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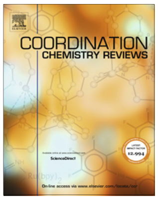

Review

Conformation versatility of ligands in coordination polymers: From structural diversity to properties and applications

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ABSTRACT

Coordination polymers (CPs, including metal–organic frameworks, MOFs) have become an active topic in chemical and materials science. The construction of CPs depends heavily on the organic ligands as well as the metal centers, and the versatility of ligands contributes to the structural and property diversities of CPs. Here, the structural diversity in CPs achieved by the conformation versatility of ligand is systematically reviewed. In addition, the effect of ligand conformation on the properties of CPs is highlighted with discussions of potential applications of CPs in areas of storage, separation, and luminescence.

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1. Introduction

Coordination polymers (CPs, including metal–organic frameworks, MOFs) have become an active topic in chemical and materials science [1–4]. Since the late 1950s when the concept of CPs arose, a large amount of CPs have been reported, and the related research has covered a lot of fields [5–8]. The wide scientific attention on CPs not only arises from their intriguing topologies and diverse structures [9–12], but is also driven largely by their high potential applications in gas adsorption and separation [13], luminescent materials [14], and catalysis [8], *etc* [15,16]. The CPs are constructed from inorganic vertices (metal ions/clusters) and organic linkers *via* coordination bonds and usually feature uniform infinite crystalline networks. The diverse structures and properties originating from the inorganic-organic hybrid nature of CPs contribute a lot to their versatility, which is beyond that of many other inorganic materials. Therefore, much efforts have been made in the investigation of new CPs with unique structures and specific functions, and various strategies and methods have been developed accordingly [17–19]. It should be noted that the contribution of metal ions to the diversity of CPs is limited in comparison with organic ligands. This fact is largely due to the limited number of metal-center species and their relatively restricted coordination modes. In contrast, benefiting from the almost unlimited potential of organic ligands in species and conformations, more effort has been dedicated to the design and application of unique organic ligands for the construction of CPs, leading to the blooming of CPs research [20,21].

Among the various organic ligands, multi-donor organic ligands with versatile conformations have attracted much attention [22]. The different conformations of the ligands often give rise to a variety of symmetries and connection modes. It should be noted that since the construction of CPs is mainly based on the self-assembly of metal centers and organic ligands, the conformations of the ligands are greatly determined by the physical factors (temperature, pressure, *etc*) and chemical factors (concentration, pH, solvent, *etc*) of reaction conditions. Therefore, it is challenging to precisely acquire and regulate the structures of the CPs based on this kind of ligand. On the other hand, the ligand in the framework of CPs may respond to external stimuli (temperature, pressure, guest molecules, *etc*) to change their conformations, which could trigger the structure transformation and dynamic behaviors of the CPs. As a consequence, much effort has been devoted to making use of conformation versatility to realize the structural diversity of CPs.

According to the origin of the conformation versatility, the organic ligands could be mainly classified into two classes: (i) ligands with "flexible" spacers (alkyl chains and ether chains, *etc*.) showing tunable relative distance and orientation between the coordination sites. (ii) ligands with "non-flexible" spacers showing potential multiple conformations contributed by the bending and rotation of chemical bonds between the coordination sites. Typically, ligands with flexible spacers are more varied in the coordination assemblies and tend to generate versatile and distorted framework due to their structural features. In contrast, the conformational change of non-flexible linkers, originating mainly from the rotation of coordination sites around single bonds and bending of ligand backbones, is relatively inconspicuous but can also contribute to the diversity of CPs. Aiming at the structural diversity of CPs, many flexible organic moieties, such as alkyl, amide, sulfur ether, azo, *etc*, have been applied as versatile spacers of ligands. Beyond the contribution to the diversity of CPs' structures, the versatile conformation of organic ligands may also endow the according CPs with variable pore geometry and ligand originated emissions, which will benefit the achievement of dynamic behavior of CPs and their potential applications as storage/separation materials and luminophores.

The continuous exploration of chemists has led to considerable progress to comprehend the coordination behaviors of ligands in the assembly process [23], and some methods have been developed to achieve multiple conformations of the ligands and the structural diversity of CPs [24–26]. However, the structural diversity as well as the properties and applications of CPs based on the ligands with conformation versatility have been rarely summarized. Here, we focus on the structural diversity of CPs constructed from ligands with versatile conformations (Scheme 1) to illustrate the key role of these ligands in tuning structures and functions. Considering the extensive reports, some representative examples and several common rules or design strategies for ligand conformation targeted constructions, such as "pillaring strategy", "positional effect", and "confined conformation", have been summarized. In addition to the presentation of structural diversity of CPs, recent advances of CPs in terms of their potential applications due to the structural diversity and conformation versatility of the ligands are thoroughly reviewed to demonstrate their critical roles. On the basis of all the points mentioned above, this review is expected to provide useful instructions for structure and function targeted construction of CPs.

2. Structural diversity of CPs

CPs are attractive for their diverse structures and applications, which were mainly determined by the characteristics of inorganic and organic building units. Compared with the inorganic building units with limited number of species and coordination modes, the organic ligands exhibit diverse configurations and conformations, and are supposed to contribute greatly on the construction of CPs with multiple structures, topologies, and distinct properties (All the network topology symbol are presented according to that collected and summarized by the Reticular Chemistry Structure Resource (RCSR) [27–29]). To date, although an overwhelming number of ligands have been developed through convenient synthesis, the definite prediction of the structures of CPs from organic ligands is still a challenge due to the ungovernable freedom of the conformation of ligands. Hence it is quite advisable to discover some common rules to understand the influence of ligands with conformation versatility on the structural diversity of CPs, which could further benefit the rational design and synthesis of CPs. In this section, we will emphasize the impact of organic ligands (flexible and non-flexible) featuring conformation versatility on structural and topological diversification of CPs. Some strategies including "pillaring strategy" and "positional effect" are introduced to reveal that how the configuration of the ligand could be regulated in the CPs to promote the rational design and construction. Many factors impacting the conformation of ligands, such as temperature, solvent, and template in the assembly process, and the external stimuli that could affect ligands in the CPs have also been introduced. Notably, since the definition of "flexible ligand" and "non-flexible ligand" is somewhat crossed considering different moieties of the ligand, some ligands with flexible spacers (usually containing C, O, N, S, *etc* hybrid atoms and –$(CH_2)_n$– moieties) are categorized as flexible ligands according to their observed conformations. The construction of CPs on the basis of mixed-ligands are also included in this section.

2.1. Structural diversity of CPs based on flexible ligands

In general, the spacers of flexible ligands contain rotatable covalent bonds, which stem from at least one sp^3 hybrid atom (usually

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