



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.

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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 ratio 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

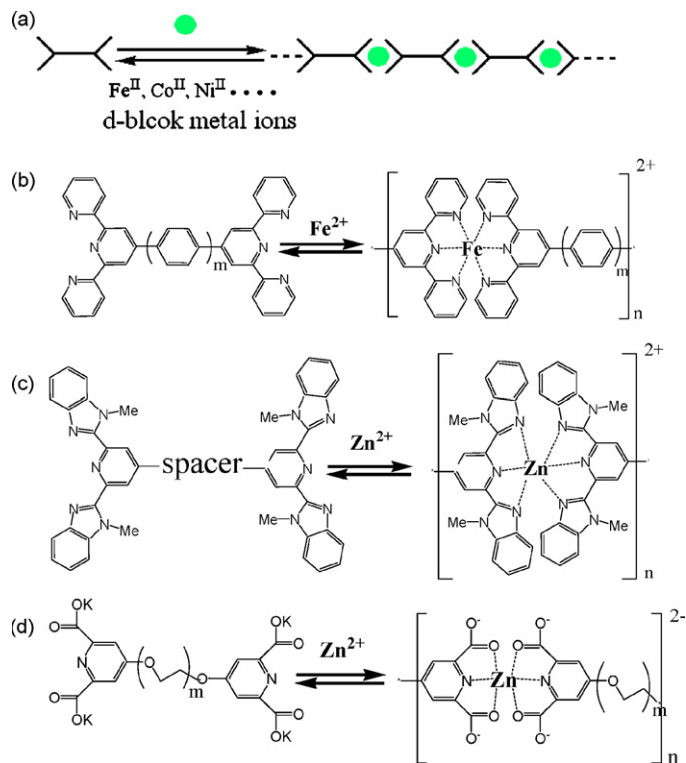


Fig. 1. (a) Illustration of formation of linear coordination polymer and (b–d) are examples taken from Refs. [23,27,26], respectively.

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].

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 Zn²⁺ 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 Nd³⁺ or La³⁺ 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 Zn²⁺ 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

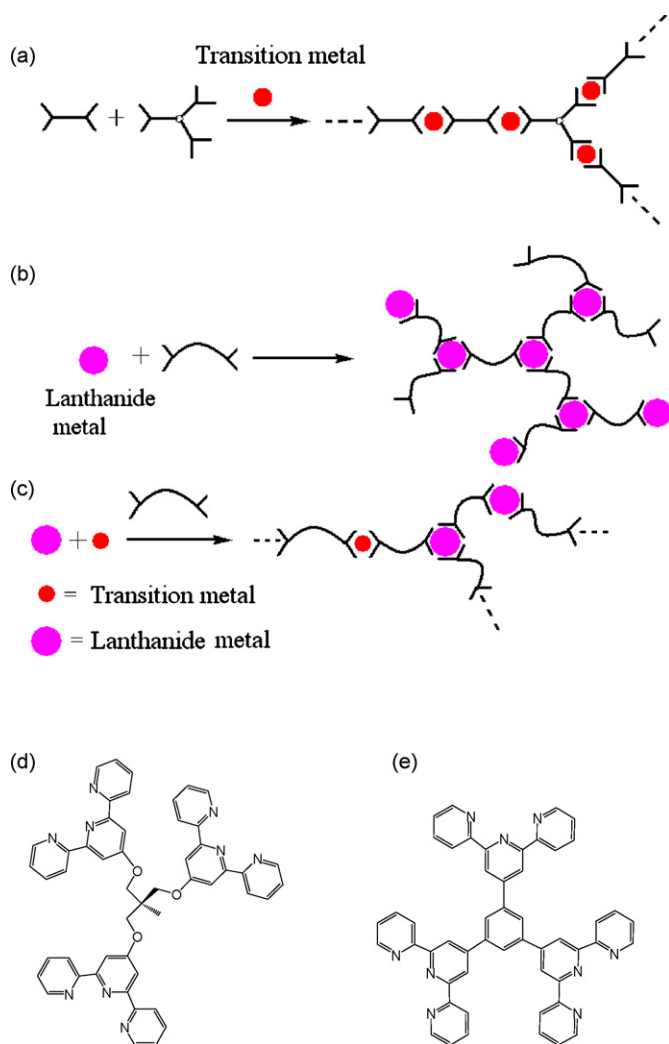


Fig. 2. (a–c) Illustration of branched coordination supramolecules and (d and e) examples for branched ligands [29,30].

that the spherulites form through a process of radial lamellar crystallization. XRD results suggest that parallel assembly of the coordination centers may occur in the spherulites. The aggregation of such spheres at higher concentration forms the skeleton of the gel.

3.2. Hierarchical self-assemblies of block coordination supramolecules

However, the self-assembly of coordination supramolecules can be readily accessed in block coordination polymer system if long hydrophobic and hydrophilic polymeric blocks coexist in one supramolecular chain. Schubert et al. demonstrated the formation of micelles in the solution of PEO₇₀-[M]-(CH₂)₁₆-PEO₇₀

[38], PEB₇₀-[M]-PEO₇₀ [37], PS32-b-P2VP13-[M]-PEO₇₀ [40], PS_x-[M]-PEO_y [35], and PDMS_n-[M]-PEO₇₀ [44] ([M] indicates the position of coordination bond). For the PS containing coordination block copolymers, addition of the sodium salt of hydroxyethyl-ethylenediaminetriacetic acid (HEEDTA) results in detachment of the PEO block, and leaves the chelating groups on the surface of the micelles. The PEO block can be recovered if the detached polymer chains are allowed to mix with the micelles again (Fig. 5). This represents one of the environmental responsiveness of the coordination supramolecular micelles. Interestingly, tri-arm star-like metallo-supramolecular block copolymer was observed to self-assemble into vesicles in acetone, but the tetra-armed analogue give micelles again [41] (Fig. 6).

4. Hierarchical co-assemblies with other modules

For most coordination supramolecules, the coordination center carries charges so that they were named metallopolyelectrolytes (MEPE) by Kurth et al. [45]. This allows interaction with oppositely charged modules, such as polymers, colloids, or molecules which carry opposite charges [13,45–48]. Both linear and branched coordination supramolecules have similar properties when interacting with an oppositely charged module, but block coordination supramolecules are not very characteristic in this aspect due to the lower number of coordination centers. Therefore, in the following we discuss some typical examples of the hierarchical co-assemblies without sorting linear or branched coordination supramolecules.

4.1. With oppositely charged polyelectrolytes: layer-by-layer assemblies

Kurth et al. [48] successfully fabricated layer-by-layer assemblies using Fe(II)-MEPE as the positively charged polyelectrolyte (Fig. 7a). In this strategy, multilayer fabrication is achieved by repeated immersion of the substrate in solutions containing Fe(II)-MEPE and oppositely charged polyelectrolytes, respectively (Fig. 7b). The obtained films are UV active owing to the presence of coordination supramolecules, and replacing linear coordination supramolecules by branched ones does not affect the formation of lbl multilayers [29].

In addition, the deposition process is independent of the substrate geometry. When colloidal particles are used as the substrate, multilayer fabrication is readily achieved by repeatedly dispersing the particles in a solution of Fe-MEPE and sodium polystyrene sulphonate (PSS) [49]. The alternating negative and positive zeta-potentials of the particles measured after each deposition step are consistent with an alternating particle. Removal of the colloidal template core yields multilayer capsules composed of coordination supramolecules and covalent polyelectrolytes (Fig. 7c). These can be potentially used as microreactors. The multilayers containing coordination supramolecules are very resistant to metal ion exchange. Even in the presence of a strong chelating agent that can disassemble the coordination polymer in solution, the multilayers were not influenced [48].

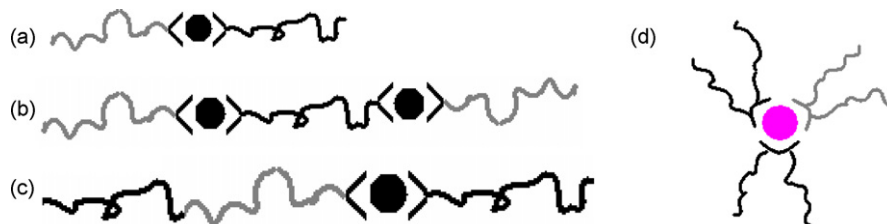


Fig. 3. (a–c) Illustration of AB, ABA, ABC type block coordination supramolecules and (d) illustration of a star-like block coordination supramolecule.

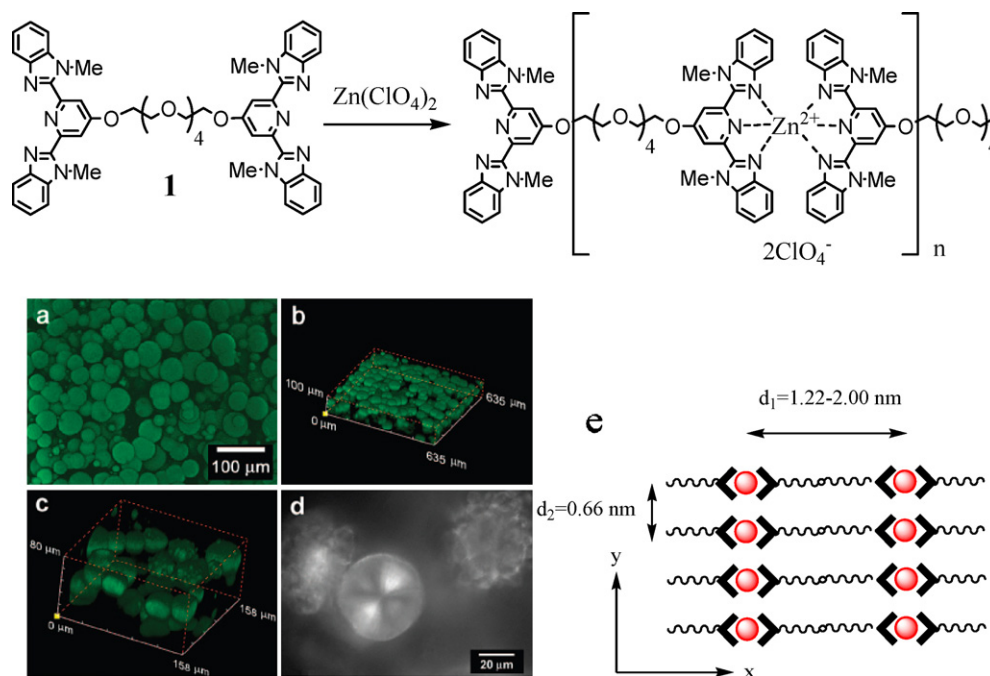


Fig. 4. Schematic representation of the formation of coordination polymeric aggregates (**1:Zn**) using ditopic ligand **1** with metal salts, $\text{Zn}(\text{ClO}_4)_2$, in polar solvents. The laser scanning confocal microscopy (LSCM) images (a) z-projection image, (b and c) 3D image of the **1:Zn** gel formed in 60/40 (v/v) DMSO/water mixture as shown in (a), and (d) polarized images of the **1:Zn** gel formed in 70/30 DMSO/water mixture (v/v) showing the coexistence of regular and irregular particles. (e) Illustrates the molecular packing mode in the aggregates. Adapted from Ref. [43]. Copyright: American Chemical Society.

4.2. With amphiphiles: polyelectrolyte–amphiphiles complex

The charged nature of the coordination supramolecules also allows them to interact with oppositely charged amphiphiles. Kurth et al. [50–53] combined the Fe(II)–MEPE and dihexadecyl phosphate (DHP) to prepare a polyelectrolyte–amphiphile complex (PAC, as shown in Fig. 8a). This PAC is hydrophobic and dissolves in organic solvents. The organic solution containing PAC can therefore spread at the air–water interface to form a Langmuir film (53). In bulk organic solution, PAC further assembles into lamellar structures

[54]. It is very interesting to find that the phase transition of the amphiphiles can tailor the magnetic properties of the MEPE [52,54]. Generally, in the presence of ligand, the crystal field around the metal ions is very strong so that the metal ions are forced into the low-spin state (LS) [55]. For Fe(II) ions, the Fe(II)–MEPE is diamagnetic since all the electrons are paired. At low temperature, the PAC assembled densely both in LB films and in crystalline state, which did not affect the strong crystal field around the Fe(II) ions. Upon increasing temperature, the energy released in the phase transition process alters the crystal field dramatically, so that the system becomes high spin and paramagnetic (Fig. 8b).

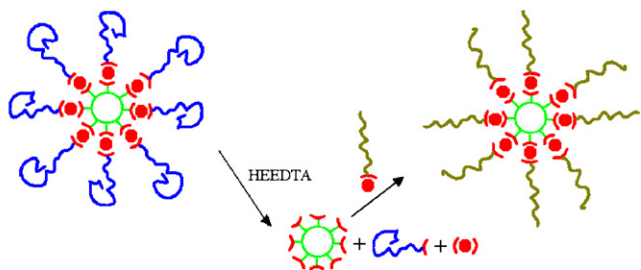
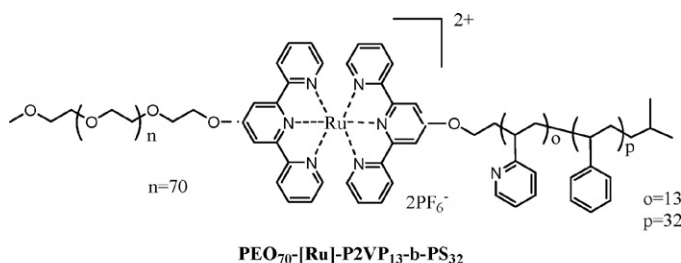


Fig. 5. The reversibility of the bis-2,2':6',2''-terpyridine-ruthenium(II) complexes allow post-modification of the micelles. The micellar hydrophobic core (green open circle) is surrounded by terpyridine (red brackets) ruthenium (red solid circle) bis-complexes; addition of a strong competing ligand (HEEDTA) allows the release of the coronal chains and the micellar core can be isolated. Reattach the coronal chains to the micellar core can be realized.

4.3. With diblock polyelectrolytes: micelles

When the coordination polymer is mixed with an oppositely charged–neutral diblock copolymer, micelles can be formed in bulk solution. The micellar core is composed of the electrostatic complex coacervate formed by the coordination supramolecules and the oppositely charged block of the coordination supramolecules, which is stabilized by the neutral block of the diblock copolymer [56] (Fig. 9a). Such micelles belong to the family of complex coacervate core micelles (C3Ms) [57], or polyion coacervate (PIC) micelles in the literature [58]. Obviously, the coordination polymer is acting as a homopolyelectrolyte in this micellar system. One should notice that the micellar formation in the coordination polymer system involves two synergistic processes: polymerization of coordination supramolecules and the formation of micelles. In the presence of oppositely charged block copolymers, the local concentration of the low molecular weight coordination complex can be increased significantly so that the polymerization degree is greatly enhanced, namely, ‘polymers’ come into formation. This long ‘polymer’ meets the ‘chain-matching’ criteria to form electrostatic micelles [56]. Interestingly, the size of the micellar core can be increased considerably by substitution of part of the diblock polyelectrolyte with homopolyelectrolytes of like charges. This is similar to the formation of microemulsions in

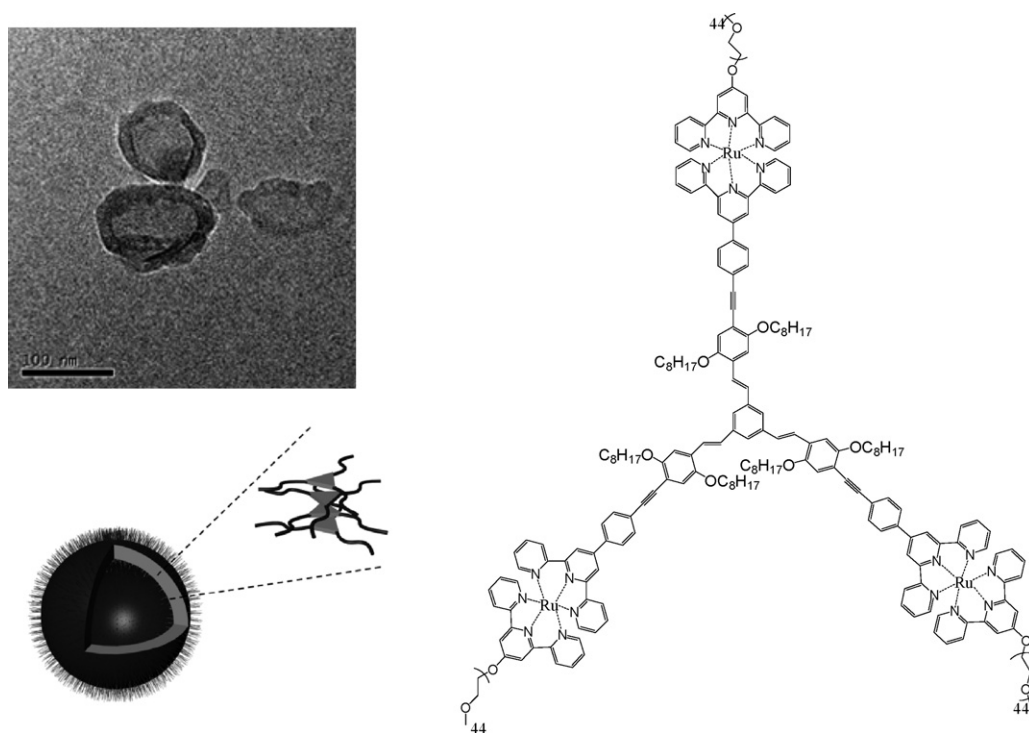


Fig. 6. Vesicles assembled from tri-armed star-like coordination supramolecules. Adapted from Ref. [41]. Copyright: Royal Chemical Society.

amphiphilic micellar systems [59]. We have successfully increased the core size of Zn-L₂EO₄/P2MVP₄₀-PEO₂₀₅ micelles by a factor of ten (Fig. 9b) [59]. Obviously, the loading amount of metal ions in the micelles can be conveniently controlled, which is very important for these micelles to be potentially used as heavy metal carriers.

Similar to covalent C3Ms, micelles containing coordination supramolecules are also sensitive to additional salt. For the Zn-L₂EO₄/P2MVP₄₁-PEO₂₀₅ micellar system, the CMC dependence on salt is exponential [60] (Fig. 10a). The micelles exhibit coordinating metal ion dependence [61]. If first row transition metals are used, excess of metal ions will not obviously influence the C3Ms, but

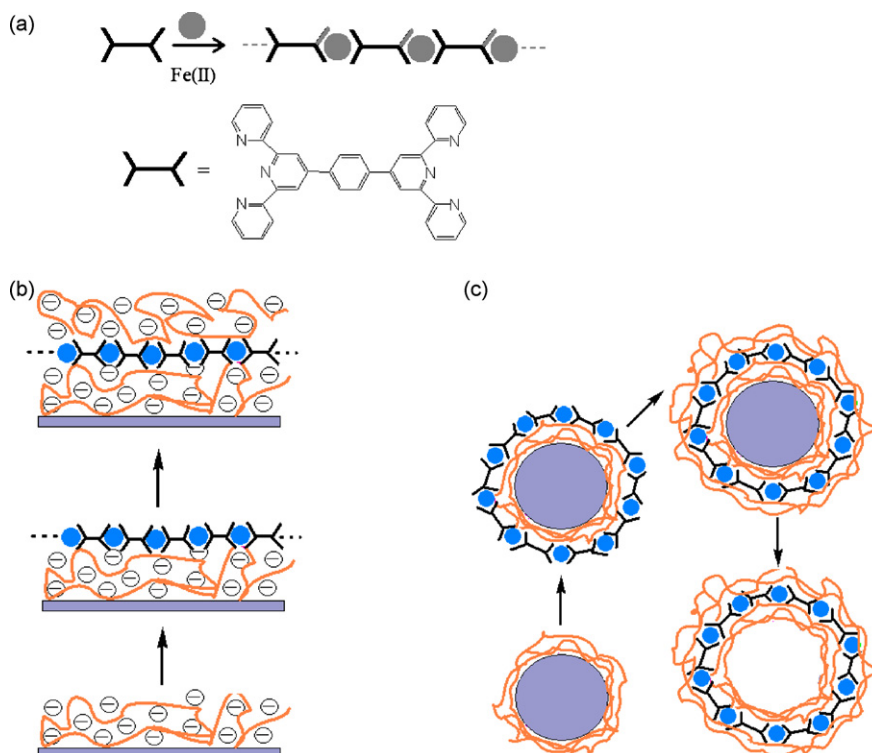


Fig. 7. (a) Formation of Fe(II)-MEPE coordination supramolecules and the layer-by-layer assembly on planar (b) and spherical (c) surface yielding from Fe(II)-MEPE and polysodium 4-styrenesulphonate (PSS) polyelectrolyte.

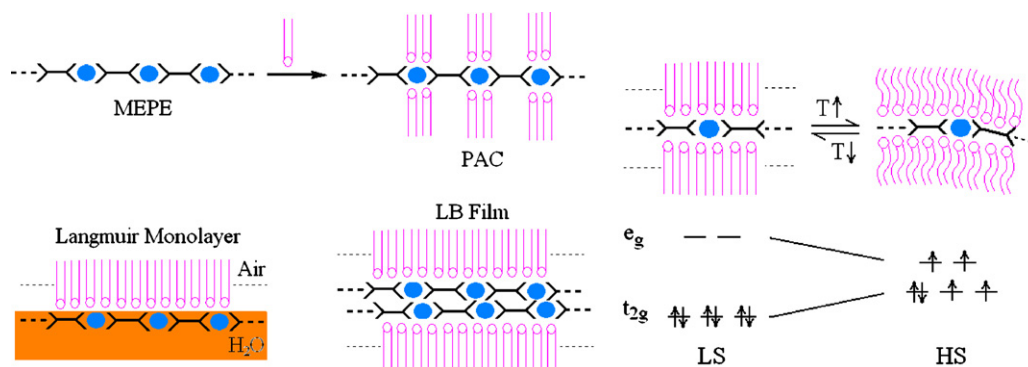


Fig. 8. Formation of Langmuir and L-B films of the polyelectrolyte–amphiphile complex PAC at an air–water interface. Melting of the amphiphilic matrix in the PAC results in a distortion of the coordination geometry of the tightly coupled metal centers, giving rise to a spin-crossover from a diamagnetic low-spin state to a paramagnetic high-spin state.

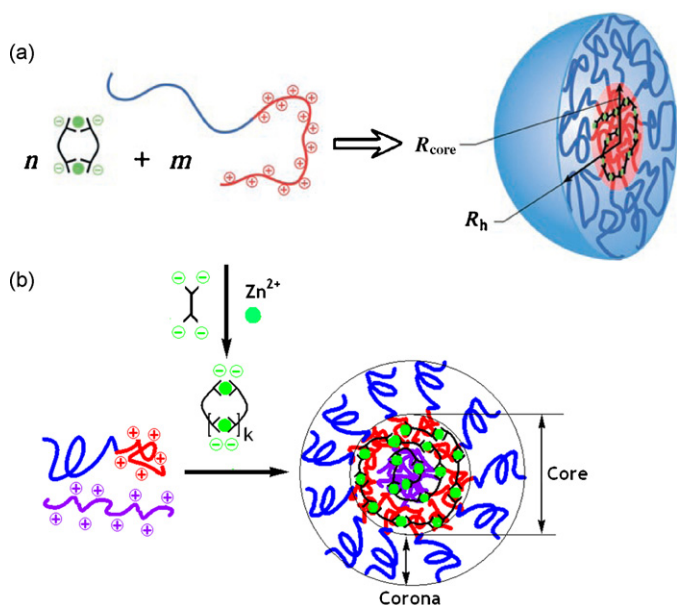


Fig. 9. (a) Schematic illustration for C3Ms in the mixed systems of Zn-L₂EO₄ and diblock copolymer P2MVP₄₁-PEO₂₀₅. (b) Enlarging of the micellar core by replacing diblock copolymers with homopolyelectrolytes. Adapted from Refs. [56(a), 59(b)]. Copyright: Wiley-VCH Verlag GmbH & Co. KGaA [56] and American Chemical Society [59].

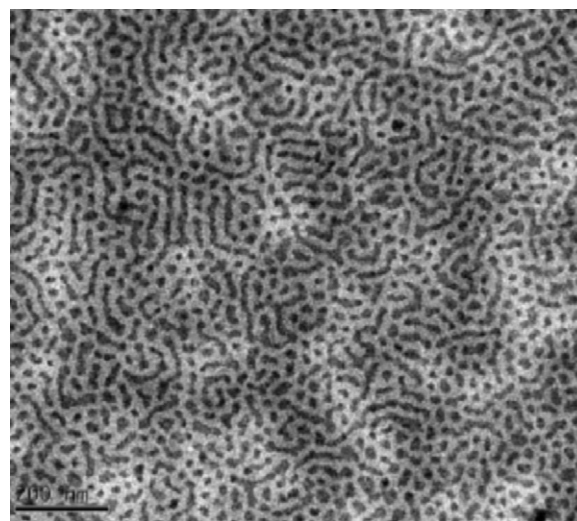


Fig. 11. Wormlike micelles formed in the system of Zn-L₂EO₄/P2MVP₄₁-PEO₂₀₅ where the negative charge ratio $f = [-]/[-] + [+] = 0.33$. Adapted from Ref. [62]. Copyright: American Chemical Society.

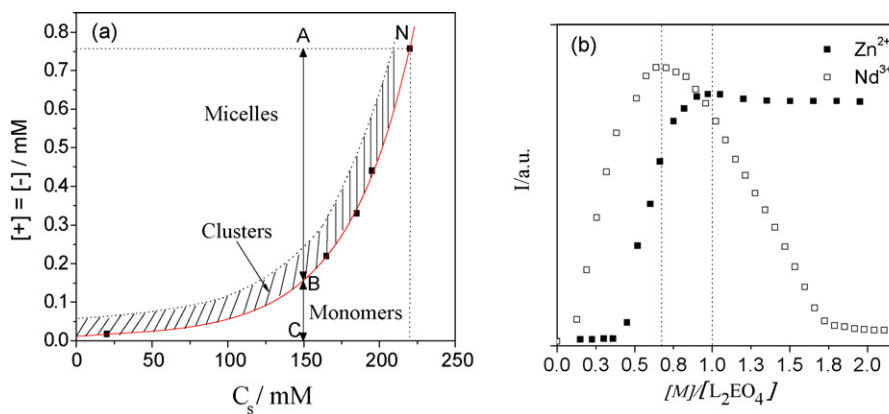


Fig. 10. (a) CMC curve (solid curve) of the micelles in the presence of NaCl. The dashed area is drawn approximately to illustrate the region where clusters are present. $T = 25^\circ\text{C}$. (b) Variation of the scattered light intensity in a solution of P2MVP₄₁-b-PEO₂₀₅ upon addition of zinc ions (filled squares) and neodymium ions (open squares). Adapted from Ref. [60]. Copyright: American Chemical Society.

when the first row transition metal ions are replaced by those in the second or the third rows, C3Ms can be destroyed by excess metal ions (Fig. 10b). This suggests that the first row transition metal ions will not extract ligands from the micellar core, but the second and third row ones do, which results in the formation of positively charged coordination chain ends and leads to the falling-apart of the C3Ms.

It is also remarkable that wormlike micelles are formed when the diblock copolymers are in excess [62,63] (Fig. 11). In cryo-TEM images, these micelles resemble strings of spherical micelles, suggesting that a weak attraction exists between these micelles. Although the mechanism of formation of these wormlike micelles is still not fully understood, solid experimental proof, including cryo-TEM, SAXS, angular dependence, and depolarized DLS results, all unambiguously confirmed their existence [62,63].

4.4. With polypeptides: nanoribbon hydrogels

The principle to combine coordination supramolecules with oppositely charged modules can be used to create a variety of assembled structures. In the case of using a polypeptide as the oppositely charged template, we can even obtain well-defined nanoribbons. Fig. 12 illustrates the ribbon structure obtained in the mixture of Zn-L₂EO₄ coordination polymer and an ABA type polypeptide [64]. Here, the middle B block is positively charged at pH < 6.8 due to the presence of histidine groups, whereas the outer A block is always charge neutral. We found that the coordination supramolecules play a crucial role in the formation of these nanoribbons, since no ribbons can be achieved by other ways of neutralizing the charges on the B block, e.g., by using either covalent polyelectrolyte polyacrylate sodium (PANa), or by increasing pH. We infer that it is the adaptable polymerization degree of the

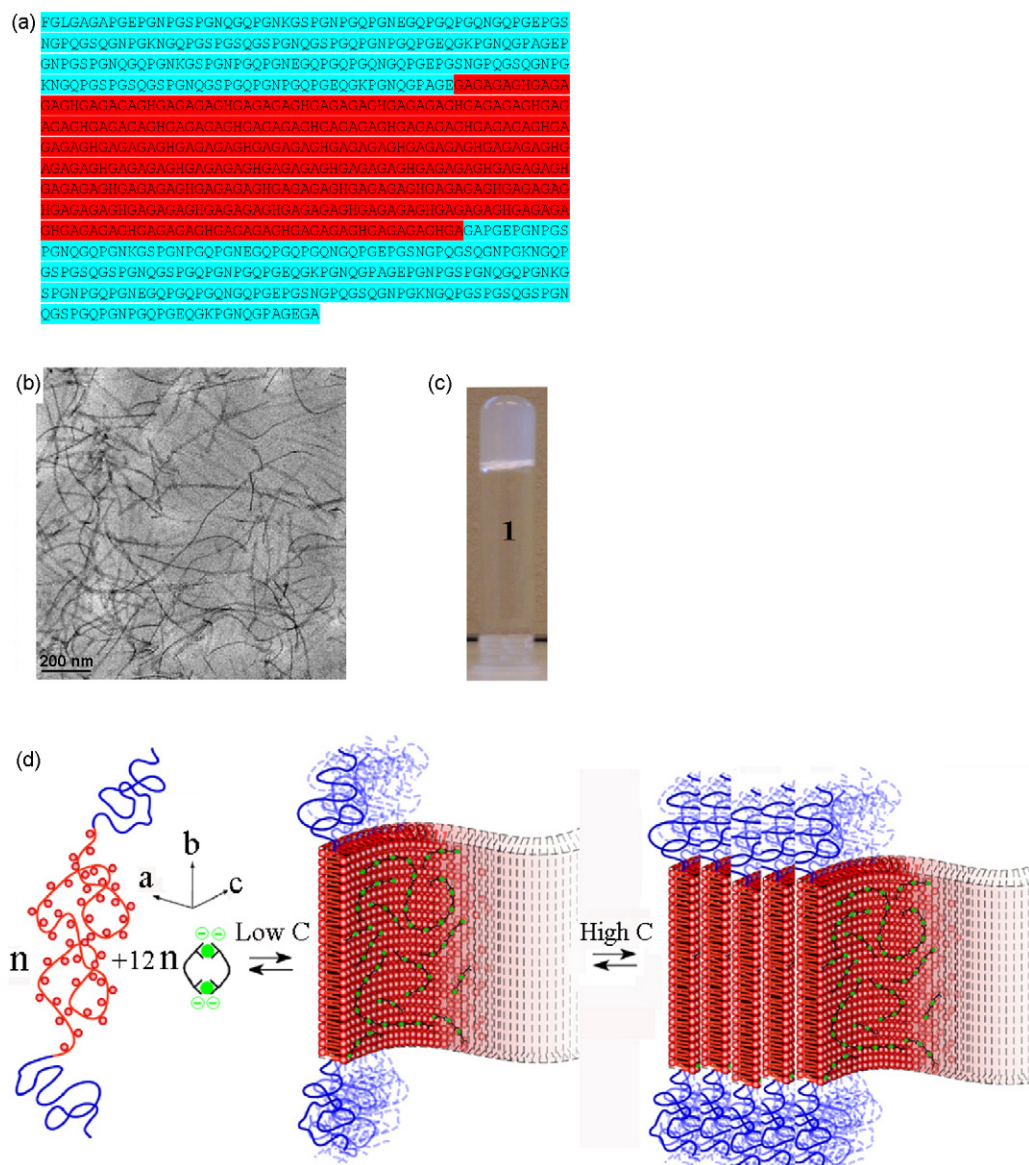


Fig. 12. (a) Amino series of the ABA type polypeptide. The middle block contains histidine groups which can be positively charged at pH < 6.8. (b) Cryo-TEM images of the nanoribbons formed out of Zn-L₂EO₄ coordination supramolecules and the polypeptide. (c) Hydrogels formed in the nanoribbon system at polymer concentration of 6.97 g/L. (d) Illustration of the formation of single ribbons at low concentrations (low C) and overlay of ribbons at high concentrations (high C) in the mixed system of ABA/Zn-L₂EO₄. Adapted from Refs. [64(a, b), 65(c, d)]. Copyright: Wiley-VCH Verlag GmbH & Co. KGaA [64] and American Chemical Society [65].

coordination supramolecules that allows uninterrupted folding and closely packing of the B block of the polypeptide. These nanoribbons bundle together to form hydrogels at higher concentration [64]. Moreover, the nanoribbons gel water more efficiently than the mixtures of PANa/ABA and pH 11 of ABA.

5. Perspectives and conclusions

Coordination supramolecules exhibit promising properties in the fabrication of molecular devices and advanced functional materials. The examples given in this review cover only a small fraction of coordination supramolecules that have been synthesized. Many systems with oppositely charged modules have not yet been explored. We expect that more coordination supramolecules with special functional groups will bring unexpected surprises to the hierarchical self- and/or co-assemblies containing coordination supramolecules. For instance, modifying the spacer structure of the telechelic ligand molecules may exert a significant influence on the function and hierarchical self-assembling properties of coordination supramolecules, and may also affect the topological feature of the co-assemblies with oppositely charged species. The coordination supramolecules can be made fluorescent upon incorporation of fluorescent group into the spacer [66,67]. Yet many questions in this respect are still unanswered, such as: Can we tailor the optical properties by using different combinations of coordination supramolecules? Can we produce materials with 'invisible' properties in a wide range of spectrum? How does the rigidity of the coordination supramolecules affect the assemblies? In addition, the

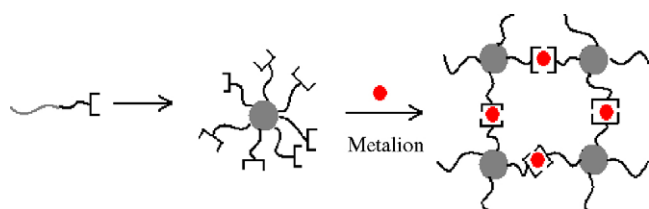


Fig. 13. Hierarchical self-assembly of a PS-*b*-PtBA-copolymer (is a terpyridine ligand) leading to the formation of a supramolecular network of micelles.

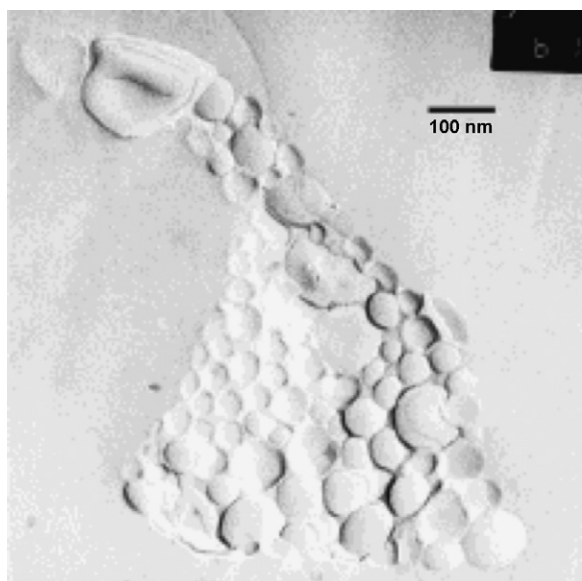


Fig. 14. Freeze-fracture electron micrograph of the second level assembly of vesicles formed by carboxylic amphiphiles in the presence of 2×10^{-4} M Cu^{2+} . Adapted from Ref. [69]. Copyright: American Chemical Society.

responsiveness of molecular assemblies, containing coordination supramolecules, to stimuli, is still not adequately explored. Work in our lab is moving toward this aim. It will be also very interesting to exploit the coordinating force to control the hierarchical interaction between molecular assemblies. For instance, Gohy et al. have used a monoligand modified amphiphile to form micelles; these micelles can form gels triggered by addition of metal ions [68] (Fig. 13). Our group also found advanced assembly of vesicles by introduction of copper ions to the carboxylic amphiphile solution [69]. Compared with the effort made to synthesize coordination supramolecules, research on molecular devices made from coordination supramolecules is still a virgin field to be explored. We expect to see more interesting work appears in this field in the near future (Fig. 14).

Acknowledgments

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