Soft Matter

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Cite this: *Soft Matter*, 2011, **7**, 6385

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REVIEW

Construction and application of tunable one-dimensional soft supramolecular assemblies

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Received 10th January 2011, Accepted 28th March 2011
DOI: 10.1039/c1sm05030c

Self-assembly of small molecules into one-dimensional soft nanostructures offers many advantages in understanding biological process and fabrication of electronically active materials. In recent decades, various one-dimensional soft nanostructures have been fabricated. The present review focuses on the following content: (1) frequently occurring forces in one-dimensional molecular self-assembly; (2) how these forces are used to construct this type of nanostructures; (3) fine-tuning one-dimensional self-assemblies by employing tools such as photo, pH, temperature, additives, and concentration; (4) some examples of the applications of one-dimensional self-assemblies in fabrication of one-dimensional hard materials are described.

Introduction

Self-assembly is ubiquitous in nature. For instance, biological cells are the ordered structures of many different molecules; the surfaces of pine needle stomata are covered by naturally occurred nanotubes; many diseases are related with the formation of fibrils or ribbon-like structures of biomolecules.[1–3] It is noted that among numerous mysterious life phenomena, one-dimensional molecular self-assembly, namely fibrils, ribbons, helical structures, and nanotubes, is often involved. Therefore, studies of this type of self-assembly have become a focus of scientists in recent years.[4–6] In addition, the discovery of unique properties of some one-dimensional molecular self-assemblies as optical and electrical materials in modern techniques has added an additional stimulus to the research of one-dimensional molecular assemblies.[7] So far, the investigation of one-dimensional self-assembly has ranged from the organic to the inorganic world. Many fascinating one-dimensional nanostructures have been successfully fabricated; for these, readers can refer to many reviews.[4–6,8–10] However, most of them focus on one type of system; an overview that covers the whole scope of soft one-dimensional molecular self-assembly is rarely touched upon.[11] Although it is not easy to do such a work, we try to summarize some general things in this field with the hope of shedding some light on future work. The following content will be included in this review: (1) frequently occurring forces in one-dimensional molecular self-assembly; (2) experimental exploration towards the rational design of one-dimensional self-assemblies; (3) tunable elements that affect one-dimensional self-assembly; (4) application of one-dimensional self-assembly; (5) conclusions and perspectives.

1. Frequently occurring forces in one-dimensional self-assembly

So far, there is not yet a universal principle that can predict the formation of any sort of one-dimensional molecular self-assembly. Although there are some theories, such as the elastic theory proposed by Helfrich and Prost[12] to describe the intrinsic bending of membranes, and some subsequent theories developed by others,[13–15] they are purely phenomenological and are only useful to explain the molecular packing. Most of the one-dimensional structures are discovered by chance, and no information can be foreseen or predicted before any solid experimental results come out. However, some molecular interactions, especially directional forces, are found to occur frequently in one-dimensional self-assembled structures. In the following we will briefly summarize the most often occurring forces in one-dimensional self-assembly.

1.1 Hydrogen bonding

A hydrogen bond is the attractive interaction of a hydrogen atom with an electronegative atom, such as nitrogen, oxygen or fluorine. Such bonds can occur between molecules (intermolecularly), or within different parts of a single molecule (intramolecularly). When a hydrogen bond is created, a specific bonding angle must be satisfied, which leads to the orientation of molecules that participated in the hydrogen bond formation. Many naturally occurring structures, such as the secondary, tertiary, and quaternary structures of proteins and nucleic acids, involve hydrogen bonds where they are partially responsible for the formation of directional structures. Inspired by nature, many

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artificial molecules that contain groups cable of forming hydrogen bonds, such as peptide amphiphiles, oligopeptides,[11,16,17] or sugar-based amphiphiles,[18] were synthesized to create desired molecular assemblies or materials using hydrogen bonds. Indeed, fibrils, helical structures, flat or twisted ribbons, were readily obtained in these systems. Recent theoretical calculations suggest that in hydrogen bonding systems, cooperative interactions occur in the process of self-assembly, where *inter or intra* molecular hydrogen bonds may contribute to the majority of the cooperative interaction.[19] This is even true for the linear supramolecular assembly of formide and other hydrogen-bond-induced supramolecular polymerization systems.[20] In a recent work in our lab, hydrogen bonds between cyclodextrins (CDs) were found to be the main driving force for the formation of rigid nanotubes in CD : surfactant = 2 : 1 (molar ratio, abbreviated as SDS@2β-CD) systems, where the hydrophobic aliphatic chains of the surfactants were completely covered by two CD molecules (Fig. 1).[21,22]

1.2 π–π stacking

π–π stacking is a noncovalent interaction between organic compounds containing aromatic moieties. This interaction is caused by intermolecular overlapping of p-orbitals in π-conjugated systems, so it becomes stronger as the number of π-electrons increases. As is a fact that molecules with just one double bond or one aromatic ring normally do not exhibit interaction, π–π stacking is significant in flat polycyclic aromatic large hydrocarbons and linear π-conjugated systems because the overlap is more effective than that in nonplanar or unconjugated cases. The strong overlap between the p-orbitals allows the face to face arrangement of π systems, which results in the orientation of the involved molecules. This is particularly true for the larger macrocyclic aromatic molecules like hexabenzocoronene[23] and the discotic liquid crystal molecules.[24–31] For example, the tubular structures formed by porphyrins (Fig. 2),[27,28] fibrils and nanobelts of perylene tetracarboxylic diimides,[5] are all mainly driven by the directional stacking of the aromatic system. Sometimes, the stacking of π-systems may be affected by some steric effects so twisting of the assembly can occur, which leads to the formation of helical structures. This can be a way to construct chiral self-assemblies from achiral molecules. Liu's group has fabricated a series of helical supramolecular structures using porphyrin derivatives at the air–water interface[32] and in hydrogels.[33] These large aromatic compounds themselves are all achiral molecules, but the helical structures are all circular dichroism (CD) active (Fig. 3).

1.3 Coordination interaction

Coordination interaction has long been applied to build molecular organized frameworks (MOFs) or other crystal clusters. In these works, single crystals are the goal to pursue. However, recently, coordination between metal ions and proper ligands has appeared as an appealing interaction that helps to construct ordered molecular self-assembled structures.[34] Delicate examples are the formation of supramolecular coordination polymers from metal ions and bis or polydentate ligands,[35–37] and the hierarchical assembly of these supramolecular polymers.[38–40] These coordination polymers are extended linear or branched structures that may dissolve in a solvent and gel it. A nice example is the hydrogel reported by Leong *et al.*, where coordination polymers formed by ligand H_2mugly, **1**, and zinc ions self-assemble into fibrillar structures in water (Fig. 4).[41] The X-ray crystal structure revealed that the mugly anion is coordinated to the Zn^{2+} center in a tridentate mode, along with a water ligand and carboxylate oxygen from a neighboring unit, thus forming a 1D coordination polymer. These 1D zigzag

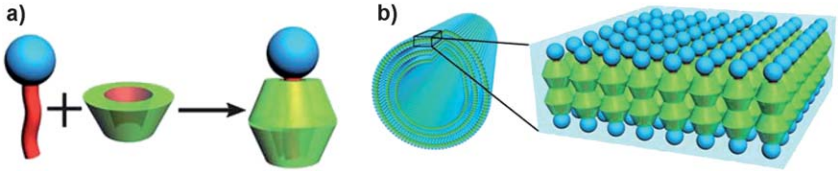

Fig. 1 Schematic self-assembly behavior of SDS@2β-CD driven by hydrogen bonding. (a) Formation of SDS@2β-CD complex. (b) The SDS@2β-CD bilayer membrane with a channel-type crystalline structure. Adapted from ref. 21.

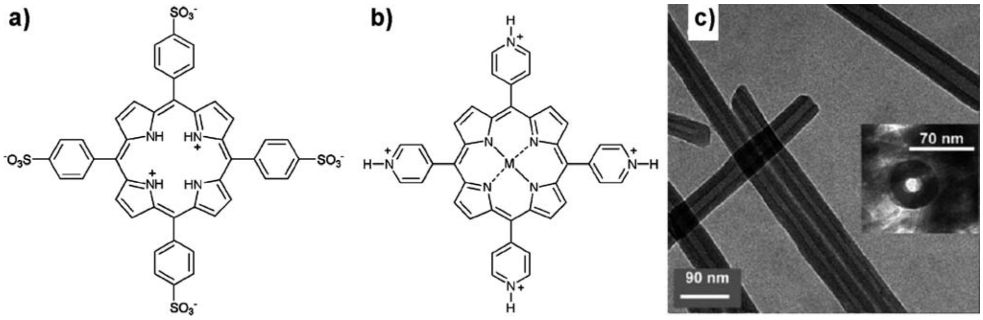

Fig. 2 Chemical structures of porphyrin ions H4TPPS^{2-} (a) and MT(4-Py)P^{4+} (b) obtained at low pH. (c) TEM image of porphyrin nanotubes obtained by ionic self-assembly of SnIVT(3-Py)P^{4+} and H4TPPS^{2-}. Adapted from ref. 28.

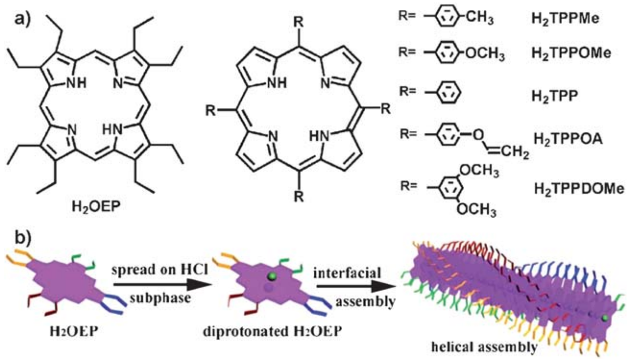

Fig. 3 A possible explanation for the interfacially assembled optically active supramolecular assemblies with helical conformation from H_2OEP by using 2.4 m hydrochloric acid as a subphase. Adapted from ref. 32.

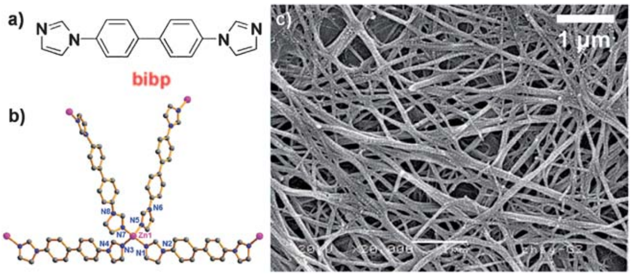

Fig. 5 Structure of bibp (a), coordination polymer of Zn–bibp (b), and fibrils formed by Zn–bibp (c). Adapted from ref. 44.

coordination polymers are arranged in a criss-crossed fashion, such that the disk-like coumarin rings stack together with the help of various hydrogen bonds.

In recent studies from our group, formation of helical structures upon simply mixing Ca^{2+} or La^{3+} ions and sodium cholate in aqueous solution was observed.[42,43] The macroscopic appearance of the coordinating systems are transparent or opalescent gels depending on the concentration. TEM microstructure observation reveals that the skeleton of the hydrogel is composed of helical structures. Further XRD analysis suggests that the resulting coordination steric effect was considered very crucial for the formation of helical structures. Another interesting example of one-dimensional self-assembly closely related to the coordination interaction is the fibrils formed in the $Zn(OSO_2CF_3)_2$–bibp system (Fig. 5).[44] $Zn(OSO_2CF_3)_2$ and bisligand molecule bipp form coordination polymers in methanol, which assemble into plate like nanoparticles; upon sonication, these nanoparticles rearrange into fibrils that gel the system. This was explained by the change of the coordination state of Zn^{2+} upon ultrasonication which further changes the torsion of the molecular arrangement.

1.4 Geometry constraints

In addition to systems that contain certain directional driving forces for one-dimensional structure formation, there are also cases such that assembly still occurs when all the specific directional forces are missing. Such examples can be frequently observed in amphiphilic systems where the geometry of the molecules prefers the formation of rod-, worm-like structures, and tubules. This is especially true in some surfactant systems where the molecular packing parameter governs the shape and type of self-assembled structures. According to Israelachvili *et al.*,[45] as the ratio between the volume of the hydrophobic chain and the multiple of the chain length and occupied area of the surfactant head falls into the range 0.33∼0.5, worm-like micelles are preferred; in certain cases in the range 0.5∼1, tubular structures can be formed. Systems that can form these structures can be the aqueous solution of a single surfactant, or the aqueous mixture of a surfactant and a proper additive. For instance, long worm-like micelles can be formed in the aqueous solution of cetyltrimethylammonium bromide (CTAB) at medium concentration or at a relatively lower concentration but in the presence of an inorganic salt or hydrophobic salt.[46,47] In a study by Hoffmann's group,[48] even the formation of rigid nanotubes was observed when mixing CTAB and a dye molecule, where the system exhibited strong birefringence (Fig. 6). It is believed that the addition of an inorganic salt or hydrophobic salt screens the repulsion between the ionic heads of these surfactants thus decreases the occupied size of the ionic heads, so that the geometry constraint allows the formation of one-dimensional worms or tubes rather than spherical structures.

1.5 Others

The above mentioned forces are, to some extent, responsible for much of the directed growth of one-dimensional self-assemblies, however, many undirectional forces that are common for all kinds of self-assemblies are also involved. For instance, solvophobic interactions are often found to assist one-dimensional self-assembly, although this interaction doesn't determine the extending direction of the one-dimensional self-assembly. Similar

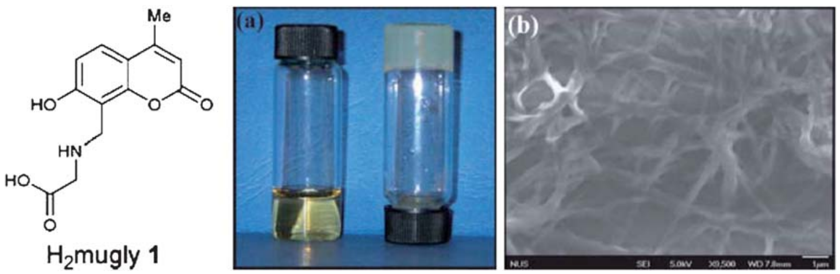

Fig. 4 Structure of ligand H_2mugly 1 (left); (a) photographs of a solution of H_2mugly, **1**, (left) and a hydrogel of **1**-Zn^{2+} (right); (b) SEM image of the freeze dried hydrogel. Adapted from ref. 41.

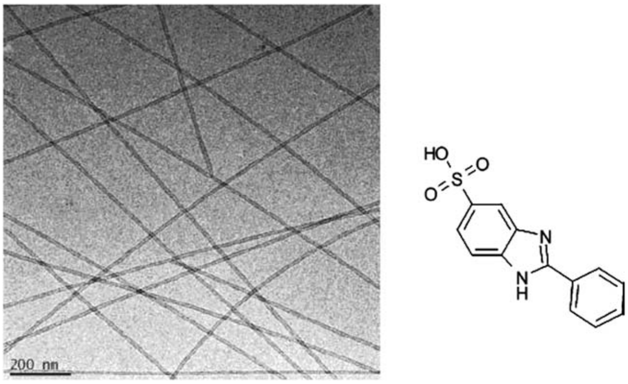

Fig. 6 Cryo-TEM micrographs of stiff nanotubes formed in a sample of 8 mM PBSA (Na salt, right) and 2 mM CTAB. (adapted from ref. 48).

unidirectional forces, such as electrostatic interactions, dipole–dipole interactions, van de Waals attraction, repulsive steric effect, *etc.* are also often present.[9,49] Actually, most systems involve combinations of these forces that counterbalance the enormous translational and rotational entropic cost caused by poly molecular aggregation.[49] By manipulating the subtle balance between these interactions, scientists are able to fabricate versatile one-dimensional assemblies. In the following section, we will briefly discuss some nice examples of the design of one-dimensional self-assemblies using certain combinations of directed and undirected forces.

2. Experimental exploration towards the rational design of one-dimensional self-assemblies

2.1 Hydrogen bonding and hydrophobic interaction governed self-assembly

This represents almost the largest category of one-dimensional self-assembly so far. Both peptide amphiphiles and long-chain sugar-based amphiphiles self-assemble mainly *via* these two interactions. Early motivation for the design of these molecules was inspired by nature where hydrogen bonding is ubiquitous in proteins and sugars. Attaching one or more alkyl chains to these groups renders the molecules with amphiphilic properties like surfactants where the hydrogen bond forming moiety resembles the hydrophilic head group. However, the presence of strong hydrogen bonds among the head groups may lead to the directional packing of these molecules which is required by the steric demands. This leads to the growth of the molecular self-assemblies along one direction so as to form fibers or ribbons, as illustrated in Fig. 7. In many cases the steric effect, which might be introduced either in the headgroup portion or in the hydrophobic chains, may further cause the twist of the molecular packing so that helical structures appear. If the pitch of the helical ribbons is small enough, hollow tubes are formed.[6,10] For instance, Shimizu *et al.* have found that upon the introduction of double bonds into the alkyl chain of long-chain sugar-based amphiphiles one may obtain helical structures (Fig. 8).[18] For a series synthetic molecules (1–7) compound 1, which bears a saturated alkyl chain, forms only straight fibers in water. However, upon the introduction of one double bond, helical ribbons appear; with an increasing number of double bonds, the helical pitch changed and long nanotubes were observed. The clear TEM images for the assemblies formed by compound 5 unambiguously demonstrate that tubes are formed by decreasing the helical pitch.

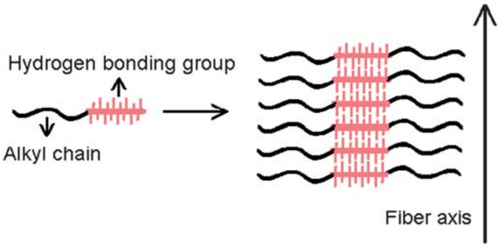

Fig. 7 Illustration of the packing mode of hydrogen bonding amphiphiles and the formation of fibers.

2.2 π–π stacking and electrostatic interaction-governed solution-based self-assemblies

Compared with planar π-conjugated molecules, formed solely by large aromatic groups, proper modification of these molecules allows for the formation of judicious self-assembled structures in organic solvents or water. For solution-based self-assembly, formation of one-dimensional structures requires that the coaxial

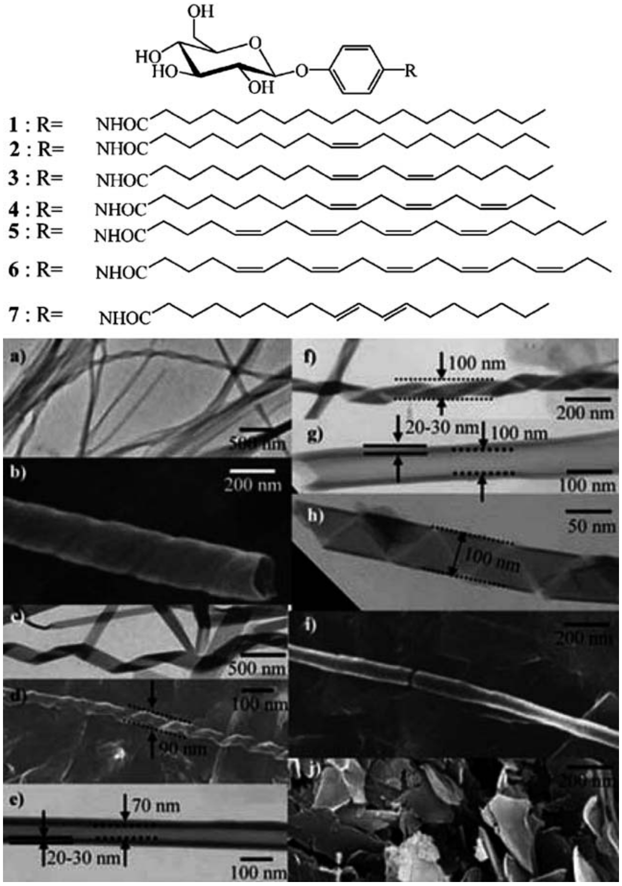

Fig. 8 SEM and TEM images of self-assembled compounds (a) 2, (b and c) 3, (d and e) 4, (f and g) 5, (h and i) 6, and (j) 7. Adapted from ref. 18.

π–π stacking between the conjugated groups must be predominant over the lateral association of attaching groups. Moore's group have synthesized a series of conjugated large ring molecules that were modified by different alkyl chains.[5] They found that the introduction of a carbonyl linkage between the side chains and the planar ring enforces the coplanar packing of the molecules, and thus promotes the formation of fibrilar structures. Variation of the structure of the side chains may decrease the steric hindrance and enhance π–π stacking to form straight fibers. The normal of the planar conjugated groups, which is in line with the stacking direction, is the axis direction of the fibers. In contrast, if charged side chains are introduced, curved self-assembly may occur. In this case, the π–π stacking direction differs significantly with the axis of the one-dimensional nanostructures. A typical example is the recent work in Parquette's group, where one-dimensional n-type nanotubes were formed by the bolaamphiphilic self-assembly of 1,4,5,8-naphthalenetetracarboxylic acid diimide (NDI) with l-lysine headgroups (Fig. 9).[50] Different from the often occurring nanotubes that were formed by the twisting of ribbons, these nanotubes were formed by the packing of nanorings. The π–π stacking occurs in the nanorings, whereas the electrostatic interaction between the edge of the rings connects them along the normal of the rings to form nanotubes.

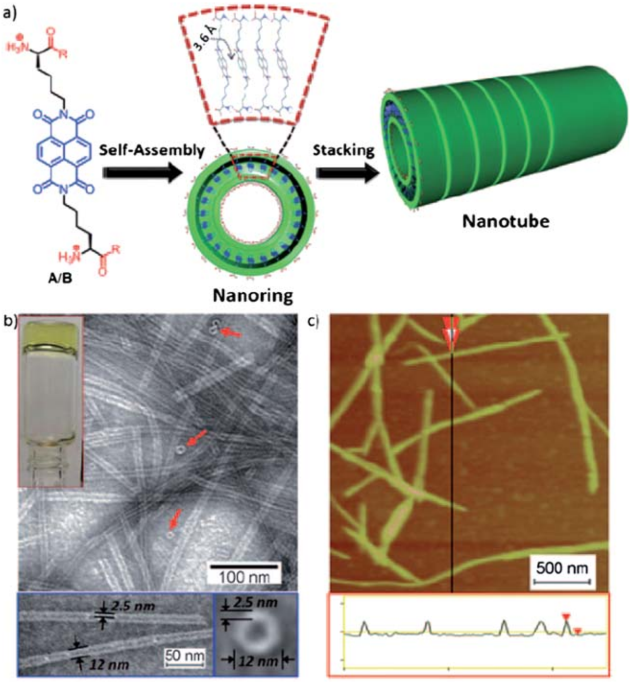

Fig. 9 (a) Structures of lysine-based bolaamphiphiles A (R = O$^-$) and B (R = OMe) and the assembly of A into rings, which stack to give tubes. (b) TEM image of bolaamphiphile A in water (250 mm; carbon-coated copper grid). (c) Tapping-mode AFM image of bolaamphiphile A in water (250 mm) on freshly cleaved mica. Adapted from ref. 51.

2.3 Metal coordination, hydrogen bond, and hydrophobic interaction-governed solution-based self-assemblies

Usually, metal coordination never occurs alone as a driving force for the formation of self-assembled structures. For instance, the helical ribbons formed in calcium-cholate systems are driven by the combination of hydrogen bonds, hydrophobic interactions, and coordination interactions (Fig. 10).[42,43] First of all, FT-IR spectra demonstrate the existence of calcium–carboxyl coordination in a bidentate chelating fashion; when replacing Ca^{2+} with Na^+ or K^+, 1D structures are not observed. Finally, the addition of EDTA is found to destroy the nanostructure. All these results indicate that the calcium–carboxyl coordination plays an indispensable role in the formation of helical structures. Furthermore, hydrogen bonds between the cholate skeleton were confirmed to exist as well in these helical structures. Owing to the intermolecular hydrogen bonds, cholate arranges into unique bilayer strips, which approach together *via* calcium–carboxyl coordination.

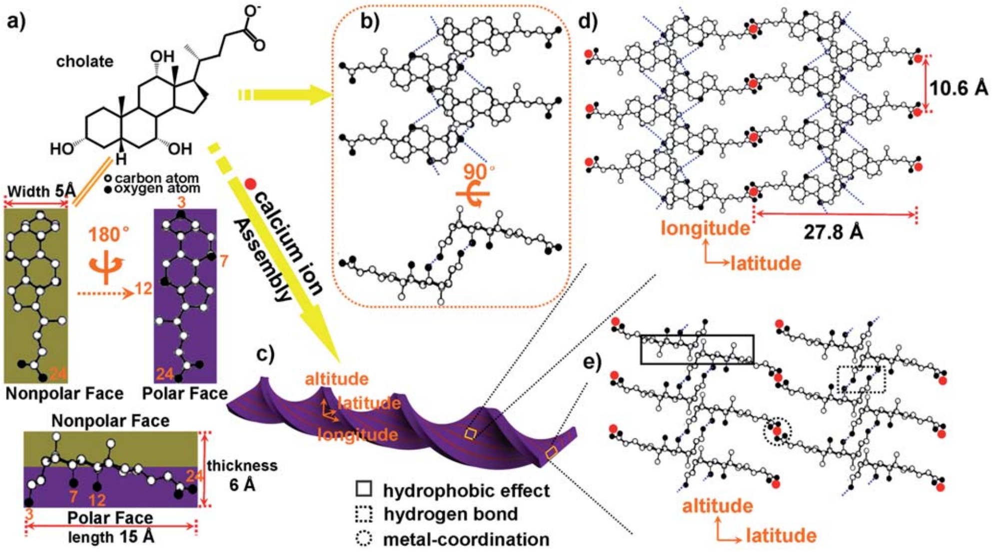

Fig. 10 (a) Molecular structure of cholate, (b) molecular aggregate of a bilayer type of cholate host framework (the blue dotted lines denote H-bonds), (c) twisted nanoribbon, (d) top view, and (e) cross-sectional view of the molecular model. Adapted from ref. 42.

A similar example using the combination of metal coordination, hydrogen bonds, and hydrophobic interactions is the fabrication of nanoribbons in the mixed system of metal ions, bisligands, and polypeptides (Fig. 11). In this mixture, a triblock polypeptide consisted of a positively charged middle block and two charge neutral end blocks. Upon mixing, coordination between the metal and bisligand occurs which produces negatively charged coordination complexes. Once the negatively charged coordination complexes are formed, they combine with the positively charged block of the polypeptide instantaneously and transform into polymeric structures. In this process, the positive charge of one block was neutralized and leads to folding of the peptide which allows the formation of a β-sheet by hydrophobic interaction and hydrogen bond formation.[40,51]

2.4 π–π stacking, hydrogen bond, and hydrophobic interaction-governed solution-based self-assembly

When compared with molecules that have one distinct group, such as a large planar π-conjugated group, long alkyl chain, or a peptide or sugar head, many molecules may not have these typical structures, or, on the contrary, have a combination of these groups. In this case, a single interaction that exists in the molecular assembly may be relatively weak, but all of them might be indispensible. To encode the cooperative contribution of different groups on the molecular self-assembly, we designed an amphiphile C_4AG that was composed of three parts:[52] butyl, azobenzene group, and sugar moiety (Fig. 12). This molecule can self-assemble into double helices in water and form viscoelastic hydrogels. This self-assembly process is so delicate that replacement of any part of these three groups failed to provide one-dimensional self-assembly. First of all, helical nanofibers cannot be observed when the azobenzene group is replaced by a saturated aliphatic chain. It is therefore suggested that π–π stacking of the azobenzene groups was crucial for the formation of one-dimensional helices. Second, when the sugar head was replaced by another hydrophilic group (*i.e.* quarternary-amine, carboxyl, or glycol), the amphiphilies would self-organize into global micelles or vesicles but not one-dimensional architectures. This means that the multiple hydrogen-bonds generated between the sugar heads can guide the orientation of molecules within aggregates. In addition, the multiple hydrogen bonds in the sugar moiety have produced a steric effect that leads to the formation of twisting in the structures. Finally, the butyl chain or longer hydrocarbon chain in the molecule was proved to be essential for the one-dimensional nanostructure, since without it, or with shorter chains, only irregular precipitates are formed. This indicates that the rigid molecules such as C_0AG and C_2AG tend to closely pack *via* π–π stacking, forming precipitates. However, the steric hindrance of the association of hydrophobic butyl or hexyl groups can interfere with the close packing between aromatic groups so that precipitates are avoided. In a later work, we found that if the sugar group was replaced by a dipeptide (C_4AzoGlyGly), straight ribbon like structures were formed.[53] The nanoribbons were formed by the nanofibers aligning in near-lamellar arrays (Fig. 12e).

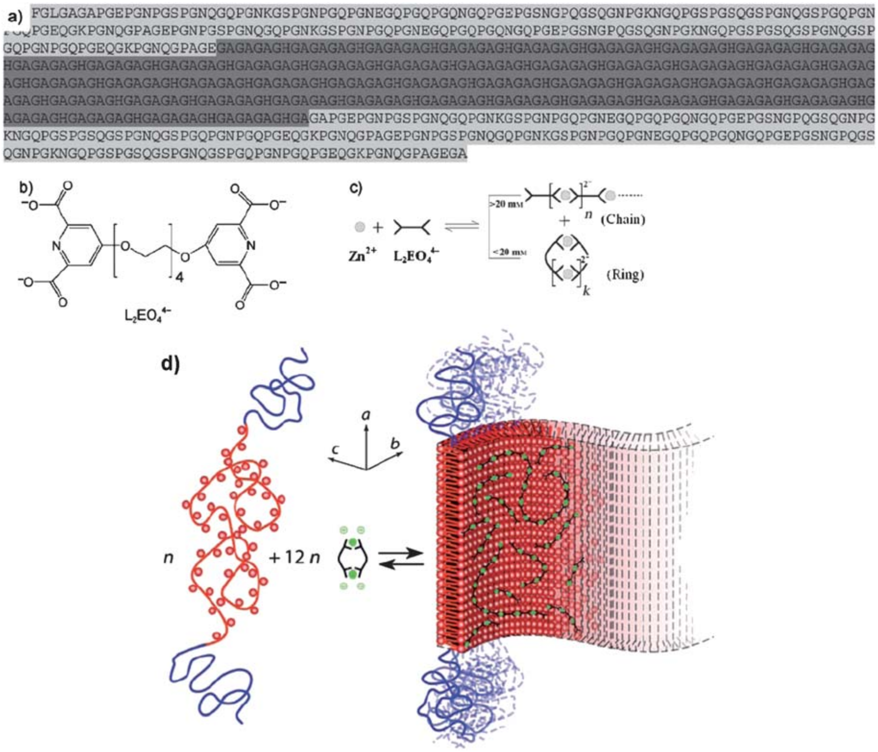

Fig. 11 Ribbon formation in the mixed system of peptide copolymer 1 and ($[Zn–L_2EO_4]^{2-}$)n. (a) Structure of the peptide polymer; (b) structure of the bisligand L_2EO_4; (c) illustration of the structure of the coordination complexes formed between zinc ions and L_2EO_4; (d) demonstration of the ribbon formation in the mixed system of peptide copolymer, zinc ions, and L_2EO_4. Adapted from ref. 40.

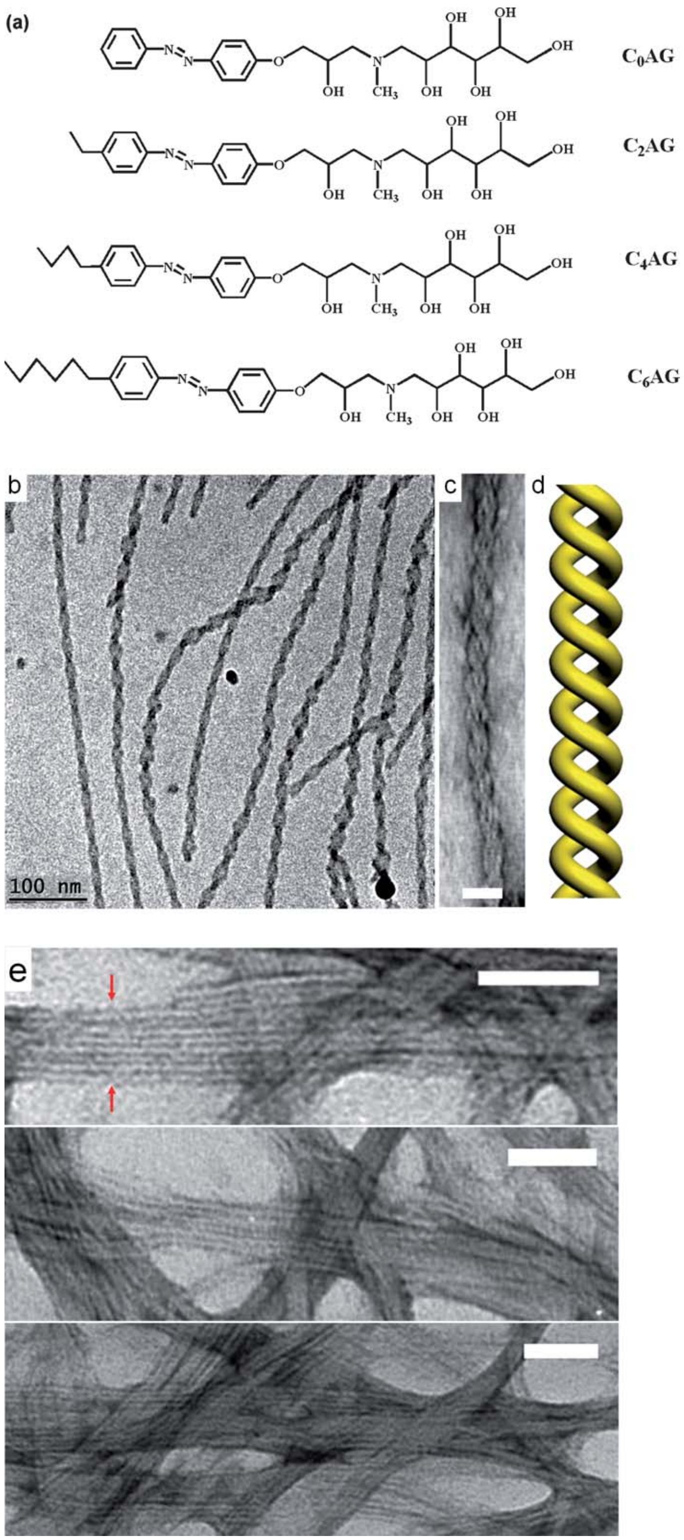

Fig. 12 (a) Molecular structure of C_4AG amphiphile and its analoges; (b) cryo-TEM image of a C_4AG double helix in solution; (c) TEM image of double helix stained with uranyl acetate (scale bar is 50 nm); (d) representative scheme of left-handed double helix; (e) ribbons formed by $C_4AzoGlyGly$ (scale bar is 50 nm). Reproduced from ref. 52 and 53.

3. Tunable elements that affect one-dimensional self-assembly

So far, many one-dimensional soft molecular self-assemblies, especially fibrils, nanobelts or nanoribbons, nanotubes, as well as a variety of helical structures, have been successfully fabricated.[5,6,10,11] Meanwhile, with the purpose of fabrication of well-designed and smart materials, there is a lot of effort aimed at controling the transition of one-dimensional self-assemblies, such as transformations between nanotubes and nanohelixes, straight fibers to twisted ones, one-dimensional to globular ones, decoupling of the double helices, *etc.* In the following we will give a brief overview of the progress in this aspect.

3.1 Photo

Photo-sensitive materials have been of interest in recent studies for the fabrication of responsive materials[54–57] since they may find application conveniently, such as in microvalves or flow sensors within microfluidic devices. In this regard, photo sensitive gels are extremely focused, especially in surfactant systems, where either photo sensitive small molecules were added to surfactant solutions, or a specific group that is sensitive to light irradiation was introduced to the surfactant skeleton.[54–57]

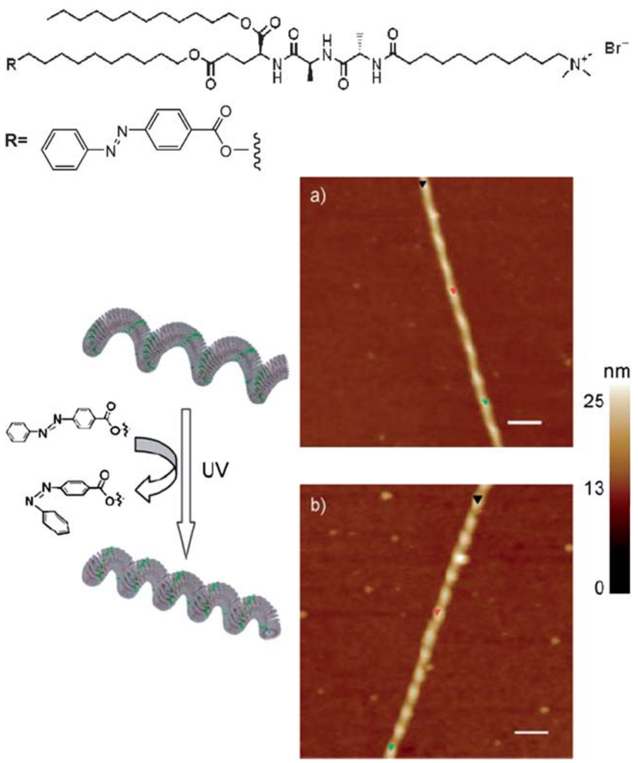

Fig. 13 Upper: Molecular structure of 1; Lower: AFM height images of the fibers: (a) before and (b) after exposure to UV light, respectively. Scale bars: 100 nm. Adapted from ref. 58.

Similarly, photo-sensitive one-dimensional molecular assemblies can also be made. For this purpose, the azobenzene group is often incorporated into the molecular skeleton to obtain such properties. For example, Stupp *et al.* found that upon incorporating an azobenzene group into molecule 1, they could tune the pitch size of the helix (Fig. 13). They found that after the *trans*-to-*cis* isomerization of the azobenzene moiety, a reduction in the pitch of the supramolecular helices from 74 to 47 nm occurred.[58] This is because the *cis* isomer is less planar than the *trans* isomer. The isomerization results in an increase of the sterically induced torque, thus leading to a reduction in the superhelical pitch. It is expected that the effect of isomerization on each supramolecular assembly is different due to the inhomogeneous isomerization degree. This is indeed the case. Our recent work on the self-assembly behavior of C$_4$AG, which contains an azobenzene group as well, as illustrated in Fig. 13, demonstrated that the *trans*–*cis* isomerization can lead to transformation from double helical structures into globular micelles (Fig. 14).[34]

3.2 pH

The study of molecular self-assembly, to a large extent, is inspired by biomolecules, therefore, pH effects that mimic biological events have been one of the main challenges in investigating molecular self-assembly. To this end, pH tunable one-dimensional self-assemblies are fabricated. This requires that the molecules contain pH responsive groups, such as peptides, carbonate groups, *etc.* Deng *et al.* found that peptide amphiphile, C12–Aβ(11–17), forms fibrils at pH 3, whereas nanoribbons are formed at pH 10 (Fig. 15).[59] Such a transition is attributed to the formation of β-sheets at pH 10. Actually, peptide or amino acid containing systems are all responsive to pH. For this readers can refer to a review article by Löwik *et al.*[11]

Zhang's group reported another type of interesting pH tunable one dimensional self-assembled system, namely, the charge transfer complex formed between a viologen-containing amphiphile (RV) and a pyrene derivative PYR, which is the pH sensitive molecule in the system.[60] The equivalent mixture of the above two components forms flexible nanofibers in pH = 9 buffer; these flexible ones become very stiff at pH 10 (Fig. 16). Such a pH dependence is ascribed to the increased repulsion at the surface of the assemblies so that the curly nanofibers are transformed into straight ones, like the conformation difference

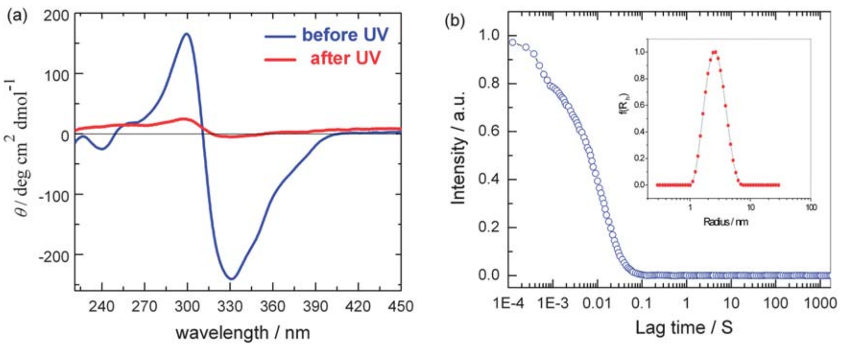

Fig. 14 (a) CD spectrum of C$_4$AG molecule in aqueous solution before and after UV irradiation; (b) dynamic light scattering of C$_4$AG solution after UV irradiation, which indicates the existence of small micelles. Adapted from ref. 52.

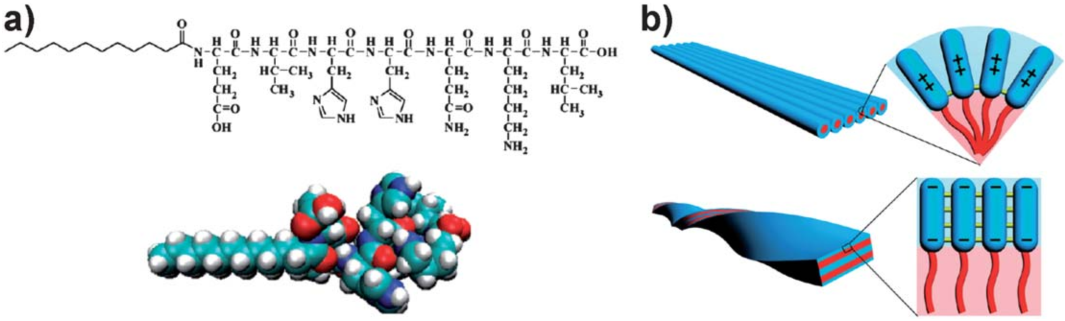

Fig. 15 (a) Chemical structure and space-filling model of peptide–amphiphile C12-Aβ(11–17), with a peptide sequence of EVHHQKL from N- to C-terminal. (b) Schematic illustration of the intermolecular interaction within the C12-Aβ(11–17) self-assemblies at pH 3.0 (top) and pH 10.0 (bottom). Yellow dashes represent hydrogen bonds. Adapted from ref. 59.

between a neutral polymer coil and a stretched polyelectrolyte chain.

3.3 Concentration

Concentration dependence of self-assembled structures often occurs in surfactant systems, where one may expect a transition from spherical micelles to rod-like ones, then to lamellar structures that pack into liquid crystals at very high concentrations.[61,62] In rare cases larger self-assemblies are formed before the occurrence of micelles.[63] It is interesting that for some one-dimensional self-assemblies, concentration dependence of the morphology also exists. For instance, we found that the annular ring-like nanotubes formed by the inclusion complexes of CD and surfactants at high concentrations may change into vesicles upon dilution.[21,22] Previously, Song[28] and Yan[64] *et al.* found that nanotubes that formed by dipeptide molecules can transform into vesicles upon dilution. It seems that at given conditions, the increased concentration which directly leads to an increase in the aggregation number will impart geometrical constraints that energetically favor the formation of larger aggregates. In some cases, it is hard to explain the concentration effect: for instance, Pagel *et al.* found that increasing the concentration of peptide VW19 promoted a conformational transformation that led to the transition from random coil to helically twisted β-sheet ribbons.[65] These results suggest that the effect of concentration cannot be neglected in one-dimensional self-assembled systems, whereas it is still not clear what effect may occur before solid experimental results are provided.

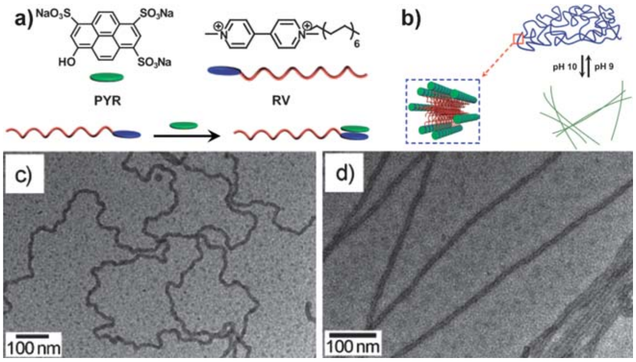

Fig. 16 (a) Structure of PYR, RV, and illustration of the complex formation between them; (b) schematic illustration of the flexible and straight fiber formation; (c) TEM image PYR–RV in pH 9 buffer solution; (d) TEM image of PYR–RV in pH 10 buffer solution. The concentration of RV is 1 × 10⁻⁴ m in each case. Adapted from ref. 60.

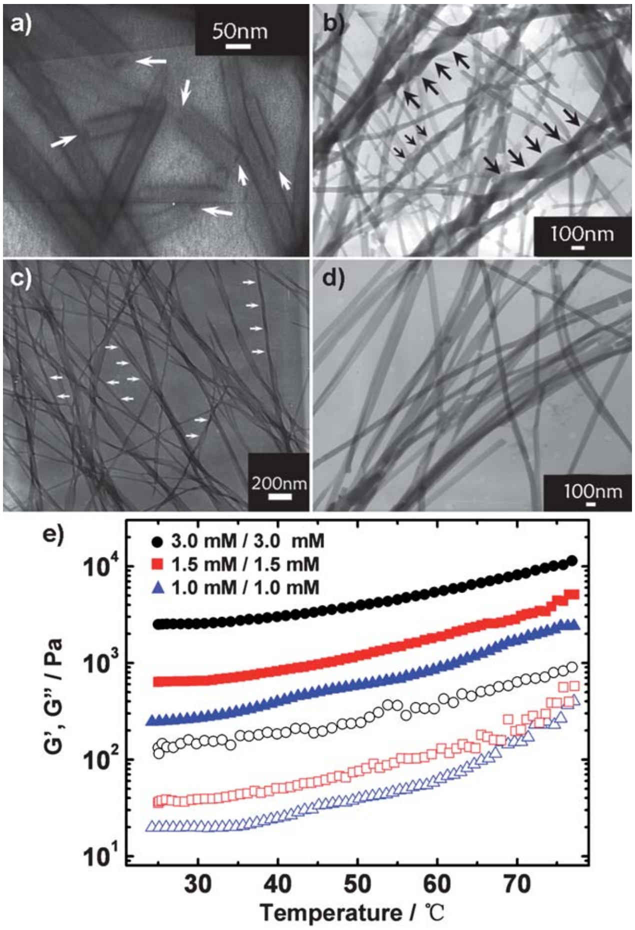

Fig. 17 (a–d) The self-assembled structures in lanthanum-cholate systems at different temperatures: from a to d: 4, 15, 25, 50 °C. (e) Temperature-sweep oscillation rheology of lanthanum cholate hydrogel at concentrations of 3 mM/3 mM (black circle), 1.5 mM/1.5 mM (red square), 1.0 mM/1.0 mM (blue triangle) of lanthanum/cholate supramolecular hydrogels. The solid symbols are G′; and the open symbols, G″. Adapted from ref. 43.

3.4 Temperature

Temperature has long been used as a convenient tool to control molecular self-assembly by utilizing the temperature sensitive phase and conformational transition of relating molecules. In practice, NIPAM (*N*-isopropyl acrylamide),[66,67] and EO (ethyleneoxide)[67] groups are often designed to be temperature sensitive units in molecular assembly. In this way, thermo-responsive micellization can be easily realized. In addition, the hydrogen bonding and hydrophobic effect are also affected by temperature. Therefore, temperature can be used to control one-dimensional soft molecular assembly as well where these interactions are present. This was indeed observed in a lanthanum-cholate supramolecular system.[43] We observed the development from nanotubes to coiled-coil helical ropes to twisted nanoribbons, and finally to nanoribbons as the temperature increased (Fig. 17a–d). In this process, the diameter of the one-dimensional self-assembly is significantly increased. This effect was supposed to arise from a change of hydration state of the hydroxyl groups of cholate molecules. The hydroxyl groups of the cholate molecules can interact with water *via* hydrogen bonds, which contribute to cholate's hydrophilicity. When the temperature is raised, the hydrogen bonds between water and cholate are weakened, leading to lower hydrophilicity, which favors the formation of larger assemblies.[43] Interestingly, the increased size of the one-dimensional self-assembled structures significantly promotes the strength of the hydrogels formed by them. As demonstrated in Fig. 17e, the shear modulus can be increased by nearly one order of magnitude as the temperature changes from 20–80 °C.

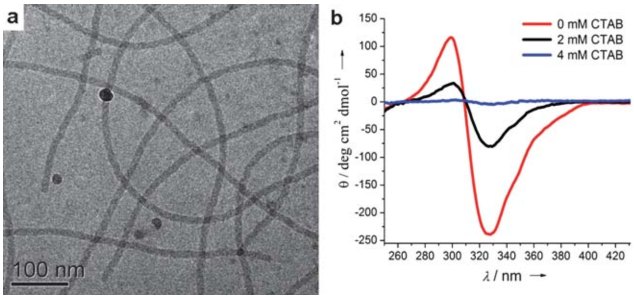

Fig. 18 (a) Cryo-TEM image of $C_4AG/CTAB$ in solution (5 mM/2 mM); (b) circular dichroism of C_4AG in solution (5 mM) with the addition of cationic surfactant CTAB. ($T = 25$ °C). Adapted from ref. 53.

3.5 Additives

Addition of appropriate additives to amphiphilic systems often triggers a change of the interaction between molecules which can lead to a transition of the molecular self-assembly. For instance, addition of trace amount of toluene may result in the transformation of vesicles into lamellar structures;[68] introducing a proper amount of ionic charges to the C14DMAO lamellar phases resulted in the bending of planar lamellae and led to the formation of vesicles.[69,70] Recently, we found that double helical structures formed by C4AG (Fig. 12b) can be decoupled simply

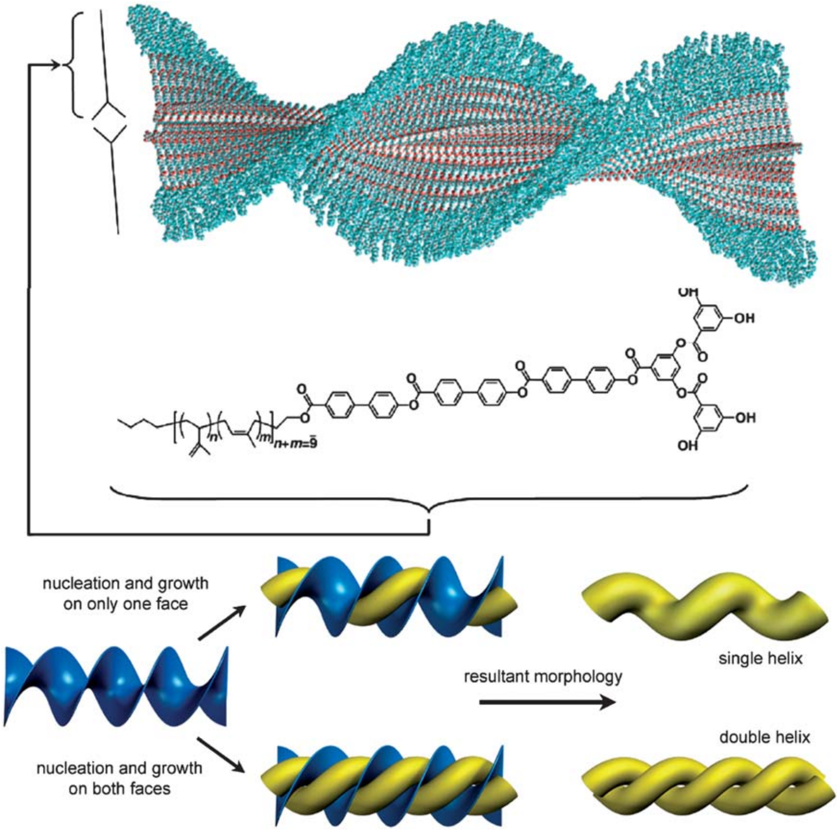

Fig. 19 Illustration of the formation of single and double helix CdS using helical structures formed by DRC molecules. Adapted from ref. 72.

by introducing ionic charges to the system to produce enough repulsion between the two helices (Fig. 18).[53] Such a repulsive force can be produced either by charging the ionizable group by increasing pH, or by the addition of charged surfactant, such as SDS, DTAB, CTAB to the double helices.[53]

4. Applications of one-dimensional self-assemblies for the fabrication of one-dimensional hard materials

One of the primary goals of creating one-dimensional soft supramolecular assemblies is for the template-synthesis of

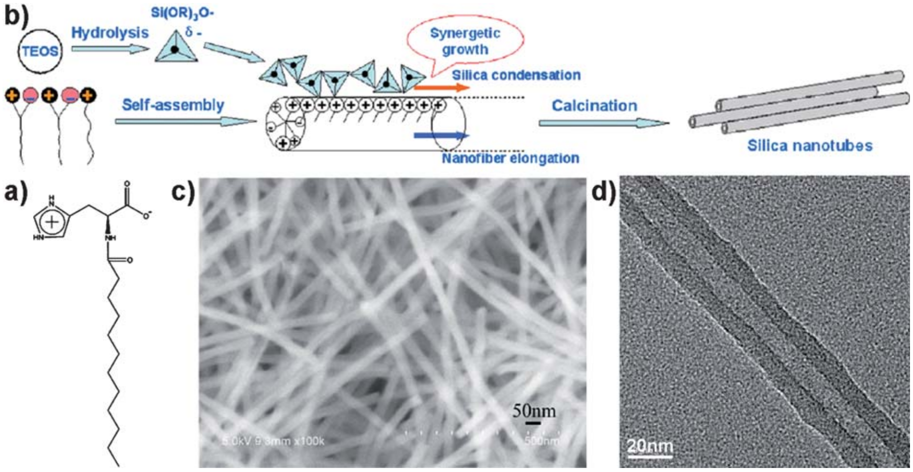

Fig. 20 (a) Structure of DHis. (b) Illustration of the templating effect of DHis/DTEAB fibers on SiO_2 nanotube formation. (c) SEM image of silica nanotubes after calcination. (d) HRTEM image of silica nanotubes after calcination. Adapted from ref. 73.

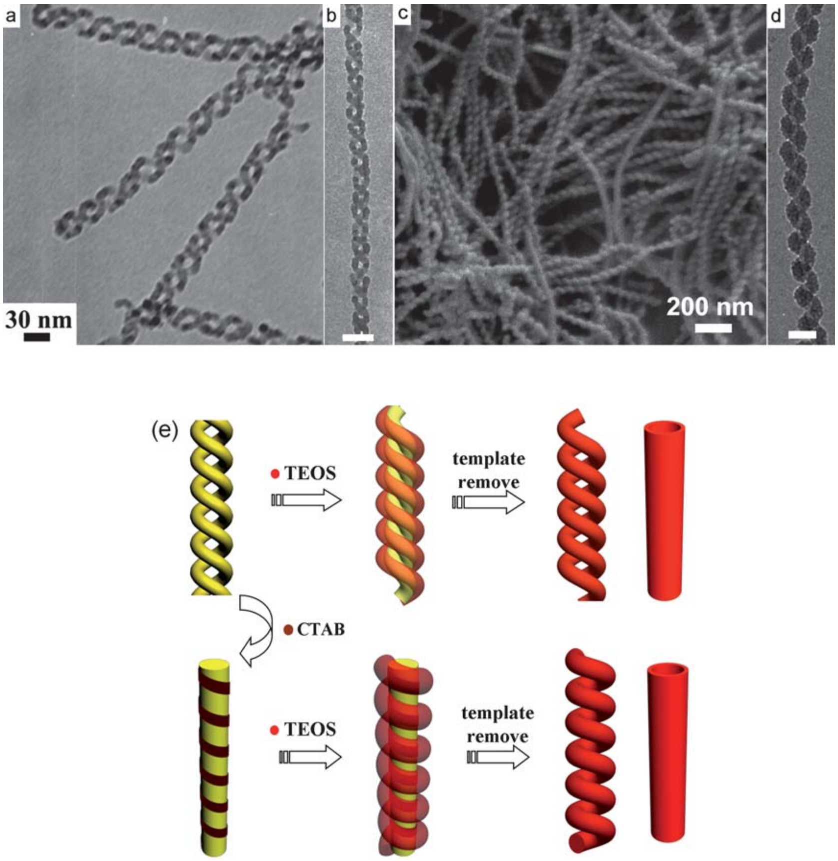

Fig. 21 (a, b) TEM images of double helical SiO_2 templated from C_4AG solution ($C_4AG/TEOS/NH_3 = 1 : 9 : 4$, pH = 10.52); (c, d) single-stranded silica helix prepared from $C_4AG/CTAB$ solution by sol–gel transcription: ($C_4AG/CTAB/TEOS/NH_3 = 1 : 0.4 : 9 : 0.8$, pH = 9.29); (e) possible scheme of helical SiO_2 nanomaterials in the system of $C_4AG/CTAB$. The brown ribbon on the $C_4AG/CTAB$ fiber gives a proposed location of CTAB, which can not be observed under TEM. Adapted from ref. 74.

one-dimensional hard materials since these materials are found to have great potential in optical materials due to their specific surface effect. So far, there are some nice examples that utilize this method to produce interesting one-dimensional hard nanomaterials. Depending on the individual molecular structure that is composed of the one-dimensional self-assemblies, one may obtain hard materials *via* different approaches.

4.1 Uptake of reacting ions by surface groups

In most cases, the one-dimensional self-assemblies themselves do not contain the elements that are required for hard materials, such as silica, metal ions, *etc.* However, these elements may be taken up by the surface of these self-assembled structures *via* proper interaction. For instance, the presence of ligand groups may allow coordination of metal ions to the soft one-dimensional structures. In this way Stupp *et al.* have successfully fabricated single and double helical CdS nanowires by using the helical structures formed by DRC (dendron-rod-coil) molecules.[71,72] In their strategy, one row of Cd^{2+} ions can be incorporated into a bilayer of helical ribbons of DRC molecules, where the heads of the DRC molecules function as ligand groups. Upon introducing H_2S gas to the system, CdS nanowires that inherit the helical structure of the DRC self-assemblies were formed (Fig. 19).

Electrostatic force is also an often used interaction to produce hard materials which is commonly used in the fabrication of SiO_2 nanotubes. For instance, in a catanionic surfactant hydrogel system formed by DHis (Fig. 20a) and DTEAB (dodecyl trimethyl bromide),[73] introducing of TEOS allows for the simultaneous growth of nanofibers with the surface covered by silica species (Fig. 20b); upon calcination, SiO_2 nanotubes that possess a similar inner radius with the soft template were produced (Fig. 20c, d). Similarly, hydrogen bonding can be used as well in the fabrication of SiO_2 nanomaterials. When TEOS is used as the source of silica, hydrogen bond formation is possible between TEOS and the sugar based surfactant, like C_4AG, for example, mentioned previously. In this way, TEOS was effectively adsorbed to the surface of the double helices formed by C_4AG, which allows for the formation of delicate double helical SiO_2 nanotubes (Fig. 21a, c).[74] Interestingly, upon decoupling the double helices by addition of CTAB to the C_4AG system, single helical SiO_2 nanotubes can be obtained as well (Fig. 21b). In the later

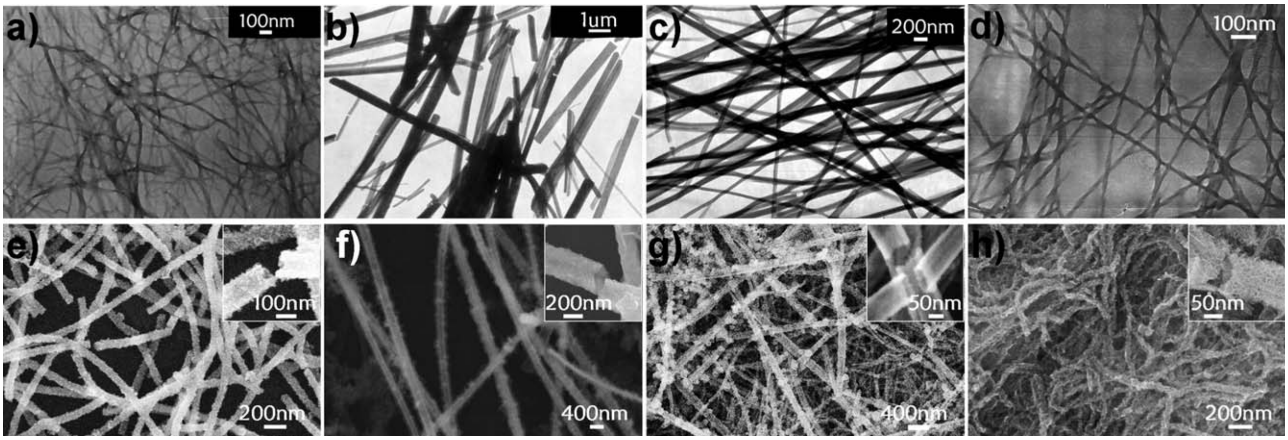

Fig. 22 Nanofibers in the system of: (a) Cu-cholate; (b) Ni-cholate; (c) Cd-cholate; (d) Co-cholate at 25 °C. Metal sulfide nanotubes prepared *via* a self-templating strategy: (e) CuS; (f) NiS; (g) CdS; (h) CoS. Adapted from ref. 75.

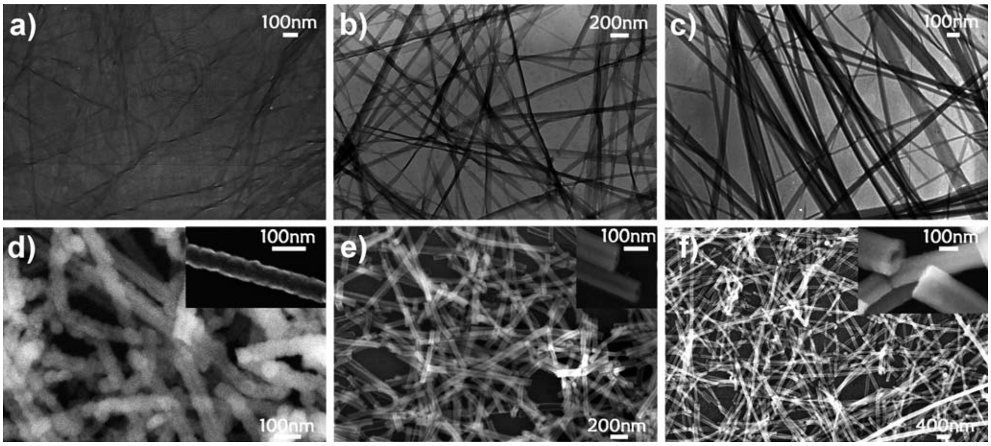

Fig. 23 Zinc-cholate supramolecular nanofibers incubated at 20 °C for: (a) 3 h; (b) 12 h; (c) 24 h. As prepared ZnS nanotubes with different incubation times: (d) 3 h; (e) 12 h; (f) 24 h. Adapted from ref. 75.

case, the silica source might be adsorbed to the single helical C_4AG template by electrostatic force between the positively charged CTAB (Fig. 21d).[74]

4.2 Self-templating

For one-dimensional self-assembled structures that form by metal coordination, the metal ions inside the assembly may directly act as both the precursor for target inorganic materials and constituent of the template. In this way, a self-templating protocol is possible to transcript the soft supramolecular structures to hard materials without additional precursors which may change the solution conditions and interfere with the soft templates. This is demonstrated by recent studies in our lab. In the metal-cholate systems, where helical and fiber structures were formed when zinc, copper, nickel, cobalt, and cadmium were used as the metal source to fabricate fibers, corresponding chalcogenide materials can be easily obtained by introducing proper chalcogenide sources, such as Na_2S, thioacetamide, Na_2Se, Na_2Te to the system (Fig. 22).[75] Moreover, the structural diversity and dynamic nature of organic architectures allow the preparation of size and shape-adjustable 1D nanotubes through conveniently temporal and thermal controls (Fig. 23). This was proved to be a general approach to fabricate one-dimensional inorganic materials where the morphology of soft templates can be fully retained and transcribed into as-synthesized inorganic nanomaterials.

5. Conclusions and perspectives

Construction of one-dimensional soft supramolecular nanostructures is an attractive topic in the field of molecular self-assembly, since these structures posses great potential for aligning elements either inside themselves or in their surroundings. So far, researchers have fabricated numerous one-dimensional soft nanostructures. The examples given in this review cover only a small fraction of them and aims to encode the forces that lead to these structures. However, as discussed in the text, this could be very complicated, and is actually system dependent. In each specific system, one may utilize only one dominant force that endows the system with the desired properties. For instance, planar π-conjugated systems may be used for studying intermolecular electronic delocalization, producing one-dimensional organized materials with efficient exciton diffusion and charge transport. Peptide and sugars may be helpful to understand phenomena in biology, such as the function of fibrils in the structural and signaling machinery of extracellular matrices, the cellular cytoskeleton, axons, dendrites, and many others. Introduction of metal ions to the system may conveniently produce half precursor for fabricating inorganic materials, which sometimes might be much easier than aligning molecules on the surface of these structures.

As for the one-dimensional structures in future studies, it is a challenging topic to map out the strategies that may achieve dimensional and shape precision of these structures. For instance, it's often that single nanoribbons were observed at low concentrations, whereas they associated into bundles spontaneously at much higher concentrations. What is the limit of the bundling? In nature, triple-helical bundles of collagen are very common in biosystems, but these bundles may behave a wide variety of different functions although they are made from a single type of nanounit. What is the machinery behind this? In addition, with the desire of fabricating smart molecular devices, highly tunable and adaptable one-dimensional assemblies with respect to structure, geometry, size, and redox properties are also expected. The examples given in this review only represent some initial trials in this field. We expect that upon proper molecular design, smart organic molecular devices of one-dimensional soft nanostructures may be produced. All these problems to be solved will be very crucial for understanding and improving the fundamental process in one-dimensional self-assembly.

Acknowledgements

This research was supported by National Natural Science Foundation of China (20903005, 21073006, 20873001, and 50821061); SRF for ROCS, SEM; and New Century Training Programme Foundation for the Talents by the State Education Commission.

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