

Supramolecular Dendritic Polymers: From Synthesis to Applications

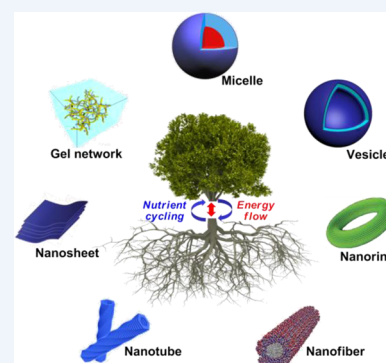
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CONSPECTUS: Supramolecular dendritic polymers (SDPs), which perfectly combine the advantages of dendritic polymers with those of supramolecular polymers, are a novel class of non-covalently bonded, highly branched macromolecules with three-dimensional globular topology. Because of their dynamic/reversible nature, unique topological structure, and exceptional physical/chemical properties (e.g., low viscosity, high solubility, and a large number of functional terminal groups), SDPs have attracted increasing attention in recent years in both academic and industrial fields. In particular, the reversibility of non-covalent interactions endows SDPs with the ability to undergo dynamic switching of structure, morphology, and function in response to various external stimuli, such as pH, temperature, light, stress, and redox agents, which further provides a flexible and robust platform for designing and developing smart supramolecular polymeric materials and functional supramolecular devices.

The existing SDPs can be systematically classified into the following six major types according to their topological features: supramolecular dendrimers, supramolecular dendronized polymers, supramolecular hyperbranched polymers, supramolecular linear–dendritic block copolymers, supramolecular dendritic–dendritic block copolymers, and supramolecular dendritic multiarm copolymers. These different types of SDPs possess distinct morphologies, unique architectures, and specific functions. Benefiting from their versatile topological structures as well as stimuli-responsive properties, SDPs have displayed not only unique characteristics or advantages in supramolecular self-assembly behaviors (e.g., controllable morphologies, specific performance, and facile functionalization) but also great potential to be promising candidates in various fields.

In this Account, we summarize the recent progress in the synthesis, functionalization, and self-assembly of SDPs as well as their potential applications in a wide range of fields. A variety of synthetic methods using non-covalent interactions have been established to prepare different types of SDPs based on varied mono- or multifunctionalized building blocks (e.g., monomer, dendron, dendrimer, and hyperbranched polymer) with homo- or heterocomplementary units. In addition, SDPs can be further endowed with excellent functionalities by employing different modification approaches involving terminal, focal-point, and backbone modification. Similar to conventional dendritic polymers, SDPs can self-assemble into diverse supramolecular structures such as micelles, vesicles, fibers, nanorings, tubes, and many hierarchical structures. Finally, we highlight some typical examples of recent applications of SDP-based systems in biomedical fields (e.g., controlled drug/gene/protein delivery, bioimaging, and biomimetic chemistry), nanotechnology (e.g., nanoreactors, catalysis, and molecular imprinting), and functional materials. The current research on SDPs is still at the very early stage, and much more work needs to be done. We anticipate that future studies of SDPs will focus on developing multifunctional, hierarchical supramolecular materials toward their practical applications by utilization of cooperative non-covalent interactions.



1. INTRODUCTION

As a bridge between supramolecular chemistry and polymer science, supramolecular polymers based on non-covalent interactions have received much attention because of their dynamic/reversible nature and unique physical/chemical properties in a wide range of fields, including biomedical applications, nanotechnology, and functional materials.¹ Hitherto, various non-covalent interactions such as multiple hydrogen bonding, π – π stacking, metal–ligand coordination, and host–guest interactions have been utilized to prepare supramolecular polymers.^{2,3} The reversibility of non-covalent interactions endows the supramolecular polymers with the ability to undergo self-adaptive/self-healing processes, in contrast to conventional covalent polymers.⁴ In addition, the responsiveness of supramolecular polymers to versatile external

stimuli involving pH, temperature, light, stress, and redox agents further provides a novel platform for the development of smart supramolecular polymeric materials and functional supramolecular devices.⁵

The topological structures of supramolecular polymers, which mainly depend on the numbers of complementary binding sites in the building blocks, play an important role in determining the physicochemical properties and functionality of the resultant supramolecular materials. In view of the molecular topological features, supramolecular polymers can be classified into four main types: supramolecular linear polymers,

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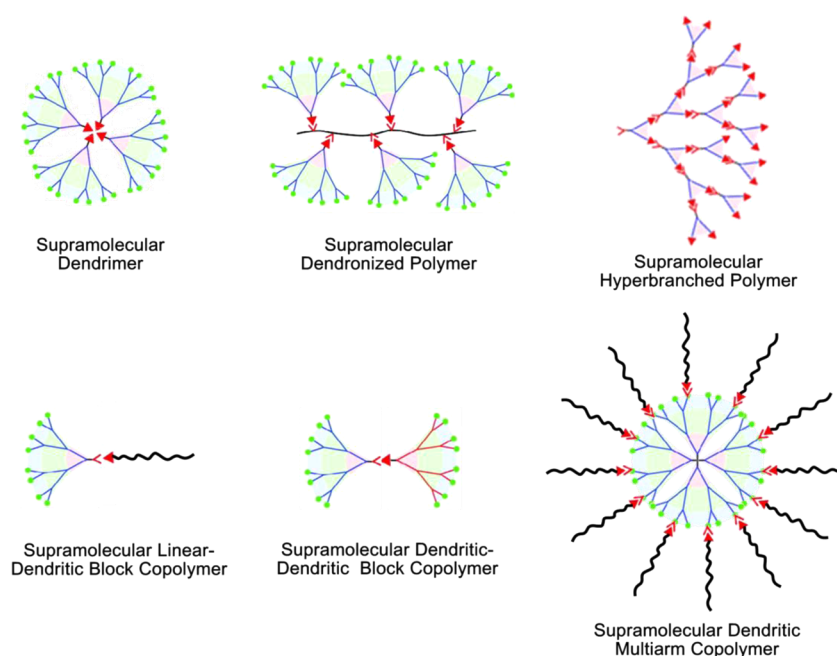


Figure 1. Classes of existing SDPs with different topological structures.

supramolecular dendritic polymers, supramolecular star-shaped polymers, and supramolecular cross-linked polymers. Generally, supramolecular linear polymers have one-dimensional linear structures, strong intermolecular entanglement, high viscosity, low solubility, and two terminal units. In striking contrast, supramolecular dendritic polymers (SDPs) show highly branched three-dimensional globular architectures, little molecular entanglement, low viscosity, high solubility, and plenty of functional terminal groups. Therefore, SDPs perfectly combine the dynamic/reversible nature of supramolecular polymers with the three-dimensional topological features and multifunctionality of dendritic polymers and thus have attracted wide interest in both academic and industrial fields.⁶ In recent years, a rapidly increasing number of publications related to the synthesis and applications of SDPs have been reported. However, a systematic summary of the synthesis strategies, modification methods, and potential applications of SDPs has not yet been published.

This Account provides an overview of SDPs, including their synthesis strategies, modification and functionalization methods, self-assembly of supramolecular nanostructures from zero- to three-dimensional, and their applications. We aim to elucidate the general concepts and structure–property relationship of SDPs and then to provide useful insights into how to realize functionalization of SDPs and their practical applications in the future. We hope to stimulate new ideas and inspire continuous endeavors in this emerging research area.

2. DESIGN AND SYNTHESIS

This section mainly focuses on the design and synthesis of three-dimensional SDPs with different topological structures. Up to now, various types of SDPs have been prepared using different non-covalent strategies based on unbalanced complementary unimers, dendrons, or dendritic building blocks. Herein we present a systematic classification scheme for SDPs according to their topological structures that contains the following six classes: supramolecular dendrimers (SDs), supramolecular dendronized polymers (SDNPs), supramolec-

ular hyperbranched polymers (SHPs), supramolecular linear–dendritic block copolymers (SLDBC), supramolecular dendritic–dendritic block copolymers (SDDBC), and supramolecular dendritic multiarm copolymers (SDMCs) (Figure 1).

2.1. Supramolecular Dendrimers (SDs)

Dendrimers are a class of perfect monodisperse macromolecules with a regular and highly branched three-dimensional architecture. Dendrimers can be synthesized using two conceptually different synthetic strategies, namely, divergent and convergent approaches. Both approaches consist of an iterative sequence of reaction steps in which each additional iteration leads to a higher-generation polymer. Thus, the tedious synthesis remains a major drawback for this class of promising macromolecules. Alternatively, supramolecular synthesis based on monofunctionalized dendritic building blocks provides an effective strategy to prepare SDs with versatile structures. Several approaches including untemplated and template-directed synthesis have been developed for the construction of SDs in bulk, organic media, or water.

Untemplated synthesis is a powerful strategy for generating well-defined SDs from monofunctionalized dendrons with self-complementary units, which guarantees structural accuracy while eliminating steps from the conventional multistep approach. As a typical example, Zimmerman et al.⁷ reported a synthetic approach for constructing disk-shaped supramolecular dendritic structures up to the fourth generation from smaller dendritic subunits by hydrogen bonding. However, this kind of SDs had limitations, in particular, low stability in even moderately competitive solvents. They further synthesized a hexameric disk-shaped aggregate with high stability using the self-complementary multiple hydrogen-bonding motif.⁸ In addition, Percec and co-workers synthesized a series of monodendrons that self-assembled through various molecular recognitions into rodlike, cylindrical, and spherical SDs. The cylindrical SDs self-organized into a thermotropic hexagonal columnar lattice, whereas the spherical ones formed a novel thermotropic cubic liquid-crystal lattice.^{6,9}

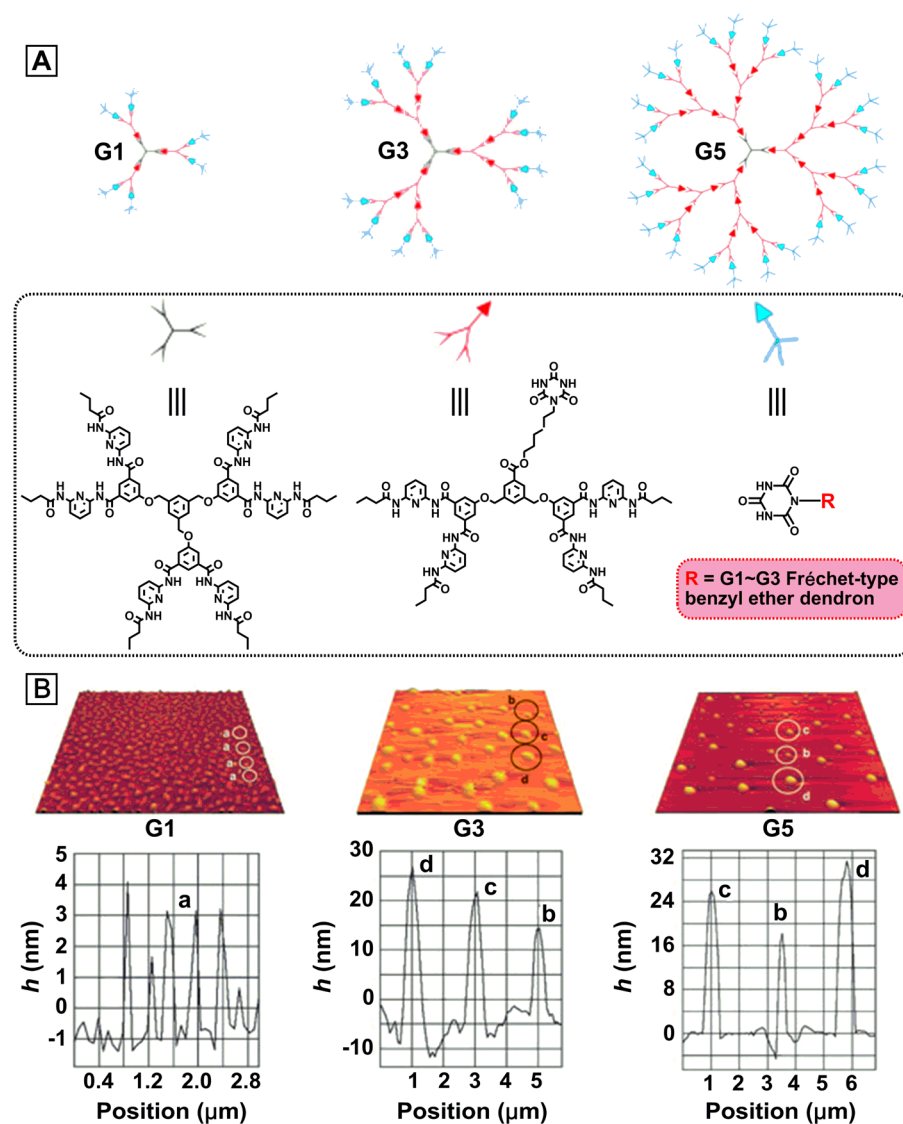


Figure 2. (A) Preparation of SDs using a homotrimeric core, heterotrimeric AB₂ branching units, and end caps. (B) Atomic force microscopy (AFM) images of SDs of different generations (G1, G3, and G5). Reproduced with permission from ref 16. Copyright 2005 Wiley-VCH.

A wide variety of template-directed approaches based on mono-heterofunctionalized dendrons have been developed to prepare SDs using various multicomplementary linkers (e.g., metal ions, homotrimeric receptors, and dendritic subunits). Vögtle, Stang, Gibson, Newkome, and others have done excellent work on template-directed synthesis of SDs. On the basis of a photoactive/redox-active [Ru(bpy)₃]²⁺-type core, Vögtle and co-workers constructed supramolecular metalodendrimers by complexation of ruthenium chloride with bipyridine ligands carrying dendritic polymers at the apex site.¹⁰ Also, Stang and co-workers reported the coordination-driven synthesis of novel cavity-cored metalodendrimers with well-defined shape and controllable size.¹¹ Besides these supramolecular metalodendrimers, Gibson and co-workers constructed different generations of self-organizing pseudorotaxane dendrimers through host-guest interactions between a tritopic ammonium salt and dibenzo[24]crown-8 (DB24C8)-functionalized dendrons.¹² Recently, Wu, Zhang, and co-workers reported a series of SDs assembled via host-guest interactions between cyclodextrin (CD) trimers and oligo(ethylene glycol) (OEG)-based dendritic guests cored with an adamantyl (AD)

group that exhibit thermoresponsive behavior at elevated temperatures.¹³

Different from the aforementioned synthesis methods, dendritic polymers with coordination centers on the periphery are prepared mostly by the divergent strategy. First, the dendritic cores are fabricated by a traditional dendrimer synthesis in which ligands or functional groups capable of coordinating metal ions are introduced in the final step. For example, Newkome et al.¹⁴ established a tailored approach for the generation of cascade metallomacromolecules with nanoscopic dimensions by utilizing a terminal-functionalized dendritic polymer as a template. Astruc and co-workers reported the synthesis of redox-active supramolecular ferrocenyl dendrimers using hydrogen bonding between polypropylenimine (PPI) dendrimers and phenol-modified ferrocenyl dendrons at the focal point and their use to recognize H₂PO₄⁻.¹⁵

Hitherto, preparations of SDs have employed preassembled dendritic building blocks in most cases. Construction of SDs from small molecules via non-covalent interactions is still a great challenge. Hirsch and co-workers presented the first

example of small-molecule-based SDs where the repetition motif was no longer from dendritic subunits (Figure 2A).¹⁶ In their design, the homotriplic Hamilton core, the heterotriplic AB₂ branching units, and the end caps were mixed with different stoichiometries, resulting in the formation of SDs of different generations with uniform size and perfect globular shape (Figure 2B).

2.2. Supramolecular Dendronized Polymers (SDNPs)

Differing from spherical SDs, SDNPs represent an emerging class of macromolecules combining the unique structural characteristics of dendronized polymers (e.g., stretching/anisotropic structure) with the reversibility of supramolecular polymers. Therefore, they are actually capable of self-healing in response to external stimuli, in contrast to conventional dendronized polymers, making them excellent candidates for supramolecular materials. Nowadays, two approaches have been established to fabricate SDNPs: the “graft-to” method for the preparation of side-chain SDNPs and the “macromonomer polymerization” method for the preparation of main-chain SDNPs.

The “graft-to” method has been developed for the preparation of side-chain SDNPs, in which dendrons are anchored to a polymer backbone by utilization of non-covalent interactions. Stoddart and co-workers constructed acid–base-switchable [G1]- to [G3]-SDNPs by employing crown ether-based host–guest interactions to graft Fréchet-type dendritic dialkylammonium salts to a DB24C8-containing polystyrene or polyacetylene backbone (Figure 3A).¹⁷ The experimental and simulation results confirmed that the length of extension of the polymer backbone increases as the size of the attached dendron increases (Figure 3B). Similarly, Jiang and co-workers disclosed that Fréchet-type dendrons with a carboxyl group at the focal point could be attached to poly(4-vinylpyridine) through hydrogen-bonding interactions, forming hydrogen-bonded SDNPs. The resulting polymers showed unique self-assembly behavior, forming stable nanosized vesicles in the common solvent under ultrasonic treatment.¹⁸ Recently, Zhang and co-workers reported a class of thermoresponsive side-chain SDNPs formed through host–guest complexation between OEG-based dendrons with an AD group and β -CD-decorated polymethacrylates.¹⁹

Main-chain SDNPs with non-covalent backbones have been prepared via the “macromonomer polymerization” method. Zimmerman and co-workers demonstrated that dendritic metalloporphyrin macromonomers could be linked together through metal–ligand coordination with succinic acid as the bridging bidentate ligand to produce an SDNP, which further formed organic nanotubes through molding of dendritic building blocks around an oligoporphyrin core.²⁰ Instead, Chow and co-workers used hydrogen bonding as the driving force to synthesize rodlike 2-ureido-4-pyrimidinone-based main-chain SDNPs from bifunctional dendritic macromonomers.²¹

2.3. Supramolecular Hyperbranched Polymers (SHPs)

As one important class of SDPs, SHPs with irregular branching display the prominent advantages of facile one-step fabrication and efficient structure–property regulation. The approaches for preparation of SHPs can be divided into two major categories: single-monomer methodology and double-monomer methodology. In the single-monomer methodology, SHPs are synthesized using AB_n-type ($n \geq 2$) heterotropic monomers. Huang and Gibson²² developed an AB₂-type SHP (Figure 4A)

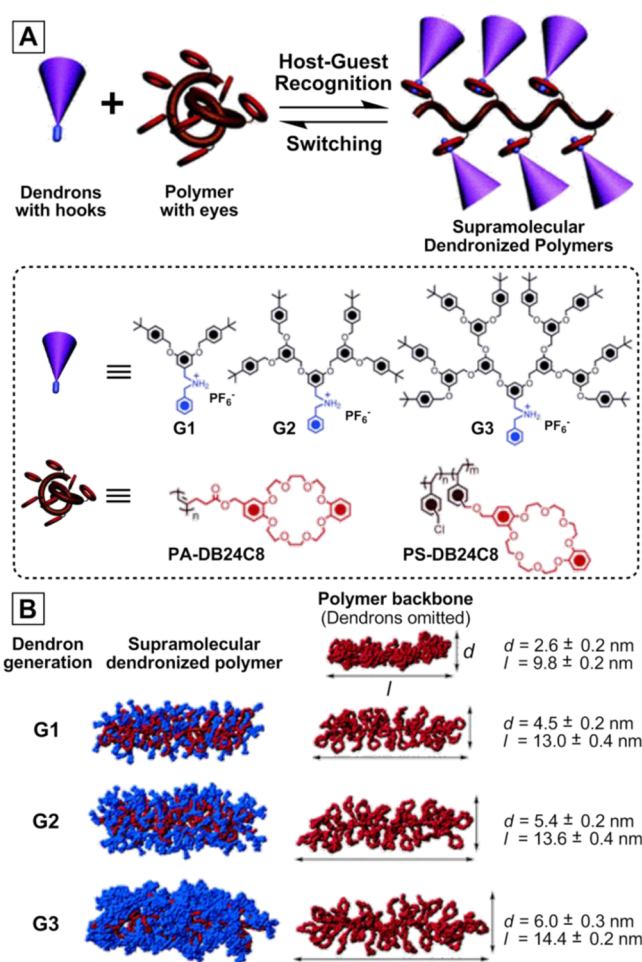


Figure 3. (A) Preparation and (B) molecular dynamics simulations of SDNPs (d = diameter and l = length). Reproduced from ref 17. Copyright 2006 American Chemical Society.

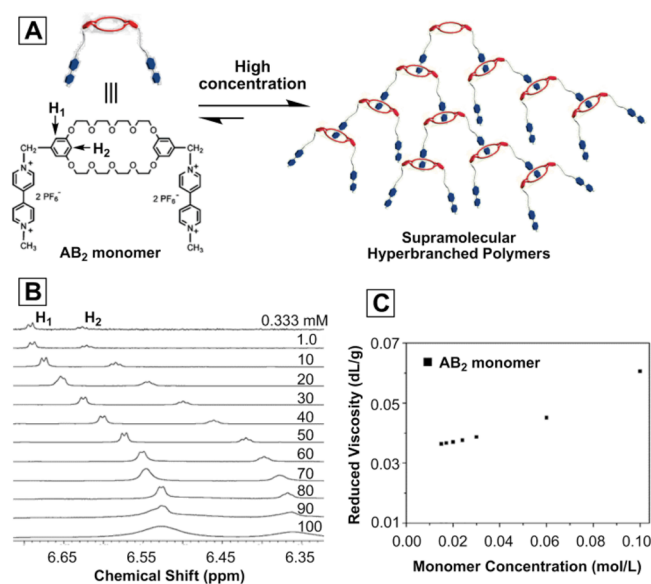


Figure 4. (A) Formation of an AB₂-type SHP from the self-organization of an AB₂ monomer. (B) Partial NMR spectra of the AB₂ monomer at different concentrations in CD₃CN at 22 °C. (C) Reduced viscosity as a function of monomer concentration. Reproduced from ref 22. Copyright 2004 American Chemical Society.

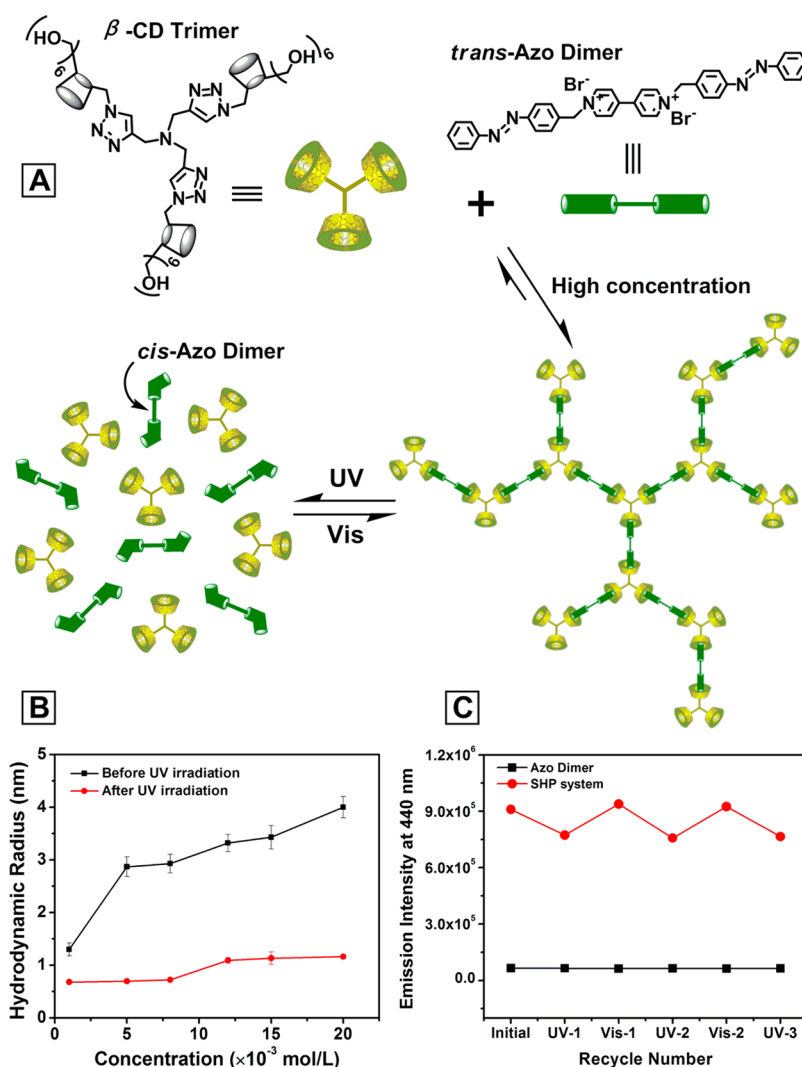


Figure 5. (A) Preparation of a photoswitchable A_2/B_3 -type SHP. (B) Change in the hydrodynamic radius of the SHP before and after UV irradiation. (C) Fluorescence variation upon alternating irradiation with UV and visible light. Adapted with permission from ref 27. Copyright 2011 Royal Society of Chemistry.

through self-organization of an AB_2 monomer containing complementary recognition sites, namely, a bis(*m*-phenylene)-32-crown-10 core and two pendant paraquat moieties. As the monomer concentration was increased, both significantly upshifted/broadened proton signals for H_1 and H_2 of the monomer (Figure 4B) and a nonlinear increase of the reduced viscosity were observed (Figure 4C), demonstrating the formation of the SHP at high concentrations. Later, Martín and co-workers designed a redox-amphoteric AB_2 monomer containing two units of the electron donor 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9*H*)-ylidene]-1,3-dithiole (exTTF) and one unit of [60]fullerene (C_{60}) that further self-assembled into an electroactive, dynamically polydisperse SHP through weak π - π interactions.²³

In the double-monomer methodology, two heterocomplementary monomers, A_n and B_m ($n \geq 2$, $m \geq 3$), are adopted to generate SHPs. Tato and co-workers reported the first A_2/B_3 -type supramolecular polymer, formed by the complexation of a β -CD trimer with sodium deoxycholate dimer via host-guest interactions. With different mixing times, a variety of dendritic aggregates with different fractal dimensions and morphologies were subsequently obtained.²⁴ Using a similar method, Zhang

and co-workers constructed water-soluble SHPs through host-enhanced π - π interactions between naphthalene trimer and cucurbit[8]uril (CB[8]), which exhibited controlled supramolecular polymerization behavior and a (ferrocenylmethyl)-trimethylammonium iodide-induced depolymerization process.²⁵ In addition, an A_2/B_4 -type SHP was prepared by host-guest recognition of a tellurium-containing CD dimer with a Mn(III)-porphyrin-based AD tetramer. This SHP showed bifunctional antioxidative enzyme activities.²⁶ It is worth noting that the supramolecular synthesis of hyperbranched polymers using A_n and B_m monomers probably leads to the formation of cross-linked structures such as microgels and even macroscopically insoluble objects at high conversion of the supramolecular polymerization.

Various types of SHPs that are responsive to external stimuli have been prepared by incorporation of either switchable non-covalent bonds or intrinsically responsive building blocks. As a first approach, we reported a novel class of photoreversible A_2/B_3 -type SHPs through the host-guest complexation of a β -CD trimer and an azobenzene (Azo) dimer (Figure 5A). Upon alternating UV and visible-light irradiation, photoswitched polymerization/depolymerization behavior can be reversibly

achieved (Figure 5B), accompanied by a periodic fluorescence change (Figure 5C).²⁷ Similarly, Bu and co-workers achieved a pH-reversible AB₂-type SHP based on DB24C8–dialkylammonium host–guest recognition that showed switchable fluorescence.²⁸ In another approach, Liu and co-workers synthesized a well-defined AB₂ unit, a poly(*N*-isopropylacrylamide) (PNIPAM) oligomer containing one AD unit and two β -CD moieties, which spontaneously formed thermoresponsive SHPs via molecular recognition between AD and β -CD in water.²⁹

2.4. Supramolecular Linear–Dendritic Block Copolymers (SLDBC)s

As a mimic of nature, SLDBC's very much resemble trees in their architecture: the linear block can be regarded as the tree trunk, while the dendritic block is regarded as the tree crown. Only a few examples of the synthesis of SLDBC's utilizing non-covalent interactions to connect the linear block with the dendritic block have been presented. On basis of their topological structures, they can be divided into two types: supramolecular linear–dendrimer block copolymers and supramolecular linear–hyperbranched block copolymers.

Supramolecular linear–dendrimer block copolymers possess a well-defined structure but require a multistep synthesis process. Wu and co-workers obtained a supramolecular linear–dendrimer amphiphile via hydrogen bonding between a hydrophilic flexible poly(ethylene oxide) with a stilbazole terminal group and a hydrophobic rigid dendritic block cored with a carboxyl group.³⁰ The supramolecular amphiphile could form various self-assemblies such as vesicles, cylindrical micelles, fibers, and hierarchical wreathlike or hollow entanglement structures. Changing the concentration and solvent polarity allowed the formation, evolution, and transformation of these aggregated morphologies to be readily achieved. In parallel, taking advantage of the β -CD/Azo host–guest interaction, Jiang and co-workers succeeded in realizing dual reversible self-assembly and disassembly behavior of a PNIPAM-based supramolecular linear–dendrimer amphiphile in response to light and heat stimuli.³¹

Supramolecular linear–hyperbranched block copolymers with less perfect structure are much easier to synthesize and show performance comparable to that of the former. We reported a novel class of supramolecular linear–hyperbranched amphiphiles (SLHAs) through non-covalent coupling of hyperbranched polyglycerol grafted from β -CD (CD-g-HPG) and AD-functionalized long alkyl chain (AD-C_n, *n* = 12, 18, 30) by the specific CD/AD host–guest interaction (Figure 6A). The resulting SLHAs further self-assemble into unilamellar vesicles in water that disassemble readily upon addition of β -CD as a competitive host. Surprisingly, the vesicles demonstrate an unexpected great ductility with an expansion of about 300% in radius under an external force (Figure 6B).³² Dual-responsive micelles were also fabricated via a CB[8]-based host–guest interaction and exhibited controlled drug release behavior in response to a competitive guest (AD) and a reducing agent (Na₂S₂O₄).³³

2.5. Supramolecular Dendritic–Dendritic Block Copolymers (SDDBC)s

SDDBC's (also termed “supramolecular Janus dendritic polymers”) resemble a tree together with its root very well in the architecture. They are constructed by the supramolecular coupling between two chemically/structurally distinct dendritic polymers via non-covalent interactions such as metal–ligand

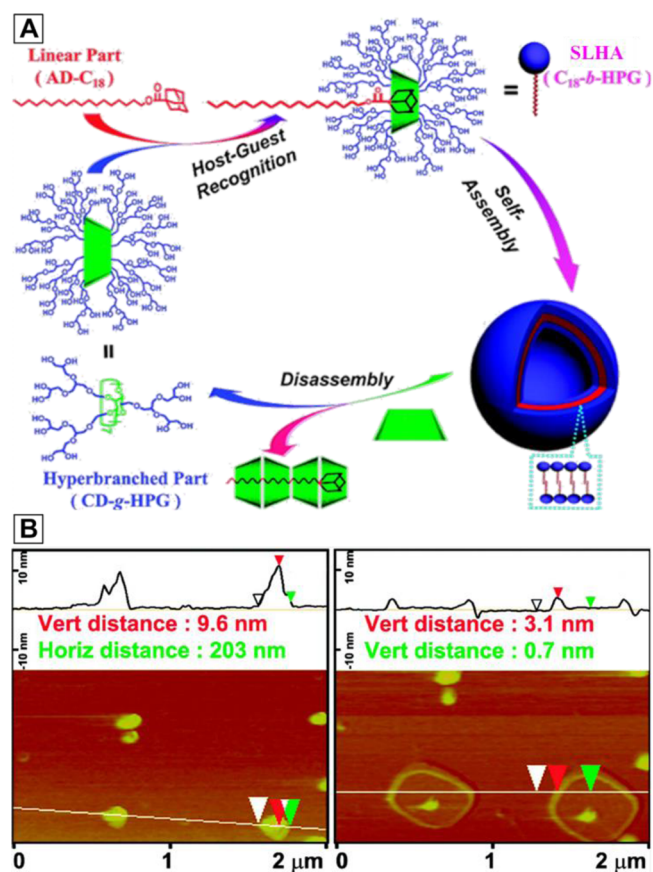


Figure 6. (A) Preparation, self-assembly, and disassembly processes of SLHAs. (B) AFM images of vesicles. The force on the AFM tip was increased to 2.1 nN (right). Adapted from ref 32. Copyright 2012 American Chemical Society.

coordination, hydrogen bonding, molecular recognition of nucleobases, and host–guest interactions. These dendritic building blocks are usually functionalized with a mono-heterocomplementary unit at the focal point. On the basis of their topological structures, they mainly comprise two major types: supramolecular Janus dendrimers and supramolecular Janus hyperbranched polymers.

Supramolecular Janus dendrimers with asymmetric structure exhibit fascinating properties as well as great potential for use as new building blocks in self-assembly. In 1995, Newkome et al.³⁴ reported the ruthenium–ligand bond-mediated synthesis of a series of well-defined Janus bisdendrimer complexes. A metallodonor dendrimer was coupled with three distinct generations of complementary terpyridine receptor dendrimers via metal–ligand coordination. Using the complementary bis(adamantylurea)/glycylurea system, Gillies and Fréchet³⁵ synthesized dendritic polyester “bow-ties” based on 2,2-bis(hydroxymethyl)propionic acid, which offered a convenient scaffold to study the effect of peripheral functionality on the association constant.

Alternatively, complementary oligonucleotides have been widely used to link nanoscale objects in precise structural arrangements through the base specificity of the resulting duplex structures. Baker and co-workers showed that two different generations of poly(amidoamine) (PAMAM) dendrimers can be linked specifically via three sets of multiple complementary oligonucleotides to form supramolecular Janus nanoclusters.³⁶ However, their approach produces a poly-

disperse array of base-paired dendrimer structures, including dimers, trimers, and larger dendrimer clusters. In contrast, Tomalia and co-workers developed a new method to covalently conjugate a single oligonucleotide to a specific single site of a thiol-functionalized PAMAM dendron, which could be held together by Watson–Crick base pairing to produce a new class of precise monodisperse Janus dendritic polymers with differentiated sizes and surface groups.³⁷

Besides these supramolecular Janus dendrimers, we prepared the first example of supramolecular Janus hyperbranched polymers (SJHPs) by the complexation between CD-*g*-HPG and hyperbranched poly(3-ethyl-3-oxetanemethanol) (HBPO) with an Azo unit at the apex (Azo-*g*-HBPO) through specific CD–Azo host–guest interactions (Figure 7A).³⁸ The resulting

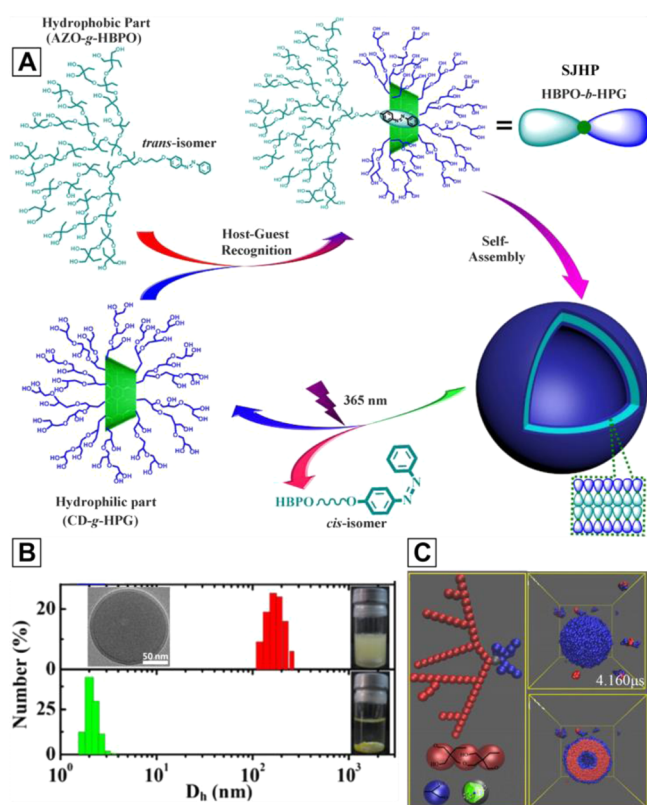


Figure 7. (A) Preparation, self-assembly, and disassembly processes of an SJHP. (B) Photographs and size distributions of vesicular solutions (top) before and (bottom) after UV irradiation as well as a TEM image of vesicles. (C) DPD simulations of the self-assembly of this SJHP. The SJHP molecular model and vesicle structure are shown. Adapted from ref 38. Copyright 2013 American Chemical Society.

supramolecular amphiphiles further self-assemble into vesicles in water, which can be disassembled under UV irradiation (Figure 7B). In addition, dissipative particle dynamics (DPD) simulations disclosed the dynamics of the self-assembly and the detailed structure of the vesicles (Figure 7C).

2.6. Supramolecular Dendritic Multiarm Copolymers (SDMCs)

SDMCs are a class of special SDPs consisting of two chemically distinct components: dendritic polymers having multiple complementary terminal units and linear polymers or dendrons with a single complementary unit. The two components can be further linked together through various non-covalent interactions to form SDMCs. Different from traditional dendritic

multiarm copolymers, SDMCs offer several unique advantages: simple synthesis and separation, tunable structures and morphologies, and stimuli-responsive properties.

The ionic bonding between carboxylic acid and amino groups has been widely used to prepare SDMCs. Crooks and co-workers first described a simple, non-covalent method to convert dendrimer exteriors from hydrophilic to hydrophobic based on the formation of ionic pairs between fatty acids and amine-terminated PAMAM dendrimers, resulting in the formation of toluene-soluble inverted-micelle-like structures.³⁹ Recently, Ros and co-workers developed an extensive series of PPI dendrimer- and hyperbranched polyethylenimine (HPEI)-based supramolecular ionic dendritic polymers bearing bent-core functional structures through the spontaneous recognition of their amine groups in the periphery by different acid-ended bent-shaped promesogenic structures.⁴⁰

Additionally, Pulpoka, Advincula, and co-workers reported a novel type of electroactive PAMAM–carbazole dendron complexes through the complexation of amine-terminated G4-PAMAM dendrimers with carboxylic acid terminal dendrons containing peripheral electroactive carbazole groups of different generations. The subsequent electrochemical oxidation of the dendrimer complexes resulted in the formation of nanoring structures during the equilibrium–decomplexation stage.⁴¹

On the basis of a newly designed host–guest system in combination with ionic and hydrogen-bonding interactions, Meijer and co-workers presented a supramolecular methodology to prepare a large variety of PPI dendrimer-based SDMCs through directional multiple secondary interactions between adamantylurea-functionalized PPI dendrimers of different generations and various ureidoacetic acid-modified molecules such as isocyanate derivatives, π -conjugated oligo(*p*-phenylenevinylene)s (OPVs), dendritic OEG, poly(ethylene glycol), and telechelic oligo(tetrahydrofuran) (Figure 8).^{42,43} The resulting PPI-based supramolecular copolymers not only displayed typical structures, properties, and functions but also further formed diverse hierarchical structures, including highly emissive homogeneous films, flowerlike structures, and transient networks. Recently, we synthesized a Boltorn H40-based amphiphilic supramolecular hyperbranched multiarm copolymer through the molecular recognition of nucleobases and showed that it can self-assemble into pH-sensitive micelles in water as a promising carrier for drug delivery.⁴⁴

3. MODIFICATION AND FUNCTIONALIZATION

As mentioned above, different types of SDPs can be non-covalently synthesized by different approaches based on various building blocks; however, most of them do not display specific functions. To realize their applications, the resulting SDPs require further modification by the incorporation of either external functional components or switchable non-covalent connections into their intrinsic backbone structures. Because of their three-dimensional globular topology, SDPs are more inclined to undergo multiple modifications compared with other types of supramolecular polymers. As shown in Table 1, strategies for modification of SDPs that notably depend on the topological structures of the building blocks generally involve terminal modification, focal-point modification, and backbone modification.

In this section, we mainly focus on supramolecular modification strategies using non-covalent interactions to realize the functionalization of SDPs, while the covalent ones

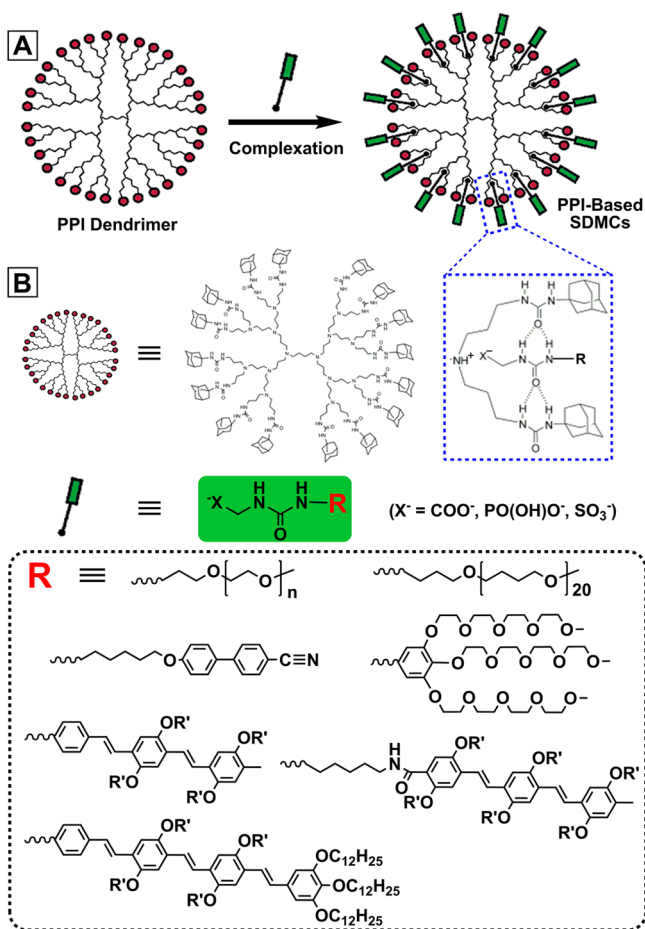


Figure 8. (A) Formation of SDMCs. (B) Chemical structures of adamantylurea-terminated PPI dendrimer and ureidoacetic acid-modified molecules.

will not be discussed here. Generally, different modification approaches are suitable for different SDPs. As an effective method to alter the surface of polymers, terminal modification is usually used to modify the dendritic-core-based SDPs. The

terminal groups of dendritic cores are first functionalized with various heterocomplementary units, such as amino groups, pyridinyl moieties, adamantylurea, nucleobases, and guest/host molecules. In that case, diverse functional components can be grafted onto the surface of the SDPs through non-covalent interactions, including liquid-crystalline, fluorescent, electroactive, and stimuli-responsive units. Focal-point modification is capable of achieving the functionalization of SDPs by means of non-covalent modification at the apex site of SDPs. In contrast to the above two modification methods, backbone modification involves altering the intrinsic nature of the SDP instead of introducing exogenous components into the original system. By this strategy, AB_n -type or A_n/B_m -type monomers can be further modified to form a series of functional SHPs via supramolecular polymerization, including electroactive, bioactive, and pH-/photo/thermo-responsive SHPs.

Besides the incorporation of functional groups, alteration of the structure parameters of SDPs has a great impact on their functionality. For example, variation of the hydrophilic/hydrophobic balance in the polymeric chains induced by the supramolecular modification remarkably affects the thermal transition behavior of SDPs.^{13,19,46}

4. SELF-ASSEMBLY AND APPLICATIONS

In this section, we will briefly summarize the recent advances in the self-assembly of SDPs and their applications in a wide range of fields, including controlled drug/gene/protein delivery, bioimaging, biomimetic chemistry, nanoreactors, catalysis, and molecular imprinting.

4.1. Self-Assembly

Similar to conventional dendritic polymers,⁴⁸ SDPs have displayed great potential to be excellent precursors in solution/interfacial/hybrid self-assembly. In general, the self-assembly process of SDPs is mostly composed of two stages: the formation of SDPs and their further hierarchical assembly. SDPs can self-assemble into a variety of impressive supramolecular structures at all scales and dimensions (Figure 9), such as spherical/cylindrical micelles,^{39,44,45,49} spherical/tubular vesicles,^{18,31,32,38} fibers,³⁰ nanorings,^{41,50} helical tubes,⁵⁰ and many hierarchical structures.^{30,43} In addition, benefiting from

Table 1. Strategies for Modification of SDPs

modification strategy	type of SDP	building block(s)	functional units	functionality	ref
terminal modification	SDMC	PPI, HPEI	mesogenic units	liquid-crystalline	40
		PAMAM	carbazole	electroactive	41
		PPI, HPEI	OPVs, calcein	fluorescent	42, 45
		HPG	cationic β -CD	tunable charge, tunable LCST	46
focal-point modification	SD	polyether dendron	lanthanide	luminescent	–
		OEG dendron	β -CD trimer	thermo-responsive	13
		PPI	ferrocene	redox-active	15
	SDNP	Fréchet dendron	DB24C8/ NH_2^+	pH-responsive	17
		OEG dendron	polymethacrylate	thermo-responsive	19
		SLDBC	Fréchet dendron	PNIPAM, β -CD/Azo	photoresponsive, thermo-responsive
backbone modification	SHP	AB ₂ monomer	PNIPAM	thermo-responsive	29
			C ₆₀ , exTTF	electroactive	23
		A ₂ /B ₃ monomer	DB24C8/ NH_2^+	pH-responsive	28
			A ₂ /B ₄ monomer	β -CD/Azo	photoresponsive
		porphyrin	photosensitizer	47	
		Mn(III) porphyrin, tellurium	antioxidative enzyme	26	

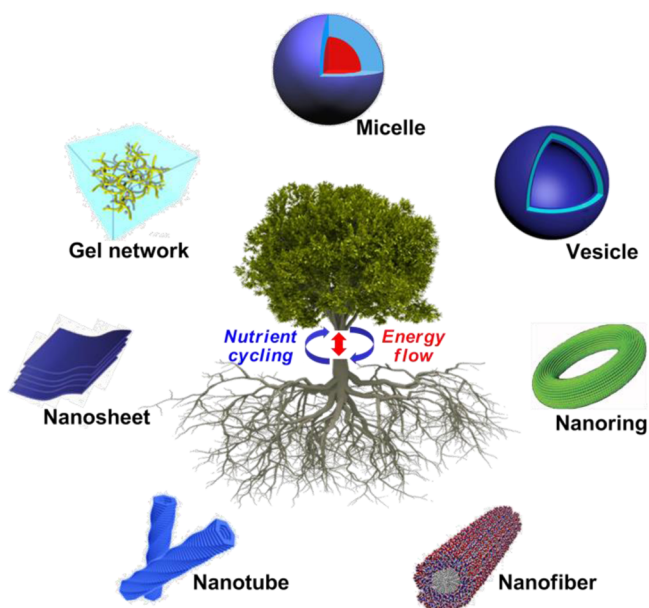


Figure 9. Various nanostructures self-assembled from SDPs.

the dynamic/tunable natures of non-covalent bonds, SDPs also demonstrate unique characteristics or advantages in supramolecular self-assembly behaviors, including controllable morphologies and structures, specific properties, and facile functionalization.

4.2. Applications

In recent years, SDP-based supramolecular systems have been widely exploited as promising vehicles in biomedical fields because of their three-dimensional architectures and multifunctionality. For example, Tseng and co-workers reported a modular synthetic approach for the preparation of size-

controllable supramolecular nanoparticles that could be used for *in vivo* bioimaging and diagnosis.⁴⁹ By the introduction of a calcein fluorescent dye, we explored a novel class of supramolecular fluorescent nanoparticles in combination with smart targeting capability for cancer-specific delivery, which exhibited excellent cancer imaging efficiency.⁴⁵ Very recently, we developed a facile supramolecular approach for the preparation of charge-tunable dendritic polycations via β -CD–AD host–guest interactions between primary- or tertiary-amine-functionalized β -CD derivatives and an AD-modified HPG (Figure 10A).⁴⁶ Through tuning of the molar ratios of these two cationic β -CD derivatives, the surface charge and molecular functionality of the resulting polycations can be efficiently regulated or optimized. This class of supramolecular polycations shows controlled pDNA condensing ability and enhanced *in vitro* transfection efficiency (Figure 10 B).

Synthetic vesicles have proved to be excellent model systems to mimic the dynamic and structural features of cells. By using cell-sized vesicles as the building blocks, we presented a large-scale cytomimetic vesicle aggregation process by utilization of β -CD–Azo host–guest recognition as the driving force. The vesicle aggregates could be reversibly disassembled and reassembled under alternating UV and visible-light irradiation.⁵¹ As inspired by jellyfish, we reported a novel class of polymeric vesicles that exhibited a pH-induced “breathing” behavior accompanied by jellyfish-like on–off switchable fluorescence.⁵² Importantly, this study extended cytomimetic chemistry from the morphological transformation of membranes to a combination of cytomimetic morphology with the concomitant expression of function.

Moreover, SDPs have demonstrated infinite potential to be eminent candidates in nanotechnology. We constructed a supramolecular nanoreactor through the electrostatic interaction between palmitic acid and HPEI or PAMAM, in which the synthesis and phase transfer of CdS nanocrystals could be

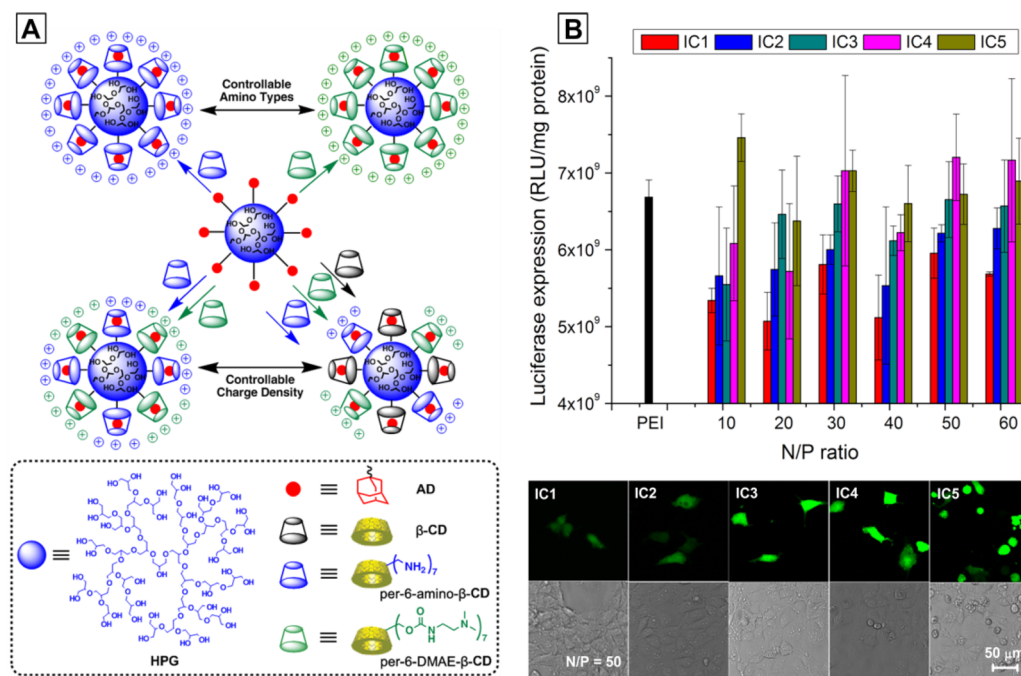


Figure 10. (A) Preparation of charge-tunable supramolecular dendritic polycations via β -CD–AD host–guest interactions. (B) Luciferase expression (top) and green fluorescent protein expression (bottom) of these supramolecular polycations in COS-7 cells. Adapted with permission from ref 46. Copyright 2011 Royal Society of Chemistry.

readily realized.⁵³ Using a similar supramolecular template, we further fabricated Au@mesoporous silica nanoparticle nanocomposites via the in situ reduction of chloroauric acid, and these nanocomposites showed excellent catalytic performance.⁵⁴ In addition, SDP-based supramolecular microcontact printing has been exploited for the preparation of controlled patterns via multivalent host–guest interactions.⁵⁵

5. CONCLUSIONS AND OUTLOOK

In this Account, we have summarized recent progress in the development of versatile SDPs, including synthesis strategies, functionalization approaches, self-assembly of nanostructures, and their applications in various fields. A series of non-covalent synthetic strategies have been established to prepare SDPs with diverse topological structures. Furthermore, different modification approaches involving terminal, focal-point, and backbone modification have been developed to endow SDPs with specific functions. As a perfect combination of supramolecular chemistry and dendritic polymers, great progress has been made in SDP-based supramolecular chemistry, and SDPs have displayed attractive potential to be excellent candidates for supramolecular self-assembly and a wide range of applications. However, the current research on SDPs is just at the very early stage, and some basic challenges still remain to be solved before SDPs can be put into practical application. In particular, it is well-expected that hierarchically structured SDPs based only on small-molecule repetition motifs will be constructed by utilization of cooperative non-covalent interactions. We envisage that this Account can further stimulate new ideas and inspire continued endeavors in this emerging research area in the future.

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