



Review

Entangled structures in polyoxometalate-based coordination polymers



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ABSTRACT

Polyoxometalates (POMs) have attracted a lot of interest due to their novel structure characteristics and various connection modes. POM-based coordination polymers with entangled structures, an indispensable branch of entangled networks, take advantage of the features of POMs, and have received increasing attention. Much effort has been devoted over the past few decades toward their preparation and the analysis of their unusual entangled topology. In this review, we will summarize a number of examples of POM-based coordination polymer that have been described according to their different entangled characteristics. Different concepts, such as interpenetration, polycatenation, polyrotaxane,

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polypseudo-rotaxane and self-penetration, are employed to describe the various types of POM-based coordination polymers with entangled structures. In addition, we further classify POM-based coordination polymers with entangled structures based on the dimensionalities of the individual motifs and the roles of the POMs. Combining the advantages of the attractive potential applications of the POMs and structure diversities of the entangled frameworks, the investigation of POM-based coordination polymers with entangled structures will be a sustainable research field in coordination chemistry.

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1. Introduction

Polyoxometalates (POMs) are early transition metal oxyanionic clusters that show a wide variety of interesting structural motifs; their diversity allows for applications in different fields such as catalysis, medicine, biology and materials science [1,2]. POM-based coordination polymers (also written as POM-based metal-organic frameworks (MOFs) in some articles) are a series of hybrid organic-inorganic materials composed of polyoxometalates and different metal-organic units [3]. Over a thousand articles related to POM-based coordination polymers have been documented by the Web of Knowledge to date [4–6] (Scheme 1). Among studies of the potential applications ranging from catalysis and adsorption of POM-based coordination polymers, the architecture and topology of entangled POM-based coordination polymers have been of particular interest [7–9]. The topological analysis of multitudinous networks is not only an important tool for simplifying complicated compounds, it also plays an instructive role in the rational design of targetable functional materials with desirable properties [10–13]. In short, topological studies make a significant contribution toward the controllable synthesis and property studies of POMs and POM-based coordination polymers.

Entangled systems, as one of the major themes of supramolecular chemistry, are comprised of individual motifs forming, via interlocking or interweaving, a periodic architecture that is infinite in at least one dimension [14,15]. In addition to the common phenomenon of interpenetration, particular attention has been devoted to characterizing these extended entanglements. The phenomenon of mechanical interlocking, which is typical of molecular structures such as catenanes, rotaxanes and knots, has been studied extensively [16–22]. Furthermore, most of these species can be considered regularly repeating infinite versions of the finite molecular motifs, and can lead to synthetic supramolecular arrays with a variety of structural features (Scheme 2). Many topologically interesting entangled structures have been discussed in comprehensive reviews by Batten, Robson and Ciani [14–16,23,24]. However, a review on the progress of POM-based coordination polymers with entangled structures has not yet appeared.

POMs in the framework may exhibit numerous connecting modes, which have a great effect on the formation of the final structure [25–29]. When analyzing different roles of POMs in the entangled POM-based coordination polymers, we separate them into two categories. (I) Systems with POMs as linkers (from the perspective of mathematical theory), in which POMs serve as versatile inorganic linkages by providing terminal and/or bridging oxygen atoms to connect with different metal-organic units to construct POM-based multifunctional hybrid materials. (II) Systems with POMs as templates, where POMs, as a unique class of inorganic metal oxide clusters, have been regarded as excellent candidates for templates to obtain POM-based coordination polymers due to their tunable size and high negative charge.

In this review, we will investigate examples of POM-based coordination polymers in the literature and describe their different entangled characteristics. Additionally, we further classify POM-based coordination polymers with entangled structures based on the dimensionalities of the individual motifs and the roles of the

POMs, because inclusion of POMs in the assembly has a significant impact on the formation of the entangled structure.

In the first section, we will briefly review interpenetration-involved POM-based coordination polymers in an attempt to accomplish an initial classification of the different interweaving and interlocking aspects (2D layer or 3D network). Later sections use different concepts, such as polycatenation, polyrotaxane, polypseudo-rotaxane and self-penetration, to describe other types of entangled structures in POM-based coordination polymers (Scheme 3) [14,15,24].

2. Interpenetration in POM-based coordination polymers

Among the different types of entangled systems, interpenetration is the most common form of entanglement and has been extensively studied over the past decade. The longer, flexible ligands usually yield compounds with high connectivity and larger voids, but these kinds of compound are always unstable. Thus, interpenetration reasonably occurs to reduce pore space in order to decrease the instability. It is almost impossible not to mention polycatenation when describing interpenetration because of their close relationship [14,23].

Generally, for interpenetration systems: (1) all individual motifs with identical topologies are usually extended infinitely into 2D or 3D networks; (2) the number of interpenetrated motifs is finite; (3) the resulting dimensionality equals the number of component motifs; (4) each single network is interlaced with all the other ones to create the final structure. Conversely, for polycatenation: (1) the motifs can be 0D, 1D (with closed circuits) or 2D, of the same or of different types and result in an infinite periodic entangled array; (2) the number of entangled motifs can be finite or infinite; (3) all of the constituent motifs have lower dimensionality than that of resultant architectures; (4) each individual motif is catenated only with the surrounding motifs, but not with all the others, etc. As is the case with MOFs and other coordination polymers, the terms polycatenation and interpenetration are sometimes not rigidly defined as outlined above.

The number of interpenetrated POM-based coordination polymers is limited; according to the classification standards mentioned above, the existing examples of interpenetration are classified into two categories: a single motif in 2D (Section 2.1) and a single motif in 3D (Section 2.2).

2.1. Interpenetration based on 2D layers

The compounds in this category are composed of 2D frameworks and usually have large open voids in a single network. After interpenetrating, these voids are filled and a 2D → 2D interpenetrating framework is formed. The *n*-fold 2D nets may stack directly on top of each other, generating a 3D supermolecular crystal packing structure, but strictly speaking, they are still 2D frameworks. As for the example which has an increased dimensionality after interpenetrating, just like the 2D + 2D → 3D framework, this will be described in detail when discussing polycatenation.

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