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Review

Supramolecular Nanostructures Constructed from Cluster-based Hybrid Macromolecules

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Molecular clusters are valuable building blocks to synthesize hybrid macromolecules, and consequently achieve diverse supramolecular nanostructures *via* self-assembly. Hybrid macromolecules can be synthesized by covalently linking different molecular clusters and grafting organic molecules onto cluster surface, or through complexation *via* non-covalent interactions. Through regulation of solution conditions such as solvent polarity, ionic strength, and type of cations, well-defined hybrids exhibit versatile self-assembled behavior determined by their molecular structures including shape, composition, volume fraction, topology, and surface functionality. The incorporation of molecular clusters into polymers can tune the flexibility and architecture of cluster-based copolymers, which fills the phase diagrams with different molecular packings as well as supramolecular nanostructures. The complexation between molecular clusters and other organic molecules provides a promising approach to construct multi-dimensional nanostructures through non-covalent interactions.

Introduction

Since the concept of macromolecules introduced by Staudinger [1], the progress of macromolecular science has been extended from traditional homo- and block- polymers to many other areas such as dendrimers [2], macrocycles [3], nanocages [4,5], polyrotaxanes [6], *etc*. Typically, macromolecules are synthesized by connecting a large number of small organic molecules (monomers) *via* covalent bond, *i.e.*, polymerization. Meanwhile, extensive covalent bonds among proper inorganic building blocks are found to form large, finite inorganic molecular clusters, including polyoxometalates (POMs) [7], fullerene (C_{60}) [8], polyhedral oligomeric silsesquioxane (POSS) [9], silver and gold nanoclusters [10,11], and polyhedral boranes [12]. The molecular clusters mostly with the size (~ 1 nm) between small molecules and colloidal nanoparticles, have well-defined sizes, shapes, compositions, and atomically precise structures. They have been used as valuable building blocks to synthesize hybrid macromolecules with organic components. Such hybrid materials, possessing both attractive physical properties (*e.g.*, catalytic, optical, luminescent, and electronic activities [13-17]) from the inorganic components, and good processability due to the organic ligands, have been demonstrated as promising functional materials.

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Self-assembly provides a powerful toolbox for the button-up construction of supramolecular nanostructures in multiple dimensions [18]. Besides the primary chemical structures, self-assembly is often driven by various non-covalent secondary interactions. In this regard, cluster-based hybrid macromolecules provide an excellent platform to study the self-assembly behavior regulated by different driving forces [19] and consequently achieve controllable supramolecular nanostructures [20-22], owing to the following reasons: (1) The molecular clusters have rigid structures with advantage of no polydispersity, which helps us build a better understanding between the primary chemical structures and consequent self-assembled nanostructures; (2) The multiple functional sites on clusters enable us to tailor their surface properties (*e.g.*, hydrophilic *vs.* hydrophobic, charged *vs.* non-charged), and meanwhile create hybrid macromolecules with different compositions, shapes, sequences, and topologies; (3) A large library of clusters can be chosen as building blocks, aiming for the superstructures with multiple functions. In this mini-review, we present some representative progress in fabricating supramolecular nanostructures *via* solution self-assembly of hybrid macromolecules based on POM, C_{60}, and POSS clusters, with the major focus on the work in the past five years.

Design of Cluster-based Hybrid Macromolecules

Molecular clusters with well-defined structures and independent functionalities, have been recently recognized as ‘nanoatoms’ or ‘superatoms’ for the concept of materials by design, because of their dual roles in structural construction and functionality integration [23–26]. As the transition regime between small molecules and colloidal nanoparticles, molecular clusters possess well-characterized surface sites, providing great opportunity for the surface modification with desired functional groups, molecules or polymers [23,27]. Thanks to the wide availability of organic synthetic strategies, the surface functional groups of molecular clusters can be covalently engineered by grafting polymers and/or other clusters in designed sequences for various nano-scaled architectures, *e.g.* dumbbell, star, and dendron shapes [23,26,28]. Especially, due to its high yield of products and excellent selectivity, click chemistry [29] plays vital roles in the precise synthesis of target hybrids. Specifically, copper-catalyzed alkyne-azide cycloaddition (CuAAC) and thiol-ene reaction, as the best-known click reactions, have been frequently applied for the construction of cluster-based hybrids due to the convenient introduction of corresponding functional groups in clusters and polymers (Fig. 1a). It is worth noting that the symmetrical distribution of surface functional groups imposes more efforts for the synthesis of hybrids with asymmetric architectures, *e.g.* half dendron, and strategies for the selective protection of functional groups and effective separation of target isomers have been developed for the synthesis of cluster-based hybrids [30–32].

Meanwhile, the enriched stock of functional groups on molecular clusters enable multiple types of non-covalent interactions for the supramolecular synthesis strategy of cluster-based hybrids [26,28]. For example, molecular clusters attached with large aromatic rings functionalize as molecular tweezer and complex with fullerene *via* π-π interaction (Fig. 1b) [33]. Organic ligands can also be applied to modify the surface of molecular clusters and the obtained multidentate compounds can coordinate to metal ions with matched symmetry for the formation of cluster complex with various morphologies, including dumbbell and polygon shapes (Fig. 1b) [34-37]. Similarly, hairy cluster-polymer hybrids can be assembled from the coordination between polymers bearing bidentate ligands and proper metal ions [24,38]. Thanks to the availability of abundant anionic molecular clusters, positively charged molecules can form complex with various clusters through the electrostatic interaction and usually star-shaped hybrids are obtained (Fig. 1b) [39,40].

Supramolecular Nanostructures Assembled by Well-defined Hybrids

Although the precision in molecular structure is not always necessary, well-defined macromolecules (no polydispersity) are certainly valuable by providing great control for a deep insight into their self-assembly process. In the past decade, intense attentions have been focused on creating well-defined hybrid macromolecules containing different molecular clusters [23,27,28]. These hybrid macromolecules, sometime called “giant molecules”, can be synthesized by either connecting different clusters with organic linkers, or grafting organic motifs onto clusters, as shown in Fig. 2. To facilitate their self-assembly in solution, the design of hybrid macromolecules usually follows the principle of amphiphilicity, with one part being hydrophilic and the other being hydrophobic. Mixed solvents are commonly used as the selective solvents to tune different intermolecular interactions and induce microphase separation, as widely applied in other systems such as small-molecule surfactants and block copolymers [41,42].

Janus Co-clusters

Hybrids with different cluster heads (Janus co-clusters) are synthesized by coupling two types of dissimilar molecular clusters (shown in Fig. 2). Overall, the Janus clusters (AB_n) can be treated as amphiphilic block copolymers with rigid A and B blocks, where A and B represent two distinctive clusters and *n* value represents the number of clusters. The dissimilarity can be achieved by choosing different types of clusters, for example, POM-POSS [43-50], POM-C_{60} [51,52], and C_{60}-POSS [46,53]. Meanwhile, it can also be achieved by using the same type of clusters but with different surface functionalities, such as C_{60}-AC_{60} composed of hydrophobic C_{60} and hydrophilic AC_{60} (functionalized with -COOH) [54]. In solution, the Janus co-clusters possess good shape-persistence, endowing them as a good model to study the effect of molecular structure (*e.g.*, size, shape, composition, volume fraction, and surface functionality) on self-assembled nanostructures.

Effect of Cluster Number and Type

Cheng’s group designed a series of POM-POSS Janus co-clusters by connecting one Keggin-type POM with $XPOSS_n$ (X=B or C, n=1, 2), where BPOSS is functionalized with crystalline isobutyl groups and CPOSS is functionalized with non-crystalline cyclohexyl groups (Fig. 3a) [44]. Their packing in the assemblies strongly depends on the polarity of solvents.

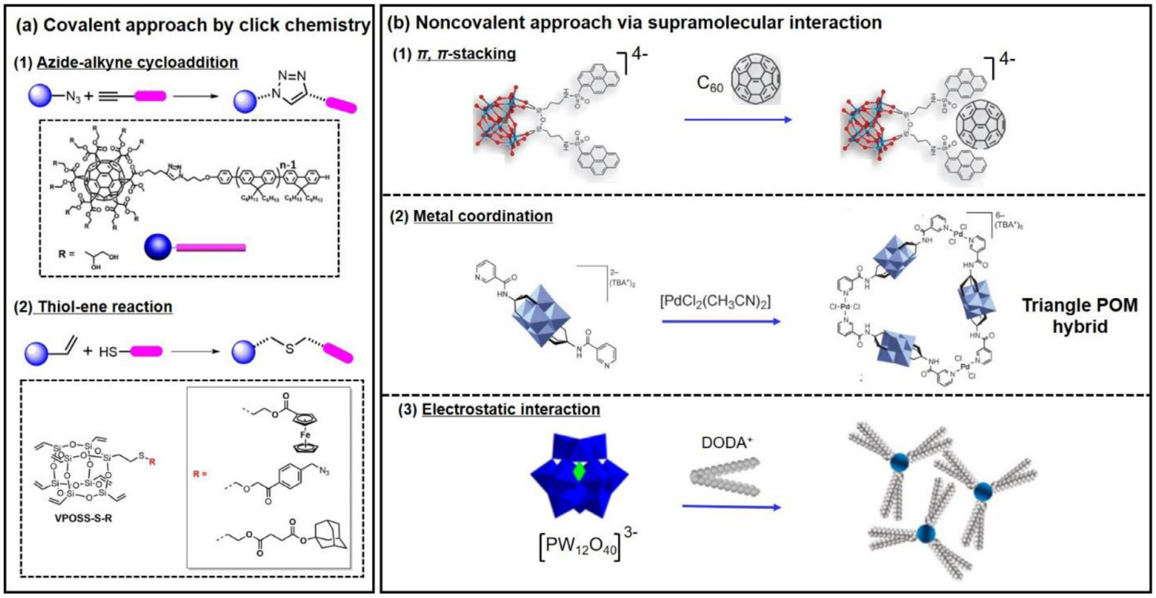

Fig. 1

Cluster hybrids constructed from (a) covalent approach and (b) noncovalent approach. Adapted with permission from ref 32-34,40, and 65. Copyright 2012 and 2014 Royal Society of Chemistry; 2009 and 2017 American Chemical Society.

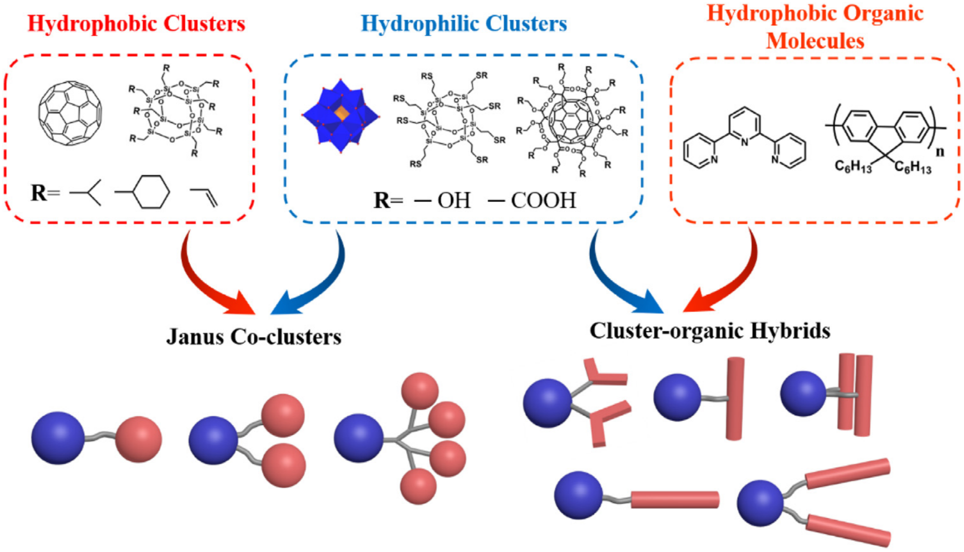

Fig. 2

Schematic illustration of typical approaches to create well-defined, cluster-based hybrid macromolecules.

In polar acetonitrile/water mixed solvents, the dumbbell-shaped Keggin-BPOSS initially forms small colloidal spheres (~30 nm) with internal lamellar structures, and continuously transforms into 1D nanobelts up to several micrometers in length after a few days period of incubation, as characterized by transmission electron microscopy (TEM) and dynamic light scattering (DLS). In contrast to polar solvent condition, the non-polar chloroform/methanol solution is much less favorable over the Keggin clusters, and the Keggin-BPOSS exhibits different self-assembly behavior by forming stacked lamellar structures. Surface property of clusters also shows important roles in determining the supramolecular nanostructures. Selected area electron diffraction (SEAD) reveals that the crystallinity of BPOSS is critical to drive the transformation from spheres to nanobelts. By replacing BPOSS clusters with CPOSS ones, the Keggin-CPOSS only forms spherical colloids in acetonitrile/water solution. Interestingly, 2D nanosheets with one bilayer thickness are observed when studying the Keggin-CPOSS in chloroform/methanol, where the interaction between Keggin POMs is dominant to drive the nanosheet formation. The contribution of POSS can be significantly enhanced by increasing the cluster number. Accordingly, 2D rhombic nanosheets with BPOSS dominant in the internal layers are formed in solution of Keggin-2BPOSS. In another study of Janus co-clusters (Fig. 3b), bare C_{60} and -COOH functionalized C_{60}

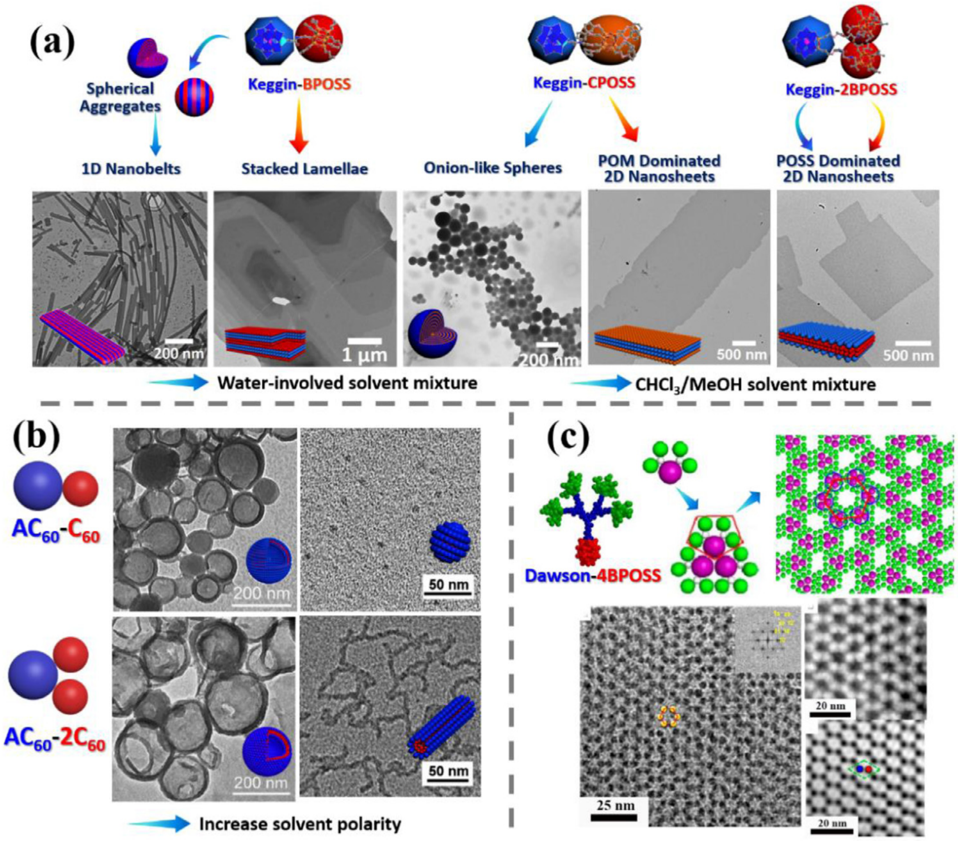

Fig. 3

(a) Structures of Keggin-POSS co-clusters and their diverse supramolecular nanostructures in solution. (b) Different self-assembled structures formed by AC$_{60}$-C$_{60}$ co-clusters. (c) Structure of Dawson-4BPOSS co-cluster and its formation of graphene-like superstructures. Adapted with permission from ref 44,48, and 54. Copyright 2014 Wiley-VCH; 2016 and 2018 American Chemical Society.

(AC$_{60}$) are used to synthesize AC$_{60}$-(C$_{60}$)$_n$ co-clusters (n=1, 2) [54]. As the deprotonation degree of carboxylic acids varies in different solvents, the size of hydrophilic parts (AC$_{60}$) can be tuned by simply adjusting the solvent polarity. On the other hand, the relative volume fraction betweenhydrophilic and hydrophobic domains changes when different number (n) of C$_{60}$ clusters are attached. These changes lead to morphological evolution of assemblies from micelles, to worm-like micelles, and vesicles.

Janus co-clusters with special geometry can be created by increasing the number of cluster (n), as demonstrated by Wang's group [48]. Fan-shaped Janus co-clusters are synthesized by linking one Dawson-type POM and four BPOSSes together (Dawson-4BPOSS in Fig. 3c). In THF/water solution, the Dawson-4BPOSS can slowly self-assemble into honeycomb structures with micrometers in size, as observed by TEM. A detailed TEM analysis reveals that the honeycombs possess well-ordered hexagonal pattern, that is, graphene-like nanostructures. Coarse-grained simulations suggest that three Janus co-clusters firstly form a triangular building block *via* the counterion-mediated attraction from charged Dawson (Fig. 3c). Driven by the entropic forces, these building blocks further self-organize into hexagonal honeycomb layers. During the growth of honeycomb layers, the van der Waals forces start to play a dominant role for the interlayer attraction, therefore, honeycombs with 1-3 layers coexist in solution. It is worth noting that the formation of hexagonal honeycomb is largely due to the fan-like shape of AB$_4$ type Janus co-clusters, which in turn originates from the rigid structures of both cluster heads and organic linkers. Recently, Janus co-clusters with very unbalanced heads, such as AB$_8$ type [55], are designed with sophisticated synthetic approach, providing an opportunity to explore the self-assembly behavior in highly asymmetric situation.

Effect of Organic Linkers

Besides the choice of cluster type and the number of cluster heads, organic linkers also show a very important role during the self-assembly of Janus co-clusters, likely due to the variation of interfacial areas between hydrophilic and hydrophobic domains. Wang's group explore a series of Dawson-BPOSS Janus co-clusters with different organic linkers in the middle. In a Dawson-BPOSS case with C$_4$ as the linker, filled-honeycomb-structured crystals are observed in acetonitrile/water solution (Fig. 4a) [43]. The results from TEM and simulation show that the BPOSS can pack closely to form bilayers with hexagonal cylinders. The cylinders continuously grow to outer layers and eventually honeycomb crystals are observed in solution. When the middle linker is replaced by phenyl group (Dawson-Ph-BPOSS in Fig. 4b), nanotubes with uniform diameter are

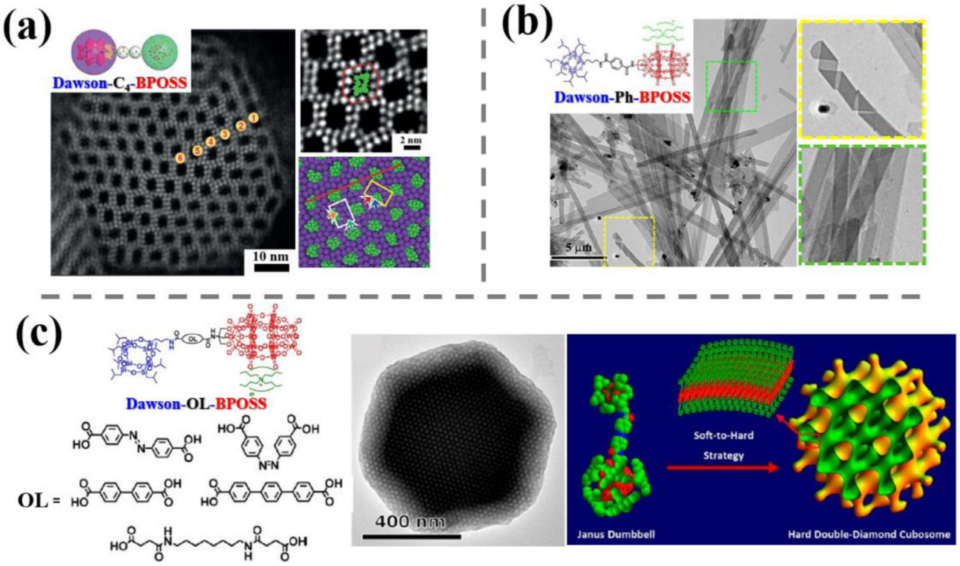

Fig. 4

(a) Structure of Dawson-C$_4$-BPOSS and its formation of filled-honeycombs. (b) Structure of Dawson-Ph-BPOSS and the nanotube formation from twisted helical ribbons. (c) Structure of Dawson-OL-BPOSS with various organic linkers, and the formation of cubosomes with internal double-diamond nanostructures. Adapted with permission from ref 43,49, and 56. Copyright 2015 and 2018 Wiley-VCH; 2019 American Chemical Society.

formed in acetone/n-hexane solution [56]. Zoomed-in TEM images clearly show that the self-assembled nanotubes are grown from twisted helical ribbons. In addition, several organic linkers (OL) are used to construct Dawson-OL-BPOSS (Fig. 4c), and cubosomes with internal double-diamond structures are achieved by slowly evaporating acetone in acetone/n-decane mixed solution [49]. TEM studies show that the formation of cubosomes involves multiple intermediate stages including vesicle formation, membrane fusion, inner-structure reorganization, and cubic-crystal growth. This study provides an alternative strategy to fabricate double-diamond nanostructures beyond the traditional block copolymers.

Cluster-organic Hybrids

In addition to the Janus co-clusters built by two or more inorganic blocks, organic molecules are commonly used as the building blocks for cluster-organic hybrid macromolecules. Many types of organic molecules (*e.g.*, flexible alkyl chains [57,58]) have been successfully attached to different clusters, as summarized in a number of reviews [23,27,28,59-62]. Here we focus on the organic molecules with rigid molecular structures, as shown in Fig. 2. Yam's group designed a series of hybrid macromolecules by combining POSS clusters and platinum complex [63,64], for example, the molecule composed of BPOSS and alkynylplatinum terpyridine complex in Fig. 5a [63]. By adjusting water contents in water/THF solution, the hybrids can self-assemble into various supramolecular nanostructures including nanofibrils, colloidal particles, nanorings, nanobelts, and ring-like aggregates. Interestingly, dramatic color change is observed during the morphological transformation among different superstructures, which is likely due to the intermolecular Pt-Pt interaction involved in self-assembly process. The terpyridine molecules have been used to connect with Dawson-type POMs, as explored by Izzet's group [35,36]. Taking advantages of strong metal coordination bond between terpyridine and metal cations, the Dawson-2tpy hybrids can form triangular-shaped discrete macrocycles with the presence of Fe^{2+} in DMSO (Fig. 5b), while mixtures of triangular- and square-shaped macrocycles are observed by using Co^{2+} (Fig. 5c). By changing DMSO to MeCN, these discrete macrocycles further self-organize into dense nanoparticles driven by the inter-macrocycle electrostatic interaction. Meanwhile, the orientation of macrocycles can be significantly changed by adjusting the valence of metal cations from Co^{II} to Co^{III}, leading to the formation of worm-like micelles in MeCN. Remarkably, the transition between discrete macrocycles and large supramolecular nanostructures is highly reversible with the switch of solvent type, demonstrating apromising strategy to fabricate controllable and reversible supramolecular structure formation in cluster-based materials.

Rod-like organic molecules have also been used as building blocks for hybrid macromolecules. Cheng's group connected spherical DC$_{60}$ (functionalized with -OH groups) and rod-like oligofluorenes (OFs) to create sphere-rod shaped hybrids with various rod lengths and rod orientations: DC$_{60}$-2TOF$_n$ and DC$_{60}$-2IOF$_n$ (Fig. 6a), where n represents the number of OF repeating units, and I- or T- means the overall molecular shape of hybrids [65]. In THF/water solution, DC$_{60}$-2IOF$_n$ shows morphological transformation from hollow vesicles to 2D nanosheets by increasing the rod length [66]. On the other hand, DC60-TOF$_n$ hybrids, which are topological isomers to DC60-IOF$_n$, show different self-assembly behavior by forming hollow vesicles or solid colloidal particles in solution. Combined analyses from TEM and small-angle X-ray scattering (SAXS) show ordered hexagonal columnar structures inside the colloids assembled by DC$_{60}$-TOF$_4$ and DC$_{60}$-TOF$_6$. In a similar molecular design reported by our group, sphere-rod hybrid macromolecules with Keggin-

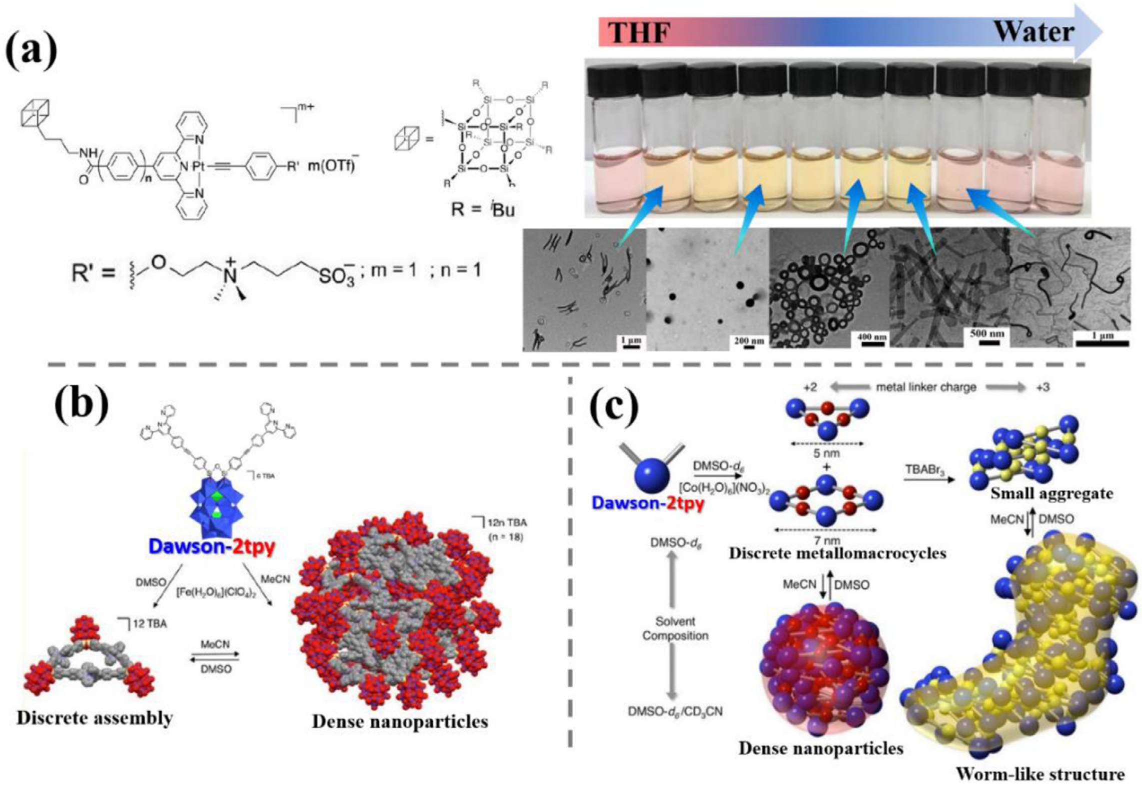

Fig. 5

(a) Molecular structure of hybrids composed of BPOSS and alkynylplatinum terpyridine complex, and diverse self-assembled structures in THF/water solution. The color of solution changes in response to different superstructures. Molecular structures of Dawson-2typ hybrids and their self-assembly processes with addition of Fe^{2+} (b) and Co^{2+}/Co^{3+} (c). Adapted with permission from ref 35,36, and 63. Copyright 2016 American Chemical Society; 2017 Royal Society of Chemistry; 2018 National Academy of Sciences.

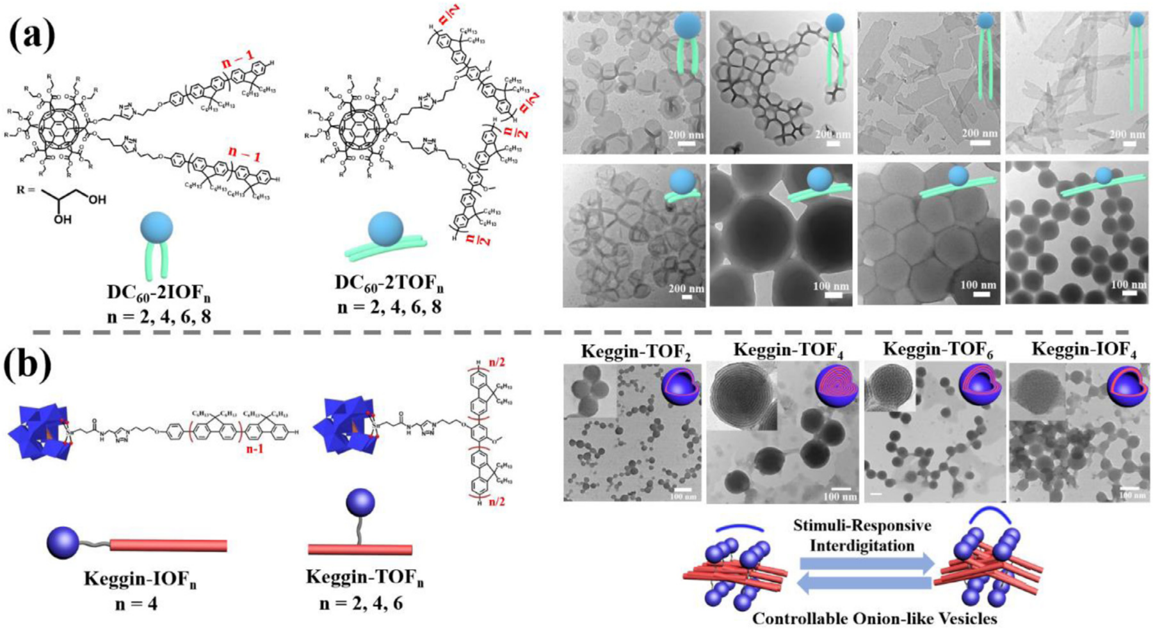

Fig. 6

(a) Molecular structures of sphere-rod hybrids constructed from DC_{60} clusters and OF rods, and their self-assembled nanostructures in THF/water solution. (b) Molecular structures of sphere-rod hybrids composed of Keggin-type clusters and OF rods, and their self-assembled nanostructures in acetonitrile/water solution. A scheme is used to demonstrate the change of rod interdigitation controlled by solvent stimuli. Adapted with permission from ref 66-67. Copyright 2020 Wiley-VCH; 2020 American Chemical Society.

type POMs as inorganic heads exhibited interesting solution behavior (Fig. 6b) [67]. In acetonitrile/water solution, all T-shaped hybrids (Keggin-TOF$_n$, n=2, 4, 6) can self-assemble into spherical superstructures. However, zoomed-in TEM images show that these spherical assemblies possess distinct internal nanostructures. That is, hollow vesicles, onion-like vesicles, and multilayered vesicles with a few outside layers are observed in Keggin-TOF$_2$, Keggin-TOF$_4$, and Keggin-TOF$_6$ solutions, respectively. Interestingly, the size and layer number in onion-like vesicles can be accurately controlled by multiple solution conditions including solvent polarity, ionic strength, hybrid concentration, and temperature, which comes from the significant rod interdigitation shown in Fig. 6b. Similar to DC$_{60}$-OF$_n$ system, the self-assembled structures also change dramatically by switching the rod orientation from Keggin-TOF$_4$ to Keggin-IOF$_4$. These sphere-rod hybrid macromolecules provide a nice comparison to other shaped hybrids such as sphere-sphere, sphere-coil, and sphere-chain.

Cluster-based Hybrid Copolymers for Versatile Superstructures

Combination of molecular clusters and polymers creates a new type of block copolymers [68-73]. The incorporation of rigid clusters brings semi-flexibility and architectural constraint to the overall copolymers. In solution, both clusters and polymer chains have shown their important effects on regulating the conformation of copolymers, consequently leading to different packings of clusters in the self-assembled nanostructures.

The POSS-PS linear copolymers present a good showcase to demonstrate the role of packing parameter [74], which is also used to regulate the self-assembled structures in other systems such as traditional block copolymers and small-molecule surfactants. The packing parameter (p) is determined based on the formula: $p = v_o/al_o$, where v_o is the volume of hydrophobic heads, l_o is the critical length of hydrophobic parts, and a is the contact area of hydrophilic heads. With the synthetic approach of step-by-step addition, the POSS clusters can be arranged into copolymers with different cluster numbers and topologies (Fig. 7a) [75], and even precise control in sequence (Fig. 7b) [76]. The different arrangements change the contact area between hydrophilic APOSS heads a (pink areas in Fig. 7) and the length of hydrophobic part l_o. Meanwhile, the size of hydrophilic APOSS heads (a) can also be affected by changing the deprotonation degree of carboxylic acids *via* solution condition, such as different hybrid concentrations in Fig. 7b. These changes lead to different values of packing parameter. Accordingly, the POSS-PS copolymers show diverse supramolecular nanostructures including spherical micelles, worm-like micelles, vesicles, and nanoribbons in solution (water/DMF). It is worth mentioning that the rich library of cluster type and their surface group could benefit the construction of cluster-based copolymers with multifunctional property in the future.

Star-shaped hybrid copolymers have been created by using molecular clusters as central cores or arms. Two triarmed hybrids (Fig. 8a) are synthesized by connecting three hydrophilic APOSS clusters with short organic linkers (Tri-APOSS) or PS linkers (Tri-PS-APOSS), and they show completely different behaviors in water/acetone solution [77]. The introduction of PS linkers can enhance the molecular flexibility of Tri-PS-APOSS, and meanwhile contribute strong hydrophobic interaction to bend the whole hybrid molecules. Accordingly, the PS linkers packed closely with each other, leading to the formation of vesicular structures. By contrast, Tri-APOSS hybrids with short linkers are fully hydrophilic and have only limited flexibility, due to the domination of charged APOSS clusters. As a result, they show similar behavior as other hydrophilic macroions, forming single-layered blackberry-type structures in solution. In another case of star-shaped hybrid copolymers (Fig. 8b), POSS clusters are used as the core for surface functionalization of polyethylene glycol (PEG), in order to improve hybrid solubility in water [78]. The disulfide bonds between POSS core and eight PEG arms can undergo ligand exchange with thiol groups in pH=12 solution. The thiol–disulfide exchange reaction further induces “polymerization” among the individual hybrid copolymers, and consequently trigger the self-assembly process. Interestingly, the exchange reaction can be terminated by simply adjusting the solution condition to pH=7. This feature provides an interesting living and programable self-assembly strategy to achieve different controllable supramolecular structures, like spherical micelles, cylinders, vesicles, worm-like micelles, hollow spheres, and elliptic nanoparticles in aqueous solution, as observed by both experiment and simulation.

In a recent report, zwitterionic hybrid copolymers containing PS chains, negatively charged C$_{60}$, and positively charged C$_{60}$ are designed (NC$_{60}$−AC$_{60}$−PS$_n$ in Fig. 9a), where n=62, 86, and 120 [79]. In water/THF solution (pH=5), well-ordered 2D nano-coins are observed by both TEM and AFM techniques (Fig. 9c-d). The 2D nano-coins are formed by microphase separation between hydrophilic C$_{60}$ clusters (both NC$_{60}$ and AC$_{60}$) and hydrophobic PS chains, as shown in Fig. 9b. During self-assembly process, the non-crystallized nature of hybrid copolymers favors the anisotropic growth of coin-shaped superstructures rather than other shapes such as triangle or square. Moreover, the diameter/thickness of nano-coins can be easily tuned by changing PS chain length. Due to pH-responsive property of zwitterionic groups, the interactions on the surface of nano-coins can be tailored *via* adjusting solution pH. Interestingly, the nano-coins start to stack together and form grana-like 3D superstructures in pH=7 solution (Fig. 9f), where the repulsions between the surface of nano-coins significantly decrease due to less positive charges on NC$_{60}$. The design of NC$_{60}$−AC$_{60}$−PS$_n$ provides a strategy to achieve nonconventional 2D nanostructures and their hierarchical self-assembly into higher ordered superstructures in solution.

Cluster-based Hybrid Complexation

Instead of covalent bonds, using non-covalent interactions has also shown as a promising approach to construct inorganic-organic hybrid macromolecules, as summarized in several reviews [21,39,80,81]. Here, we focus on some recent progress in fabricating novel low dimensional nanostructures by hybrid complexation. With the use of different non-covalent interactions (*e.g.,* electrostatic interaction, hydrogen bonding, and π-π stacking), clusters can strongly attract other molecules and spontaneously co-organize into superstructures. The specific

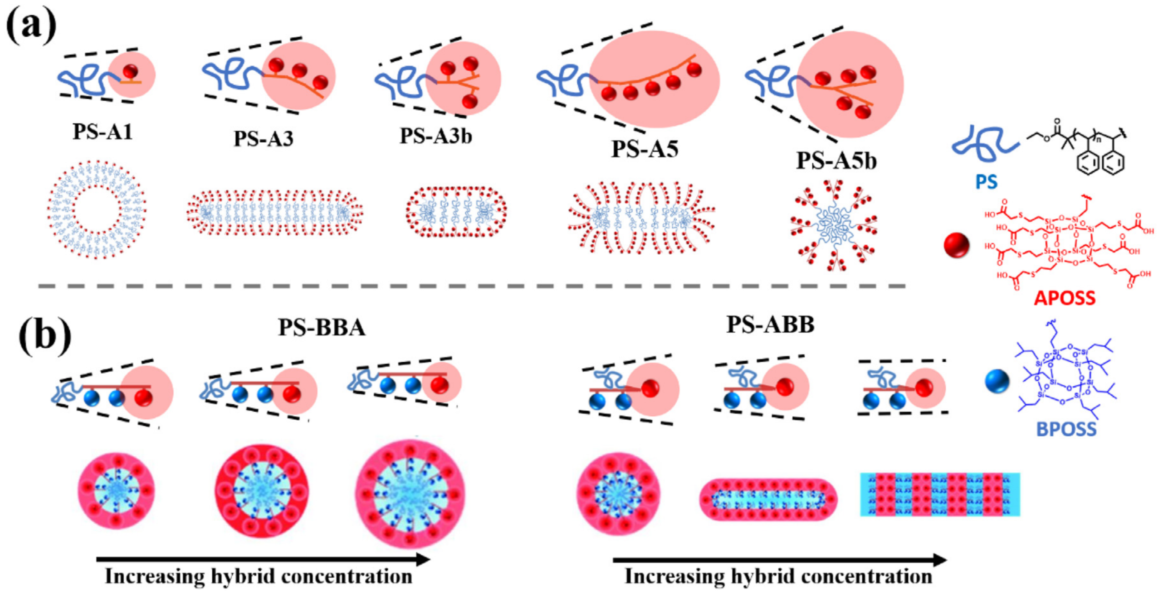

Fig. 7

POSS-PS hybrids with different cluster numbers, topologies (a), and sequences (b). These variables lead to morphological transformation in self-assembled nanostructures. Adapted with permission from ref 75-76. Copyright 2016 and 2019 Royal Society of Chemistry.

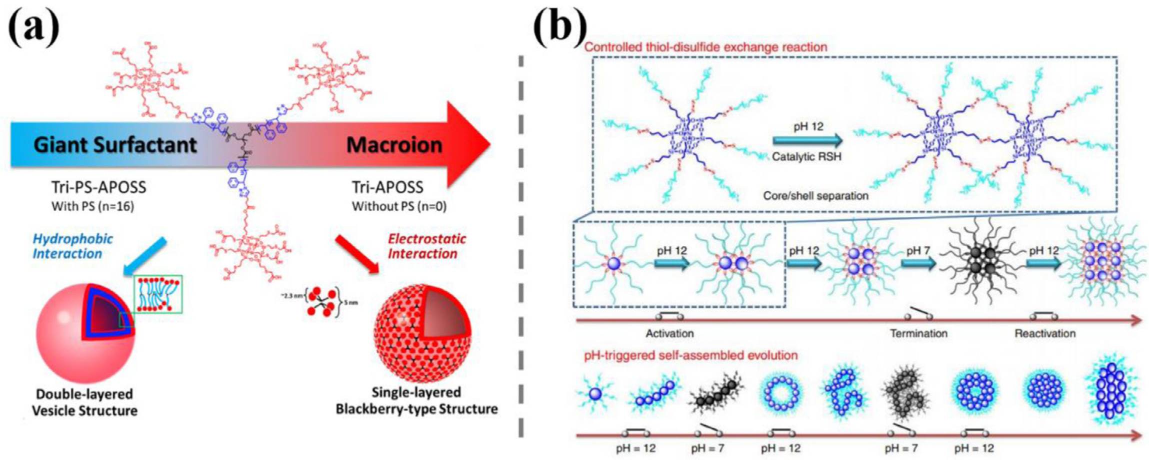

Fig. 8

(a) Structures of two triarmed hybrids with APOSS clusters, and their self-assembly behavior. Short organic linkers are used for Tri-APOSS, and PS linkers are used for Tri-PS-APOSS. (b) Star-shaped hybrid with POSS cluster and PEG chains. Induced by thiol-disulfide reaction, the hybrid shows programable self-assembly behavior with the switch of solution pH. Adapted with permission from ref 77-78. Copyright 2017 American Chemical Society; 2018 Springer Nature.

hydrogen bonding between Keggin-type POMs and neutral cyclodextrins (β- and γ-CDs) is first explored by Stoddart's group [82]. In a later study, Cadot's group report an interesting helicoidal tubular structure *via* the complexation of three components: Dawson-type POM, γ-CD, and Ta_6 cluster (Fig. 10a) [83]. The tubular chains are formed through multi-step recognition in water. Firstly, Ta_6 cluster enters the cavity of γ-CD through the host-guest interaction, and then anionic Dawson and cationic $[Ta_6@\gamma\text{-CD}]^{2+}$ undergo self-organization with the help of directional hydrogen bonding and electrostatic interaction, leading to periodic alternation building blocks in the tubular chains. Meanwhile, two-dimension nanostructures can be fabricated by taking advantages of strong electrostatic interaction between organic cations and anionic molecular clusters. An ammonium cation with oligoether chains is synthesized by Kimizuka's group, in order to interact with anionic Keggin-type POM (Fig. 10b) [84]. In aqueous solution, 2D nanosheets are formed with the molar ratio of cation:Keggin=1:1. The self-assembled nanosheets are micrometers in length but only 15-30 nm in thickness, showing as novel materials for photo-related applications such as photoetching. Recently, Wu's group deigns a hybrid complexation system to fabricate 2D nanosheet membranes, with only single-layered thickness (~1.5 nm, Fig. 10c) [85]. The membrane is achieved *via* a two-step self-assembly strategy. In the first process, an azobenzene cation forms host-gust complexes with α-CD. The corresponding complexes are

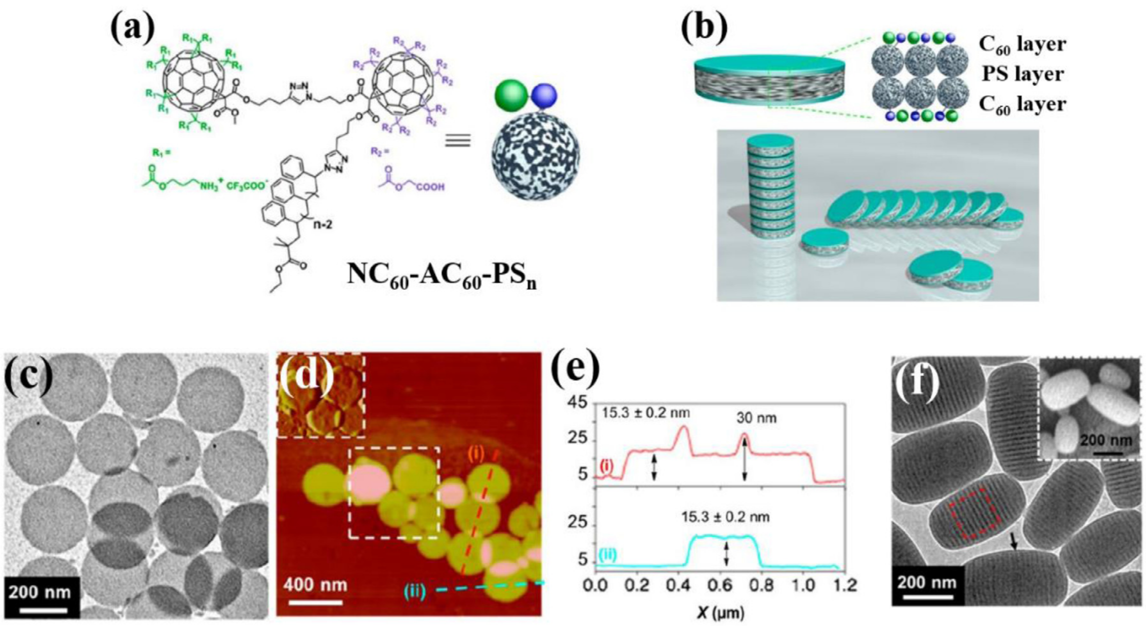

Fig. 9

(a) Molecular structure of NC$_{60}$-AC$_{60}$-PS$_n$. (b) Schematic illustration of 2D nano-coins and 3D grana-like superstructures. TEM (c), AFM (d), and line profile (e) of 2D nano-coins. (f) TEM images of 3D grana-like superstructures. Adapted with permission from ref 79. Copyright 2017 American Chemical Society.

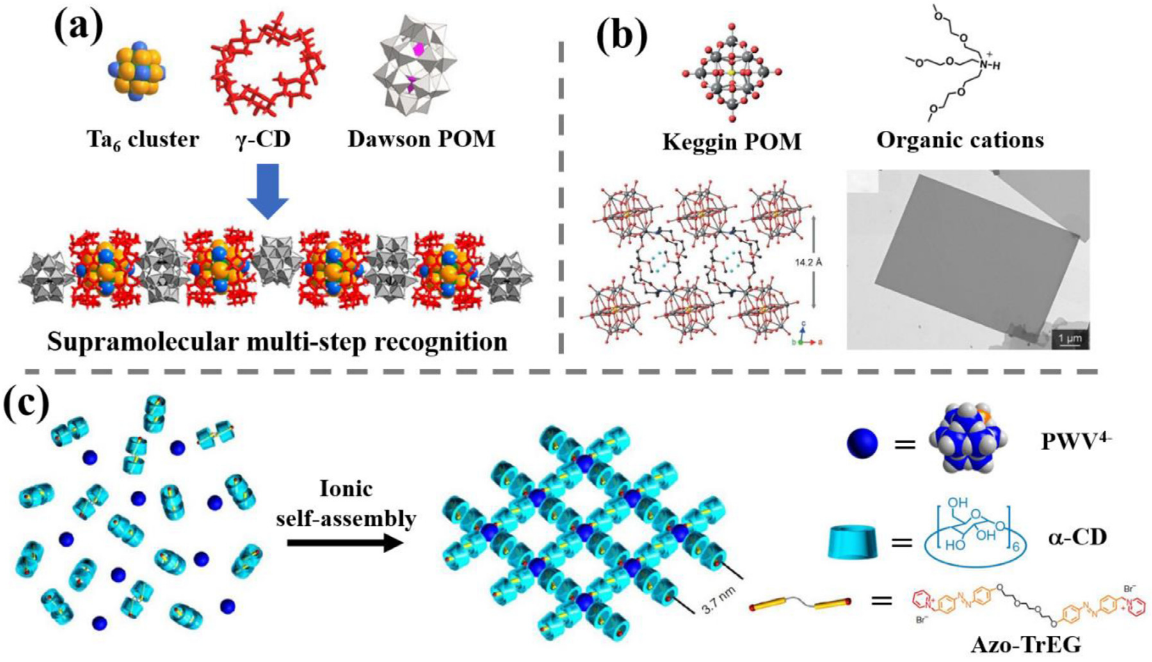

Fig. 10

(a) Structures of Ta$_6$ cluster, γ-CD, Dawson POM, and their co-assembly into 1D tubular chain. (b) Structures of Keggin POM, oligoether cation, and the 2D nanosheet formation *via* complexation. (c) 2D monolayered nanosheet achieved by the complexation of Keggin POM, α-CD, and azobenzene cation. Adapted with permission from ref 83-85. Copyright 2016 Springer Nature; 2017 American Chemical Society; 2017 Wiley-VCH.

further mixed with Keggin-type POMs (PWV^{4-} in Fig. 10c) at the molar ratio of [Azo-TrEG@CD]$^{2+}$: PWV^{4-}=2:1. The self-assembled 2D membranes have uniform mesh structures with edge length of 3.7 nm. Due to highly uniformed mesh size, the membranes show remarkable ability to separate two similar sized CdTe quantum dots (D=3.3 nm and 4.4 nm) with high separation efficiency.

The ability to manipulate hybrid complexation into multi-dimensional superstructures is highly desired. Wang's group explores the interactions between a series of Dawson-type

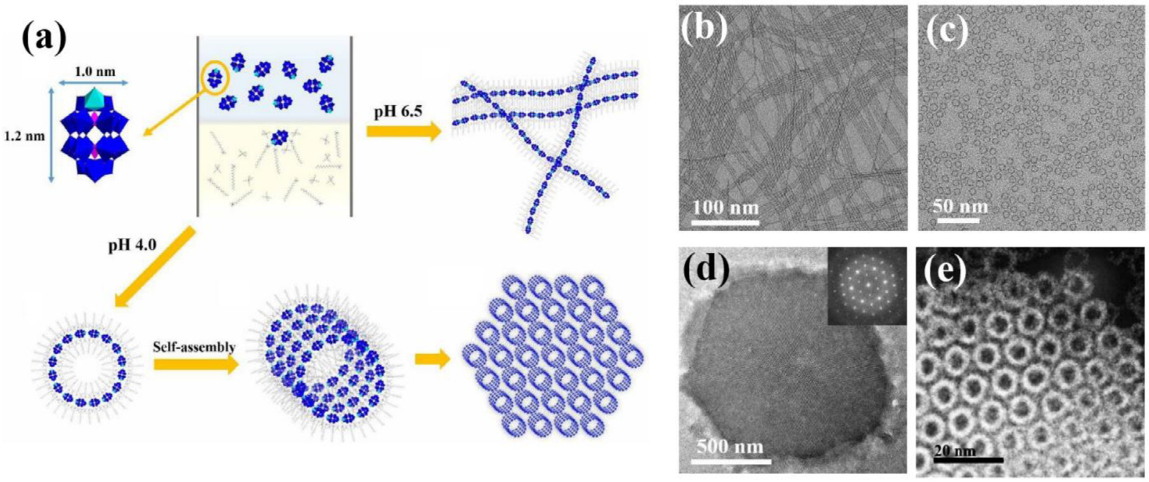

Fig. 11

(a) Schematic illustration of multi-dimensional superstructure formation *via* complexation. (b) TEM image of nanowires. (c) TEM image of nanorings. TEM image of 3D superstructures (d) and a zoomed-in TEM image (e). Adapted with permission from ref 86. Copyright 2019 American Association for the Advancement of Science.

POMs and cationic surfactants in solution (Fig. 11a) [86]. In neutral pH condition (pH=6.5), the mixing of Dawson POM ($P_2W_{17}Ln$) and surfactant leads to the formation of 1D ultrathin nanowires, with several hundred nanometers in length (Fig. 11b). By simply changing the solution pH to 4.0, the morphology of nanostructures transforms into 2D nanorings (Fig. 11c). Molecular simulation reveals that this transformation is attributed to different types of POM-POM configuration, which comes from the change in intermolecular interaction between single POM cluster. Interestingly, the nanorings can spontaneously self-organize into highly ordered 3D superstructures with uniform pores (Fig. 11d and 11e). Such multi-dimensional transformation has been observed in 15 different Dawson POMs, suggesting that this approach is general and might be extended to other cluster systems. Moreover, the self-assembled nanostructures show excellent activity in catalytic and electrochemical sensing, endowing them as promising advanced materials for a wide range of applications.

Summary and Outlooks

In this mini-review, we summarize some recent progress about cluster-based hybrid macromolecules and their supramolecular structure formation in solution. The hybrid macromolecules can be synthesized *via* both covalent and non-covalent approaches. In covalent approach, highly efficient reactions (*e.g.*, click reaction) are commonly used to connect molecular clusters and other molecules together. While non-covalent interactions such as π-π interaction, electrostatic interaction, and hydrogen bonding, are applied to construct cluster-based hybrid complexes. The well-defined hybrid macromolecules can generally be divided into two categories, Janus co-clusters and cluster-organic hybrids. In solution, they can form diverse self-assembled nanostructures controlled by their molecular structure of hybrids including size, shape, composition, topology, volume fraction, and surface functionality. On the other hand, solution conditions such as solvent polarity and extra added cations, also show significant effects on molecular interactions and their solution behavior. The copolymers composed of clusters and polymer chains exhibit semi-flexibility property in solution. The explorations in their overall molecular architecture, type of cluster heads, and polymer chains enhance our understanding of molecular arrangement and regulation in the supramolecular nanostructures. In addition to covalently linked macromolecules, the complexation driven by non-covalent interactions provides a strategy to achieve novel hybrid nanostructure in multiple dimensions.

Based on current knowledges in manipulating cluster-based hybrids into highly ordered and controllable supramolecular nanostructures, the future focus might be to explore the structure-property relationship of supramolecular nanostructures as functional materials. The rapid development of synthetic approach in other cluster systems, such as silver and gold clusters, could enrich the library of hybrid macromolecules and lead to attractive functional materials *via* self-assembly. The currently reported approaches mostly involve the incorporation of various functional groups to clusters or the arrangement of clusters, in order to achieve the goal of varying the intermolecular interactions and the consequence of supramolecular structures based on the competition of driving forces. It would be challenging but interesting, if functionalization approaches can be developed to modify the physical features of the cluster themselves (such as electron energy band gap), so that the application of such clusters can be further expanded. Currently, it is still beyond our capability to promote electron communications among assembled clusters and tune the electronic structures of their assemblies, which is a key to their applications for semi-conducting. Meanwhile, cost-effective and large-scale synthetic protocols for the functional materials of cluster assemblies are urgently needed for the extension of their practical applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.giant.2020.100013.

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