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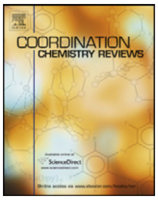

Review

Hierarchical assemblies of coordination supramolecules

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ABSTRACT

Hierarchical assemblies of coordination supramolecules are reviewed. These assemblies are self-organized by coordination supramolecules themselves or co-assemblies with other modules. By utilizing electrostatic interaction, the coordination supramolecules can be incorporated into films, liquid crystals, micelles, and hydrogels, etc. These coordination supramolecules-containing novel materials exhibit many switchabilities and other desired properties. The following contents are covered in this review: (1) coordination supramolecules of different architecture; (2) hierarchical molecular devices containing these coordination supramolecules; (3) short perspectives and conclusions.

1. Introduction

Recently, the construction of coordination supramolecules or coordination polymers has emerged as a powerful and versatile strategy for engineering metallo-polymers [1–5]. Different from covalent conventional polymers, the coordination supramolecules are based on metal–ligand coordination bonds [6–11]. The advantages of coordination supramolecules over those covalent ones are obvious: on the one hand, the presence of metallic elements allows the coordination supramolecules to offer special optical, electrical, magnetic and mechanical properties [12–18]; on the other hand, the dynamic nature of the coordination bonds endows switchability to the system, mimicking the behavior of natural supra-structures [19,20]. Another advantages of such metal–ligand interactions, in part, lies in the large catalogue of accessible ligands, along with applicable metal ions comprising nearly half the periodic table, which means there are a vast range of metal–ligand complexes that can be easily accessed [21]. Therefore, the coordination supramolecules offer a broad platform for the development of smart materials.

In the past decades, accompanied by the burgeoning study on the synthesis and solution property of coordination

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supramolecules [12–18], some efforts were also made in construction of molecular devices utilizing these supramolecules [22–25]. These devices include both self-assembled nanostructures of coordination supramolecules themselves and co-assembled objects with other modules. They are all hierarchical assemblies of the self-organized coordination supramolecules. Although there are quite a few review articles about coordination supramolecules [6–11], most of them focus on the structure of the coordination supramolecules [6–11], or on one sort of hierarchical assembly of these supramolecules [21]. An overview that covers the full scope of hierarchical assemblies based on coordination supramolecules is still absent. Therefore, we focus our aim in the present discussion on the progress in the field of hierarchical assemblies made of, or containing, coordination supramolecules. For clarity, we will briefly introduce the main architecture of coordination supramolecules, then discuss their hierarchical assemblies.

2. Architecture of coordination supramolecules

The category of coordination supramolecules depends on the location of the metal ions: main chain or side chain. When the coordination bond is present in the side chain, the polymeric structures still hold characteristics of covalent polymers, and do not represent a revolutionary change to the polymer properties. Therefore, main chain coordination supramolecules are of particular interest in the field of metallo-supramolecular research. In the main chain coordination supramolecules, metal–ligand coordination bonds are the linking force between repeating units. In this framework, linear, branched, and block copolymers, can be formed. In the following section, these three architectures will be briefly introduced.

2.1. Linear coordination supramolecules

Linear coordination supramolecules are usually formed between ditopic ligand (bisligand) molecules, which possess two chelating heads, and metal ions, as illustrated in Fig. 1a. The chelating heads of these ditopic ligand molecules often contain di or terpyridines, or sometimes carbonyl groups. Fig. 1b–d demonstrates some examples of linear coordination supramolecules [26,27,13–19]. The polymerization degree of linear coordination supramolecules is highly concentration and mixing ratio dependent [26,28]. Long chains can be formed only at 1:1 metal to ligand ratio at high concentrations. Deviation from 1:1 mixing leads to formation of chain ends so that the growth of the chain stops. The concentrated 1:1 mixed system of bisligands and metal ions can be very viscous and elastic whereas when dilute, the system is water-like with small ring-like oligomers present [26].

2.2. Branched coordination supramolecules

When three-head telechelic ligand molecules are used, branched coordination supramolecules can be formed [29,30], as illustrated in Fig. 2a. Branched coordination supramolecules can also be formed in the mixed system of ditopic ligands and f-block metal ions [31–34,18], where the f-block metal ions can hold three chelating heads that act as cross linkers (Fig. 2b). Concentrated branch coordination supramolecules are effective gelators. The cross-linking effect is so strong that a small fraction of branched coordination supramolecules in coexistence with linear ones, is sufficient to yield a gel [25,32].

2.3. Block coordination supramolecules

Using the strategy of metal–ligand coordination, linear or star-like block copolymers can also be prepared [10,35]. By attaching one or two chelating heads to a polymer chain end, one may connect polymer chains by a metal–ligand coordination bond. In this way, di- and tri-block (A-[M]-B [36–38], A-[M]-B-[M]-A [38,39], or A-[M]-B-b-C [38,40], where [M] represents coordination center) copolymers can be readily made (Fig. 3a–c). If the A, B, and C blocks are immiscible, these coordination supramolecular block copolymers can behave as amphiphilic block copolymers, with self-assembly behavior. For construction of star-like coordination supramolecules, 2,2′-bipyridine ligand is very often used [35,41]. This ligand forms complexes with a large variety of metal ions, and is an ideal candidate for the preparation of multi-arm stars because bipyridines functionalized at the 4- and/or 4′-position can be rather easily prepared. For more work in this area, one can refer review paper [35].

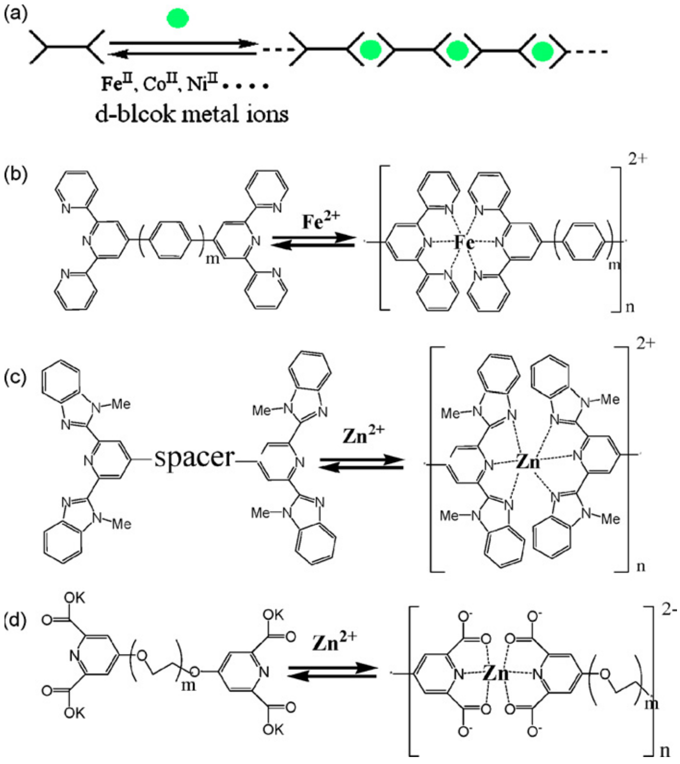

Fig. 1. (a) Illustration of formation of linear coordination polymer and (b–d) are examples taken from Refs. [23,27,26], respectively.

3. Hierarchical self-assemblies of coordination supramolecules

3.1. Hierarchical self-assemblies of linear/branched coordination supramolecules

So far, most coordination supramolecules were reported with respect to their bulk solution properties. The linear coordination supramolecules formed by Zn^{2+} and the ditopic ligand in Fig. 1d reported by Vermonden et al. forms a highly viscous solution when dissolved in water [26]; whereas the branched ones formed by Nd^{3+} or La^{3+} with the same ligand forms a hydrogel under similar conditions [32]. For the large variety of linear and branched coordination supramolecules made out of small telechelic ligands and metal ions, hierarchical self-assembled structures can hardly be formed due to their homopolyelectrolyte nature. However, Rowan et al. found that the coordination supramolecules formed by Zn^{2+} and the ditopic ligand illustrated in Fig. 1c may organize into spherulites in gels formed by these coordination supramolecules [18,42,43] (Fig. 4). Typical Maltese cross patterns under crossed polarizers indicate