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ARTICLE

Dendronized Supramolecular Polymers

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Supramolecular polymers formed from topological building blocks pave a new avenue for creating novel supramolecular structures and functional materials. Dendronized supramolecular polymers (DSPs) combine the topological characteristics of dendronized polymers and dynamic nature from supramolecular chemistry, and are promising in forming supramolecular structures and functional assemblies. These topological supramolecular polymers are characteristic in cylindrical shape, high rigidity, multivalency, as well as the inherent thickness. These structural characteristics make them idea candidates for supramolecular assembly. DSPs can be formed through non-covalent interactions, such as hydrogen bonding, π-π stacking, and metal coordination, and classified into main-chain, side-chain and block types. This feature article will summarize methodologies for the preparation of homo- and block DSPs with a focus on their supramolecular structure formation. A particular attention is put on structural effects from DSPs on their supramolecular assembly.

1. Introduction

Supramolecular polymers formed from monomeric building blocks of various architectures have received considerable attention in last decades.[1-3] Various types of topological building blocks, such as linear, block, cyclic, star, discotic and dendritic ones, have been elegantly designed and applied for the construction of topological supramolecular polymers.[4-10] The permanent interest in topological supramolecular polymers relies on their ability in creating ordered supramolecular structures and affording promising functional properties, which are not only dependent on the dynamic characteristics from noncovalent interactions, but also governed by the topological structures of the building blocks.[11-13] For example, peptide amphiphilic segments can self-assemble cooperatively into ordered filamentous supramolecular polymers with intriguing bioactive properties based on their heterogeneity and phase separation.[14,15] Discotic molecules with rigid planar cores and flexible side chains tend to aggregate axially to form one-dimensional ordered nano-structured polymers in solutions or in bulk through π-π stacking or hydrogen bonding, which leads to chiral amplification or affords semiconducting properties.[16,17] Star-polymers as building blocks for supramolecular assembly lead to the formation of hydrogels with improved properties. For example, reactions between hydrophilic and thermoresponsive star-polymers afforded non-swellable hydrogels through synergistically swelling and shrinking of different components after injection.[18] The hydrogels endure a compressive stress up to 60 megapascals, and can be stretched more than sevenfold without mechanical hysteresis. Dendritic molecules as building blocks possess distinguished structural features, such as highly branched and compact geometry, as well as multivalent functional groups, and have received considerable attention recently for supramolecular assembly in different length scales.[19-21] For example, amphiphilic hyperbranched copolymers bearing linear arms can self-assemble into macroscopic tubes in selective solvents.[22] Telechelic dendritic macromolecules carrying guanidinium pendants on the peripheries were found to bind strongly to clay nano-sheets through multiple ionic interactions, leading to the formation of supramolecular hydrogels with outstanding mechanical properties.[23] Therefore, through consciously tailoring the topological structures of building blocks, morphologies and properties of supramolecular polymers can be finely controlled and tuned.

Dendronized polymers are conventionally formed through attaching dendrons densely along a linear polymer main chain,[24-26] and most of them were prepared with covalent linkages through macromonomer, "graft-to" and "graft-from" strategies.[27-29] With increase of dendron generation, these polymers show reduced flexibility as wormlike nano-objects, and in some extremely cases, may attain constrained and stretched conformations. At the same time, the corporation of dendrons with the linear polymer backbone affords these polymers tunable thickness, which is dominated by dendron generation. Furthermore, these polymers are capable of having multivalency functional groups in the interior or/and on periphery, dependent on the dendron structures. These major structural features make dendronized polymers unique candidates for self-assembly to achieve versatile ordered structures.[30] The cylindrical wormlike morphology of these polymers is important to shield interior structures with the

peripheral units.[31-33] For example, thermoresponsiveness of oligoethylene glycol (OEG)-based dendronized polymers is dominated by the peripheral units, irrespective of hydrophobic or hydrophilic interiors.[34-36] Their thickness has been proven to be responsible for the unprecedented thermoresponsiveness of these dendronized representatives and the heterogeneous dehydrations,[37-38] and can mediate transition of guest molecules during the thermally-induced aggregation processes.[39-42] The shielding effects from dendritic components also work nicely in dendronized polyfluorenes.[43,44] Poly(benzyl ether) dendrons along the main chain reduced aggregation/excimers of the conjugated polyfluorene backbones both in solution and in bulk, which improved the luminescence properties of the polymers. In addition, positively charged third- and fourth-generation dendronized polystyrenes were found to spontaneously form networks in aqueous media whereby the net segments comprise of loosely braided double helices.[45] Here, thickness of dendronized polymers endowed the homopolymers amphiphilic characteristics to phase separate perpendicularly. Polymers' thickness also offers propensity for second-generation 4-aminoproline or lysine-based chiral dendrons to orient helically around a flexible polymethacrylate main chain, irrespective of the backbone's tacticity.[46-48] Dendronized polymers carrying crown ether branching units can be stretched upon complexation with potassium ion.[49] The multivalency of dendronized polymers makes it possible for these flexible polymers carrying donor or acceptor pendants to complex efficiently through donor-acceptor interactions, leading to co-assemble in bulk into supramolecular nanometer-scale helical columns.[50] These columns contains in their cores π-stacks of donors, acceptors or donor-acceptor complexes exhibiting high charge carrier mobilities.

Despite the significant progress in synthetic strategies for dendronized polymers, the tedious synthetic procedure remains a major drawback for this promising class of polymers. In contrast, combination of dendronized polymers and supramolecular chemistry leads to the formation of dendronized supramolecular polymers (DSPs), where less synthetic effort will be necessary for their preparation. In this feature article, DSPs are referred to the class of topological supramolecular polymers which are formed from dendron-based motifs through non-covalent interactions. DSPs inherit structural characteristics from their parent dendronized and supramolecular polymers, and possess outstanding features of (1) cylindrical topology, (2) thickness, (3) multivalency, as well as (4) dynamic structures. Therefore, they are promising candidates for forming new level ordered and functional supramolecular assemblies. Report on formation of DSPs can be dated back to the early 2002. Positively charged dendronized polymers of different generations complexed with DNA, resulting in wrapping of smaller charge density DNA around the more highly charged dendronized polymers, where the interplay between the electrostatic energy and elastic energy was proposed to define both the overall charge of the complex and the different helical pitch sizes for the wrapped DNA.[51] Up to now, numerous types of DSPs have been

reported via various strategies, and their supramolecular assembly as well as their functional properties investigated. DSPs can be mainly divided into main-chain, side-chain, and block types. Their fabrication can be performed through non-covalent linkages, including hydrogen bonding, metal coordination, π-π stack, acid-base (ionic) interactions, and host-guest inclusions. The cartoon presentation for construction of DSPs is shown in Fig. 1. In this feature article, we will mainly outline supramolecular formation of DSPs, their assembly morphologies, as well as the promising functional properties of the assembled structures.
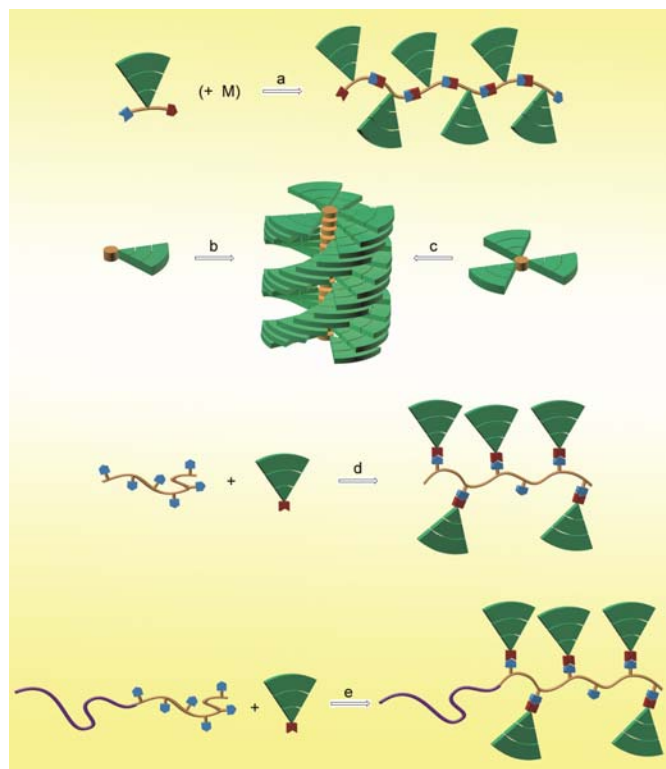

Fig.1 Cartoon presentation of different synthetic strategies for DSPs: (a) Main chain DSPs formed through dendritic macromonomers with or without metal (M) coordination, (b) main chain DSPs formed via one-dimensional assembly of dendritic components, (c) main chain DSPs formed through one-dimensional stacking of C_3 molecules, (d) side chain DSPs formed through interactions of linear polymer with dendrons, and (e) dendronized supramolecular block copolymers (DSBCs) formed through interactions of linear block copolymer with dendrons.

2. Main-chain dendronized supramolecular homopolymers

Through interactions of dendritic macromonomers bearing supramolecular motifs at their cores, main-chain type of DSPs can be formed. Hydrogen bonding, metal coordination, π-π stacking and solvophobic interactions have been reported to efficiently form main-chain DSPs with various architectures.

2.1 Hydrogen bonding

Hydrogen bonding-mediated self-assembly has been proven to be a powerful strategy for the formation of ordered structures

from smaller subunits. Through self-complementary motifs with multiple hydrogen-bonding units, the relatively weak hydrogen bonding can be strengthened to give more stable assemblies.[52] Therefore, dendrons cored with 2-ureido-4-pyrimidinoned (UPy) quadruple hydrogen-bonding unit[53-55] were reported by several different groups for supramolecular assembly (via route a in Fig. 1), and molecular structures of several representatives are shown in Fig. 2. Their self-assembly efficiency to form DSPs is dependent on both polarity and steric hindrance from the dendrons. When non-polar aliphatic dendrons were used (1-3 in Fig. 2a), the binding strength from UPy motifs was enhanced significantly, and DSPs with high polymerization degrees were achieved.[56] The solubility of DSPs increased with dendron generations, indicating the enhanced shielding effect of the dendrons to the hydrogen bonding. Increase of monomer concentrations led to nonlinearly increase of associative interactions between monomers, which could cause stacking of individual DSP chains to form J-aggregates.
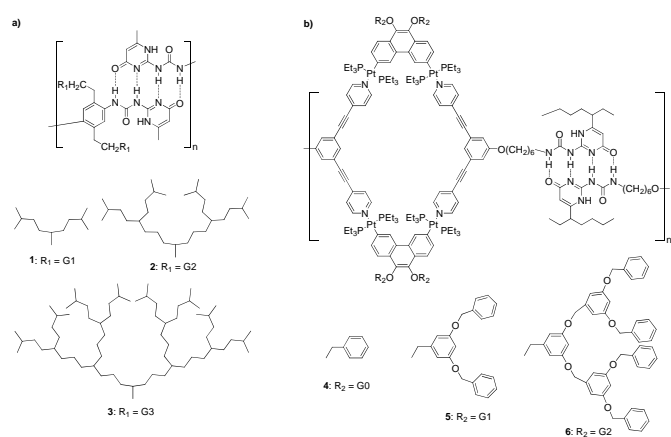

Fig.2 UPy mediated supramolecular polymerization to DSPs.

Combination of metal coordination and hydrogen bonding has also been proven to be efficient for the hierarchical formation of DSPs with ordered structures. Upon mixing a donor decorated with UPy moiety and acceptors pendanted with G0–G2 dendrons, rhomboidal metallacycles were first formed (Fig. 2b), followed with subsequently polymerization into dendronized metallacyclic polymers 4-6 through hydrogen bonding (Fig. 3a).[57] TEM results proved G2 metallacycle self-assembled into worm-like single polymeric chain with thickness in the range of 6 nm, which subsequently aggregated in CH_2Cl_2 to fiber bundles (Fig. 3b & 3c). However, the same species maintained a monomeric nature in DMSO, where intermolecular hydrogen bonding was believed to be disrupted by the polar solvent.

Hydrogen bonding interactions within constrained environments have been proven to efficiently mediate high level supramolecular assembling. For example, dendronization of dipeptides led to the formation of hierarchical assembly in solutions or in bulk (route b in Fig. 1). When G2-G3 poly(benzyl ether) dendrons 7-8 cored with the dipeptides Boc-Tyr-Ala-OMe or Boc-Tyr-Ala-OH (Fig. 4a) were dissolved in
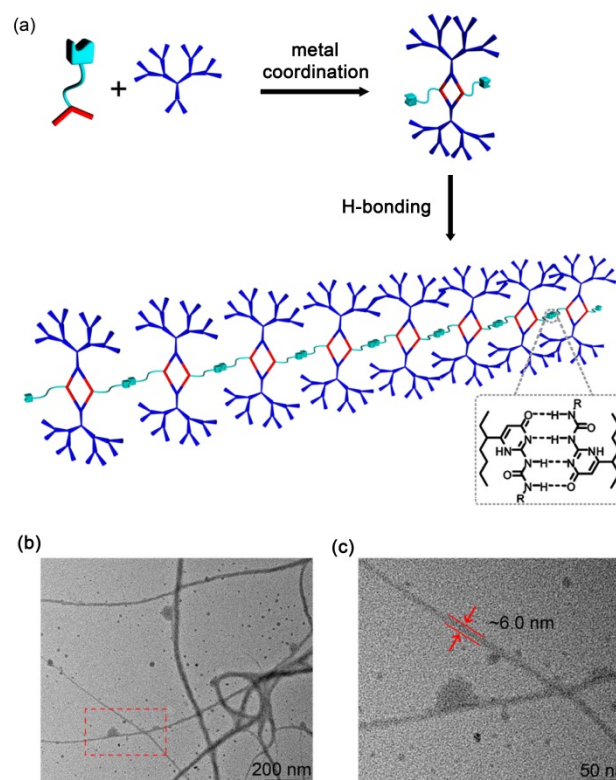

Fig. 3 Cartoon presentation for DSPs formation through combination of metal coordination and multiple hydrogen-bonding (a), TEM image of nanofibers formed in dichloromethane from 6 (b) and the enlarged image (c). Reprinted with permission from ref. 57. Copyright 2013 American Chemical Society.

solvents like acetonitrile, acetone, ethyl acetate, chloroform, or benzene, they formed fibril gels in a helical manner. This gelation was found to be dependent on solvent type, concentration, as well as dendron generations. With increase of dendron generation, gelation tendency was enhanced, which indicates shielding effects from the dendritic wedge is prerequisite for the hierarchical assembly. The driving force for assembly was proposed to be the hydrogen bonding from the peptide motifs, since addition of small amount of polar solvent like DMSO or presence of inorganic salt like LiCl prohibited the gelation.[58] Similar amphiphilic dendritic dipeptides 9-16 (Fig. 4b) were found to self-assemble in solutions or in bulk into helical porous supramolecular columns (Fig. 4c) through recognitions.[59] These recognitions are sufficiently robust to tolerate a range of modifications to the amphiphilic structures. The self-assembled conformation was mediated by a solvophobic effect in solution or by the micro-segregation of the aliphatic and aromatic parts of the dendrons in solid state.[60] The stereochemistry of the peptides determined the sense of the helical pores.[61] Even the protection group of peptide played a role in controlling the assembly.[62] Notably, the assembled pores could be stabilized through enhanced π-stacking interactions on the periphery, which are functional for proton and water transportation.[63]

a)

7: R4 = G2

8: R4 = G3

R3 = H, CH3

b)

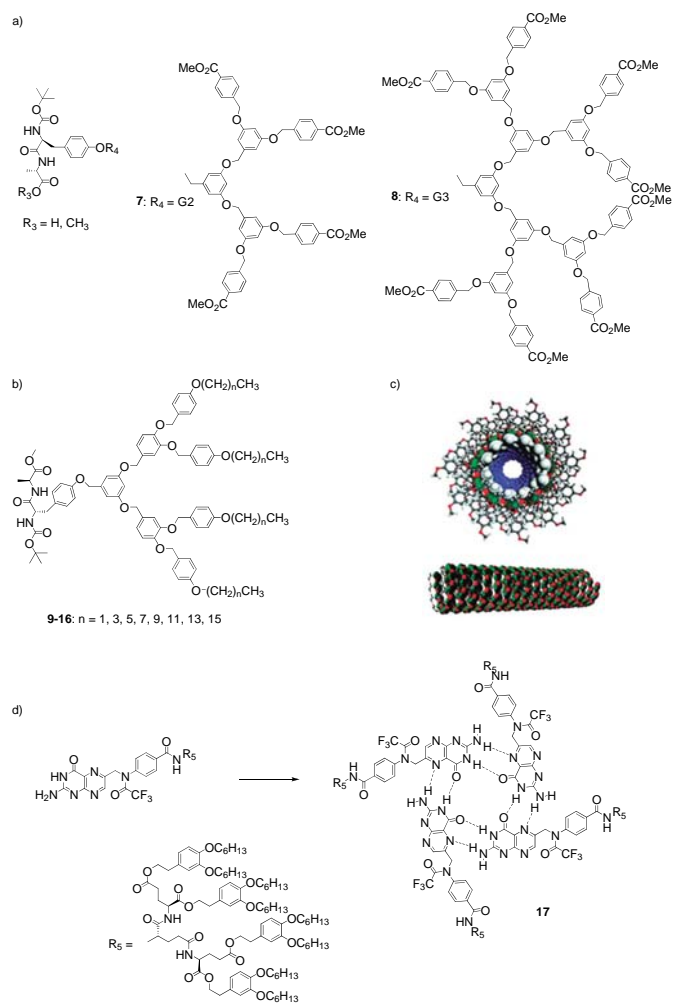9-16: n = 1, 3, 5, 7, 9, 11, 13, 15

c)

d)

17

Fig. 4 (a) Molecular structures of Frèchet-type dendronized dipeptides **7** and **8**. (b) Molecular structures of Percec-type dendronized dipeptides **9-16**. (c) Top and side views of the supramolecular helical pores form from self-assembly of **9-16**. Reprinted with permission from ref. 30. Copyright 2008 American Chemical Society. (d) Molecular structure of chiral dendron bearing UPy at its focal point, which preorganized into tetramer before supramolecular polymerization.

Alternatively, dendritic shielding effect on the self-assembly mediated by hydrogen bonding was also verified for fan-shaped molecules in the formation of DSPs. Dendronized molecules carrying H-bonding amide groups in proximity to their polar aromatic core self-assembled in bulk into columnar geometry with spontaneous polarization along the columnar axis (route b in Fig. 1).[64] When a polar amide dendron was used, dendritic building blocks bearing a focal pyrene moiety self-assembled in aqueous media into vesicles, which could be reversibly transformed into nanotubes through inclusion of pyrene moieties with α- or β-cyclodextrins.[65] Through intermolecular hydrogen bonding driven cyclization of G2 dendronized folic acids into the disklike tetramers **17**, columnar supramolecular assembly was enhanced, resulting in the formation of DSPs (route c in Fig. 1) with preferential helicity governed by stereochemistry of the chiral dendrons (Fig. 4d).[66] Similarly, peptide macrocycles bearing G1 dendrons self-assembled through intermolecular hydrogen bonding from

peptide motifs into columnar liquid crystal (LC) superstructures, which can be induced via an E-field to orient homeotropically over a large area.[67]

2.2 Metal coordination

Metal-ion mediated polymerization of dendronized aromatic modules has been proved to be another efficient methodology for preparation of DSPs (route a in Fig. 1). The assembled morphologies are dominated by the balance among the coordination interactions, van der Waals interactions and π-π stacking of aromatic segments, and the efficiency of supramolecular polymerization is dependent on the coordination constant, dendritic steric hindrance, and also counteranions. For example, coordinated metallacycles of achiral dendrons self-assembled via metal-metal interaction to form luminescent superhelical fibers. A series of pyrazole-anchored poly(benzyl ether) dendrons with generations of 2 to 4 were complexed with Cu^I, Ag^I, or Au^I, and resulted in formation of helical fibers through a helically twisted edge-to-edge stacking.[68] Through equivalent coordination of platinum compounds with first (G1) to third generation (G3) of bis(ethynyl)-functionalized dendrons, necklace-like and yellow-coloured dendronized polymers were obtained (**18**, Fig. 5a), which were confirmed by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy.[69] The molecular weights determined by LLS and GPC measurements revealed these DSPs possessing high degrees of polymerization (DPs) in the range of 30-880. Monomer concentration in polymerization and sample concentration in measurements did not show any influence on their molecular weights, indicating the high coordination ability of the comonomers and high stability of the supramolecular polymers. Steric hindrance was found to play a major role in achievable DPs. Depending on the structures of platinum compounds, formation of cyclic oligomers can be enhanced or suppressed. [70] Furthermore, by introducing trifunctional platinum compounds, cross-linked SDPs were formed.[71] However, by complexation of silver ion with dendronized diazadibenzoperylene (DABP) dyes, G1 to G2 π-conjugated DSPs **19** and **20** with low molecular masses formed (Fig. 5b), which were confirmed with ^{1}H diffusion ordered NMR spectroscopy.[72] These DSPs showed excellent solubility through shielding of π-π stacks from the aromatic moieties by dendron encapsulation. However, for G3 dendron, the shield effect from dendrons dominated even during polymerization, and no obvious supramolecular polymerization was observed. For supramolecular complexation of metal ions with bent-shaped, chiral bipyridine ligands carrying oligoethylene glycol (OEG)-based G2 dendron, the structures of supramolecular polymers **21-24** are dominated by counteranion sizes, type of metal ions and bipyridine structures. Complexation with silver ion resulted in chiral supramolecular assemblies, whose secondary structures are dependent on counteranion sizes (Fig. 5c).[73] In bulk, the secondary structures of these coordination chains changed from helical chains, via a dimeric cycle, to zigzag chains with the increase of anionic sizes. The coordination chains based on small anions such as nitrate and tetrafluoroborate self-

assembled into helical DSPs that organized into 2-D hexagonal lattice. In contrast, the coordination chain based on a larger anion, such as heptafluorobutyrate, organized into a lamellar structure. While in dilute solutions, these complexes exhibited a columnar structure in polar solvents which spontaneously jellified. Solvation ability to silver salts and shielding ability of dendrons to the conjugated backbone are responsible for controlling the morphologies.[74] In aqueous solutions, the helical complexes formed through silver ion-mediated coordination from the bent-shaped, OEG-based dendronized ligands showed thermoresponsiveness, and their helical pitches changed reversibly around their phase transition temperatures, leading to the formation of supramolecular springs[75] or responsive hydrogels.[76] When different Cu^{II} ions were used for the complexation with the bent-shaped bipyridine ligands, the coordination polymers formed double-stranded helices, driven by interstranded, copper-chloride dimeric interactions.[77] By elongating aromatic segments within the bent-shaped bipyridine ligands, enhanced π-π stacking led to the formation of helical tubules. The tubular structures can be switched reversibly into nonchiral flat sheets upon dissociation of silver-mediated complexation (Fig. 5d). This structure transformation was proposed to be originated from the competition between the π−π stacking interactions between the zigzag polymer chains and silver-initiated strong coordination.[78]
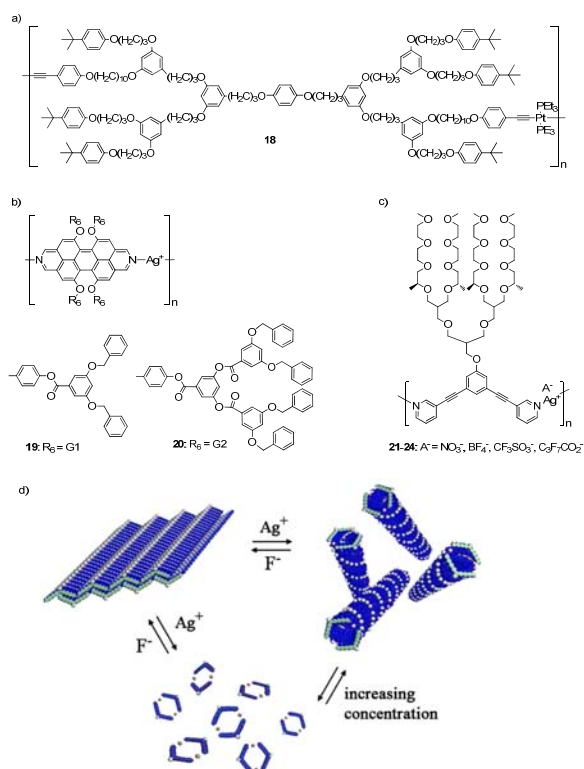

Fig. 5 (a) Molecular structures of G2 necklace-like DSP **18** formed through Pt mediated coordination. (b) Molecular structures of dendronized DABPs **19** and **20** formed via coordination of silver ions. (c) Molecular structures of DSPs **21-24** from silver-mediated coordination of bent-shaped amphiphiles, whose secondary structures are dependent on counteranion sizes. (d) Schematic representation of reversible transformation through flat sheets, helical tubules

and discrete toroids. Reprinted with permission from ref. 78. Copyright 2013 American Chemical Society.

2.3 π-π stacking

Supramolecular assembly through π-π stacking from dendronized rod-coil amphiphiles consisting of rigid rod segments and hydrophilic flexible OEG dendrons leads to the formation of various nanostructures in aqueous solutions (route a in Fig. 1).[79] Self-assembly of aromatic facial amphiphiles formed nano-fibril DSPs,[80] which can further form thermoresponsive nematic gels,[81] while amphiphilic dumbbells formed nanorings or long cylindrical morphology.[82] The latter can also form reversibly helical coil and nanofibers, as well as straight rods.[83,84] These different supramolecular morphologies are governed by π-π stacking between the aromatic units, but related to the balance between molecular geometry, amphiphilic nature, and microphase separation between incompatible components (Fig. 6).[85,86]
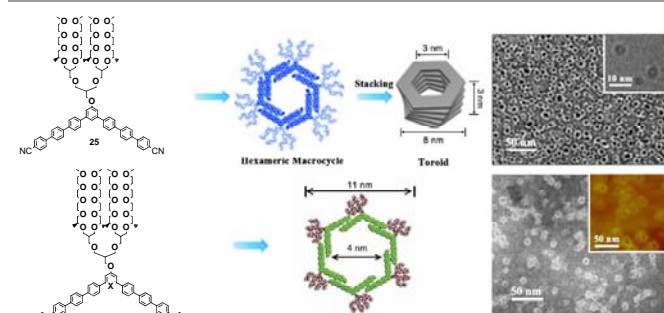

Fig. 6 (a) Molecular structure of bent-shaped rod amphiphile **25** and schematic representation of helical stacking of hexameric toroidal macrocycles and negatively stained TEM image. The inset is a cryo-TEM image. (b) Molecular structure of bent-shaped rod amphiphile **26** and negatively stained TEM image from an aqueous solution. The inset is an AFM image on mica. Reprinted with permission from ref 79. Copyright 2013 American Chemical Society.

Supramolecular assembly of symmetrical C_3 molecules mediated synergistically by π-π stacking and hydrogen bonding to form columnar stacks is another efficient strategy for the preparation of DSPs (route c in Fig. 1). For example, discotic trisamides and trisureas formed from 1,3,5-benzenetricarboxylic acids **27** and **28** (Fig. 7a) columnarly stacked in apolar solvents into elongated, helical DSPs, which turned into gels.[87] The urea stacks were found to be more rigid than the corresponding amide ones. While amide disks immediately reached their thermodynamic equilibrium, kinetic factors seemed to dominate urea aggregation. Both "sergeants-and-soldiers" principle and "majority-rules" effect are operative in chiral columnar stacking of these discotic molecules.[88] Achiral solider discotic molecules **29-32** carrying peripheral olefinic groups mixed with tiny amount of chiral sergeant component **33** led to the formation of helix with one handedness, which can be preserved through ring-closing olefin metathesis polymerization after removal of chiral component (Fig. 7b).[89] Furthermore, breaking the symmetry of these C_3 molecules afforded them amphiphilicity through orthogonally attaching polar or apolar pendants, which facilitated the

hierarchical self-assembly into bundled (triple helical) structures.[90] Differently, both dendronized cyclotriveratrylene (CTV) derivatives and dendronized triphenylene derivatives of three-folded symmetry adopted crown-like rather than discotic conformation, which could also self-assemble in bulk through π-π stacking into one-dimensional stacks with preferential helicity.[91,92]
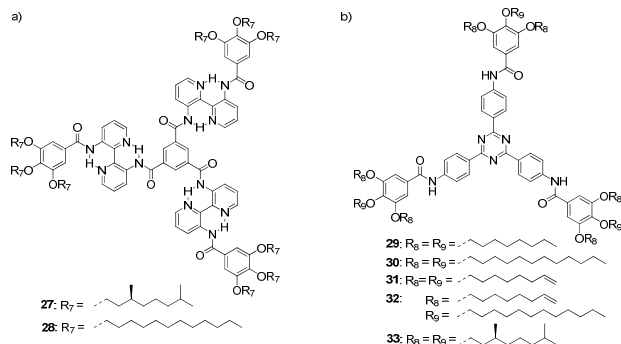

Fig. 7 Molecular structures of discotic C_3 molecules for columnar stacking to form DSPs: (a) discotic trisamides from 1,3,5-benzenetricarboxylic acid, (b) discotic molecules with 1,3,5-triazine as the core.

3. Side-chain dendronized supramolecular homopolymers

The major challenge for efficient synthesis of covalent dendronized polymers through "graft-to" strategy is the low coverage, which is mainly aroused by steric hindrance from the dendritic wedge. This problem also exists for in the formation of side-chain DSPs through "graft-to" strategy via non-covalent interactions. However, the coverage of dendritic wedge becomes less important issue here, and instead, more attentions were put on the supramolecular assembly through non-covalent, multivalency interactions between linear polymer main chains and dendritic side units through non-covalent interactions, such as acid-base interactions, hydrogen bonding, or host-guest complexation. Molecular structures of some representative side-chain DSPs are shown in Fig. 8.

3.1 Hydrogen bonding

Hydrogen bonding mediated formation of side-chain DSPs can be efficiently conducted through interactions between poly(4-vinylpyridine)s (P4VPs) and dendritic sulfonic acids (route d in Fig. 1). Upon protonation of P4VP chains by G1 dendritic sulfonic acids, cylindrical complexes **34** and **35** were formed (Fig. 8a). These complexes formed a liquid crystalline phase at low degrees of substitution, but tended to form hexagonal columnar mesophase at neutralization degrees above 80 %.[93] AFM visualization indicates individual supramolecules consisting of P4VP backbone wrapped by non-covalently bound sulfonic acid moieties. The length of the supramolecules is controlled by the length of P4VP core.[94] When P4VP complexed with carboxyl groups at the core of G2 or G3 poly(benzyl ether) dendrons (Fig. 8b), the resulting DSPs (**36** and **37**, respectively) can assembled in common solvents into
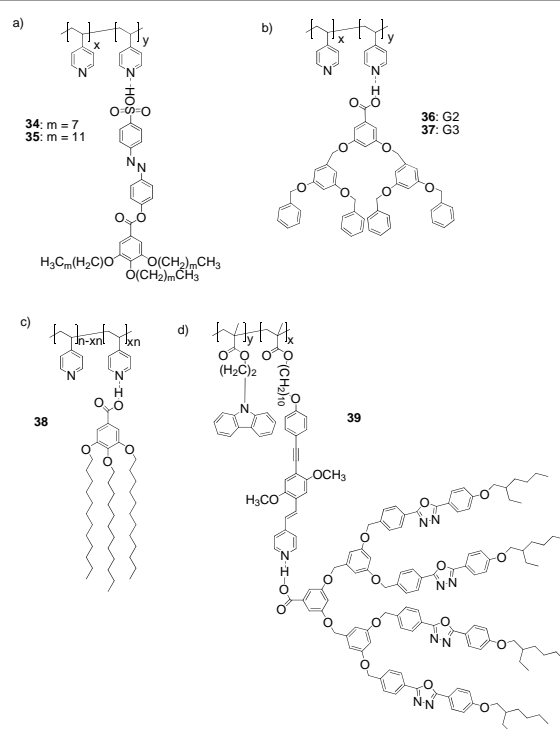

Fig. 8 Molecular structures of side-chain DSPs. All these polymer have the P4VP backbone, and their supramolecular formation is based on strong hydrogen bonding interactions between pyridine and the acid moieties.

vesicles, and the thickness of vascular membrane increased with molar ratio of dendrons to P4VP (Fig. 9).[95] This morphology was proposed to be initiated by the strong hydrogen bonding, and stabilized through π-π stacking from the higher generation dendrons. Phase behaviour of supramolecular complex **38** from P4VP and 3,4,5-tris(dodecyloxy)benzoic acid is dependent on the ratio of two components (Fig. 8c). With increase of the molar ratio of dendrons to P4VP, the morphologies transform from homogeneous to lamella phase, and then to cylinder or hexagonal columns.[96] Through hydrogen bonding mediated interactions between pyridine moieties from carbazole-containing light-emitting polymethacrylates and benzoic acid at the focal point of a G2 dendron (Fig. 8d), the supramolecular copolymer **39** show improved electrochemical and electroluminescence properties.[97] High generation dendrons afforded stronger isolation (shielding) and dilution effects, resulting in better energy-transfer phenomena. Besides, hydrogen bonding interactions between P4VP and different dendrons with benzoic acid at the focal point mediated the supramolecular columnar polymers in bulk to adopt helical conformation, whose handedness was biased by the stereogenic centres in peripheral tails of the dendrons.[98]
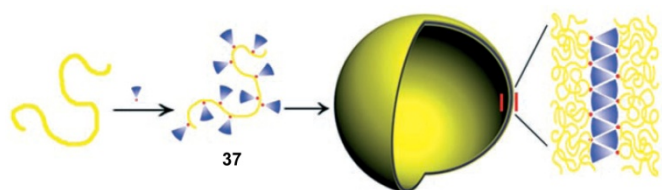
Fig. 9 Cartoon presentation for the formation of the soft vesicle from **37** in chloroform. Adopted with permission from ref. 95. Copyright 2007 John Wiley and Sons.

3.2 Host-guest complexation

The successful supramolecular formation from polymers with small molecular components usually requires high-affinity binding recognition motifs. One permanent recognition motif is the complexation between dialkylammonium and crown ether, which can form pseudorotaxane complex held strongly by hydrogen bonds between acidic $R_2NH_2^+$ protons and the oxygen atoms from crown ether ring.[99] Thus, DSPs **40 - 42** were efficiently formed (route d in Fig. 1) through complexation of G1 to G3 dendrons cored with dialkylammonium and polyacetylenes pendant with crown ethers, respectively (Fig. 10a).[100] The formation of DSPs was demonstrated to be controllable by acid-base reactions, indicating the system can be switched to rigid dendronized polymers and to flexible polymers reversibly (Fig. 10b). Host-guest interactions between G2 dendronized alternative copolymers carrying crown ether moieties and secondary amine derivatives were also utilized for the formation of supramolecular dendronized copolymers with brush structures.[101]
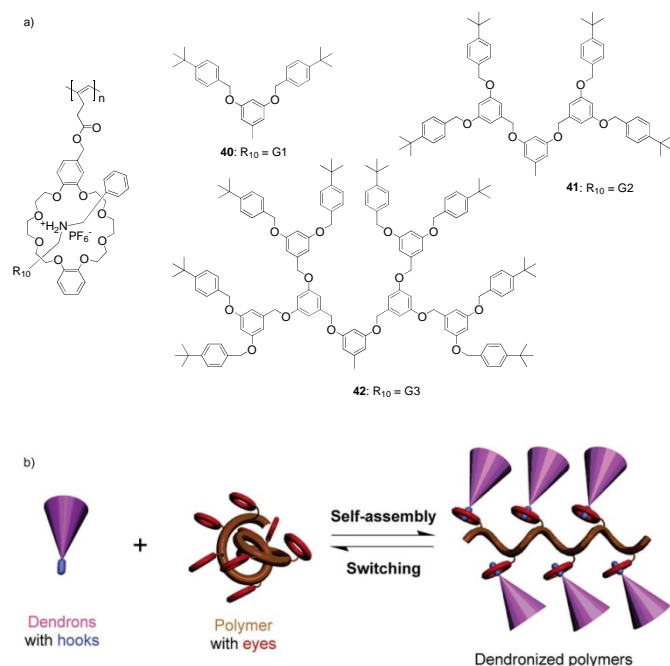

Fig. 10 (a) Molecular structures of DSPs formed through host-guest interactions between polyacetylene bearing crown ether pendants and Frèchet-type G1-G3 dendrons. (b) Schematic representation of the supramolecular formation of DSPs constructed through host-guest interaction between dendritic dialkylammonium

salts (hooks) and the crown ether (eyes) containing polymer. Reprinted with permission from ref. 100. Copyright 2006 American Chemical Society.

Another important recognition motif is the inclusion complexation of host cyclodextrins (CyDs) with guest hydrophobic moieties of appropriate sizes.[102-105] Thus, side-chain DSPs can be conveniently formed through complexation of host linear polymers with dendron guests. For example, taking the linear polymethacrylate (as the backbone) attached in each repeat unit with a β-CyD moiety as the host, and three-fold branched oligoethylene glycol (OEG)-based G1 and G2 dendrons cored with an adamantyl (Ada) as the guest, DSPs **43** and **44** were formed efficiently through inclusion complexation (Fig. 11).[106] β-CyD and Ada were selected as both can form inclusion complexes in water with a high binding constant in the range of 1×10^5 M^{-1}. The inclusion complexation to form DSPs was confirmed with ^{1}H NMR spectroscopy and dynamic light scattering measurements. These supramolecular polymers are soluble in water at room temperature, but show characteristic thermoresponsive behaviour at elevated temperature with sharp phase transitions and small hysteresis. Their phase transition temperatures are dependent mainly on the hydrophilicity of OEG dendrons.[35-37] The hydrophilicity from β-CyD within the polymers was shielded completely by the cylindrical architecture of dendronized polymers and showed no obvious contribution to the phase transition temperature. However, polymer concentration and molar ratio of host/guest had minor contribution to the phase transition temperatures, suggesting remarkable macromolecular effects. Notably, thermally-induced OEG chain dehydration and collapse caused decomplexation of the host and the guest as evidenced by ^{1}H NMR spectroscopy, and the tendency enhanced with a further increase of solution temperature. However, this decomplexation did not show significant influence on the thermoresponsiveness of the complexes, indicating that increase of solution temperature showed a dual effect by favouring the dissociation of dendrons, and at the same time, inducing the aggregation of the free dendrons within loops of the polymer main chains (Fig. 11b). Based on the dynamic nature of DSPs, their thermoresponsive properties could be tuned by complexation of guest dendrons with different hydrophilicities. For example, inclusion complexation from a linear β-CyD polymer and a mixture of two Ada-cored G2 OEG dendrons with different hydrophilicity led to the phase transition temperatures tunable continuously in the range of 34–56 °C, simply through variation of the ratios of the dendritic guests.[107] Furthermore, the dehydration and collapse of the OEG units initiated decomposition of the dendritic guests from the supramolecular copolymers, and the more hydrophobic guest dissociated at a much lower temperature than that for the more hydrophilic one.

When hyperbranched polymers carrying Ada moiety at the focal point was used as guests, complexation with a linear host polymer bearing β-CyD led to the formation of DSPs with hyperbranched side chains. By using linear-block-hyperbranched polymers as the guest, dendronized

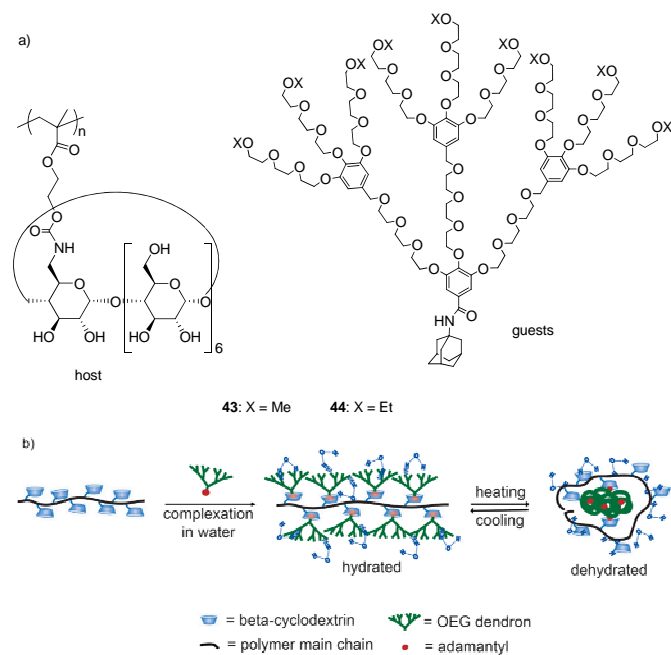supramolecular copolymers grafted with linear-block-hyperbranched polymers were formed.[108]

Fig. 11 (a) Molecular structures of host polymer bearing β-CyD in the pendants and OEG-based dendron guests. (b) Illustration of DSPs prepared via host-guest inclusions and their collapse in water. Reprinted with permission from ref. 106. Copyright 2011 John Wiley and Sons.

3.3 Acid-base (ionic) interactions

Although acid-base (ionic) interactions are relatively weak, the multivalency of dendronized architectures provides sufficient compensation to it, and thus leads to the efficient formation of abundant supramolecular structures. For example, through ionic interactions between poly(styrenesulfonic acid)s and G1 to G3 L-aspartic acid dendrons, DSPs **45-47** were successfully prepared (Fig. 12a).[109] Ionic interactions between conjugated poly(phenylacetylene)s and chiral glutamic acid dendrons formed supramolecular polymer **48** in organic solutions, at the same time, mediated the DSP to adopt a helical conformation with preferential handedness (Fig. 12b).[110] The helicity induction was enhanced when a high generation dendron was applied, and the handedness is dominated by the stereogenic nature from the peptidic dendrons.
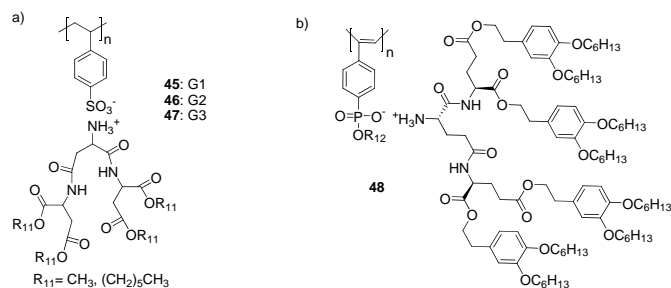

Fig. 12 (a) Molecular structures of DSPs **45-47** formed via ionic interaction from poly(styrenesulfonic acid) and peptidic amines. (b) Helical DSP **48** constituted from poly(phenylacetylene) and glutamic dendrons.

Ionic interactions between amphiphilic dendrons and oppositely charged polyelectrolytes led to enhancement of the gelation ability of the dendrons in organic solvents, mainly due to the multivalency effects from DSPs. A poly(urethane amide) (PUA) G2 dendron with long alkyl chains on its periphery was complexed through the carboxyl group at its focal point with oppositely charged polyelectrolytes, leading to the formation of DSPs **49-51** (Fig. 13). The supramolecular assembly enhanced significantly the gelation ability of the amphiphilic dendrons in organic solvents via a nucleation-elongation mechanism through complexation with poly(diallyldimethylammonium chloride) (PDADMA).[111,112] This gelation enhancement was found to be dependent on the ionic interactions between dendrons and polyelectrolytes. P4VP exhibited very strong interactions with PUAs, which hindered the pre-organization of PUAs and thus declined their gelation ability. Alternatively, PAH had very weak interactions with PUAs, therefore, its presence showed little effect on the gelation of PUAs.[113] In addition, presence of salts showed influence on the assembly morphologies, which were induced to transform from micelles to vesicles with the increase of salt concentration.[114]
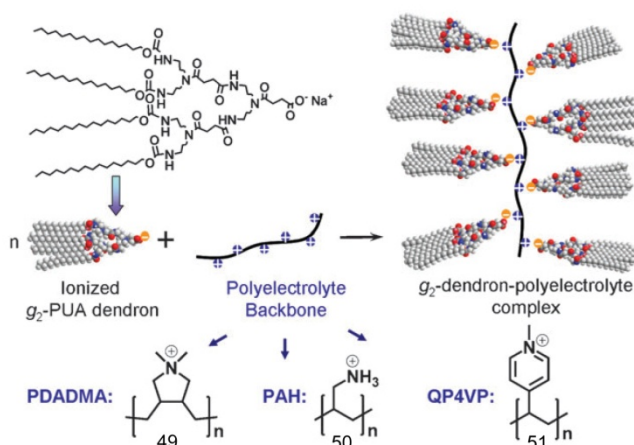

Fig. 13 Schematic drawing of DSPs formed via ionic complexation of PUA G2 dendron with polyelectrolytes. Adopted with permission from ref. 113. Copyright 2011 Royal Society of Chemistry.

Ionic interactions between linear polymers and amphiphilic dendrons enrich the morphologies in bulk. Ionic complexes of linear poly(ethylenimine) (PEI) or poly(allylamine hydrochloride) (PAH) with G1 dendrons carrying long alkyl chains on their peripheries through benzoic acid at their focal points led to the formation of DSPs, which adopted in bulk lamellar or hexagonal columnar phase, respectively. Thus, the location of binding sites at the polymer chain played an important role in determining the mesomorphous structures, since the amino groups for PEI are within backbone and for PAH at side chains.[115] When the polyelectrolytes were changed into poly(ferrocenylsilane) (PFS), complexation led to the formation of redox-active supramolecular polymers

with ionic thermotropic liquid crystalline phase.[116] Analogously, ionic interactions between charged dendronized polymers and surfactants can also form robust hierarchical assembled morphologies in bulk. Through supramolecular ionic complexes of cationic dendronized polymers (PG1–PG3) with anionic sulfonated lipids, a thermotropic liquid crystalline behavior and ordered nanostructures such as lamella, column rectangular, column hexagonal, or column square were menifested, depending on both dendron generations and lipid chain lengths.[117,118]

In addition, some other non-covalent interactions, such as metal coordination can also be used for the formation of side-chain DSPs. For example, through Ru[III] coordination of dendritic terpyridine and linear polymer main chain with terpyridine pendants, DSPs carrying two G2 dendritic terpyridine moieties in each repeat unit were synthesized.[119] Similarly, G2 dendronized alternative copolymers carrying terpyridine pendants coordinated through Ru[II] with terpyridine terminated PEG component, led to the formation of supramolecular dendronized polymer brushes.[120]

4. Dendronized supramolecular block copolymers

Conventionally, dendronized block copolymers (DBCs) are constituted covalently with linear polymer block(s) together with dendronized block(s), which combines the structure characteristics of both conventional block copolymers and dendronized polymers. Based on the structural characteristics from dendronized polymers, DBCs form a class of highly modular macromolecules, whose nature of the polymer backbone and the dendritic wedges, as well as the length of the constituent blocks can be independently varied to afford these block copolymers with precisely controlled chemical structures. They are therefore interesting candidates for supramolecular constructions and for fabricating stimuli-responsive materials. Due to the specific dendron generation-dependent thickness (d) of the dendronized polymer block, this construction allows preparation of copolymers with the same length ratio (l_1/l_2) but varied segment fractions (Fig. 14). Therefore, DBCs are able to self-assemble via solvophobic effect,[121-124] thermal-induction[125,126] or host-guest inclusion[127] into abundant morphologies, such as micelles, lamella, cylinders or 2D honeycomb sheets (Figure 14).

Supramolecular construction of this type of promising block copolymers will provide alternative way to tune their constitutions, thus allowing easily to mediating their supramolecular assemblies. Consequently, dendronized supramolecular block copolymers (DSBCs) can be formed from covalent block copolymers via non-covalent interactions within one of the blocks with small dendritic components (route e in Fig. 1). The major advantage of this strategy is that less synthetic effort is needed when comparing to the preparation of their covalent counterparts. For example, diblock copolystyrene (PS) with one block bearing 2,6-diamidopyridine (DAP) anchoring groups interacted complementarily with G0 to G3 Frèchet dendrons cored with thymine (Thy) recognition units

through three hydrogen bonds to form DSBCs **52-55**, respectively (Fig. 15a and 15b). The morphologies of block copolystyrene changed upon addition of thymine dendrons from lamellar (Thy-G0) to cylindrical (Thy-G1 and Thy-G2) to spherical (Thy-G3), which indicates addition of increasingly larger dendronized thymine derivatives resulted in a progressive increase in the effective volume fraction of the PS/DAP block, crossing the lamellar/cylindrical phase boundary at G1 and the cylindrical/spherical phase boundary at G3 (Fig. 15c).[128]
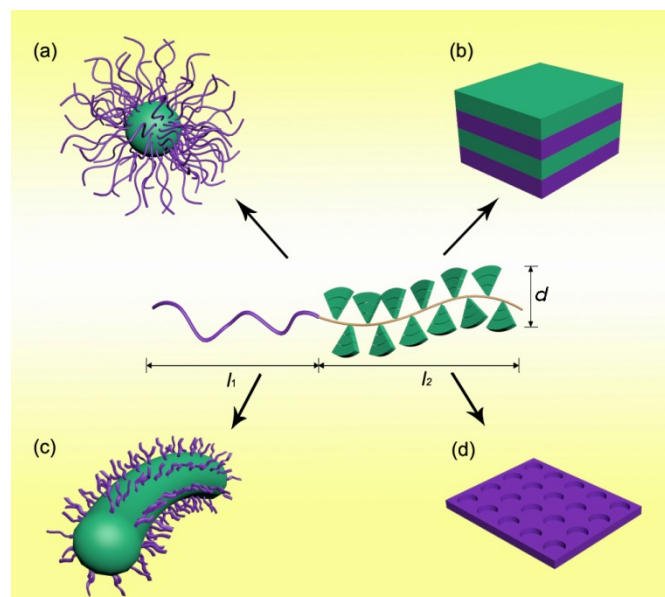

Fig. 14 Illustration of structural features of DBCs and several representative morphologies formed from their self-assembly: (a) micelles, (b) lamella, (c) cylinders and (d) honeycomb film.

The strong hydrogen bonding between pyridine and acid moieties has received considerable attention for the fabricating DSBCs. For example, complexation of diblock copolymer poly(2-vinylpyridine)-b-poly(ethylene oxide) (P2VP-b-PEO) with dendrons cored with a sulfonic group via proton transfer afforded DSBCs with tunable morphologies in thin films.[129] Degrees of neutralization at P2VP block controlled thin film morphologies of the block copolymers. At degree of neutralization equal to 0.25, perpendicular PEO cylinders formed initially, which merged upon solvent-vapor annealing, resulting in a mixed lamellar-cylindrical morphology. With increase of neutralization degree to 0.50, ordered amorphous PEO cylinders were observed to orient perpendicularly to the substrate. It was proposed that formation of liquid crystalline layers parallel to the interfaces is the major driving force determining the final morphology of the thin film. Similarly, symmetric block copolymer PS-b-P4VP interacted with nonmesogenic 4'-(3,4,5-trioctyloxybenzoyloxy)benzoic acid (TOB) to form DSBC **57** with tunable bulk morphologies.[130] The amphiphilic TOB features in its three alkene tails expanding out for a wedge-like shape and the extended benzoic acid head for both hydrogen bonding with P4VP and π-π stacking in self-alignment. When blended with PS-b-P4VP,

TOB moieties preferred to bind to pyridine moieties from P4VP rather than self-aggregate, which induced several LC phases of DSBC **57** depending on the overall binding fraction ratio x (Fig. 16b). With increase of TOB grafting density, the global morphology of the complexed block copolymer can be tuned from lamellar, hexagonal, face-centered-cubic to tetragonally perforated layer structures, successively. Since the hydrogen bonding between P4VP and TOB is temperature sensitive, it is also possible to tune the mesomorphic ordering of **57** via temperature.
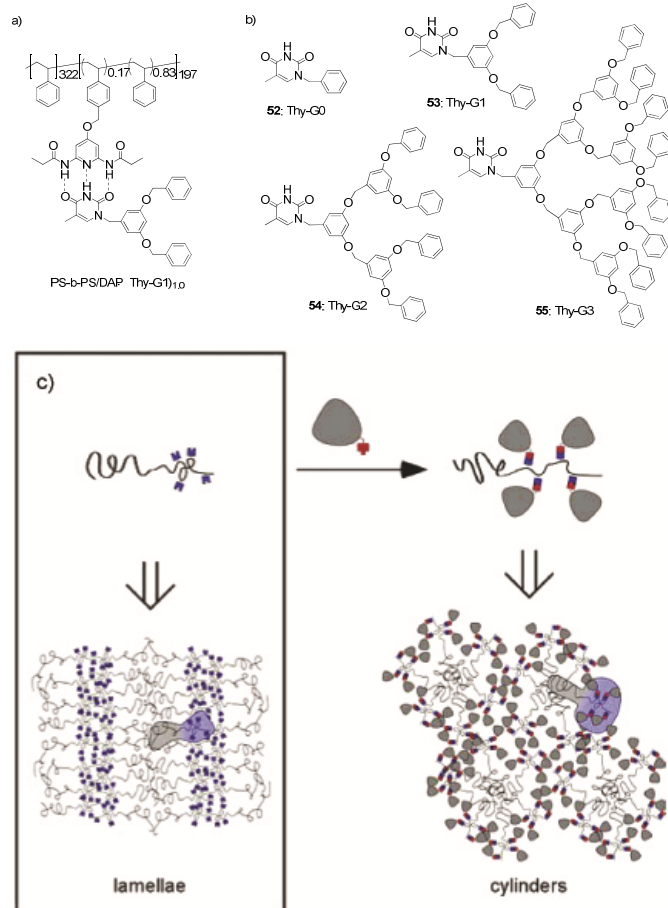
both are attractive qualities in optical applications. The dendritic structure of dAZO favors the interactions between pendant azobenzene units, thus enhancing the photo-response of the complexes. Photo-induced orientation of azobenzene units was obtained in films of the supramolecular complexes, and the achieved photo-induced anisotropy is promising for optically sensitive materials.
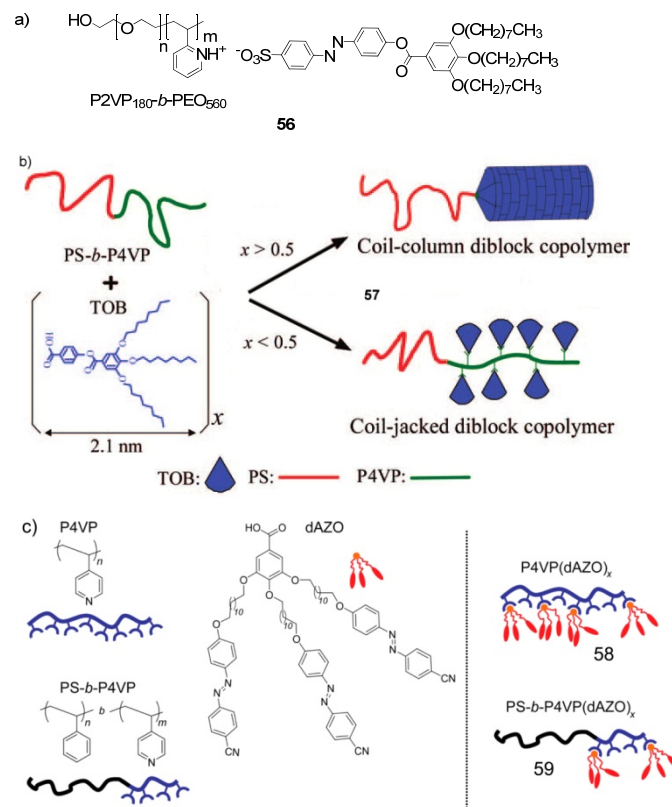

Fig. 15 Chemical structures of DSPs formed from block copolystyrene carrying DAP anchoring groups in one block (a) and Frèchet dendrons (G1 to G3) cored with thymine (b), as well as illustration for supramolecular assembly into different morphologies upon dendronization via complementary interactions between DAP and Thy (c). Adapted with permission from ref. 128. Copyright 2005 American Chemical Society.

Fig. 16 (a) Molecular structures of DSBC formed from P2VP. (b) Cartoon presentation for the supramolecular assembly from complexation of PS-b-P4VP with TOB. (c) Molecular structures and schematic representations of P4VP, PS-b-P4VP, dAZO, and their complexes P4VP(dAZO)x and PS-b-P4VP(dAZO)x. Reprinted with permission from refs. 130 and 131. Copyright 2009 and 2014 American Chemical Society.

Recently, complexation of a carboxyl-terminated azodendron, dAZO, with pyridine-containing homopolymer P4VP **58** and block copolymer PS-b-P4VP **59** was investigated and compared (Fig. 16c).[131] Complexation from the block copolymer translated into more abundant phase morphologies by tuning the ratio x between P4VP and dAZO moieties, and spherical, cylindrical, as well as lamellar structures were observed. The P4VP block from PS-b-P4VP can selectively encapsulate the dAZO moieties, whereas the PS block conferred processability and transparency to the system, and

Alternatively, DSBCs can also be formed through ionic complexation of charged DBCs with surfactants. The main advantage of this structural construction is based on the multivalency of dendronized polymers, which favors the multiple interactions in the dendronized block, leading to the formation of hierarchical structures. Thus, DBCs containing the thermoresponsive block bearing comb-like OEG chains and G1 and G2 positively charged dendronized blocks showed a better phase separation in bulk, a property which could be exploited in terms of three-dimensional bulk structure design.[132] The positively charged dendronized blocks were complexed with negatively charged lipids of different lengths (n = 8, 12, 14, 18) to afford DSBCs **60-63**, respectively (Fig. 17a). Their bulk structures investigated by X-ray diffraction and TEM revealed that, increasing alkyl length led to an order-to-order transition from the columnar-tetragonal to lamellar structure, and 3D

hierarchically organized structures with columnar phases at the small length scales can be formed. Dendronized block architecture makes it possible to engineer these approximately nanometer-scaled columnar phases into square, rectangular, and hexagonal lattices (Fig. 17b) through tuning the structural parameters, including block ratio l_1/l_2, thickness d related to dendron generation, and surfactant chain length.

a)

R_{13} = -(CH$_2$)$_{n-1}$CH$_3$

60: n = 8
61: n = 12
62: n = 14
63: n = 18

b)

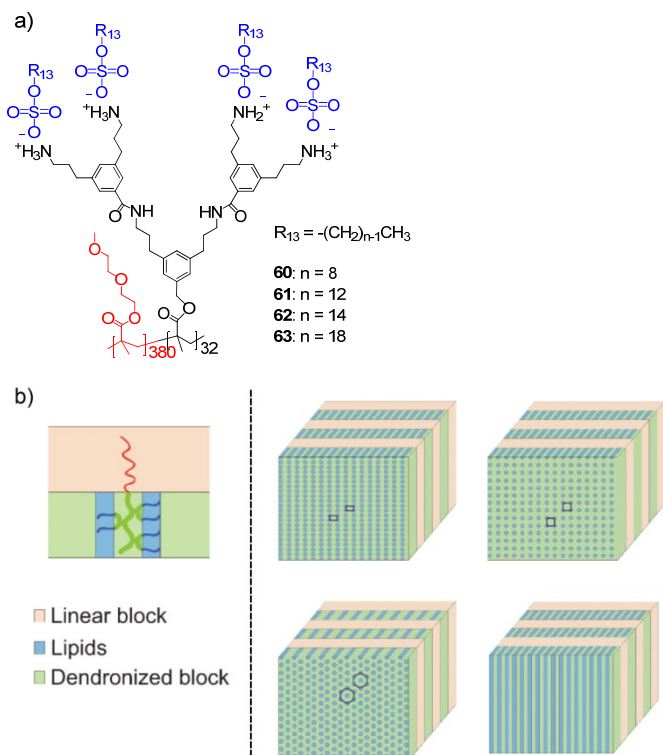☐ Linear block
☐ Lipids
☐ Dendronized block

Fig. 17 Molecular structures of supramolecular complexes from DBCs and lipids of different lengths (a), and schematic drawings of topological chemical connectivity of DBC components in the microphase-separated state and hierarchical nanostructures obtained, including rectangular-within-lamellar, tetragonal-within-lamellar, hexagonal-within-lamellar, and lamellar-within-lamellar structures (b). Reprinted with permission from ref. 132. Copyright 2008 John Wiley and Sons.

Conclusions and perspectives

Dendronized supramolecular polymers (DSPs) represent one intriguing type of topological supramolecular polymers, which inherit structural features from supramolecular construction and dendronized polymers. These structural characteristics, including bulkiness, cylindrical geometry and multivalency, have translated them into formation of abundant and unique hierarchical supramolecular structures. The thickness from dendrons affords shielding effects, which in one side enhance the solubility of the supramolecular motifs, and at the same time, mediate the supramolecular assembly. Cylindrical geometry guarantees the formation of morphologies which are not available from other supramolecular approaches. Multivalency from DSPs is especially attractive to compensate for the weak non-covalent supramolecular interactions, and to strengthen the supramolecular driving force and efficiency. Overall, many DSPs with different structures and of various architectures have been reported, and their supramolecular assembly to form versatile morphologies were explored. Some

promising functional properties from DSPs, such as electric, optical, chiral, gelating, as well as stimuli-responsive properties have received considerable attention. These investigations provided numerous strategies by using DSPs as scaffolds for supramolecular constructions, and revealed substantial advantages for developing novel functional materials based on DSPs.

However, researches in this area are still in its infancy, and more questions were raised than answered. For instance, much attention in DSPs was focused in last decade on their formation and supramolecular assemblies. Most supramolecular polymers were based on low generation dendrons (G1 and G2), consequently, dendronized architecture effects may not be sufficiently magnified for the supramolecular construction and assembly. Researches on effects of dendron structures on the formation of DSPs and their assemblies need to be enhanced. Only few types of dendrons were reported for the construction of DSPs, and most of them have no functions, which limit the exploration of functional properties for the formed DSPs. Efficient strategies for preparation of functional dendrons and formation of DSPs are required. Compared to other non-dendronized supramolecular entities, more DSPs need to be explored. To make use of the structural features from DSPs for material design, such as self-healing or stimuli-responsive functional materials is still a challenge.

Acknowledgements

Author Biographies

Jiatao Yan received his B.E. and M.S. in Polymer Engineering from Zhengzhou University in 2006 and 2009, respectively. In 2012 he received his Ph.D. in Polymer Chemistry and Physics from Fudan University under the supervision of Professor Peiyi Wu and Professor Afang Zhang, where he worked on synthesis and stimuli-responsive properties of dendronized supramolecular polymers based on inclusion complexation of cyclodextrins and adamantane. After the graduation, he joined Professor Afang Zhang's group at Shanghai University as a postdoctoral researcher. His main research interests are design and synthesis of stimuli-responsive supramolecular macromolecules, including dendronized supramolecular polymers and cyclodextrin-based supramolecules.

Wen Li received her B.E. degree in 2004 from Zhengzhou University, China. Subsequently she moved to Germany and studied in a Joint Master Program of TU, HU, FU and UP in Berlin and obtained her M.S. degree in 2007 under the direction of Professor Andre Laschewsky. In 2010, she obtained her Ph.D. from ETH Zürich under the supervisions of Professor A. Dieter Schlüter and Professor Afang Zhang, where she focused on developing stimuli-responsive dendronized polymers. Thereafter, she joined Shanghai University, and is currently an Associate Professor. Her research interests include stimuli-responsive polymers, dendronized polymers and functional dendritic nanomaterials.

Afang Zhang earned his M.S. (1988) and Ph.D. (1999) in Polymer Chemistry & Physics from University of Science & Technology of China and Peking University, respectively. He began his research work from 1988 at Chemistry Institute of Henan, where he became an associate professor in 1992 and a full professor in 1998. After three years working at the Deutsches Kunststoffinstitut and Free University of Berlin, he joined Zhengzhou University, China as the distinguished professor in Polymer Chemistry & Physics. In 2005, he started working in ETH Zürich. By the end of 2009, he returned back to China and joined Shanghai University as the distinguished professor in Polymer Chemistry & Physics. Thereafter, he became a 1000plan Scholar affiliated to Shanghai Government. His main research interest comprises dendritic supramolecular polymers, peptide-related helical polymers, and polymers with switchable properties.

Notes and references

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