

Materials Science

From low-dimensional materials to complex superstructures: A review and outlook

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Abstract: Low-dimensional materials have attracted increasing attention due to their guiding significance for material preparation and potential wide-ranging applications. Through the controllable synthesis and suitably designed fusion of low-dimensional materials into ordered complex superstructures, it has become an effective way to explore new properties of materials and construct structures meeting new application needs. Based on low-dimensional materials such as metal oxides, copolymers, metal-organic complexes, and organic crystals, great efforts have been devoted to the design and construction of complex superstructures with regular repeatability. A series of unique cases including multi-block, core/multi-shell, hyper-branched and network structures have been reported, which has promoted the development of the field of material preparation. Herein, we summarize representative progress of low-dimensional complex superstructures in a reasonable structure classification manner. Ultimately, the existing challenges are discussed, and an outlook is given for future study of precise construction of superstructures as well as exploitation of potential applications.

Keywords: low-dimensional materials, complex superstructures, structural composite, designable fabrication, functional application

Introduction

Complex superstructures with high unit repeatability are widespread in nature or in human life as a means to achieve a range of their practical functions [1–4]. This phenomenon has attracted widespread attention in the field of materials science [5]. The preparation of such superstructures is believed to enable the exploration of new properties of materials to meet new application requirements. In the field of materials, micro- and nano-scale low-dimensional materials, including metal oxides/sulfides, metal complexes, polymers, and inorganic organic crystals, exhibit rich and diverse properties, which have become the focus of research in recent years. Low-dimensional materials typically have large specific surface area and unique particle confinement effects and are considered potential micro/nano sized electrical and optical transport media [6–8]. Taking low-dimensional materials as the basic unit, the fusion of structures through suitable strategies has become a feasible approach to prepare complex superstructures with ordered repeating structures for exploring new functions [9]. Efficient control of the fabrication process and precise construction of structures are crucial for

the study of superstructures. Therefore, a great deal of effort is devoted to the precise synthesis of basic building materials [10–12]. At the same time, effective construction strategies and synthetic methods have been continuously proposed to realize the controllable preparation of low-dimensional complex superstructures [13,14].

In the past two decades, a series of low-dimensional complex superstructures (LDCSs) with different configurations have been prepared and reported, including multi-block [15,16], core/multi-shell [17,18], hyperbranch [19,20] and network [21,22] structures. Through methods such as gas/liquid phase self-assembly and structural transformation, these complex superstructures are usually fused by multiple similar repeating basic units, including micro nanowires, micro nanosheets/discs, micro nanospheres, and micelles (Figure 1) [23]. Under the condition of retaining the properties of the basic unit materials, through the overall synergistic effect, LDCSs realize the exploration of new properties and functions of materials [24] and show a wide range of application prospects in the fields of catalysis [25,26], drug delivery [27,28], optics [29,30], and electricity [31,32]. Among them, the selection of basic unit materials, the design of composite structures, and the control of the fusion process are crucial [33,34]. However, there are still many challenges in designing and fabricating complex superstructures, and there is a lack of guiding sufficient experience. Therefore, it is necessary to systematically summarize and prospect low-dimensional complex superstructures, which will lead readers pay attention to this exciting field and guide researchers' development of the preparation and application of more complex superstructures in the future.

Herein, we conduct a generalization of recent progress in LDCSs from multiple aspects of material selection, preparation, and structural classification in this review. Firstly, we will describe the materials selection and preparation strategies of low-dimensional superstructures. Then, we classify and summarize various reported complex superstructures from the perspective of structure and introduce their preparation strategies and some applications. Finally, we will summarize the challenges facing the field of low-dimensional superstructures and give these challenges our outlook for the future development of this field.

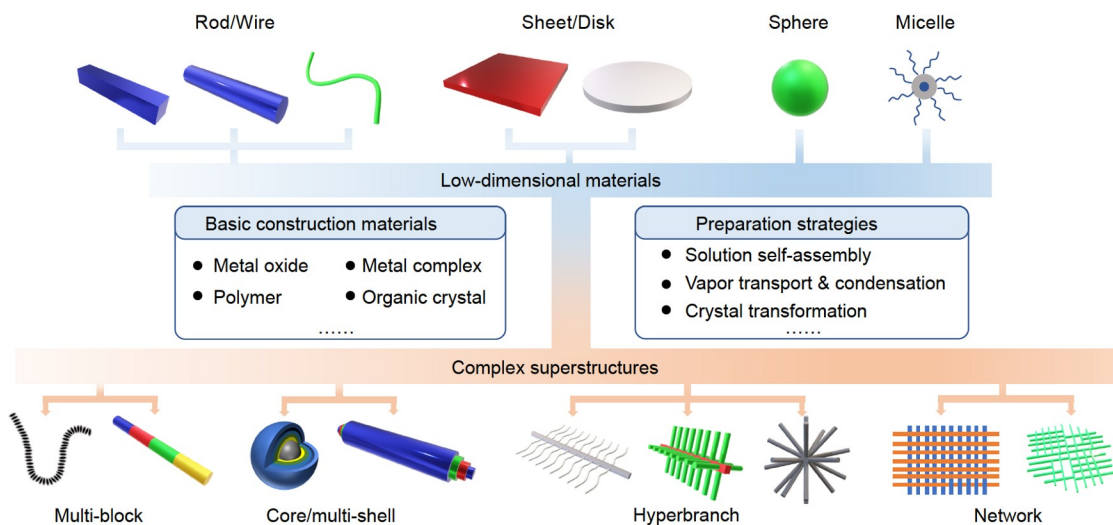


Figure 1 Organization of this review. Construction of complex superstructures through the composite of typical low-dimensional materials. Basic construction materials include metal oxides, metal complex, polymer and organic crystal. Preparation strategies include solution self-assembly, vapor transport & condensation and crystal transformation. The superstructures reviewed in this paper are divided into multiblock, core/multi-shell, hyper branched, and network structures.

Basic materials for constructing superstructures

In the past 20 years, due to their unique properties in electrical [35–37], optical [38–42], magnetic [43,44] and other fields, and their significance to the field of basic materials, many low-dimensional materials have attracted extensive attention of materials researchers, and especially, have been widely invested in the preparation of LDCSs [45,46]. Inorganic compounds such as zinc oxide and lead sulfide, as important semiconductor materials, have always been widely concerned by researchers. These inorganic semi-conducting nanomaterials, such as nanotubes, nanowires, nanorods, and nanoribbons [47–50], also play a role in related fields such as optoelectronics, arousing widespread interest among researchers [51–54]. For a long time, researchers have been committed to guiding nano-low-dimensional inorganic compound materials to form ordered and complex superstructures, and constantly exploring their new properties and application prospects. Notable studies include ZnO nanobridges [55], nano propeller arrays [56], PbS hyperbranched nanowire networks [57], etc. [58–64]. Besides, silicon-based low-dimensional self-assembly materials, such as silicide nanowires, have both metal-like electronic transmission properties, high physical chemical stability, and good mechanical properties, showing broad application prospects in the fields of nano electrical interconnection, integrated devices, etc. [65,66]. These low-dimensional materials of inorganic compounds have successfully achieved ordered multilevel recombination through self-assembly growth that does not require templates and become available basic components for the preparation of complex superstructures. Correspondingly, in this field, researchers in the field of organic materials have also invested a lot of efforts. Small organic molecules are often molecularly tailorable and structurally designable, exhibiting a rich variety of optoelectronic properties [67–71]. Micro-nano crystals self-assembled by small organic molecules have the advantages of regular structure and few defects, and are widely recognized optical transmission medium materials [72–75]. A series of reported work are devoted to the construction of complex superstructures by the directed growth of organic crystal constructions [76]. Under the guidance of the lattice matching mechanism, through rational design, a series of multi-level complex structures, including branches, blocks, and core-shells, have been constructed, showing the broad prospects of organic crystals in the field of complex structure research. In addition, metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) have uniform and abundant microporous structures with large specific surface areas, which are useful in many practical functional fields such as gas adsorption and desorption carriers, catalytic reaction micro-cavities, and drug delivery media [77,78]. Similarly, when synthesizing superstructures, their shape, size, and pore structure can be tailored with reasonable design and controllability to achieve the desired structure and function. Coincidentally, the size and morphology of polymer micelles can be designed through monomer polymer selection, chain composition structure design, and control of solution conditions (e.g., solvent mixtures, acid-base environment, reactant concentration, and ambient temperature). Therefore, it has relatively high designability and selectivity in the preparation of superstructures based on polymer micelles [79,80].

Strategies for preparing superstructures

With the continuous in-depth exploration and practice of researchers, the simple self-assembly process has

become an increasingly mature method for preparing low-dimensional materials at the micro- and nano-scale [81,82]. According to the physical and chemical properties of different materials, the specific preparation methods and processes are different, for example, the preparation of low-dimensional structures of a series of metal oxides and metal sulfides via a self-assembly process by high temperature steam condensation [83,84]. MOF/COF materials are usually grown through self-assembly via hydrothermal or solvothermal reactions. The high-temperature gas-phase method or solvothermal method are suitable for the preparation of nanostructures of metal compounds, which can produce a large quantity of structures with good crystallinity and high purity but is usually only suitable for the preparation of high-temperature resistant materials [85–87]. In contrast, organic materials generally use liquid-phase self-assembly at room temperature to achieve structure growth and construction. The room temperature solution method is usually simple to operate, low in cost, and does not require conditions such as high temperature and pressure. In addition, the reaction process of solution method is easy to control, which provides great convenience for the design of superstructure [88,89]. However, the solution method is also limited by the solubility of the material [90].

Generally, these self-assembly processes are accomplished spontaneously through interactions between molecules or atoms. By changing the conditions and environment of self-assembly, such as time, temperature, concentration, and ratio, the control of the self-assembly process and the further rational design of the composition of complex superstructures are the focus of the reported work for the preparation strategy. With the increase of components, the interactions within the system become more and more complex, and the problem of phase separation is easy to occur through a simple one-step self-assembly process, which makes it difficult to be competent for the preparation of multi-component complex superstructure. The multi-step self-assembly method has been developed to control the self-assembly sequence between different components more reasonably, so as to realize the controllable preparation of multi-component superstructure [91,92].

Above all, most of the methods can be accomplished only by the hierarchical directed self-assembly of different components without the existence of templates. However, for some more complex structures, such as hyperbranched network structures, the crystal transformation process using sacrificial templates appears to be more effective [93–97]. In addition, some substances do not exist in the final complex structure but promote the fusion and formation of complex structures by affecting the interaction between substances. The introduction of such catalyst-like substances also provides ideas for the design of feasible strategies for preparing complex superstructures.

Characterization methods and techniques

As the basic characterization equipment, high magnification microscopes can be used for the quick preliminary characterization of the micron scale structure and observation of the overall morphology of the superstructure. Furthermore, fluorescence microscopy (FM) is more suitable for characterizing some luminescent materials or structures [98,99]. It is difficult for ordinary optical microscope to characterize the specific structural details of superstructures, especially for smaller superstructure. For nanoscale structures and structural details of superstructure, scanning electron microscope (SEM) or transmission electron microscope (TEM) and other microscope equipment with higher resolution and magnification are required. SEM and TEM can stereoscopically observe and characterize the structural details of superstructure, such as

interface and surface, at a large magnification. Selected area electron diffraction (SAED) analysis can efficiently characterize and analyze the crystal structure of superstructure, such as crystal plane spacing and crystal orientation [100–104]. However, due to the principle of electronic imaging, electron microscopy is difficult to distinguish components with similar conductivity, and other characterization methods are needed to assist. Energy dispersive spectroscopy (EDS) is used to conduct element analysis on each component or part of the superstructure to better characterize it [105,106]. In addition, atomic force microscope (AFM) is usually used to characterize the thickness and flatness of superstructure. High resolution atomic force microscope (HRAFM) can be used to characterize and analyze the molecular arrangement structure of nanomaterials [107–109]. Similarly, X-ray diffraction (XRD) analysis is often used to characterize the crystal structure of superstructure [110,111]. Spectral tests include ultraviolet-visible-near infrared spectroscopy, infrared spectroscopy, Raman spectroscopy and most of the transient spectral tests can be used to characterize the luminous characteristics of superstructure, molecular structure, excited state properties, and other parameters [112–114]. Besides, with the rapid development of computer technology and artificial intelligence technology, simulation, deep learning, visualization, and other technologies have been gradually applied to molecular design, material structure simulation, self-assembly process analysis and other aspects [115–117]. In general, for the characterization of complex superstructure, it usually requires multiple characterization methods to cooperate at the same time to achieve the best analysis results [118].

Classification of low-dimensional complex superstructures

Multiblock superstructures

One-dimensional multiblock complex superstructures integrate multiple identical or different base structures in the same axis. These basic structures often have fundamental unique properties such as length-dependent optical, electrical properties. When integrated into a multi-block structure, the synergistic effect of the multiblock as a whole endows the structure with new properties. Because of this, researchers have put a lot of efforts into exploring this exciting field. Under this circumstance, numerous multiblock structures with different properties have been controllably prepared and reported, especially the proposal of targeted strategies and the exploration of advanced applications including optics and other fields.

Cui *et al.* [119] particularly produced the complex one-dimensional multiblock superstructures by taking advantage of the difficulty in achieving global equilibrium of the amphiphilic charged block copolymers in the system. This strategy relies on the combined action of divalent organic counterions and mixed solutions to drive the aggregation and dispersion of block copolymers to form complex one-dimensional multiblock structures in a specific way. The specific assembly route to prepare the multiblock copolymer structure is as shown in Figure 2A. By adjusting the composition of mixed solvents to achieve the kinetic manipulation of charged, amphiphilic block copolymers (Figure 2B), the formed morphology can be changed without changing the chemical properties of block copolymers (Figures 2C and 2D). The selectivity of water for the PAA moiety allows control of the interfacial curvature between the hydrophilic crown and the hydrophobic core in the spherical micelle, thereby controlling the local shape of micelles. Therefore, it is able to generate different nanoscale structures with simple block copolymer chemistry (Figure 2E). Based on a similar strategy raised by Wan *et al.* [120], the synthesis of multiblock copolymer superstructures made of Pd^{II} and

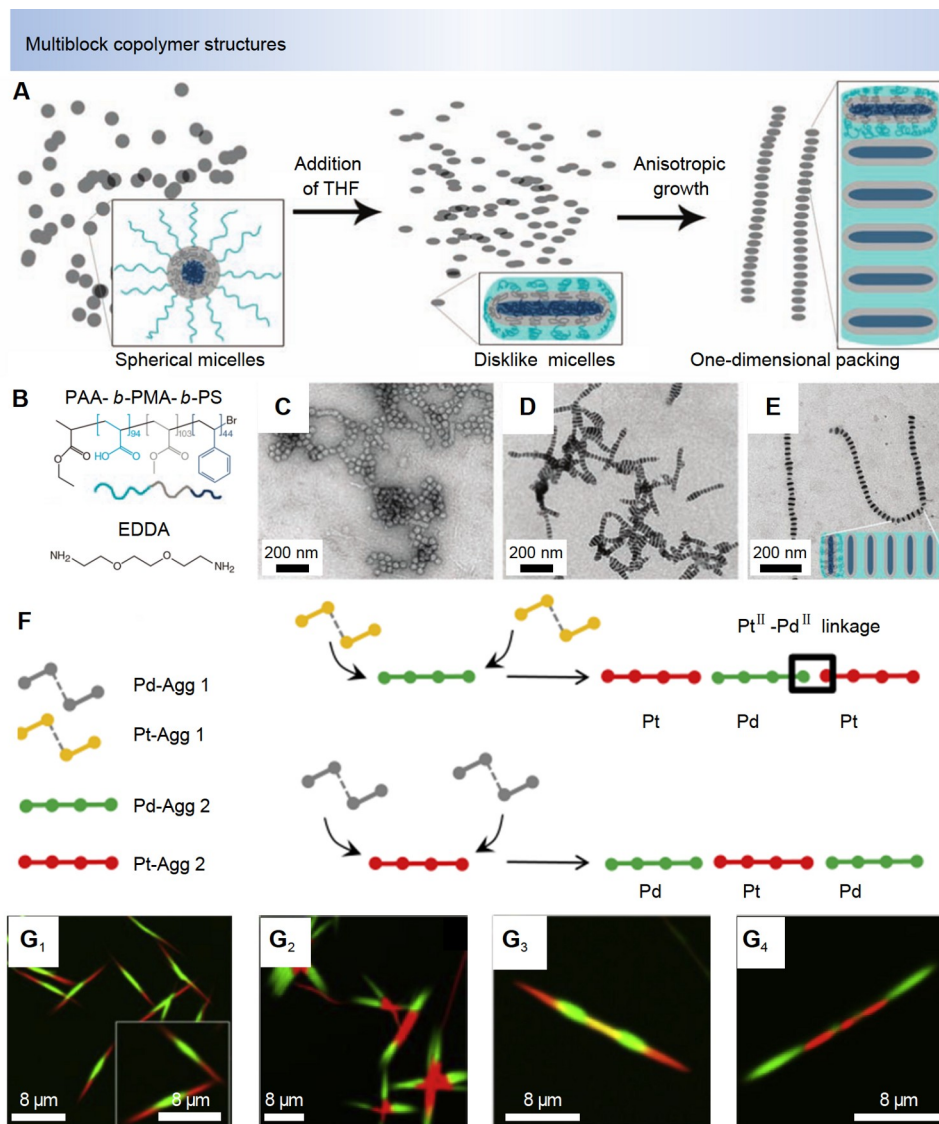


Figure 2 (A) Growth mechanism of multiblock copolymer. The addition of tetrahydrofuran (THF) first triggered the sphere-disk transition. The anisotropic shape enables disklike micelles to form multi-block chain copolymer structures through one-dimensional preferential growth. (B) Molecular structures of PAA-*b*-PMA-*b*-PS and organic diamine (EDDA). (C) In the presence of EDDA, PAA₉₄-*b*-PMA₁₀₃-*b*-PS₄₄ formed into spherical micelles at the 1:4 ratio of THF to water (molar ratio of amine groups:acid groups = 1:1). Scale bar: 200 nm. (D) TEM image of spherical micelles aggregated one-dimensionally immediately after continued addition of THF to the original solution to achieve a final THF to water ratio of 2:1. Scale bar: 200 nm. (E) TEM image of the one-dimensionally assembled PAA₉₄-*b*-PMA₁₀₃-*b*-PS₄₄ multiblock structure in 67% THF/water solution. The sample shown here was stained with an aqueous solution of uranyl acetate. Scale bar: 200 nm. Inset: schematic drawing of cross section of one-dimensionally assembled structures (Reproduced from Ref. [119]. Copyright©2007, The American Association for the Advancement of Science). (F) Schematic illustration of the prepared Pt^{II} and Pd^{II} multiblock copolymers through a living supra-molecular polymerization method. (G₁) Confocal image of sample A, triblock red-green-red copolymers. Scale bar: 8 μm. (G₂) Confocal images of sample B, triblock green-red-green copolymers. Scale bar: 8 μm. (G₃) Confocal images of sample C, pentablock copolymers. Scale bar: 5 μm. (G₄) Confocal images of sample D, multiblock copolymers. Scale bar: 5 μm (Reproduced from Ref. [120]. Copyright©2020, Elsevier Inc.).

Pt^{II} organometallic complexes was achieved (Figure 2F). By controlling the sequence and size of supra-molecular Pd and Pt multiblock copolymers, multiblock structures with different luminescent sequences were obtained (Figures 2G₁–2G₄).

In the field of organic materials, work on multiblock complex superstructures is more abundant. Due to the

easy processability and unique optoelectronic properties of organic materials, the multi-block structural platform enables them to exert more advanced applications and functions. Yao *et al.* [121] fabricated a one-dimensional Ln-MOF multi-block heterostructure with photonic encoding applications by a stepwise epitaxial growth strategy. These Ln-MOFs, composed of different lanthanide ions and organic linker 1,3,5-benzenetricarboxylic acid (BTC), exhibit distinct lanthanide center luminescence and similar crystal structures. On this basis, through a simple stepwise solvothermal synthesis, one-dimensional multicolor Ln-MOF heterostructures are able to be fabricated. As shown in Figure 3A, in a typical fabrication experiment, a Tb-MOF structure with a green emission color was first fabricated by a liquid-phase self-assembly method, which could be used as a seed for the second-stage MOF epitaxial growth. Subsequently, the Eu^{3+} ion solution was added to the solution system in which the prepared Tb-MOF crystallites existed. After 2 h of epitaxial self-assembly process, the composite Ln-MOF one-dimensional structure was finally obtained. The hierarchically assembled Ln-MOF microstructures exhibited red-green-red triblock heterostructures under ultraviolet (UV) lamp irradiation, which indicated the successful secondary epitaxial growth of new MOF blocks on prefabricated block, as expected (Figure 3B₁). These Ln-MOFs have an isostructural structure with high crystallinity, which is favorable for the epitaxial growth of different MOF blocks. Therefore, by changing the order in which Ln ion precursors are added in the reaction and controlling the ratio of different ions in the host framework, the luminescence of different blocks can be adjusted, resulting in triblock structures with different color sequences (Figure 3B₂). By doping Eu^{3+} ions in the Tb-BTC host and adjusting the doping ratio, a hybrid Ln-MOF with efficient orange emission can be fabricated, resulting in a triblock red-orange-red heterostructure (Figure 3B₃). Multiblock Ln-MOF heterostructures with identifiable features provide the opportunity to encode each microstructure. The fingerprint of each segment's microstructure is assigned based on the wavelength positions of distinct peaks in the PL spectrum. A typical barcode contains a series of black bars of varying widths that represent specific digital information. For bulk heterostructures, the solid line of each fragment corresponds to the wavelength position of each peak in its PL spectrum, resulting in a specific barcode pattern for each fragment. In this way, different block heterostructures can be easily converted into different barcodes with corresponding patterns. In addition, by adjusting the concentration of epitaxial precursor solution and controlling the molar ratio of epitaxial precursor to seed after growing seeds of roughly equal length, the block lengths of different blocks can be precisely controlled, endowing the heterostructure with length encoding features, which provides a platform for developing complete graphics coding. More importantly, thanks to the flexible step-by-step self-assembly process, more complex multiblock heterojunctions can be fabricated. In the reaction system, the Tb^{3+} ion precursor was again added to the existing triblock Tb@Eu-MOFs heterostructure (Figure 3C), resulting in alternating red-green multiblock heterostructures (Figure 3D). The preparation of complex heterostructures with more fragments will further enhance the coding ability (Figure 3E).

Sun *et al.* [122] prepared multicolor block heterostructures by doping, and realized more complex Ir/Ru acceptor host-guest multiblock heterostructures by finely controlling the process of co-assembly and epitaxial growth. First, Ir donors are nucleated from a mixed solution ($\text{CH}_3\text{CN}/n\text{PrOH}$, 1:50) and grown into green-emitting microrods (Figure 3H, Stage 1). Subsequently, a few amount of Ru acceptor was added into the suspension containing the Ir donor microrods. Afterwards, the two components co-assembled along the axis of the microrod to form a triblock structure with two tips emitting red (Figure 3I, Stage 2). During the final stage, still exist Ir donor in solution is further epitaxially grown on the two tips of the asformed triblock

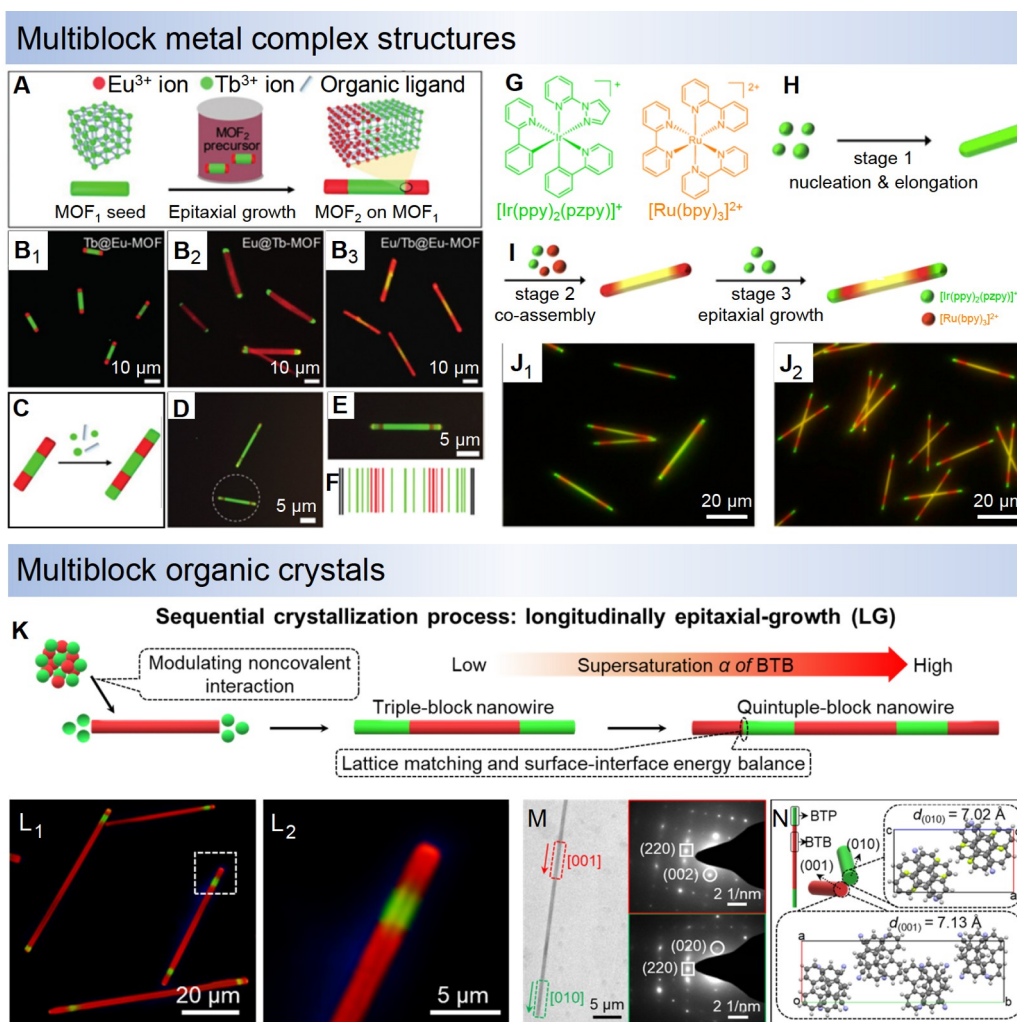


Figure 3 (A) Schematic illustration of the multiblock MOF structure fabricated by the epitaxial growth process of BTC and different Ln ions. (B₁)–(B₃) PM images of the Ln-BTC triblock heterostructures under UV irradiation. Scale bars are 10 μm . (C) Schematic illustration of penta-block superstructures fabricated by further epitaxial growth. (D) PL image of the 1D penta-block superstructures. Scale bar is 5 μm . (E), (F) The magnified PM image and corresponding barcode of the penta-block superstructures. Scale bar is 5 μm (Reproduced from Ref. [121]. Copyright©2019, Wiley - VCH Verlag GmbH & Co. KGaA, Weinheim). (G) Chemical structures of the Ir donor $[\text{Ir}(\text{ppy})_2(\text{pzpy})]^+$ and the Ru acceptor $[\text{Ru}(\text{bpy})_3]^{2+}$ (counteranions are PF_6^-). (H)–(I) Schematic representation of the three-stage growth process for preparing Ir(III) and Ru(II) multiblock nanorods. (J₁)–(J₂) Fluorescence microscopy images of multiblock nanorods doped with (J₁) 0.5%, (J₂) 1%, Ru acceptor under UV irradiation. Scale bar is 20 μm (Reproduced from Ref. [122]. Copyright©2018, American Chemical Society). (K) Longitudinal epitaxial growth strategy for the preparation of organic multi-block microwires through a continuous self-assembly process. (L₁), (L₂) FM images of organic quintuple-block microwires prepared with the acceptor molecular content η_{TTP} of 6%. The scale bars of (L₁) and (L₂) are 20 and 5 μm , respectively. (M) TEM image of one typical organic triple-block microwire. Scale bar is 5 μm . The upper right and lower right insets are SAED patterns collected from the central part (marked by red grid lines) and end parts (marked by green grid lines) of triblock microwires, respectively. (N) Molecular arrangement and orientation of BTP and BTB crystals at the junction of multiblock structure (Reproduced from Ref. [123]. Copyright©2021, The Author(s)).

rods to obtain the pentablock microrod superstructure (Figure 3I, Stage 3). By adjusting the amount of incorporated Ru acceptor, the luminescence of the triblock structure in the middle can be tuned (Figures 3J₁ and J₂). In addition to the construction of materials in the form of host and guest, micro-nano crystals composed of small organic molecules are also widely used in the preparation of hierarchical block structures. Zhuo *et al.* [123] achieved horizontal epitaxial growth of organic crystals through a step-by-step crystal-

lization strategy to fabricate one-dimensional multiblock heterostructures. As shown in Figure 3K, they first performed crystalline growth of BTB blocks, followed by horizontal epitaxial growth of BTP blocks on both ends of the existing BTB blocks, forming a triblock heterostructure. Due to the high concentration of BTB components in the system, after the triblock structure is formed, the excess BTB components will continue to undergo epitaxial growth again at both ends of the triblock structure, and finally a complex pentablock superstructure is obtained. The pentablock superstructure exhibits length-discriminated dichromatic emission properties as can be seen from the fluorescence microscopy picture of Figure 3L₁ and the locally enlarged PL picture of Figure 3L₂. The BTB and BTP blocks correspond to the red and green moieties, respectively. The same growth tendency and good lattice matching between the BTB and BTP blocks are the keys to their ability to perform compound epitaxial growth in the system (Figures 3M and 3N). Similarly, in the work of He *et al.* [124] and Zhang *et al.* [125], a series of other multicolor block superstructures with different luminescence properties were also prepared and reported. Benefiting from the good optical properties of organic crystalline materials, length-discriminated multicolor multiblock superstructures show potential applications in the fields of optical logic gates and photonic coding.

Core/multi-shell superstructures

The core/multi-shell structure can be considered as an extension of the multi-block structure on the three-dimensional scale. The multi-shell structure has a larger specific surface area and a hollow shell space, which shows application potential in catalysis and other fields. MOFs themselves have orderly and tunable porous structure with large specific surface areas, and are expected to be applied in various fields including gas adsorption [126], separation [127], catalysis, [128,129] and drug delivery [130]. Therefore, the development of multicore-shell superstructures based on MOF materials becomes a logical option. Liu *et al.* [131] demonstrated a reasonable method to prepare a hollow multi-shell single-crystal superstructure through stepwise crystal growth and following etching processes. Scheme in Figure 4A illustrates the processes of forming the MSHMs structures. Firstly, uneven octahedral MIL-101 crystals were obtained by a hydrothermal reaction using 1,4-benzene dicarboxylic acid (H₂BDC) as the organic linker and chromium ions as metallic node (Figure 4B₁). When the obtained product was under the treatment with aqueous acetic acid at 180°C for 4 h, the internal less stable (ls) part of the crystal were firstly etched, resulting in cavities formed inside the MOF crystals (Figure 4A, Graphic 2). It can be seen that each crystal structure has a spherical cavity and a more-stable (ms) outer shell (Figure 4B₃). Subsequently, when these as-prepared “LS@MS” hollow MIL-101 particles were used as templates to combine with added chromium ions and H₂BDC aqueous solution for 4 h, an additional layer of MIL-101 continued epitaxial growth (Figure 4A, Graphic 3). The result was as wished, the further grown MOF layer by epitaxial growth also has a “LS@MS” hierarchical structure. After further immersion of these newly obtained particles in aqueous acetic acid for 4 h (Figure 4A, Graphic 4), double-shelled hollow MOFs (DSHMs) were obtained (Figure 4B₅). Following such steps to perform multiple epitaxial growth and etching processes, a multi-shelled hollow MOF superstructure can be obtained (Figure 4B₇). Each shell in the same MSHM sample has a similar thickness, around 50 nm. High-resolution transmission electron microscopy (HRTEM) images and corresponding fast Fourier transform (FFT) patterns confirmed that the multiple shell layers of MSHM all have the same crystal orientation (Figures 4B₂, B₄, B₆, B₈, and the insets). The cavities between these porous shell structures can function as

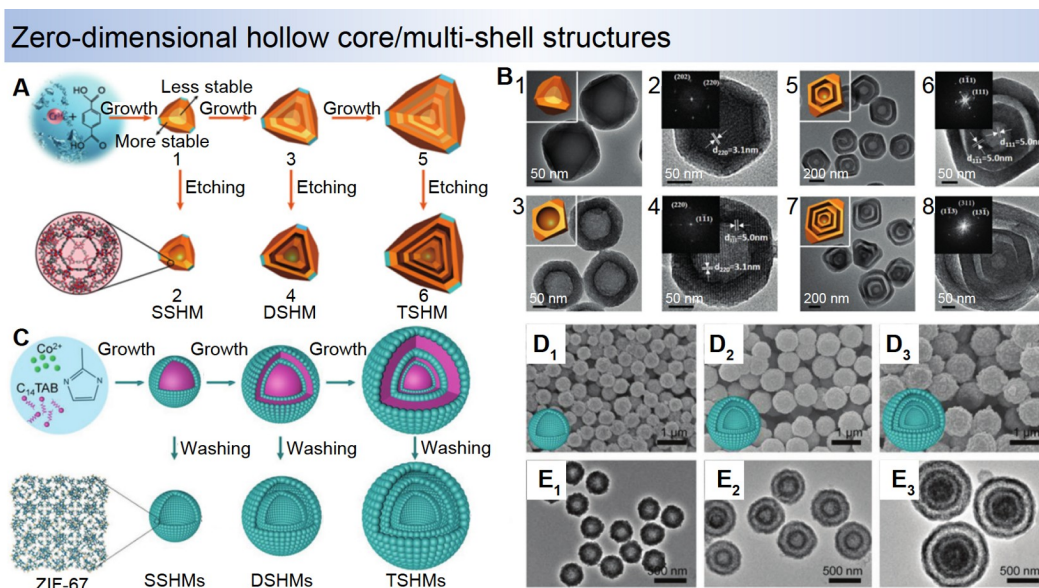


Figure 4 (A) Schematic illustration of the fabrication of single-shell (SSHM), double-shell (DSHM), and triple-shell (TSHM) hollow MIL-101 superstructures by layer-by-layer self-assembly growth and etching processes. (B₁)–(B₈) TEM ((B₁), (B₃), (B₅), (B₇)) and HRTEM ((B₂), (B₄), (B₆), (B₈)) images of solid MIL-101 ((B₁), (B₂)), SSHM ((B₃), (B₄)), DSHM ((B₅), (B₆)), and TSHM ((B₇), (B₈)). Scale bars: (B₁)–(B₄), (B₆), (B₈), 50 nm; (B₅), (B₇), 200 nm. Insets of (B₂), (B₄), (B₆), (B₈): the corresponding FFT patterns (Reproduced from Ref. [131]. Copyright©2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim). (C) Schematic illustration of the synthesis of single-shelled (SSHMs), double-shelled (DSHMs), and triple-shelled (TSHMs) hollow MOFs through shell-by-shell soft-templating method, respectively. (D₁)–(D₃) SEM images of SSHMs (D₁), DSHMs (D₂), and TSHMs (D₃). (E₁)–(E₃) TEM images of SSHMs (E₁), DSHMs (E₂), and TSHMs (E₃) (Reproduced from Ref. [134]. Copyright©2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

nanoreactors for catalytic reactions or containers for drug storage [132,133]. The experimental results demonstrate that the hollow-structured MIL-101 can maintain much higher catalytic activity compared with the solid MIL-101 crystal, and the catalytic activity increases with the number of layers in the MSHM. A similar structure was also realized in the work of Sun *et al.* [134]. They reported a highly uniform multi-shelled hollow cobalt (II)-imidazolate-based MOF (ZIF-67) superstructure prepared by rational shell-by-shell soft-templating strategy (Figure 4C). After the same growth and etching process, the transformation from single-shell structures to double-shell and multi-shell structures are also obtained (Figure 4D). As can be seen from the TEM images, these spherical multi-shell superstructures also possess uniform hollow regions that can be used as catalytic mediators and drug delivery (Figure 4E). These studies not only proposed a simple and efficient stepwise crystal growth-subsequent etching method to fabricate hollow multi-shell superstructures with superior properties compared with the solid nanomaterials, but also may provide new opportunities for the preparation of various complex advanced superstructures with multi-functional applications based on multi-shell hollow MOF-structured meta structural materials.

The advantages of the core/multi-shell structure are not only manifested in the hollow space brought by the multi-shell layers, the synergistic effect between the multi-shell layers can also endow the multi-core-shell structure with unique properties and functions. Zhuo *et al.* [135] reported a strategy to fabricate multi-shelled organic crystal microrod superstructures via a simple horizontal epitaxy growth strategy. Based on the regulation of non-covalent interactions between organic semiconductor molecules and lattice matching between organic co-crystals, the synergistic effect of different red-green-blue luminescent shells is effectively realized, and the application of multi-source white light is proposed. The specific process of the

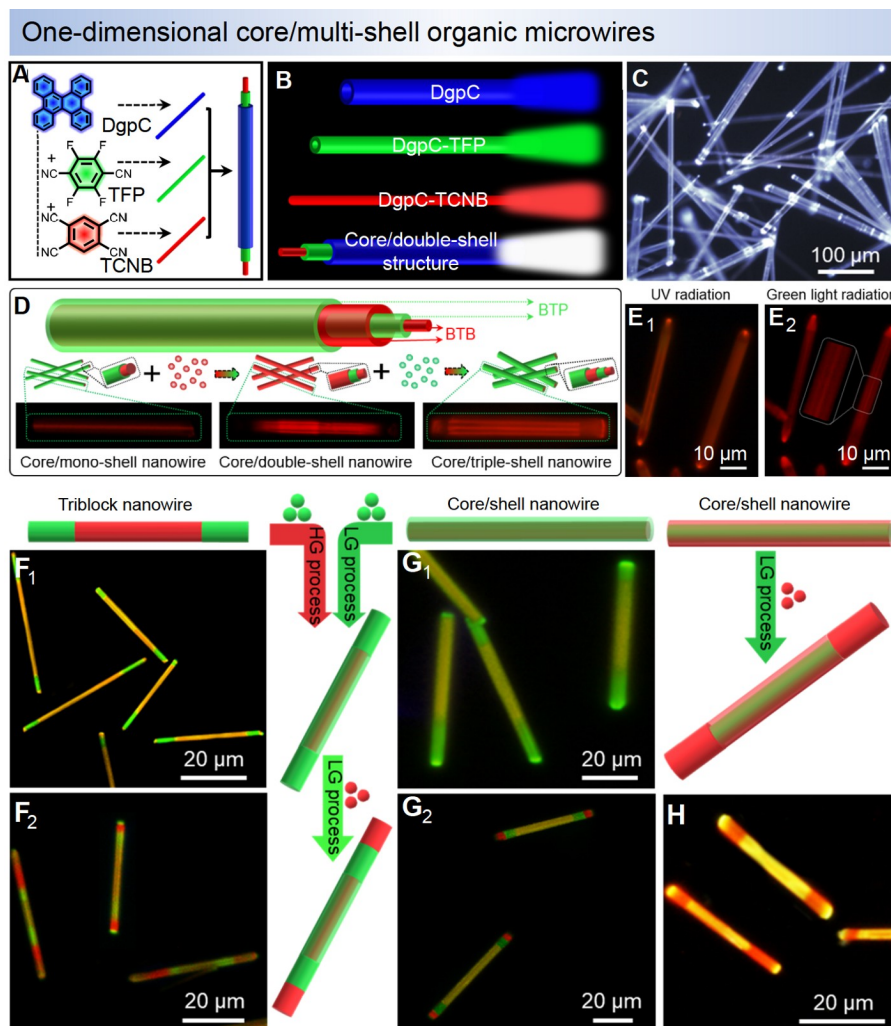


Figure 5 (A) Schematic illustration of single-component DgpC cocrystal microrods fabricated by primary self-assembly and core/shell microrods based on DgpC cocrystal fabricated by horizontal epitaxy process (Adapted with permission from Ref. [135]. Copyright©2021, Wiley-VCH GmbH). (B) Schematic of the specific structures and emission properties of each layer in DgpC-TCNB/DgpC-TFP/DgpC core/double-shell microwires. (C) FM image of DgpC-TCNB/DgpC-TFP/DgpC core/double-shell microwires showing white emission due to the synergistic effect of the multishells. Scale bar is 100 μm (Reproduced from Ref. [135]. Copyright©2021, Wiley-VCH GmbH). (D) The process of preparing BTB/BTP core/multi-shell organic microwires by horizontal epitaxial growth method and the specific structure diagram of the core/multi-shell microwires. (E₁), (E₂) FM images of core/triple-shell organic microwires excited with ultraviolet light (E₁) and green light (E₂). The obvious shell structure can be seen in the photo excited by green light. Scale bars are 10 μm (Reproduced from Ref. [123]. Copyright©2021, The Author(s)). (F)–(H) Schematic illustration of the rational design and elaborate synthesis of organic superstructure microwires combining multiblock and multishell structures and the corresponding fluorescence microscopy images. (F₁), (F₂) FM images of different types segmented-core/shell organic superstructure microwires. (G), (H) FM images of different types core/shell-segmented organic superstructure microwires. Scale bars are all 20 μm (Adapted with permission from Ref. [123]. Copyright©2021, The Author(s)).

horizontal epitaxial growth strategy is shown in Figure 5A. DgpC molecules with a unique twisted conformation form crystals by tightly and offset face-to-face stacking through π - π interactions, while eutectic microrods are formed by giving strong CT forces between acceptor molecules. DFT calculation result of the intermolecular interaction ($|E_{\text{CT}} \text{DgpC-TCNB}| = -18.35 \text{ kcal mol}^{-1} > |E_{\text{CT}} \text{DgpC-TFP}| = -13.45 \text{ kcal mol}^{-1} > |E_{\pi-\pi} \text{DgpC}| = -6.81 \text{ kcal mol}^{-1}$) (Figure 5A)) suggests that the DgpC-based cocrystals have different binding forces. As the force increases, the emission of the crystal exhibits a red-shift trend, and the growth order of the crystal also appears successively (Figure 5B). On this basis, hierarchical self-assembly based on DgpC

co-crystals is beneficial for the development of core/multi-shell heteromicrorod structures. Typically, DgpC-TCNB cocrystals with stronger CT interactions first self-assemble into seed lines, then DgpC-TFP cocrystals with slightly weaker CT interactions grow horizontally on the outer layer of DgpC-TCNB cocrystals, and finally the DgpC crystals with weak π - π interacting continued to grow horizontally on the surface of the core/shell crystals, forming a DgpC-TCNB/DgpC-TFP/DgpC core/double-shell heterostructure (Figure 5B). Due to the synergistic effect between the different luminescent multilayer crystals, the prepared core/multi-shell structures exhibit unique white luminescence. Benefiting from the low lattice mismatch rate between crystals of the same eutectic system and the precise manipulation of the self-assembly process dominated by intermolecular non-covalent interactions, the preparation of more complex organic core/multi-shell superstructures is possible. At the same time, due to the excellent optical properties of organic crystals and the effective synergistic effect after recombination, the superstructure of complex multicore-shell organic crystals will undoubtedly greatly promote the exploration of optical applications including the generation of polychromatic light sources. In other work by Zhuo and co-workers [123], they prepared BTB/BTP multi-shell microwire structures by a similar stepwise growth strategy of organic crystals (Figures 5D and 5E). At the same time, they combined this strategy with a forementioned longitudinal stepwise growth process to prepare a series of complex microwire superstructures with unique multiblock and core/multi-shell composites (Figures 5F–H). These studies show that it is a mature strategy to control the step-by-step growth process of crystals by controlling the interaction between organic molecules, thereby realizing the processability of complex structures.

Hyperbranched superstructures

Penniform structures

In the reported work, amphiphilic copolymer blocks have been shown to be effective modifiers for crystal growth that can be used to control the crystallization process of inorganic molecular particles in solution state. Previously, we reviewed strategies for the preparation of multiblock superstructures from amphiphilic polymers. Using cationic reversed micelles formed from a mixture of cationic-anionic surfactants, Shi *et al.* [136] reported a peculiar strategy for the synthesis of highly branched single-crystal BaWO₄ penniform-like nano superstructures. Individual penniform structures based on BaWO₄ nanowires were synthesized in a synthetic system of a double-hydrophilic block copolymer poly(ethylene glycol)-block-poly(methacrylic acid) (PEG-*b*-PMAA). In a typical preparation, a cationic surfactant mixture made up by combining equimolar amounts of undecanoic acid and decylamine is firstly dissolved in decane with gentle heating. Next, Na₂WO₄ solution and PEG-*b*-PMAA aqueous solution were added to the system and shaken, and then BaCl₂ was added and shaken vigorously. Finally, the resulting mixture was incubated at 50°C for 8 h, and a white precipitate gradually formed. The growth process of the nano-penniform structures was observed, and after aging for 0.5 h, the formation of penniform BaWO₄ nanostructures with an axis width of about 220 nm and a hair tuft length of about 200 nm was achieved. When the aging time reaches 1 h, tuft length increases to about 400 nm, while its axial width remained almost unchanged. If the aging time was further increased to 8 h, the tuft length increased to 2 μ m, after which the tuft length remained essentially unchanged with time, indicating that the growth was basically over. This result indicates that the rod-like BaWO₄ axis is first formed (Figure 6A₂), and then BaWO₄ nanowires are gradually attached and grown along the crystallographic [001]

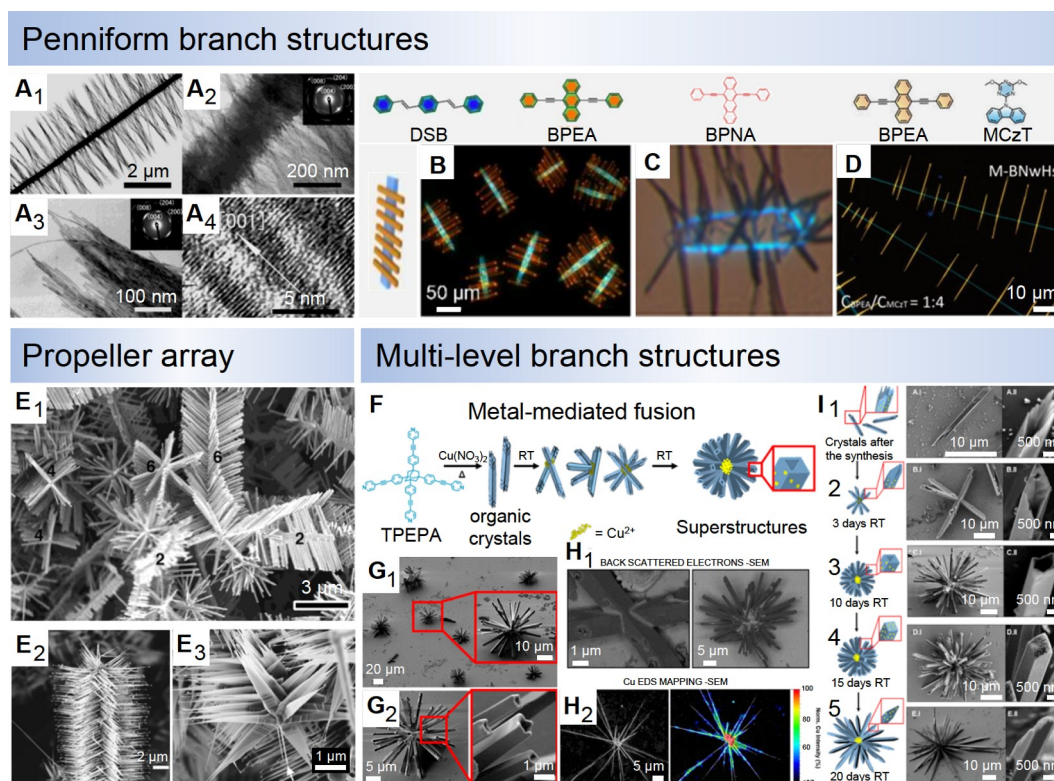


Figure 6 (A₁) The low magnification TEM image of penniform BaWO₄ nanostructures. (A₂) Locally enlarged TEM image of the shaft of the penniform BaWO₄ nanostructure. (A₃) Locally enlarged TEM image of the barbs of the penniform BaWO₄ nanostructure. The upper right inset shows the corresponding electron diffraction patterns of the main core and tufts. (A₄) A magnified image of the tuft portion of the penniform structure. Scale bars: (A₁) 2 μm; (A₂) 200 nm; (A₃) 100 nm; (A₄) 5 nm (Reproduced from Ref. [136]. Copyright©2003, American Chemical Society). (B)–(D) FM images of DSB-BPEA (B), DSB-BPNA (C), and BPEA-MCzT (D) highly branched superstructures. Scale bars: (B) 50 μm; (D) 10 μm. (B)–(D) Reproduced from Refs. [138–140], respectively. Copyright©2022, Wiley - VCH GmbH; Copyright©2021, The Author(s); Copyright©2022, Royal Society of Chemistry. (E₁) SEM images of ZnO propeller-like nanostructures containing various symmetric structures marked as 6-, 4-, 2-fold. Scale bar is 3 μm (Reproduced from Ref. [141]. Copyright©2002, American Chemical Society). (E₂) SEM image of the ZnO nanopropeller array. (E₃) SEM image of the front view of the ZnO nanopropeller array (Reproduced from Ref. [142]. Copyright©2004, AIP Publishing). (F) Schematic representation of the formation of a hollow multi-level branch superstructures through metal-mediated fusion of TPEPA crystals. (G₁), (G₂) SEM images of TPEPA multi-level branch superstructure after 12 days of aging, showing the formation of complex branch structures and their hollow morphology. Scale bars: (G₁) 20 μm, inset 10 μm; (G₂) 5 μm, inset 1 μm. (H₁) SEM backscattered images of hollow TPEPA superstructures. Scale bars: left 1 μm, right 5 μm. (H₂) SEM secondary electron image (left) and mapping of copper by EDS-SEM (right) of a superstructure. Scale bars: 5 μm. (I) Right (1–5): schematic illustration of the process of recombination of TPEPA crystals into a multi-level branched superstructure as the reaction time continued. Right: Time-correlated *ex situ* SEM images showing specific changes in the fusion of TPEPA crystals into the superstructure. Inset: the evolution of the branch tip, showing the formation of the hollow topography. Scale bars are 10 and 500 μm (Reproduced from Ref. [143]. Copyright©2018, American Chemical Society).

direction on both sides of the axis (Figures 6A₃ and A₄), and finally the penniform-like BaWO₄ nano superstructures are formed (Figure 6A₁). This facile, mild, and controllable synthesis strategy validates a new method for the preparation of hierarchical hyperbranched structures based on the liquid-phase direct self-assembly growth of inorganic nanowires. Similar approaches were also adopted by Shi *et al.* [137] to prepare other structurally similar BaXO₄ penniform nanowire superstructures. In the studies of Su, Zhang and Yang *et al.* [138–140], a similar multi-branched brush-like superstructure was achieved through the directional epitaxial growth of organic crystals, including the composite of BPEA with DSB (Figure 6B) and MCzT (Figure 6D), respectively, and the composite of BPNA and DSB (Figure 6C). These organic crystalline superstructures also show unique applications as potential optical logic gates.

Propeller array structures

Except for the brush-like structures, Lao *et al.* [141] reported a series of propeller-like hierarchically hyperbranched ZnO complex superstructures fabricated by thermal vapor transport and condensation techniques. Hierarchical ZnO complex structures were prepared via high temperature gas phase transport and condensation self-assembly on In_2O_3 core nanowires. First place the well-mixed ZnO, In_2O_3 and graphite powders in a port-sealed quartz tube. The entire reaction assembly is finally placed into the ceramic tubes of a Tube furnace with rotary pumping. The vacuum in the reaction vessel was maintained at approximately 0.5 to 2.5 Torr. The mixed powder is heated to a high temperature of 950 to 1000°C for 30 min. Then, during the nanostructure growth stage, the reaction temperature was controlled at about 820–870°C, so that a temperature gradient was generated in the ceramic tube. As shown in the SEM pictures, after the reaction, a large number of propeller-like highly branched structures were obtained. These highly branched branches all have some symmetry with respect to the In_2O_3 major core, three main structural symmetries obtained, marked as 6-, 4- and 2-fold (Figure 6E₁). When the diameter of the major core nanowires is small, the newly formed nanorods grow in a single row on both sides of one axis of the major core, as shown in Figure 6E₁, marked as 2. As the nanowire of main core grows large enough, more secondary grown nanorods form along other sides of the main core, which can be seen in Figure 6E₁, marked as 4 and 6. Since the main core is hexagonal, the secondary branches are mainly arranged in sixfold symmetry along the main core, and the secondary branches are also hexagonal. This suggests that, to a certain extent, by controlling the size of the main core, highly branched hierarchical structures with different forms of symmetry can be achieved. In general, with some adjustments according to the actual situation, the synthesis method of this hierarchical branched nano superstructure reported in this paper is also applicable to many other oxides, carbides, nitrides and other non-polar compound materials. This not only opens a feasible path for the synthesis of nanomaterials, but also creates prerequisites for their application in numerous fields. Similarly, the work of Gao *et al.* [142] reported a polar surface-dominated ZnO nano propeller array fabricated by a step-by-step high temperature solid-vapor deposition process (Figures 6E₂ and 6E₃). These fabricated ZnO propeller array superstructures are considered to be very important for electrical, optoelectronic, photovoltaic device, and sensor applications, which can be applied in sensing, microfluidics, electromechanical coupled devices and sensors. Their work not only introduces the nano propeller superstructure and growth process, but also illustrates the effect of temperature gradient and material surface polarity on the growth structure during the reaction, which provides a reference for the preparation of other superstructures.

Multi-level branch structure

The previous reviews are highly branched secondary branch structures epitaxially grown on one primary branch. From the perspective of morphology evolution, the brush-like highly branched structure is a 2-fold symmetric structure grown by axial epitaxy, while the propeller-like structure is a multi-symmetric structure grown in two or more axial directions. The helical structure can be considered as an extension of the brush-like structure. di Gregorio *et al.* [143] reported a multi-branched structure composed of multiple organic hollow nanotubes. The formation of hyperbranched superstructures can be divided into two crystallization processes. First TPEPA with a four-fold excess of $\text{Cu}(\text{NO}_3)_2$ in chloroform/dimethylformamide at 105°C

(DMF) mixed solution for two days of solvothermal treatment to obtain uniform hollow constitutive organic crystals. The reaction system is then brought to room temperature and undergoes a series of successive fusion processes, these TPEPA organic crystals combine to form a multi-branched superstructure (Figure 6F). To gain insight into the formation mechanism of the hierarchical branch superstructure, *ex situ* time-correlated SEM studies were started directly after the solvothermal reaction. SEM images acquired during 20 days reveal the process of superstructure generation and evolution (Figure 6I). The crystals formed after the solvothermal reaction are morphologically homogeneous with a rectangular geometry. As the time progressed, the first observation is that the number of initially formed rectangular crystals keeps decreasing, while an increase in the number of superstructures assembled from these crystals was observed. After three days at room temperature, the length of the branches in the superstructure was comparable to that of the initially formed crystals, confirming that the superstructure was formed by fusion of TPEPA crystals obtained from a solvothermal reaction. During this process, copper salts play an important role in fusing crystals and stabilizing the structure at the junction. During the self-assembly process of the solvothermal reaction, the crystal surface generated by the pyridine moiety of TPEPA interacts with the metal salt to induce uniformity and stability of crystal growth. During the subsequent fusion process, this coordination facilitates the fusion of crystals formed in solution into larger superstructures. Backscattered electron SEM images show extremely bright regions at the junction due to copper salts localized, and EDS mapping also confirms the presence and location of copper (Figures 6H₁ and 6H₂). In general, this strategy of guiding crystal fusion through metal salt coordination to obtain superstructures provides an unprecedented idea for the preparation of superstructures directly through crystal construction.

Network structures

The multi-branch structure can be regarded as a structure with high-speed repeatability formed by the ordered fusion of micro-nanowires/rods. When the micro-wires/rods form a staggered and ordered array stack in a two-dimensional plane, it exhibits a network structure. In the work of Li *et al.* [144], a 2D template topological transformation method was used to prepare complex disk-like network superstructures composed of Bi₂S₃ single-crystal nanorods aligned perpendicular to each other. The synthesis of Bi₂S₃ nanorod networks was obtained by adding thioacetamide (TAA) to the hydrolysis solution of BiCl₃ followed by a mixing reaction at 60°C for 60 h. Specifically, first, before adding TAA, a white precipitate was formed in the aqueous solution of BiCl₃, and the solid precursor template was collected after aging for 2 h. As shown in Figures 7A₁ and A₂, the precursor templates are presented as micrometer-scale disks with smooth surfaces and about 20–50 nm thicknesses. It can be seen from the XRD pattern that the disk-shaped precursor template is pure BiOCl crystals with a tetragonal structure. Subsequently, after adding TAA to the solution containing BiOCl disks, the BiOCl disks gradually transformed into a disc-like nanorod network, and after the process lasted for 4 h, some diffraction peaks representing Bi₂S₃ appeared in the XRD pattern of the product, indicating that the disks are partially transformed into Bi₂S₃ micron wires. After the reaction time was 10 h, the apparent morphology of the product remained basically unchanged, but the diffraction spots corresponding to BiOCl hardly existed in the ED image, indicating that the BiOCl disc was further transformed into Bi₂S₃. However, the XRD results showed that some characteristic peaks of BiOCl still clearly existed when the reaction time was 10 h, and this phenomenon was weakened but still existed when extended the

reaction time to 44 h, which indicated that the transformation still not completely finished. Finally, the reaction time was further extended to 60 h, and the XRD results showed the same peak shape as pure Bi_2S_3 , indicating the formation of pure Bi_2S_3 nanorod network. As shown in the SEM and TEM photos (Figures 7A₃ and 7A₄), the formed Bi_2S_3 network structure is composed of Bi_2S_3 nanowires arranged in an orderly manner with obvious network holes. The transformation of the initial single-crystal BiOCl disks to the final disk-like network consisting of intersecting single-crystal Bi_2S_3 nanorods reflects a topological reaction process driven by lattice matching (Figure 7b). Layered Bi_2S_3 , held together by van der Waals interactions, elongated along the c -axis into ribbons of microwires/rods. Moreover, in addition, there is a tight lattice match between the c -axis of Bi_2S_3 and the a -axis or b -axis of BiOCl , so these Bi_2S_3 single-crystal nanorods tend to be oriented along the two perpendicular $[100]$ and $[010]$ crystallographic orientations of BiOCl , resulting in the transformation of the top surface of the BiOCl disc into a layer of disc-like network composed of intersecting nanorods.

A similar strategy is also applicable to the construction of complex nanorod networks from organic crystals. A simple crystal transformation strategy is proposed by Sun *et al.* [145] for the epitaxial growth of nanorod networks containing benzoperylene 1,3-dicyanotetrafluorobenzene (BP-1,3-DTFB). Two-dimen-

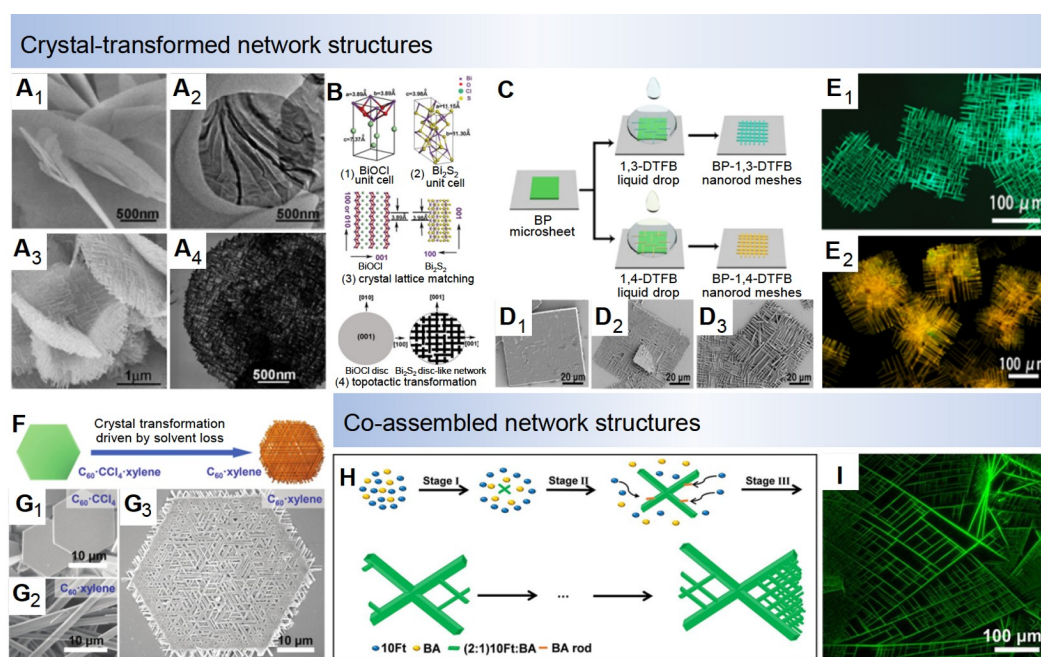


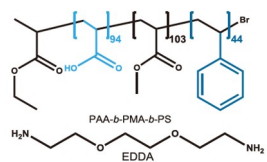
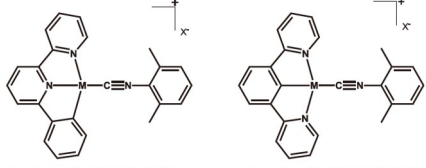
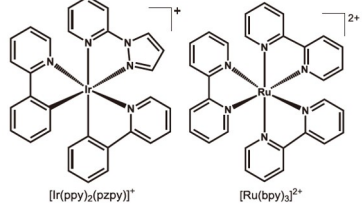
Figure 7 (A₁), (A₂) SEM image (A₁) and TEM image (A₂) of the BiOCl precursor discs. Scale bars are 500 nm. (A₃), (A₄) SEM image (A₃) and TEM image (A₄) of disc-like networks consists of Bi_2S_3 nanorod. Scale bars are 1 μm and 500 nm, respectively. (B) (1) Schematic diagram of BiOCl tetragonal unit cell; (2) Bi_2S_3 orthorhombic unit cell; (3) lattice matching between BiOCl and Bi_2S_3 ; (4) schematic diagram of the crystalline topological transition of BiOCl disc structure to Bi_2S_3 disc-like network superstructure (Reproduced from Ref. [144]. Copyright©2008, WILEY - VCH Verlag GmbH & Co. KGaA, Weinheim). (C) Schematic illustration of the fabrication of BP-based cocrystal nanorod network structures through the crystallographic transformation process induced by etching BP microsheets. (D₁)–(D₃) Evolution process of different stages from BP microsheets to BP-1,3-DTFB nanorod networks. Scale bars are 20 μm . (E₁) FM image of BP-1,3-DTFB nanorod network structures. (E₂) FM images of BP-1,4-DTFB nanorod network structures. Scale bars are 100 μm (Reproduced from Ref. [145]. Copyright©2020, American Chemical Society). (F) Schematic illustration of the transformation from C_{60} plates to network structures driven by solvent loss. (G₁), (G₂) SEM images of (G₁) C_{60} disks and (G₂) C_{60} rods synthesized in the presence of CCl_4/IPA and m -xylene/IPA mixtures, respectively. (G₃) SEM image of a typical C_{60} network superstructure. Scale bars are all 10 μm (Reproduced from Ref. [146]. Copyright©2003, 2020, RSC Pub). (h) Schematic showing the mechanism for the preparation of hyperbranched (2:1)10Ft:BA MW networks through a stepwise co-assembly process. (I) FM image of the co-assembled network of 10Ft and BA excited by UV light. Scale bars are all 100 μm (Reproduced from Ref. [147]. Copyright©2021, Wiley-VCH GmbH).

sional (2D) nanorod network composed of benzoperylene-1,3-dicyanotetrafluorobenzene (BP-1,3-DTFB) formed by crystallographic transformation of pre-prepared BP microsheets (Figure 7C). Specifically, the preparation of single-crystal BP microplate templates was first completed, and then the microplate templates were dissolved and etched by the solution system to form oriented BP-1,3-DTFB nanorods. Surprisingly, BP microsheets were transformed into nanorod meshes by immersing them in a solution of 1,3-DTFB in isopropanol (IPA, CDTFB = 100 mM) and then slowly evaporating the suspension. To this end, the specific evolution process of the 2D nanorod grid at different growth sections was recorded to reveal more structural information about the crystal transitions (Figures 7D₁–D₃). When the preparation progressed to 10 min, it could be seen that the smooth-appearing BP microsheets became rough, indicating that etching had occurred (Figure 7D₁). Due to the intermolecular interaction of BP with the high concentration of 1,3-DTFB, BP molecules are slowly etched and dissolved into solution. As the IPA solvent evaporates, the dissociated BP molecules will co-crystallize with adjacent 1,3-DTFB molecules to form BP-1,3-DTFB cocrystal rods. At 60 min, a fraction of the region of the BP sheet remained unetched, and lots of the 1D nanorods were interconnected to form an inconsecutive 2D nanorod network (Figure 7D₂). When the reaction finally proceeded to 120 min, almost all the microsheets of BP completely depleted, and a very inerratic nanorod network is obviously identified (Figures 7D₃ and 7E₁). The CT and AP interaction forces between BP and 1,3-DTFB molecules are greater than the π - π interaction force between BP-BP molecules, and when the BP microsheets are immersed in the solution of high concentration 1,3-DTFB, the stronger interaction drives the transformation of the crystal. At the same time, due to the space matching between BP microsheets and 1,3-DTFB microrods, partially consumed BP sheets provide a sacrificial template for the orderly growth of BP-1,3-DTFB nanorods, and finally build neat organic microrods network superstructure. Subsequent supplementary experiments demonstrate that this crystallographic transformation strategy can also achieve the preparation of BP-1,4-dicyanotetrafluorobenzene (BP-1,4-DTFB) nanorod networks (Figures 7D₃ and 7E₂). It is believed that with careful selection of electron acceptors, this strategy can easily achieve two-dimensional nanorod grids with different luminosity. A similar process was proposed in the work of Sun's colleague Lei *et al.* [146] (Figure 7F), which achieved the crystalline transformation of C₆₀ microdisks (Figure 7G₁) to the size corresponding C₆₀ network superstructure (Figure 7G₃) through changes in the solvent environment. Such crystallographic transformation processes blaze new trails for designing complex network superstructures and potential functional application. In addition to the crystal transformation strategy, Feng *et al.* [147] also reported the synthesis of highly ordered multigenerational branched network superstructures made from (2:1)10Ft:BA-AP co-crystals via a facile solution co-assembly method (Figure 7H₁). And the transition of the network superstructure from green to red is also achieved by doping with different concentrations of acceptor BN. Hierarchical network superstructures based on such light-emitting organic semiconductors are expected to realize unprecedented and unique optoelectronic properties, such as multi-channel optical waveguide devices and laser arrays.

Conclusions and outlook

In this review, we summarize the basic theory of basic material selection and fabrication strategies for low-dimensional complex superstructures (Table 1). At the same time, in the form of classification, a series of

Table 1 Representative examples of superstructures

Structure	Components	Material classification	Method	Strategy	Years	Reference
Multi-block	 PAA-<i>b</i>-PMA-<i>b</i>-PS EDDA Poly(acrylic acid)-block-poly(methyl acrylate)-block-polystyrene (PAA-<i>b</i>-PMA-<i>b</i>-PS) 2,2'-(Ethylenedioxy)diethylamine (EDDA)	Copolymers	Solution assembly	Regulation of hydrophilic and hydrophobic interactions	2007	[119]
	 M = Pd X = PF₆ Pd-1-PF₆ X = ClO₄ Pd-1-ClO₄ X = OTf Pd-1-OTf M = Pt X = PF₆ Pd-1-PF₆ X = OTf Pd-1-OTf M = Pd X = ClO₄ Pd-2-ClO₄ X = OTf Pd-2-OTf M = Pt X = PF₆ Pd-2-PF₆ X = ClO₄ Pd-2-ClO₄	Copolymers made by organometallic complexes	Solution assembly	Out-of-equilibrium assembly	2020	[120]
Pt ^{II} and Pd ^{II}						
Ln-MOF		Metal organic framework (MOF)	Solvothermal synthesis	Step-by-step epitaxial growth	2019	[121]
	 [Ir(ppy)₂(pzpy)]⁺ [Ru(bpy)₃]²⁺	Transition metal complexes	Solution assembly	One-pot/stepwise growth	2018	[122]
	[Ir(ppy) ₂ (pzpy)](PF ₆) [Ru(bpy) ₃](PF ₆) ₂					
	Benzo[ghi]perylene-1,2,4,5-tetracyanobenzene (BTB) Benzo[ghi]perylene-tetrafluoroterephthalonitrile (BTP)	Organic small molecules	Solution assembly	Hierarchical epitaxial growth Lattice matching	2021	[123]
0D hollow Core/multi-shell	Chromium (III) terephthalate MOF (MIL-101)	MOF	Hydrothermal reaction	Step-by-step Subsequent etching processes	2017	[131]
	Cobalt-imidazole-based MOF (ZIF-67).	MOF	Solution assembly	Shell-by-shell soft-templating method Solvent washing	2020	[134]
1D hollow Core/multi-shell	Dibenzo[g,p]chrysene (DgpC) Tetrafluoroterephthalonitrile (TFP) 1,2,4,5-Tetracyanobenzene (TCNB)	Organic small molecules	Solution assembly	Non-covalent interaction regulation Lattice matching	2021	[135]
	Benzo[ghi]perylene-1,2,4,5-tetracyanobenzene (BTB) Benzo[ghi]perylene-tetrafluoroterephthalonitrile (BTP)	Organic small molecules	Solution assembly	Hierarchical epitaxial growth Lattice matching	2021	[123]

(To be continued on the next page)

(Continued)

Structure	Components	Material classification	Method	Strategy	Years	Reference
Hyperbranch	BaWO ₄	Metallic oxide	Solvothermal synthesis	Double-hydrophilic block copolymers modification	2003	[136]
	Bis(phenyl-ethynyl)anthracene (BPEA) 9,10- <i>p</i> -distyrylbenzene (DSB)	Organic small molecules	Solution assembly	Temperature regulation Lattice matching	2022	[138]
	<i>p</i> -Distyrylbenzene Tetracene 9,10-Bis(phenylethynyl)anthracene 5,12-Bis(phenylethynyl)naphthacene	Organic small molecules	Solution assembly	One-pot co-assembly route Stepwise seeded growth method	2021	[139]
	Bis(phenyl-ethynyl)anthracene (BPEA) 9-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-9H-carbazole (MCzT)	Organic small molecules	Solution assembly	Concentration regulation Lattice matching	2019	[140]
	ZnO	Metallic oxide	Vapor transport and condensation technique	Lattice matching	2002	[141]
	ZnO	Metallic oxide	High temperature solid-vapor deposition	Two-step process	2004	[142]
	1,3,5,7-Tetrakis(4-(pyridyl-4'-yl-ethynyl)phenyl)adamantine (TPEPA) Cu(NO ₃) ₂	Organic crystal	Solvothermal synthesis	Metal-Coordination-Induced	2018	[143]
Network	Bi ₂ S ₃	Metal sulfide	Solvothermal synthesis	Solvent etching Crystal transformation	2008	[144]
	Benzoperylene (BP) 1,3-Dicyanotetrafluorobenzene (1,3-DTFB) 1,4-Dicyanotetrafluorobenzene (1,4-DTFB)	Organic crystal	Solution assembly	Template sacrifice Crystal transformation	2020	[145]
	C ₆₀ -xylene	Fullerenes solvate crystals	Solution-phase strategy	Free energy difference drive Template sacrifice Lattice matching	2019	[146]
	1,4-Bis(pentafluorostyryl)benzene (10Ft) 9,10-Bis(phenylethynyl)anthracene (BA) 5,12-Bis(phenylethynyl)naphthacene (BN)	Organic crystal	Solution co-assembly	Lattice matching	2021	[147]

research progress of low-dimensional complex superstructures is introduced. These advances cover the precise synthesis of fundamental materials including inorganic salts, polymers, metal-organic frameworks, and small organic molecules. More importantly, a series of effective fabrication strategies are proposed to provide guidance for solving composite structure design and precise design fusion process. We note that the review of low-dimensional complex superstructures further explains their application prospects in numerous fields and broadens the application scope of low-dimensional materials.

On this basis, it is also recognized that the preparation of low-dimensional complex superstructures still faces some challenges currently (Figure 8).

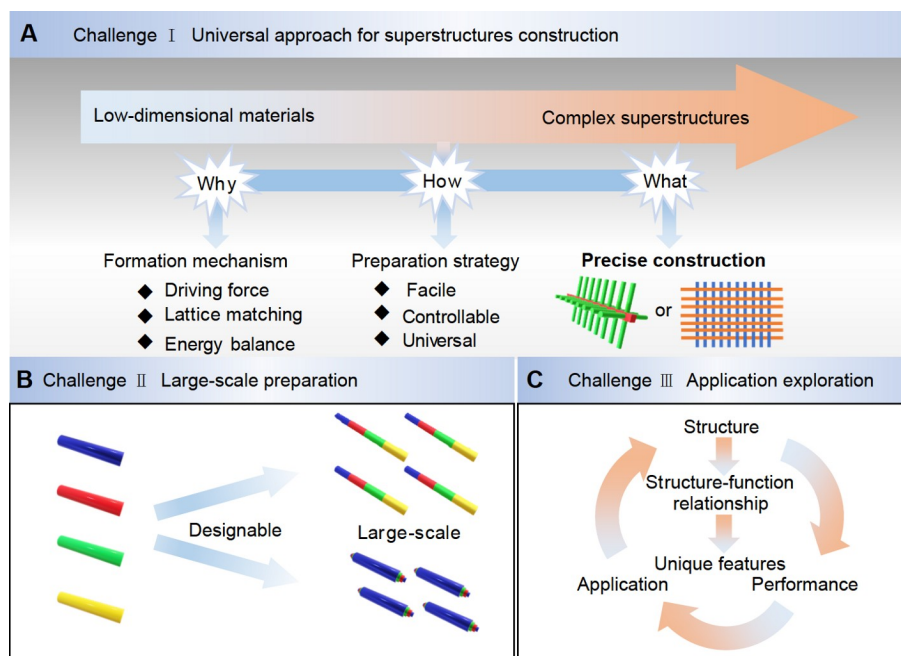


Figure 8 Existing challenges in the field of low-dimensional complex superstructure research. (A) Challenge I: universal approach for superstructures construction. (B) Challenge II: designable large-scale preparation of superstructures. (C) Challenge III: exploring potential applications of superstructures.

(1) Firstly, although existing work reports many unique and efficient strategies to achieve low-dimensional complex superstructures, these successes are mostly presented on a case-by-case basis, so there is still lack of universal research methods with broad instructive significance. In the context of this challenge, three crucial questions remain to be addressed. Based on observations of a large number of work, it is believed that clarifying the formation mechanism of complex superstructure is an important prerequisite for research in this field. Numerous typical cases show that the interaction between reactants, the lattice matching required for structural recombination, and the energy balance of the system are all important drivers for the formation of complex structures. Systematic research is needed to achieve controllability of the self-assembly process. The development of universally applicable basic materials based on a certain material system is an urgent issue that needs to be addressed. In order to facilitate the progress in the field of complex superstructure preparation, simple, controllable and universal methods and strategies are also essential, which is related to the precise construction of complex superstructures with potential applications.

(2) Due to the lack of mechanistic studies, despite the appreciable presence of complex superstructures observed in the reported experiments, there are still many obstacles to realize the large-scale preparation of designable structures of complex superstructures, especially the small number of repeating units. In addition, for the practical application of superstructure, the orderly and regular growth of the structure is also crucial, which requires the development of an effective localization limited preparation strategy. The rational use of positioning templates and catalysts, such as amphiphilic materials, is a direction worth considering.

(3) In the presence of the first two challenges, the application development of low-dimensional complex superstructures is still in the initial stage, limited by the understanding and testing methods of the system, and the structure-activity relationship between structure and performance yet has been widely reported. Corre-

spondingly, the development of unique applications of the structure is far less than the research on the preparation of the structure. The research on the integration of superstructure is the main breakthrough, and integrated photonics applications, catalysis and other fields are very promising development directions at present. In summary, We hope that the classification and summary of existing work in this review will be helpful in overcoming these challenges to facilitate further progress in low-dimensional superstructures with a wide range of new applications.

Data availability

The original data are available from the corresponding authors upon reasonable request.

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Conflict of interest

The authors declare no conflict of interest.

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