Introduction to the themed issue "Coordination polymers: structure and function"

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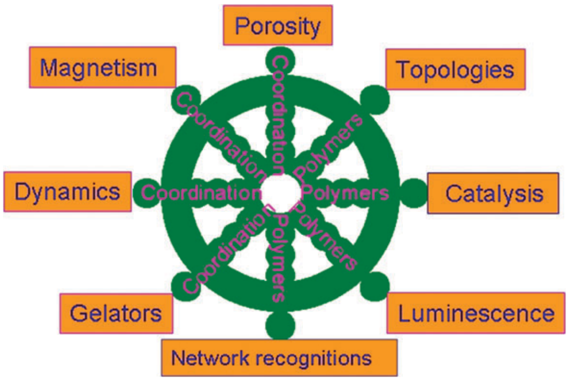
Transition metal complexes in which the ligands link the metal atoms in an infinite array *via* coordination bonds are traditionally regarded as coordination polymers (CPs). At present, there exist several other terminologies for CPs, such as metal–organic frameworks (MOFs), metal organic materials (MOMs), porous coordination networks (PCNs) and porous coordination polymers (PCPs).[1] Prussian Blue, in which Fe(II) and Fe(III) centers are linked *via* CN^- ions into a three-dimensional cubic network, was one of the first coordination polymers studied systematically. Although the term coordination polymer has existed in the literature since the 1950s, the potentiality of CPs was realized only at the beginning of the 1990s. The initial foundations of the field were laid by the work of A. F. Wells, who introduced the concept of looking at inorganic crystal structures as networks by reducing them to well defined nodes and connections.[2] The adoption of this approach by Robson to describe coordination polymers was hugely successful and elicited widespread interest among chemists for the creation of new topological networks exhibiting interpenetration, cavities or channels.[3] In this regard, the work with bis-pyridyl based ligands by Fujita, Kitagawa, Robson, Yaghi and Zaworotko immensely contributed to the growth of the field in its initial stages.[4] Subsequently, convincing demonstrations of the porous properties of CPs by Kitagawa and Yaghi in the late 1990s allowed the potential of CPs to be realized to mimic the properties of zeolites.[5] These studies have led to an explosion of literature on CPs in the current decade. Apart from porosity, CPs have demonstrably exhibited several other important properties (Scheme 1).

Despite the plethora of literature, the mechanism of formation of CPs is as yet not well understood. Often several factors, such as metal–ligand ratio, metal coordination mode, the presence of anions or guest molecules, pH of the reaction mixture, reaction conditions and so on, are thought to contribute to the resultant network topology. Indeed, CPs are truly modular in nature, as for a given ligand and metal, numerous different networks are possible. Furthermore, the term secondary building unit or block (SBU or SBB) is in frequent use in the literature of CPs, referring to polymetallic clusters that act as nodes for linking organic ligands.[6] The term SBU was first used in the literature for zeolites to simplify or understand their complicated structures. Overall, the crystallization of CPs by various methods raises several intriguing but so far unanswered questions: What is the true building block of a framework? Is there a limit to the size of a building block in solution? Is it possible to predict chemical building blocks that, through an iterative self-assembling process, will lead to higher-dimensional frameworks with complete control of network topology? What is the contribution of template effects by solvents, guest molecules and anions? The answers or insights to some of these questions are expected to lead to more control over network prediction and properties in CPs.

Kitagawa's classification of CPs into three types based on their properties is worth mentioning here. According to this classification, first generation CPs are ones in which the network collapses after the removal of guest molecules (type-I, non-permanent porosity), second generation CPs are ones in which the network remains intact after removal of the guest (type-II, permanent porosity), and third generation CPs are ones in which the networks are flexible and exhibit a dynamic response to external stimuli (type-III).[7] I am sure that in the future several other categories will be added to this classification; for example, one can add the post-functional covalent modification of CPs as a new type of CP.

Back in 1998, *NJC* published a thematic issue on "Molecular Networks", guest edited by Mir Wais Hosseini. Twelve years later, the editorial board of *NJC* felt that a themed issue on the versatile and exotic field of coordination polymers would be very timely and attract the attention of both active practitioners of CPs and researchers in other areas alike for further progress in the field. This themed issue covers all the above-mentioned aspects from a spectrum of researchers located



Scheme 1 Some of the important functional properties of CPs.

across the globe. Lastly, we would like to thank all the authors for readily accepting our invitation to write for this themed issue.

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