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Importance of pyrazole carboxylic acid in MOFs preparation

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Abstract

Metal–organic frameworks (MOFs), constructed by organic linkers and metal nodes, are a new class of crystalline porous materials with significant application potentials. Featured with extremely high surface area, large porosity, tunable pore size, and flexible functionality, MOFs have gained extensive explorations as a highly versatile platform for functional applications in many research fields. This short review presents the applications of metal-organic frameworks (MOFs) synthesized from pyrazolate derivatives. In fact, many pyrazolate ligands were examined: These ligands were used to synthesize a variety of MOFs that were subsequently investigated for batteries, luminescent sensing, gas storage, catalytic performance etc.

Keywords: Metal-organic frameworks; batteries; luminescent sensing; gas storage; catalytic performance.

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1. Introduction

The discovery of metal–organic frameworks (MOFs), as a new class of porous materials with high surface areas, tunable pore size and other engineerable properties has unlocked the potential opportunities for scientists to solve some pressing problems related to sustainable energy and environment [1]. Similar to other technologies, the research activities in the first 20 years have been

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focused on the discovery phase [2-5], and in the next 30 years research interests will shift towards applications [6-8]. Metal−organic frameworks (MOFs) are fabricated from the metal ions or metal-oxo units coordinating with electron-donating organic ligands, so they can be designedly synthesized with tunable high porosities, large specific surface areas, uniform pore sizes, and functional structures [9]. These structural features make them favorable luminescent sensing candidates. It has been observed that organic ligands play crucial roles for the designed synthesis of some interesting coordination networks, such as the donating type, the flexibility, and the geometry of the organic ligands [10-13]. Especially the coordination compounds synthesized from transition metal ions and N-heterocyclic carboxylic ligands which containing heterocyclic nitrogen atoms, this type of compounds with open frameworks have been continuously explored with multiple applications in many fields, such as catalysis, ion exchange, selective separation and fluorescence probe, etc [14-28].

2. Examples of MOFs based on pyrazole carboxilic acid

Different MOF architectures were prepared using pyrazole carboxylic acid ligand as it can be observed from Fig.1. The compound 1 of Fig.1 is a flexible, multifunctional and an excellent material for the construction of novel coordination compounds and can be taken as an example to reveal the role of the pH value of the reaction in controlling the structure of the supramolecular architecture [29]. The Mannich catalytic reaction of zirconium MOFs based on compound 2 of Fig.1 and its derivatives showed a good conversion compared to other nitrogen ligands [30]. Furthermore, the compound 3 (1H-pyrazole-4-carboxylic acid) has been used in mechanical and electrochemistry synthesis methods, for preparing attractive MOF porous materials [31]. The preparation of luminescent Tb-MOFs based on compound 4 of Fig.1 was demonstrated to exhibit high sensitivity and detection of uric acid in aqueous media [32]. The compound 5 of Fig.1 (1-H- pyrazole-3,5-dicarboxylic acid), strongly bent linker molecule was used to prepare MOFs with specific topologies [33]. The compounds 6 and 7 of Fig.1 were used to synthesize a variety of MOFs that were subsequently investigated for luminescent sensing, gas storage, and catalytic performance [34].

The perfluorinated MOF materials based on compound 8 of Fig.1 has shown an excellent magnetic property [35], whereas the compound 9 in Fig.1 (N-rich pyridyl-pyrazole) was used as a linker in a synthesis of Ln-MOFs with good gas storage, magnetic and luminescence properties [36]. The post-synthesis of metallation used compound 10 of Fig.1 for enhancing catalytic performance of MOFs materials [37]. A luminescent sensor 3D MOF based on compound 11 of Fig.1 has been prepared with interesting topology [38]. The asymmetric tritopic pyrazole carboxylate ligand (compound 12 of Fig. 1) was used as a subunit to synthesis MOFs for acetone sensor application [39]. The bifunctional pyrazoleisophtalate ligand (compound 13 of Fig.1) was used in the synthesis of flexible porous MOFs with dynamic CO_2 sorption isotherm [40].

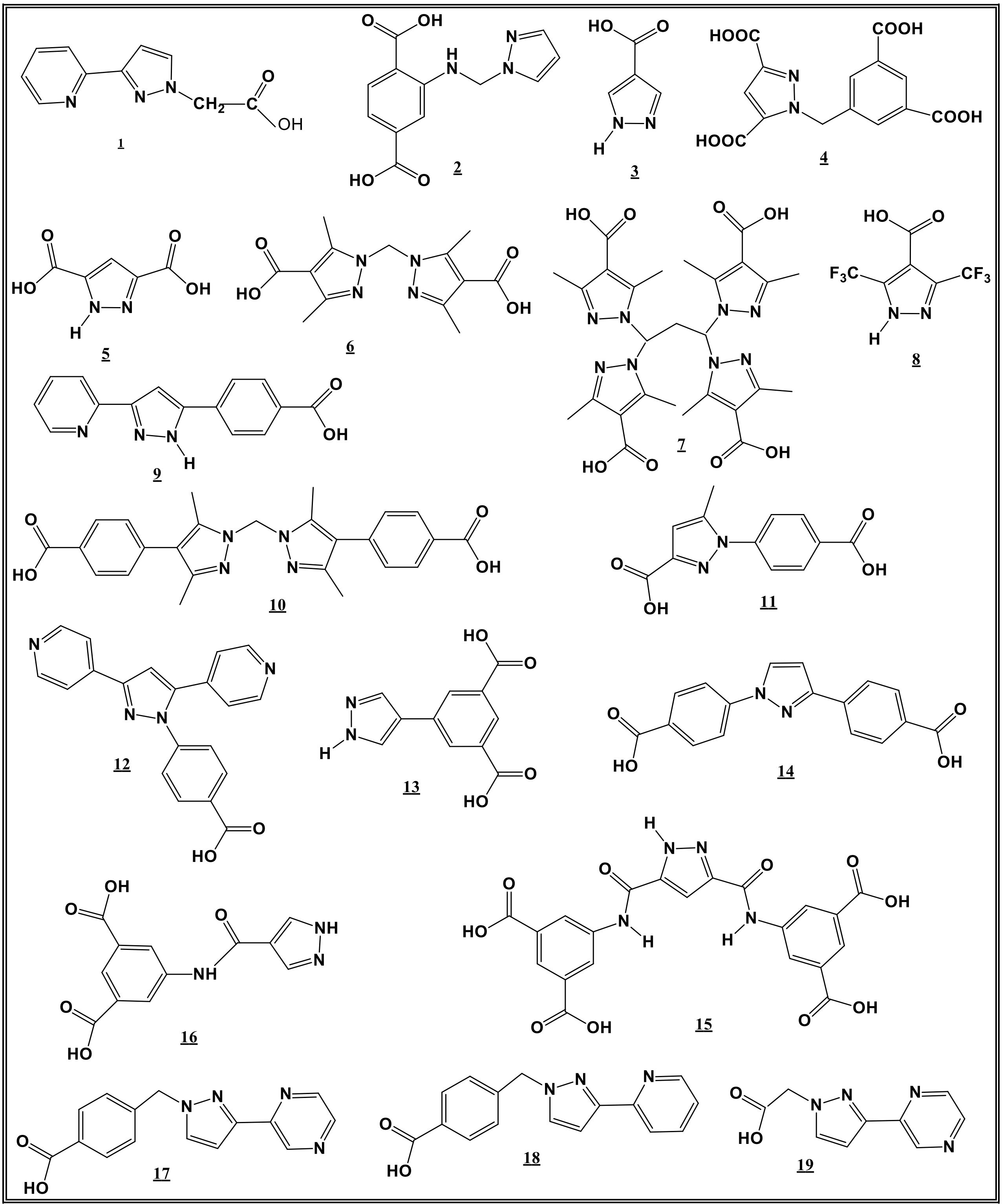

Figure 1: List of organic linkers used in the synthesis of MOFs described in this review.

A two-dimensional MOFs were prepared using compound 14 of Fig.1 for a fluorescent sensor application, particularly for ascorbic acid detection [41]. A new luminescent MOFs based on compound

15 of Fig.1 were prepared and used for selective sensing of nitroaromatic explosives [42]. The compounds 16 of Fig.1 has been used by Bu et al. in a Co-MOF and a Zn-MOF, which show good CO_2-sorption properties [43,44]. A series of metal–organic frameworks based on flexible ligands with nitrogen heterocycles and carboxyl (compounds 17 and 18 and 19 of Fig.1) were prepared and used in catalysis, ion exchange, selective separation and fluorescence [45]. The compounds in Figure 1 are not an exhaustive list of all the pyrazole carboxylic acid, but the main compounds involved in the preparation of MOFs as linkers.

3. Some applications of MOFs

Metal–organic frameworks (MOFs) are a class of porous materials first defined by Yaghi and co-workers [46], which recently have attracted extensive research interests both in LIBs and supercapacitors [47-54]. For example, Tarascon et al. have done pioneering work on the use of MIL-53 (Fe) as a cathode material [55] (Figure 2). Besides, Kang and Yaghi et al. have reported 23 kinds of different MOFs doped with graphene as supercapacitors, and several members of them give high capacitances [56].

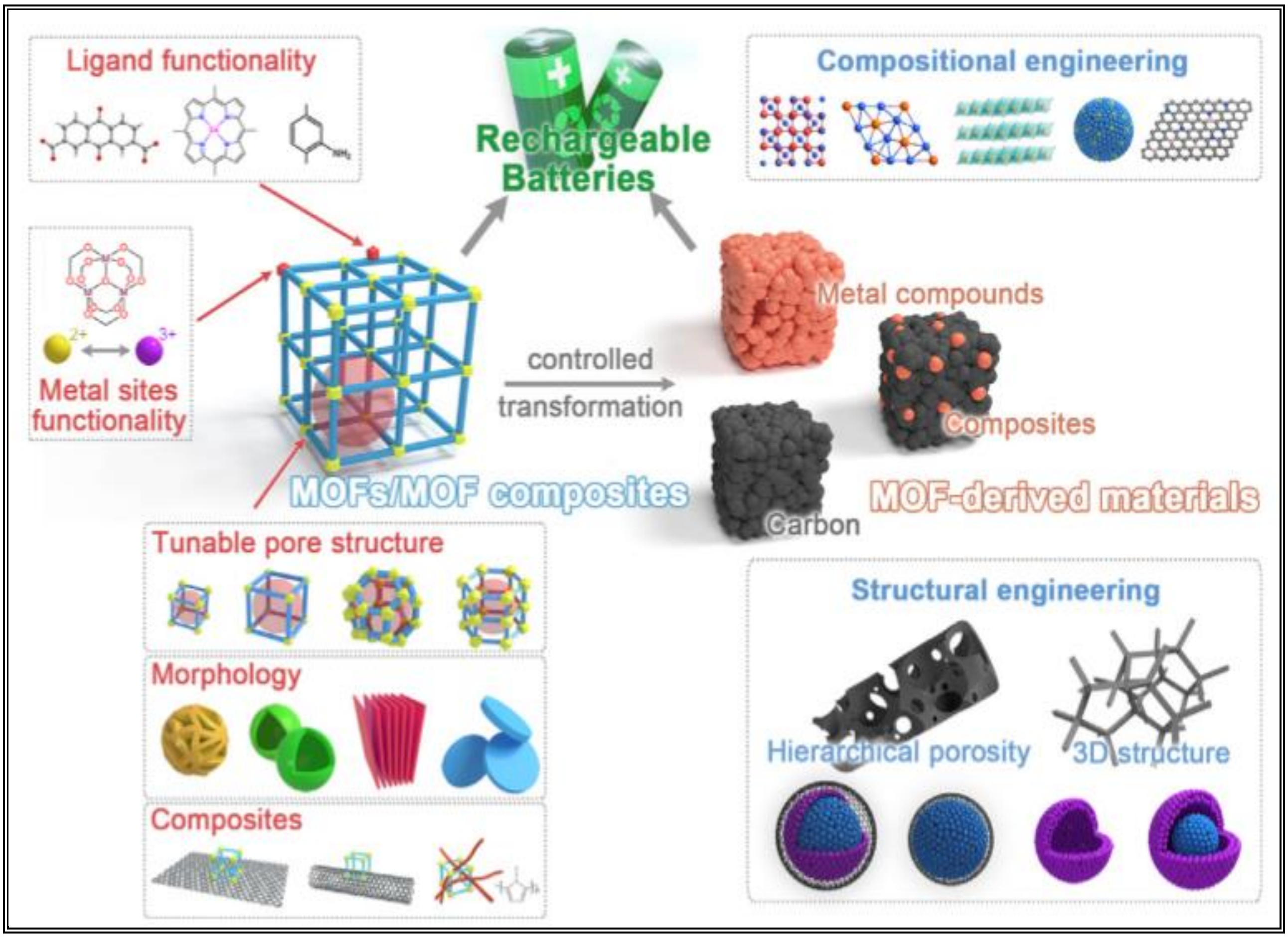

Figure 2: Schematic Illustration of MOF-Related Materials for Rechargeable Batteries

Simultaneously, polyoxometalates (POMs) with multi-electron redox properties, stability, and structural diversity are well-suited to achieve a high capacity for energy storage applications (LIBs and pseudo capacitance) [57-61]. In addition to that Metal–organic frameworks have emerged as desirable cross-functional platforms for electrochemical and photochemical energy conversion and storage (ECS) systems owing to their highly ordered and tunable compositions and structures [62]. MOFs have been extensively explored in different battery systems in the past decades. Their adjustable porous structures and controllable compositions at molecular level are advantageous for the search of advanced electrode materials for batteries (e.g., LIBs, LSBs, LOBs, and SIBs) [63] (Figure 2). Pyrazole is a very versatile ligand and can play many different roles in chemical systems. Different pyrazole compounds were used to synthesize MOFs for many applications. Among them some are cited above in figure 1. A New MOFs constructed from Carboxylate Functionalized Bispyrazolylmethane (compound 6 of Fig.1) for Coal Mine Methane Capture and synthesis of gas storage materials [34]. The MOFs based on pyrazole compound 5 Fig. 1, were used for water adsorption and it was demonstrated to be a crucial material for many applications such as dehumidification, thermal batteries, and delivery of drinking water in remote areas [64,65].

4. Conclusion

In summary, MOFs have received tremendous advances from structural design and controllable synthesis to their functional applications in the past two decades. Although many obstacles remain to be solved on their way to the industrial applications, the academia and chemical industry are beginning to join hands to realize practical applications of MOFs. We expect a bright future for MOFs with the collaborative efforts from researchers in different fields including chemists, materials scientists, engineers, medical professionals, and others.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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