with 82% capacity retention after 500 cycles. The great performance was contributed by the uniform porosity, conjugated structure and good stability, confirming the high potential of these COF materials for both gas selective capture and energy storage. We envision that such COFs could facilitate the development of green energy storage devices such as Li-air, Li-O₂ and Li-CO₂ batteries.

4.6 References

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Chapter 5: Summary and Outlooks

5.1 Summary

In this thesis, we have summarized our recent progress on pore and function engineering to develop functional porous framework materials and improve their performances in gas transportation and filtration, enantioselective separation, luminescence sensing and emitting, as well as electrode material and energy storage materials. Since we can readily design and tune the porosities, pore sizes and functional sites of framework materials, this makes them very promising for gas storage, gas separation and enantioselective separations. We can certainly target functionalizing such materials beyond their porosities through the incorporation of a variety of metal ions/metal clusters, organic linkers and encapsulating the species within pores of unique physical and chemical properties. Theoretically speaking, an infinite number of these linkers can be assembled into frameworks to have variable structures and porosities and to introduce physical and chemical functionalities. Furthermore, the pore spaces within frameworks can encapsulate a number of exotic superior objects, like inorganic nanoparticles, organic small molecules, polyhedron and bio-macromolecules, providing such materials the potential and variability for further development being superior to the other functional materials. In addition, the commercialization of some classical porous framework materials has certainly inspired the continuous research motivation for the further post-functionalization and the targeted decoration. Multidisciplinary collaboration between chemists, physicists, biologists and engineering scientists with different expertise as well as the industrial partners will not only open more new opportunities to explore and develop the

properties of porous framework materials in various fields, but also open up the option and capability of applying such materials in our daily life.

Inspired by these achievements, we also carried out in-depth works to explore the porous framework materials in the aspect of chemical sensing and lithium ion storage. In the first chapter, recent advancements of porous framework materials regarding synthetic strategies, morphology tuning and their performance optimization, were discussed, which formed the basis of my research motivation in the field. Subsequently, three related works inspired by these advancements were showcased.

In the second chapter (our first work), we utilized these characteristics and the inherent advantages to cage functional polymers inside for molecular recognition and investigated the stimuli-responsive behavior with high selectivity caused by different pore sizes. Through inducing the electron-rich polymer, the resulting functional material showed specific interactions with some acceptor molecules, particularly nitro compounds, which are the major components in explosives. This interaction led to a charge-transferring process, observed as an obvious red shift on optical signal and a visible color change. In conventional materials for molecular recognition, a synergy effect is expected, where polymer-threaded MOFs might enhance the stability of the hybrids and the MOF porosity could be used to realize the selectivity towards different guest molecules. In this case, the caged polymers served as the responsive components and could induce multifunction to MOF for enhanced sensitivity. Notably, some shortcomings should be avoided during the preparation of polymer-caged MOF, including complicated structures, poor response performance, and uncontrolled response degree. This novel sensing approach with simple synthesis and

colorimetric output showed broader prospects in practical analysis and sensing applications based on MOF materials.

In the third chapter (our second work), we fabricated a Zn-based cubic MOF in which 12-crown-4 were covalently integrated into the backbone of the structure, in which the active entities with specific interactions with energy-related molecules and ions were introduced. With a high surface area of $1101.4 \text{ m}^2 \text{ g}^{-1}$, this MOF was capable of docking Li^+ ions by the supramolecular interactions between Li^+ and the crown ether units, achieving a high density of 0.73 Li per crown ether in MOF crystals. The MOF after Li^+ ions docking showed 45% enhancement for H_2 storage at 77 K and 67% increase for CO_2 capture at 273 K as compared to the MOF without Li^+ , confirming the specific interactions between the guests and lithium in the MOF. Furthermore, with the host-guest interactions between the crown ethers and Li^+ ions, the lithium ion batteries exhibited enhanced charge capacities of 273 and 348 mAh g^{-1} when the Li^+ ion-free and Li^+ ion-loaded MOFs were employed as the anode materials, respectively. Interestingly, the Li^+ ion-free MOF-based battery showed improved cyclability, with 88% capacity retention after 500 cycles. This research presents a new outlook for crown ether-based MOFs towards further development in chemical strategies for new energy materials.

In the fourth chapter (our third work), we presented two fully conjugated porous COFs with high capability of selective gas adsorption and large capacity of Li ion storage. In the aspect of gas selective adsorption, the selectivity ratio of H_2 and CO_2 to N_2 reached $\sim 15:1$ and $7:1$ respectively. In the Li ion storage, COFs exhibited high capacity ($\sim 700 \text{ mAhg}^{-1}$) and stable long life (500 cycles). Their superior performance displayed the potential of COFs to be employed for eco-friendly energy storage. Importantly, the usage of conjugated COFs not

only avoid complex synthesis of classical conjugated polymers and multilayered or doped hybrids, but also combines their superior properties including structural diversity, flexibility and high electrochemical activity. The present work opens up a promising route for further utilization of COFs in energy-related fields such as electrode materials, supercapacitors and Li-gas batteries.

Lastly, we have presented an outlook for the rapid development of MOF composites with the promising blueprint in structural design, post-functionalization and large-scaled application, together with the many challenges that still exist. The increasing appreciation and acceptance of their properties and behavior will fuel continuous study interest and it is expected that their applications to our daily life will be realized in the near future.

5.2 Outlook

The field of porous materials is at an exciting stage of its evolution. In comparison with its status quo 20 years ago, the types of functional porous solids to choose from have expanded greatly. In particular, porous MOFs, while being a mature technology and have been commercially established, are still developing rapidly. For example, two-dimensional zeolites¹ open up new possibilities for what were hitherto thought of as three-dimensional materials. However, the diversity can make it a dilemma when it comes to select the best material for a specific purpose. For long-termed and large scaled applications, computational structure/property prediction tools will be developed to augment experiment, ultimately to allow the de novo design of new porous solids. This would have strong translational benefit because the same prediction challenge exists for a wide range of nonporous solid-state materials.

During the development and generalization of these predictive tools, materials design will proceed mainly *via* more qualitative and empirical rules, iterated with syntheses and property measurements. In this aspect, opportunities and challenges could be identified. Carbon dioxide capture is an important yet unsolved problem and porous materials could potentially be the solution but the obstacles to commercialization are daunting, not least because of the enormous scale: a single power plant can produce more than 20 billion kg of CO₂ annually. Chosen materials must therefore have low cost and long service lifetimes (i.e. good stability). Although substantial progress has been made on selectivity, both for adsorbents and for membranes,²⁻⁵ the scaling up potential is dependent on kinetics. For membranes, selectivity and permeability are usually studied together, but for adsorbents, kinetics is less commonly investigated and this is an area that requires more attention. In order for membranes to displace commercial high-free volume polymers in large scale separations, or to establish entirely new separation processes, it will be important to solve the physical aging problems associated with these materials.⁶ Improved water purification and water recovery^{7,8} technologies are also of pressing importance worldwide. In principle, many of the material classes outlined in thesis could translate into water purification technologies, and this will likely be a future growth area, although the scale of these processes also necessitates improved performance, low cost and high durability to compete, for example, with commercial desalination membranes. Heterogeneous catalysis is a mature field, hence new porous solids must showcase specific advantages over well-established catalysts and catalyst supports such as zeolites, alumina, silica or simple polymer resin technologies. So far, many heterogeneous MOF catalysts are simply variants of these classical materials. However, a range of new opportunities exists; for example, the rise of asymmetric molecular

organocatalysis⁹ predates the rapid expansion in porous organic polymers by just a few years. It is likely, therefore, that a range of metal-free porous heterogeneous polymer organocatalysts will soon follow,¹⁰⁻¹² especially given the enormous synthetic versatility in porous polymers. More specifically, conjugated chromophores that are not present in more traditional heterogeneous catalysts, but instead by coordinating in the porous frameworks.¹³ The recent discovery of an organic, metal-free photocatalyst that performed photochemical water splitting for 200 days without a reduction in activity¹⁴ suggested that for some of the organic materials, long-termed photostability that matches or exceeds that of traditional inorganic semiconductors could be achieved. More active polymer photocatalysts for water splitting could in turn stimulate the search for improved porous separation media for the hydrogen and oxygen gas streams that would be produced. Alternatively, it might be possible to design a porous membrane material that not only produces hydrogen and oxygen gas but also separates them—for example, by tailoring the pore size.

Separation, adsorption, and nanochannels are what might be called “traditional” areas for porous materials. There are also recent studies that demonstrate new possibilities for porous solids where the advantages over materials such as zeolites are perhaps more clear-cut. For example, in battery and supercapacitor technologies, new porous solids¹⁵ will be competing with conventional materials such as graphite and graphene. New porous electronic materials have developed rapidly in recent years, where crystalline porosity in COFs, for example, has been used to position functional units with respect to one another in space more than to achieve porosity per se. In short, dopable, solution processable porous molecular solids, perhaps designed using crystal structure prediction methods, would be a logical future development.

Scheme 5.1 Selected advances in functional porous solids. Both experimental and computational methods have progressed rapidly in the past decade to yield a range of materials with new or improved functions. Nnumbers in parentheses denote relevant references. Reproduced with permission from ref. 16. Copyright 2015 Science.

5.3 Reference

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