Hierarchical molecular self-assemblies: construction and advantages

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Hierarchical molecular self-assembly offers many exotic and complicated nanostructures which are of interest in nanotechnology and material science. In the past decade, various strategies leading to hierarchical molecular self-assemblies have been developed. In this review we summarize the recent advances in the creation and application of solution-based self-assembled nanostructures that involve more than one level of arrangement of building blocks. The strategies for construction hierarchical self-assembled structures and the advantages brought up by these assemblies are focused on. The following contents are included: (1) general approaches to fabricate hierarchical self-assembly, including self-assemblies based on supramolecules and specially designed block copolymers; (2) the advantages brought about by the hierarchical self-assembly, including the fabrication of special self-assembled structures, rich responsiveness to external stimuli, and the materials’ performance.

1. Introduction

The concept of self-assembly, which implies small structural motifs, such as atoms, molecules, macroions, or nanoclusters, self-organized into much more complicated structures via non-covalent interactions, has drawn strong attention in the past decade. The self-assembled structures have shown great potential for the fabrication of various functional materials and nano-devices via a bottom-up strategy. The forces involved in the self-assembling process can be hydrogen bonds, electrostatic interactions, hydrophobic effects, host–guest interactions, metal–ligand coordination, etc. Since all these interactions are dynamic, self-assembling systems are able to respond to external stimuli.

Simple molecular self-assemblies can be easily obtained as a result of one of the aforementioned driving forces via a one-step approach. This can be viewed as the first level of molecular self-assemblies which are now playing fundamental roles in daily industry, such as cosmetics, pharmaceuticals, and detergents. In recent years, much more complicated molecular self-assembling systems that involve more than two levels of self-assembling steps or orders are emerging. Compared with the limited structures and related functions of their first
level counterparts, the multi-level dynamic nature of these hierarchical self-assemblies is able to provide more structural and functional possibilities.  

In this review, we briefly summarize recent progresses in the fabrication of hierarchical molecular self-assemblies. Here we mainly tackle the structures self-assembled via more than two levels self-assembling processes or more than one step assembling approaches; Janus structures that are asymmetrical in functional groups and topologies are not included. The following topics are involved: (1) general approaches to construct hierarchical self-assemblies which include a structural hierarchy resulting from primary self-assembled structures, and stepwise control of the self-assembling processes; (2) Advanced properties of hierarchical self-assemblies, which include (i) the structural advantages derived from the hierarchical structures, and (ii) the responsiveness of the hierarchical self-assemblies; (3) Material advances and perspectives.

2. General approaches to construct hierarchical self-assemblies

As mentioned in the previous text, the approaches to hierarchical self-assemblies often involve multi-level driving forces or multi-step procedures. In case of multi-level driving forces, a pre-assembled structural motif is formed in advance, which then acts as the basic block that further self-assembles into more complicated structures. The pre-assembled structural motif can be a pair of donor–acceptor molecules stacked via a charge–transfer interaction, a supramolecular structure based on a host–guest interaction, or a metal–ligand coordination interaction. The multi-step approach usually occurs in block copolymer systems, where stepwise aggregation of the different blocks can be controlled so that the resultant structures possess a structural hierarchy which contains multi-compartmental. In the following we summarize some typical self-assemblies achieved via these two approaches.

3. Structural hierarchy based on supramolecules

Some molecules have the ability to self-assemble into certain structures in solution. Specifically, the self-assembled structures are based on classical molecules which are an ensemble of atoms connected together via covalent bonds. In contrast, the structural units for hierarchical self-assemblies are often supramolecules that pre-assemble via non-covalent interactions. These supramolecules then arrange into higher-ordered structures which are driven by various inter-supramolecular interactions. In the following, we briefly introduce three types of interactions that drive the supramolecular building blocks to self-assemble into higher ordered structures.

3.1 Hydrogen bonding: tool for host–guest inclusion supramolecules to self-assemble

Host–guest inclusion was found in the 1960’s by Schlenk and Sand in the mixed solution of cycloexetrins (CD) and fatty acids, and later was found to be a general phenomenon in the mixed systems of amphiphiles and CDs. In the inclusion complexes, the hydrophobic hydrocarbon chains are enclosed in the cavity of the CDs. Then the inclusion complex as a whole becomes hydrophilic due to the presence of plenty of OH groups on the outer surface of the CDs. For about half a century, these host–guest inclusion complexes were not considered as motifs that can self-assemble due to their ‘hydrophilic’ nature. However, recent studies in our group suggest that at high enough concentrations hydrogen bonds are capable of forming between the inclusion complexes, so that a self-assembled structure with secondary order can be formed. In our studies, ionic surfactant sodium dodecyl sulphite (SDS) and β-CD were mixed at a molar ratio of 1 : 2 to form an inclusion complex SDS@β-CD (Fig. 1a). The whole hydrophobic section of the SDS molecule is embedded in the cavities of the two β-CDs via a host–guest interaction. The inclusion complexes then assemble into various topologies in water at room temperature at concentrations beyond 5% (wt%). Vesicles, multi-lamellar microtubes, and lamellae can be realized with increasing the overall concentration of the system. However, the final self-assembled structures are not necessarily limited to these topologies. In the case of surfactants with hydrocarbon chains longer than 14C, the self-assembled structures can also take a diamond shape. We found this is a general phenomenon in the inclusion system of ionic surfactants with α or β-CDs. The latest work suggests that not only ionic surfactant, non-ionic surfactant such as tween-20 (ref. 34), TX-114 (ref. 35) are all able to form inclusion supramolecules with CDs, and the supramolecules may further self-assemble into vesicles. We found that the critical concentration for the self-assembly formation depends highly on the polarity of the surfactant head groups. The lower the charges that the head carry, the smaller the critical concentration is. The critical concentration for ionic surfactant systems such as SDS systems can be as high as 5% (wt%) whereas for the non-ionic surfactant tween-20 is as low as 0.2 mM.

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3.2 Hydrophobic interaction: forces utilized by the supramolecular amphiphile (SA) to build structural complexity

The supramolecular amphiphile (SA) is a concept developed recently by Zhang and Wang, which allows the construction of structural motifs with more complexity and tenability. SAs were generally built from a pair of molecules, such as oppositely charged amphiphiles, electron donors and acceptors, a pair of amphiphiles connected by coordination, hydrogen bonding, or host–guest interactions, as demonstrated in Fig. 2.

Unlike their classical counterparts formed by covalently linked atoms, the SAs are comprised of two covalent molecules which are connected by dynamic non-covalent interactions. This provides more possibilities for the self-assemblies. For instance, upon employment of a charge-transferring interaction, a bola-type supramolecular surfactant can be built by the conjunction of 1-[11-oxo-11-(pyren-1-ylmethoxy)-undecyl]pyridinium bromide (PYR) and ethane-1,2-diyl bis(3,5-dinitrobenzoate) (DNB). The PYR has an electron-rich pyrenyl group and thus becomes an electron donor in the pair while the DNB with electron-deficient dinitrobenzene groups acts as an electron acceptor. A mixture of the two molecules (PYR : DNB = 2 : 1) generates the bola-form complexes. The PYR-DNB complex displays a vesicle morphology, which is different from the tube-like aggregates in the PYR system. The charge transfer interaction also allows the creation of SAs with

![Fig. 1 Vesicles, multi-wall microtubes, and lamellar structures formed on the basis of host–guest inclusion supramolecules of SDS@2β–CD. (A) Scheme of the inclusion complex of SDS@2β–CD. (B) Scheme of the assemblies based on SDS@2β–CD. (C) TEM image of the vesicles. (D) CLSM image of the microtubes. (E) SEM image of the lamellar structure. (F) TEM image of diamond-shape aggregates. Adapted from ref. 31 and 32.](image)

![Fig. 2 Topologies of SAs via different interactions. D and A refer to donor and acceptor, respectively. Adapted from ref. 36. Copyright: The Royal Society of Chemistry.](image)
special topologies. For instance, X-shaped and H-shaped supramolecular amphiphiles were realized with this strategy (Fig. 3). This directly led to fine hierarchical structures as one-dimensional nano-rods or 2-dimensional nano-sheets, respectively.

### 3.3 Electrostatic interaction: choice of coordination supramolecular polymers for hierarchical assembly

Low-molar mass species may self-assemble into linear or branched polymeric structures using non-covalent interactions as linkages. To build a supramolecular polymeric backbone, the strength and directionality becomes more important. Without a relatively high binding constant, the monomers are more likely to form oligomers rather than polymers. In this case, hydrogen bonds, dynamic covalent bonds, host-guest interactions, and coordinative bonds are exploited to make supramolecular polymers. Among which, a coordinative bond as one of the non-covalent interactions is widely used for constructing hierarchical molecular self-assemblies.

To build main-chain coordination polymers or metallosupramolecules, low molecular weight polytopic ligands (bisligands in many cases) are required. The metal ions exploited are usually transition metal ions with empty or unsaturated orbitals so that they can accept electrons and form coordinative bonds. Thus, metal ions act as linkers between the polytopic ligands and finally lead to polymeric structures (Fig. 4).

Kurth, Vermonden, Constable, and Rowan and co-workers have synthesized different ligands and resultant coordination polymers. Since each coordination centre usually carries net elementary charges, many supramolecular polymers have difficulties in stepping into next-level self-assemblies. However, upon introducing components with opposite charges, the assembly of supramolecular coordination polymers can occur with electrostatic interactions. Kurth and coworkers reported a layer-by-layer assembly with a positively charged coordination polymer (Fe(n)-MEPE) and negatively charged polyelectrolytes. After repeated immersion of substrate in the two candidates, a UV-active thin film was obtained. Capsules can also be prepared by this means (Fig. 5).

When further mixed with diblock polyelectrolytes, coordination polymers can form micelles, which are called polyion complex (PIC) micelles or complex coacervate core micelles (C3Ms). The diblock polyelectrolytes often comprise of a charged and a neutral blocks. The charged one is to form polyion complex with the coordination polymers via electrostatic interactions, whereas the neutral one is to stabilize this electrostatic complex. Therefore, the PIC micelles often have a core-corona topology. With this approach, Yan et al. have assembled the coordination polymer based on a low-molar mass bisligand 1,11-bis(2,6-...
dicarboxypyridin-4-yloxy)-3,6,9-trioxaundecans (L$_2$EO$_4$) and Zn$^{2+}$ into PIC micelles in the present of a diblock copolymer poly(2-vinyl-N-methylpyridinium iodide)-$b$-poly(ethylene oxide) (PMVP$_{41}$-$b$-PEO$_{205}$) (Fig. 6A). The coordination polymers just behave like classical negatively charged polyelectrolytes, which form the micellar core with the positively charged PMVP$_{41}$ block. Moreover, the size of micellar core can be controlled by replacing part of the coordination polymers with like-charged homopolyelectrolytes (Fig. 6B). In this way, the diameter of the resultant particles can be of several hundreds of nanometers. Such huge soft particles are called microemulsions.$^{55}$

Fig. 5 Assembly of MEPE on capsules. Adapted from ref. 44. Copyright: Elsevier.

4. Structural hierarchy based on the self-assembly of triblock copolymers

Amphiphilic polymers with proper blocks can spontaneously self-assemble into supramolecular aggregates like their small amphiphilic counterparts. This is especially the case for diblock co-polymers with one solvophobic block and the other solvophilic. For this reason, block copolymers often form micellar aggregates in a selective solvent, just as a conventional low molecular weight amphiphiles does.$^{56}$ The AB di-block copolymers always form a core–corona structure, with the solvophobic chains hiding inside with THE well-solved chains surrounding the outside. However, block co-polymers with more than two segments may form much more complicated structures such as multi-compartment micelles (MCMs).$^{57}$ Stepwise control over these building blocks also becomes possible to achieve advanced structures.

4.1 One-step self-assembly of triblock copolymers

Tri-block co-polymers with hydrophobic parts composed of hydrocarbon and fluorocarbon segments may have overall three incompatible chains plus a hydrophilic fragment. It is known that the strong incompatibility between hydrocarbon chains and fluorocarbon chains always leads to separated domains in surfactant systems.$^{58}$ Li et al. have reported an ABC terpolymer system,$^{59}$ in which a synthesized ABC miktoarm star block co-polymer was investigated. The star block terpolymer $\mu$-EOF ($x$-$y$-$z$) shown in Fig. 7 has one hydrophilic poly-ethylene oxide chain, one hydrophobic polyethylene chain and one hydrophobic poly-fluoropropylene oxide chain. The star terpolymer in dilute water solution formed a series of fascinating aggregates due to the different values of the block molecular weight parameters. With an increase of the molecular weight of the hydrophilic block ($\mu$-EOF (2-13-2) and $\mu$-EOF (2-13-3)), three-lobed and four-lobed micellar cores were discerned. On the other hand, the $\mu$-EOF (2-7-2)

Fig. 6 Complex coacervate core micelle systems. (A) Adapted from ref. 54. (B) Adapted from ref. 55. Copyright: John Wiley and Sons.$^{34}$ and The Royal Society of Chemistry.$^{55}$

Fig. 7 Multi-compartment micelles formed by $\mu$-EOF. Adapted from ref. 58. Copyright: The American Association for the Advancement of Science.
aggregates appeared as long strings while those for the μ-EOF (2-9-2) looked like a “segmented worm” under Cryo-TEM. The hierarchical structure of the segmented aggregates of the micelles implies an attractive interaction between the micelles and thus the molecular arrangement in the MCMs was proposed. Other strategies of block copolymer designation were also investigated to achieve multi-compartment micelles. In later works, they systematically studied the aggregates formed with various compositions of the μ-EOF terpolymer and developed a series of new morphologies. For instance, the blends of μ-EOF terpolymer and diblock polymer EO (poly-ethylene oxide) formed “hamburger” micelles (Fig. 8).

Cui et al. have worked out a kinetic manipulating strategy to generate different nano-structures with triblock copolymers. Using methods such as solvent mixing and complexation of counter ions, kinetically trapped but stable assemblies were forced to form. The linear poly(acrylic acid)-block-poly(methyl acrylate)-block-poly(styrene) (PAA-b-PMA-b-PS) triblock copolymer formed striped cylindrical one dimensional nano-structures with 2,2′-(ethylenedioxy)diethylamine (EDDA) as a diamonium counter ion. Adding another linear block copolymer poly(acrylic acid)-block-poly(methyl acrylate)-block-poly[2,3,4,5,6-pentafluorostyrene] (PAA-b-PMA-b-PPFS), a new hydrophobic block was forced to form within the cylindrical micelle core (Fig. 9).

4.2 Stepwise solvophobic interaction-directed structural hierarchy

To control the morphology of block copolymer assembly, more efforts were made. The solvophobic-driven assembly of block copolymers into multi-compartment micelles can also be controlled kinetically and thus this becomes a multi-step assembly. For instance, a delicate hierarchical architecture was constructed from stepwise self-assembly of linear terpolymers by Muller and coworkers (Fig. 10). The terpolymer SBM (polystyrene-b-polybutadiene-b-poly(methyl methacrylate)) first formed well-defined micellar subunits with a collapsed core and a mixed corona in the non-solvent of core blocks. By changing the solvent, the subunits ran into the next-level assembly and formed spherical multi-compartment micelle with a fixed amount of patches.

Recently, these authors reported that the topology of the multicompartment micelles can be finely tuned by controlling the volume of the two solvophobic blocks. They started from a group of ABC-type triblock copolymers, the so-called colloid building blocks (CBB) which contain polystyrene (S)-polybutadiene (B) or poly(3-buteneyl[(dodecyl)sulfane] (D) as core makers, and poly(tert-butyl methacrylate) (T), poly-methyl methacrylate (M) or poly(2-vinylpyridine) (V) as corona blocks (Fig. 11). Dispersion of the triblock terpolymers in a non-solvent for B or D yields B or D-core particles with S and V (or S and T) corona patches. During transfer into a non-solvent for S and B or (S and D), these develop into monovalent ABC and divalent ABCA units with sticky A patches. At the volume ratios of V_S/V_B < 1 and >1, the stick properties of the primary particles are different, so that they finally developed into different structures. Because the volumes of different blocks are experimentally controllable, they can even be used to predict what kind of structures can be formed by simply analyzing the volume ratio of the starting CBBs.

4.3 Stepwise exerted solvophobic and electrostatic interaction-directed self-assembly

Typical linear block copolymers form core–shell–corona structures, but strategies were developed to make linear terpolymer aggregates more complex. This is the case for the interpolyelectrolyte complexes (IPEC) with two oppositely charged block copolymers system illustrated in Fig. 12. In this work, Schacher et al. employed a terpolymer PB−P2VPq−PMAA which formed micelles in aqueous system at high pH. In the micellar structure, the interpolyelectrolyte complex of P2VPq and PMAA formed the middle shell, while the excess negatively charged PMAA chains formed the corona domains. Upon addition of a positively charged block copolymer P2VPq−PEO, amazing star-like aggregates occurred in which IPEC of excess PMAA and additional P2VPq
blocks formed. After 10 days’ equilibration, the nanostructures evolved into spherical core–shell–shell–corona micelles.

5. Advanced structures attained by hierarchical self-assembly

Hierarchical self-assembly does not simply include step-by-step assembling of the components in the systems. Sometimes, the simultaneously occurred cooperative interactions may lead to advanced structures that cannot be achieved in monosystems or with other protocols. In the following we raise two typical examples in this regard.

5.1 Special folding of polypeptides

Folding of polypeptides may lead to different structures under different conditions. Usually, the key to various folding modes is the native structure of the polypeptide. For instance, Stupp et al. have found that the terminating groups significantly influence the thermal stability of the fibrils resulting from amphiphile peptides. Whereas Pochan et al. reported that the D or L conformation of the amino acids composing the polypeptides determines whether they fold into single fibrils or further assemble into laminates. In some cases, special...
structures can be obtained only under proper control. We have demonstrated that a polypeptide by itself forms fibrils and may form nanoribbons when coassembled with a Zn–L₂EO₄ coordination polymer. The polypeptide is illustrated as an ABA type block copolymer in Fig. 13. The B block is positively charged at pH <6.8 due to the effect of histidine groups while the A block is charge neutral at all pHs. Upon charge neutralization of the B block with a Zn–L₂EO₄ coordination polymer, perfect nanoribbons were observed. In contrast, discharging the B block by either increasing the pH or with a covalent polyelectrolyte led only to fibrils. Circular dichroism (CD) analysis suggested that the reversible Zn–L₂EO₄ coordination polymer has led to uniform folding of the B block. This was attributed to the reversible nature of the coordination polymers. In the process of charge neutralization, the Zn–L₂EO₄ coordination polymer will change their conformation and position to avoid interfering with the stacking between the folded polypeptide. In contrast, the covalent polyelectrolyte didn’t exhibit such smart abilities.²¹,²²

5.2 Ultralong nanoladders

To fabricate a ladder structure is a challenging problem in polymer and supramolecular science. Usually, the ladders in one step self-assembly are only several nanometers long. However, upon employment of the hierarchical self-assembly of coordination polymers, we may obtain ladders of several micrometers long. To this end, a rigid bisligand TPE-C₄-L₂ was adopted. The TPE-C₄-L₂/metal coordinating complexes self-assemble polydispersed cocoon-like particles. Upon addition of a charge balancing amount of PMVP₄₁–PEO₂₀₅ block copolymer, the cocoons immediately transformed into ultralong ladders run up to several micrometers with a width of about 10 nm (Fig. 14). It is very amazing that in the nanoladders precise charge recognition has driven the vertical chain orientation for the TPE-C₄-L₂/metal coordination polymer and the PMVP₄₁–PEO₂₀₅ block copolymer.²³

5.3 Promoted formation of coordination polyelectrolytes

In the previous text we showed some examples of hierarchically self-assembled structures based on coordination polymers. However, one of the most critical parameters for the fabrication of coordination polymers is to carefully control the stoichiometric mixing ratio between the ligands and the metal ions. Polymeric structures can only be obtained at the exact stoichiometric ratio. Deviation from this ratio leads to coordination ends which are fatal to the polymeric structures. However, the layer-by-layer approach showed a level-off effect on the metal to ligand ratio regardless of their initial composition.²⁴ The formation of the coordination polyelectrolytes can be obtained at metal to ligand ratios far from chemical stoichiometry (Fig. 15). This means that the dynamic nature of the coordination bonds allows a rearrangement of the coordination complexes to reach optimal electrostatic interactions.

6. Stimuli-responsiveness imparted by the hierarchical self-assembly

Non-covalent interaction imparts the self-assembled structures with good tunability. Particles with multiple structural hierarchies have much in common with their conventional counterparts. Moreover, the unique patterns obtained in the multi-level assembling approach impart them with excellent potential for manipulating the structural hierarchy of nanosystems. In the following we summarize some typical examples of stimuli-responsiveness, advanced structures, and special materials.

6.1 pH responsiveness

One of the most widely used external stimuli is the variation of pH. The change of pH generally influences the solubility and configuration of the responsive molecules,²⁵ and thus impacts their self-assembling properties. One example of pH-responsive hierarchical assemblies is the multi-functioning three-layered nanoparticle (3LNPs) reported by Shen and co-workers.²⁶ The 3LNPs have a core–layer–layer structure with a poly-

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Fig. 13 (A) Zn–L₂EO₄ coordination polymer. (B) Amino series of the ABA type polypeptide. (C) Illustration of the formation of ribbons (D) Cryo-TEM images of the nanoribbons formed out of the Zn–L₂EO₄ coordination supramolecules and the polypeptide. (E) Hydrogels formed in the nanoribbon system. Adapted from ref. 71 and 72. Copyright: John Wiley and Sons²¹ and American Chemical Society.²²

Fig. 14 Structure of (A) TPE-C₄-L₂, and (B) schematic representation of the structures formed by TPE-C₄-L₂ and metal ions without and with polymer; the PEO₂₀₅ block is illustrated as the yellow shell that covers the ultralong ladders. Adapted from ref. 73. Copyright: American Chemical Society.
(ε-caprolactone) (PCL) core, a pH-responsive middle layer built up of poly[2-(N,N-diethylamino)ethyl methacrylate] (PDEA), and a polyethylene glycol (PEG) outer layer. Changing of the pH influenced the solubility of the PDEA layer and thus controlled the release process as illustrated in Fig. 16. At physiological pH (above 7), the PDEA layer covered the PCL core and prevented the drug release process. When the pH falls below 6.5, the middle layer is positively charged thus becomes soluble, which enables the drug release.

6.2 Redox responsiveness

When a redox-active component is involved, the hierarchical assembly may inherit redox responsiveness. For instance, we have built a micellar system consisting of Fe³⁺ ions, the bisligand L₂EO₄, and the block polyelectrolyte PMVP₄₁–PEO₂₀₅. Polyion complex micelles were formed based on the cooperative interaction of the electrostatic interaction and coordination. Fe³⁺ and L₂EO₄ form coordination supramolecules which carry one elementary negative charge at each coordinating centre. Upon complexation with charge-balancing positively charged PMVP₄₁–PEO₂₀₅, neutral polyion complex micelles are formed immediately. When the Fe³⁺ was reduced to Fe²⁺, the micelles developed negative charges, which took up positively charged species. It was interesting to find that the shape of the micelles changed when a rigid species was taken up. When a rigid positive coordination polymer was used as the cargo, the topology of the electrostatic systems gradually changed into banana-bundle-like, then became rod-like (Fig. 17). Zeta potential measurements suggested that such a change is related to the diffusion degree of the net charges on the reduced micelles. At the initial reducing stage, few negative charges were developed and they were mainly confined near the core region. Then the rigid coordination polymers may be loaded close to the core and swelling the core into a banana-like bundle; as more negative charges were developed, the charges may go further outward from the core, then the micelles may act as a mediator that connects the rigid positively charged cargos. In this way, the micelles smartly reacted with respect to the amount of the rigid cargo. However, if the positively charges species are flexible polymers or small molecules, the micelles remained spherical.

6.3 Photo responsiveness

Photo responsiveness can be also introduced into the hierarchical structures. Zhang et al. has designed a photo responsive supramolecular amphiphile (SA) by using a block copolymer poly(ethylene glycol)-b-poly-L-lysine hydrochloride, (PEG-b-PLKC) from two small organic amphiphile. Upon mixing in an aqueous medium, they formed electrostatic complexes which further aggregate into sheet-like assemblies (Fig. 18). When UV-light was applied, the solubility of the malachite green derivative increased due to its transformation into an ionic species, thus leading to a disassembly of the aggregates.
7. Advanced functions imparted by the hierarchical self-assembly

The complexity of the structural hierarchy also brought functional advantages to the self-assembled structures. First of all, structural hierarchy often involves multiple components. Then each of the components may contribute to functions. Secondly, the hierarchical structures often produce fine structures so that they can be used as templates.

7.1 Eu$^{3+}$ luminescence enhancement by hierarchical structure of coordination supramolecules

The presence of secondary self-assembly allows a rearrangement of the primary supramolecules. This naturally triggers functional improvement. Yang et al. reported the fluorescence enhancement of Eu–L$_2$EO$_4$ coordination polymers$^{77}$ through the construction of polyion micelles discussed in the previous text. Conventional methods to enhance the luminescence of europium ions in aqueous solution generally requires a high enough concentration of the fluorescent species. By using a hierarchical assembly of the coordination polymers, the luminescence emission can be enhanced at a very low concentration. The local concentration of the complexes was increased by the electrostatic attraction between the coordination complexes of europium and the oppositely charged diblock polyelectrolyte (Fig. 19), thus a high sensitivity had been achieved. It is worth noting that the rearrangement of the coordinating complexes owing to the second level self-assembly is crucial for the luminescence enhancement. If the bisligand L$_2$EO$_4$ was replaced with a chelating ligand EDTA, no luminescence enhancement can be observed in the same procedure.$^{81}$

7.2 Parallel arrayed nanoparticles

Nanoparticles have shown potential in optical and electronic devices. The fabrication of ordered arrays of nanoparticles on substrates is very important to improve the technology of nanodevices.$^{82}$ In the work of Cui et al.$^{64}$ parallel arrayed nanoparticles can be prepared in the presence of the MCM templates. The periodic PAA region induced the oppositely charged inorganic nanoparticles to construct periodic structures (Fig. 20). This work clearly showed the advantages and potential of the hierarchical structures to be used as templates in construction materials. In a recent work by Muller et al.$^{66}$ the arrays of nanoparticles can be made in a more extended way. This means the structural hierarchy of MCM micelles can be potentially used as a general approach to fabricate nanoarrays of nanoparticles.

8. Summary and perspectives

Hierarchical molecular self-assemblies are very important for mankind to understand and learn from nature. Most naturally occurring materials with fascinating functions are based on structural hierarchy. Each level of arrangement of the relating units undertakes special functions. It is the cooperative or combined interplay at different levels the makes up the wonderful chorus of mother nature. In this regard, the design of hierarchical molecular self-assemblies on demand is a step that we must make towards advanced functional materials. This is especially crucial for achieving high performance nanomaterials. In approaching a higher complexity of solution-based self-assembly, much more efforts are needed. The examples and strategies summarized in this review, although covering only part of the up-to-date studies in this field; represent a start toward this goal. The key roles that determine the easiness and possibilities of creating structural hierarchy are still to be discovered. We expect that both inspiration from nature and
basic physical laws should be employed in order to rationally design hierarchically assembled systems. This is especially helpful in guiding the molecular assemblies based on one-level order to arrange into higher ordered structures. Compared to the ordered structures ranging from nano to macroscopic scale in natural materials, mankind still has a very long way to travel to reach the realm of the hierarchical materials.

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Notes and references
