Fabrications and Applications of Cucurbit[8]uril-Based Supramolecular Polymer

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29.1 Introduction

Cucurbiturils (CB[n]s, n = 5–8, 10, 13–15), as the third-generation macrocyclic compounds, are formed by n glycoluril units bound together by 2n methylene bridges, engendering pumpkin-shaped hollow molecules with an inner

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hydrophobic cavity [1]. The binding and encapsulation properties of CBs are mainly dependent on the arrangement of glycoluril subunits. Among the common CBs, CB[8] possesses the larger cavity of ca. 1.7 times compared with the volume of CB[7], which enables a plenty of binding motifs [2, 3]. The cavity of CB[8] is highly electronegative as well as remarkably hydrophobic, benefitting the hosts capable of forming inclusion complexes with cationic/neural organic guests via cation-dipole interactions, hydrophobic forces, and optimization of host-guest packing coefficients [3–5]. Significantly, CB[8] has been demonstrated well to form ternary complexes with appropriate guests, which is the important member in the cucurbituril family [6–9]. CB[8] promotes not only 1:1:1 heteroternary but also 2:1 homoternary in aqueous solution; thus, a variety of applications including supramolecular polymers, hydrogels, and functional materials have been exploited [10–13].

Supramolecular polymers, combining the characters of polymers and supramolecular interactions, including host-guest complexation, hydrogen binding, π-π stacking, as well as dipole interactions, have brought novel and much vigor into functional and advanced material science [14–17]. Since 2008, the research CB[8]-based on supramolecular polymers has progressed quickly taking advantage of CB[8]-mediated host-guest interactions with high binding constants [18]. Supramolecular polymers based on CB[8] have been established to construct various application in many fields, such as (1) extremely stretchable and tough supramolecular polymer networks are achieved through copolymerization of functional polymers and dynamic CB[8]-mediated non--covalent cross-linking, exhibiting remarkable self-healing property [19, 20]; (2) CB [8]-based ternary host-guest complexation allows dual stimulus responsiveness of the supramolecular polymers [21]; (3) well-ordered architectures bearing excellent photophysical properties are constructed via supramolecular assembly of individual chromophore components and CB[8] [22–24]; (4) CB[8]-based supramolecular polymers are utilized to constructed soft materials with biological applications [25–28], including drug delivery, cell adhesion, and proliferation; and (5) more functional materials in other fields are also developed in supramolecular microcapsules [29–31], surface engineering [32–38], and polymer modified [39], which make the CB[8]-based supramolecular polymers prosper. In this chapter, we provide an overview of construction strategies of CB[8]-based supramolecular polymers and their application in various fields.

29.2 Construction Strategy

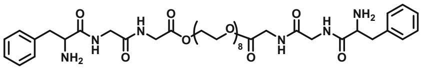
CB[8]-based polymers can be constructed taking advantage of a series of supramolecular interactions. There are a number of excellent reviews in the area of CB[8]-based polymers and more general host-guest-driven polymerization. In this section, we focus on summarizing the categories of the guest molecules and the bonding motif with CB[8], which reveals the essential construction methods.

29.2.1 CB[8]-Based Supramolecular Polymers with Homoternary

A lot of guest molecules can form double encapsulation into the cavity of CB[8] with a stable 2:1 homoternary, including napththyl cations derivatives, dipyridinium salts, anthracene derivatives, coumarin, and some specific peptide sequences (Fig. 1) [40–45]. In addition, some particular radical cations [46–48], such as dicationic viologen and tetrathiafulvalene cation radical dimers, can be trapped inside of CB[8], which would provide more opportunities to construct stimulus-responsive supramolecular polymers.

In 2014, Scherman et al. reported that CB[8] enhanced the [4 + 4]-photodimerization rate of anthracene in **12** via host-guest interaction, where the two anthracene moieties were co-included in the cavity of CB[8] in a face-to-face π-π stack orientation. Then, the authors applied the strategy in photochemical polymer ligation and cross-linking supramolecular hydrogel [49]. Subsequently, Jiang and Chen [50] designed a novel approach to realize unimolecular cyclization based on CB[8]-stabilized π-π interactions (Fig. 2). Anthracene-functionalized polyethylene glycol **13** achieved a ring-closure operation supported by CB[8] complexation in a highly diluted solution. Moreover, the cyclic polymer could be directly characterized by GPC, because of anthracene groups transferred to covalent bond through UV light irradiation, which is very rare for supramolecular polymer. The environment-friendly cyclization in water provided further applications in many research fields.

Azastilbene derivatives, also as one kind of photodimerization molecules, have drawn a great deal of interest of chemists. In 2013, Zhang et al. [51] utilized CB[7,8] to bind with photosensitive azastilbene derivatives **14** to form different host-guest complexes with various emissions, which may be potential in fabricating advanced stimuli-responsive fluorescent materials (Fig. 3a). And then, they employed CB[8] and a three-arm azastilbene derivative **10** via host-guest interactions and photochemistry to fabricated supramolecular hyperbranched polymers [52]. Lately, the authors reported a novel method of controllable supramolecular polymerization, drawing support of host-enhanced photodimerization of **17** [53]. CB[8] and bifunctional monomers with Brooker's merocyanine (BM) moiety on either end firstly formed in low-molecular-weight supramolecular oligomers and then transformed into supramolecular polymer with high molecular weight with UV light irradiation, which could be controlled by varying the irradiation time (Fig. 3b). Furthermore, the authors investigated the CB [8] catalysis effect in accelerating the photodimerization of BM [54]. A catalytic amount of CB[8] (1% of the BM units) could significantly promote the photodimerization, due to the higher binding affinity of unreacted BM units than the product with CB[8], that is, the catalytic cycle is self-driven, thus rendering CB[8] preferred bind two new BM units and encycling the catalytic process. On this basis, the authors developed a novel approach for achieving covalent polymerization [55], using CB [8] as a supramolecular catalyst and a BM unit – bifunctional monomer **18** – as the reaction substrate, to successfully prepare polyelectrolytes in aqueous solution (Fig. 3c). The line of research combined supramolecular catalysis and polymer chemistry, offering new methodology of polymerization and horizons for supramolecular polymer chemistry.



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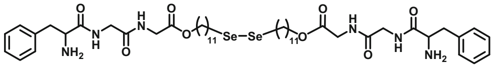

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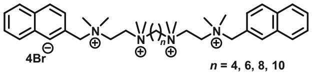

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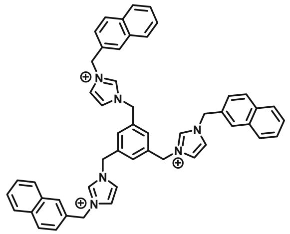

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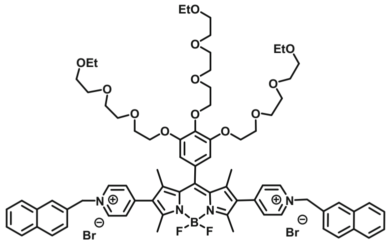

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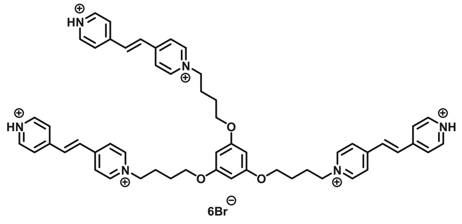

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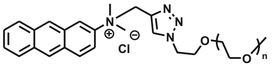

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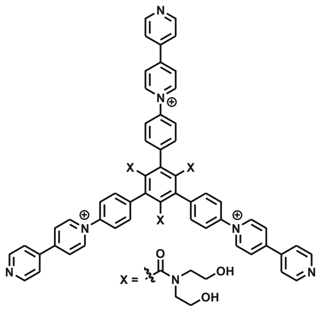

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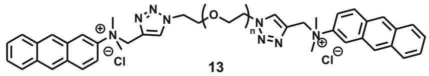

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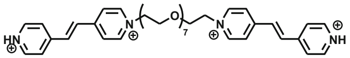

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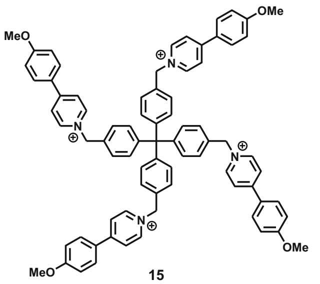

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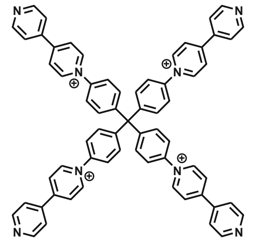

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Fig. 1 (continued)

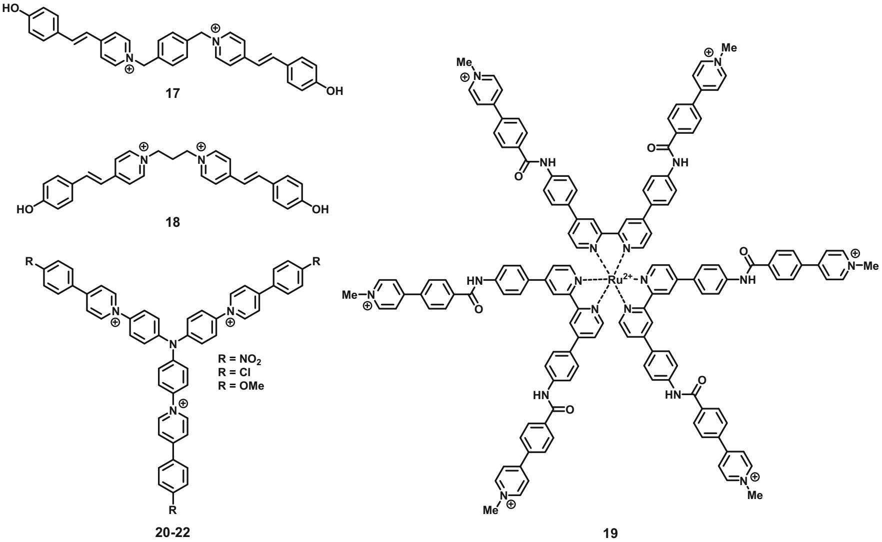


Fig. 1 Structures of monomers

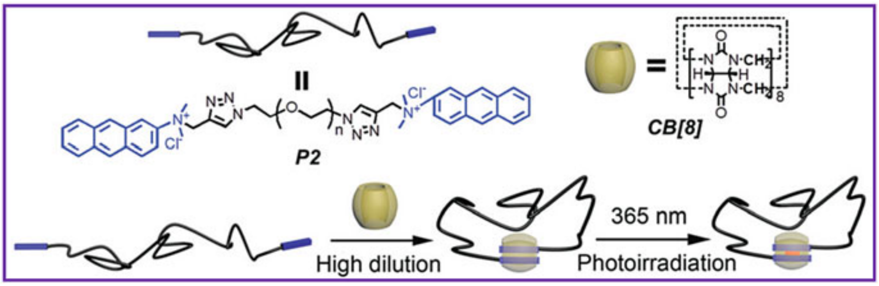


Fig. 2 Cyclization based on the CB[8]-stabilized π-π interaction in a highly diluted aqueous solution and the following covalent fixation through photo-irradiation at 365 nm [50]. (Copyright © 2015, Royal Society of Chemistry)

Recently, Li, Zhao, and other groups [56–60] constructed a series of supramolecular network polymer – supramolecular organic framework (SOF) – in water based on rigid guest molecules, which bear bipyridium derivative on periphery. In 2013, Li and Zhao [61] firstly designed and synthesized well-defined single-layer 2D SOF by triangular preorganized molecule assembling with CB[8] in a 2:3 molar ratio (Fig. 4). In the design, the hydrophilic bis(2-hydroxyethyl)carbamoyl groups as

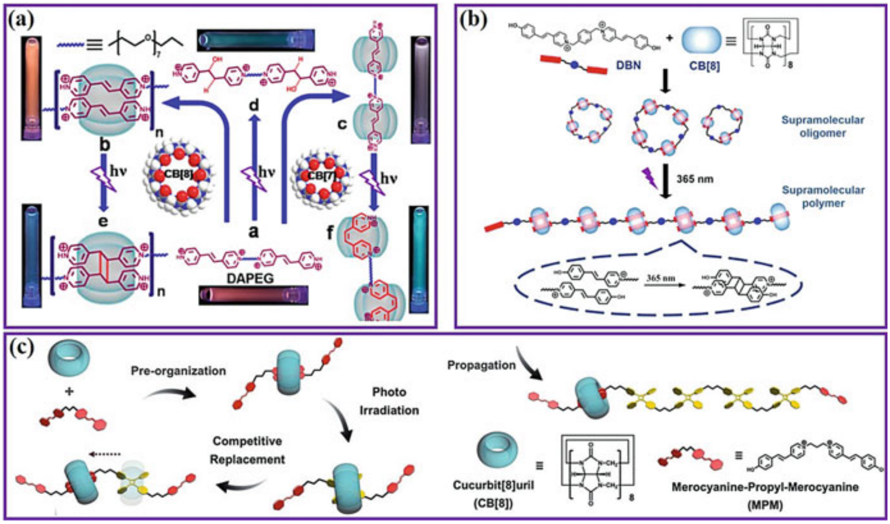


Fig. 3 Example of CB[8]-based supramolecular polymers on azastilbene derivatives. (**a**) Multicolor fluorescence supramolecular polymers by host-guest chemistry and photochemistry [51] (Copyright © 2013, American Chemical Society). (**b**) Light-promoted supramolecular polymerization of **17**@CB[8] [53] (Copyright © 2016, American Chemical Society). (**c**) A new method of supramolecularly catalyzed polymerization [55]. (Copyright © 2018, John Wiley and Sons)

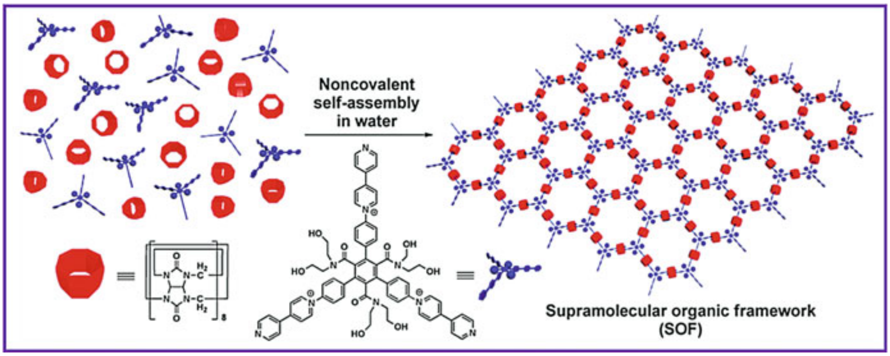


Fig. 4 2D SOF from supramolecular cross-linking of a rigid strut and CB[8] [61]. (Copyright © 2013, American Chemical Society)

steric-generating groups were tactfully induced to the triangular molecule to suppress the stacking between layers. The novel 2D porous architecture represents periodic structural ordering similar to MOFs and COFs, providing more opportunities for producing advanced materials.

Then, Li and Zhao [62] developed 3D periodic SOF ion sponge with the dimerization of two aromatic units in tetratopic molecular blocks **15** in the cavity of CB[8]. Upon evaporating water, the 3D SOF still maintained in porous microcrystals and could be used as supramolecular “ion sponge” to absorb different kinds of anionic guests, such as dyes, peptides, nucleic acids, poly (amidoamine) dendrimers, and drugs, and furthermore realized the absorbed drugs released to water with selectivity in acidic medium (Fig. 5A). Subsequently, Li et al. [63] constructed the first homogeneous supramolecular metal-organic framework (SMOF-1) in water at room temperature by the same supramolecular assembly strategy with a hexa-armed $[Ru(bpy)_3]^{2+}$-based precursor **19** and CB[8]. Remarkably, SMOF-1 can adsorb anionic Wells-Dawson-type polyoxometalates (WD-POMs) in a one-cage-one-guest manner to give a hybrid assembly (Fig. 5B). Moreover, the hybrid enabled remarkably efficient hydrogen production in aqueous media and in organic media, as a result of fast multi-electron injection from photosensitive $[Ru(bpy)_3]^{2+}$ units to redox-active WD-POM units upon visible light irradiation. Recently, the same group utilized post-modified method to observe a diamondoid 3D SOF through appending $[Ru(bpy)_3]^{2+}$ groups to the framework via formation of a hydrazone bond [64]. Thus, the 3D SOF could realize efficient visible light-induced recyclable heterogeneous catalyst for reduction of aromatic azides to amines with up to 11 runs. To summarize briefly, the authors systematically studied that trihedral and tetrahedral molecules, which contain 4-phenylpyridinium units in peripheral, assembled with CB[8] to afford periodic 2D and 3D SOF in water phase. Benefitting from complexation with CB[8], the SOF exhibits good stability and excellent order, making the opportunities to tune the physical and chemical properties through encapsulation nanoparticles or post-modified method, and then proves to be a great candidate for material applications in the future.

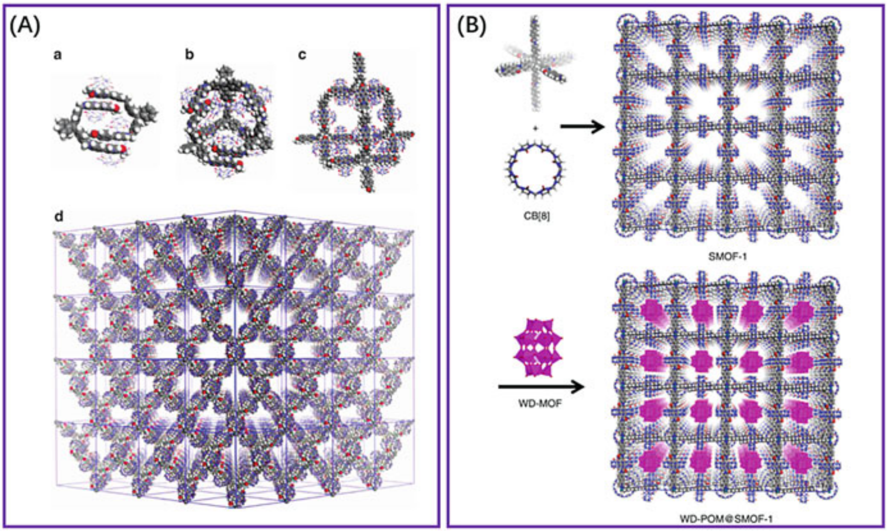


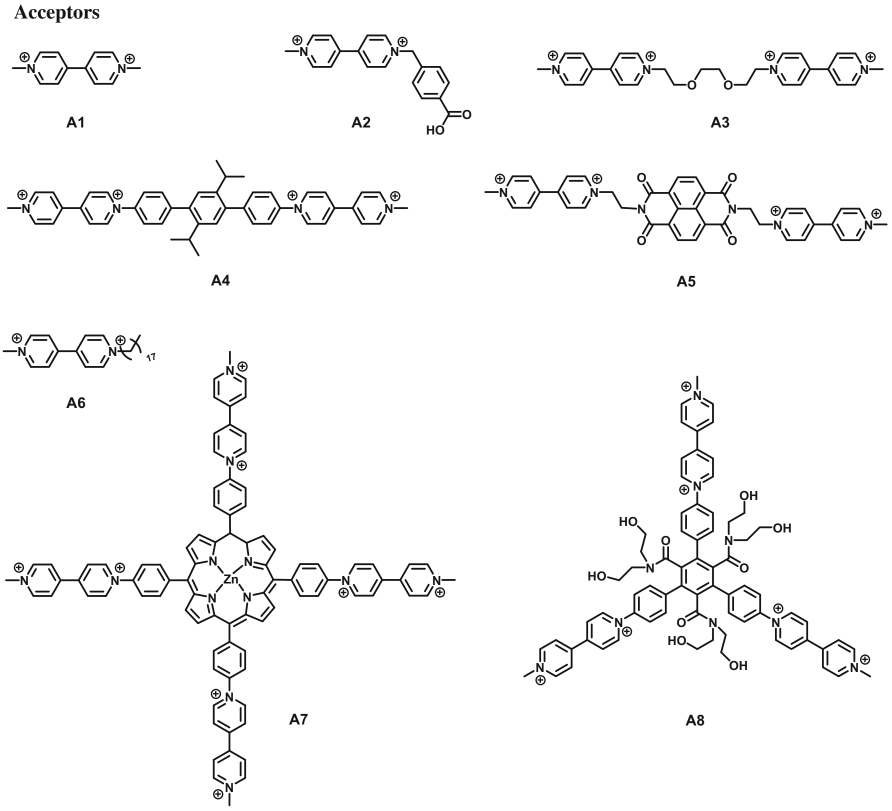
Fig. 5 (**A**) Models of one adamantane-shaped unit and the 3D supramolecular organic framework (15_n•CB$[8]_{2n}$) [62] (Copyright © 2014 NPG). (**B**) Formation of SMOF-1 ($\mathbf{19}_n$•CB$[8]_{3n}$) and WD-POM@SMOF-1 [63]. (Copyright © 2016 NPG)

29.2.2 CB[8]-Based Supramolecular Polymers with Heteroternary

On the other hand, CB[8] could form stable 1:1:1 heteroternary supramolecular complex (Fig. 6), typically an electron-deficient first guest and an electron-rich second guest, through host-stabilized charge-transfer (CT).

In 2001, Kim et al. [65] firstly discovered the CT phenomenon: the exclusive 1:1 complex formed between CB[8] and MV^{2+} could bind an electron-rich aromatic guest, such as 2,6-dihydroxynaphthalene (**D1**) or 1,5-dihydroxybenzene (**D3**). More than that, the authors also found that N,N′-dimethyldipyridyliumylethylene (MPE^{2+}) was a stronger electron acceptor than MV^{2+}, resulting in more stable CT heteroternary with electron-rich guest [66]. Remarkably, the host-stabilized intramolecular CT interaction offers new opportunities to fabricate functional supramolecular assembly, such as molecular necklace, poly(pseudorotaxane), molecular loop lock, and so on (Fig. 7) [67, 68].

Following the strategy, the amphiphilic diblock copolymers and oligopeptide self-assembly and some other supramolecular network polymers have been



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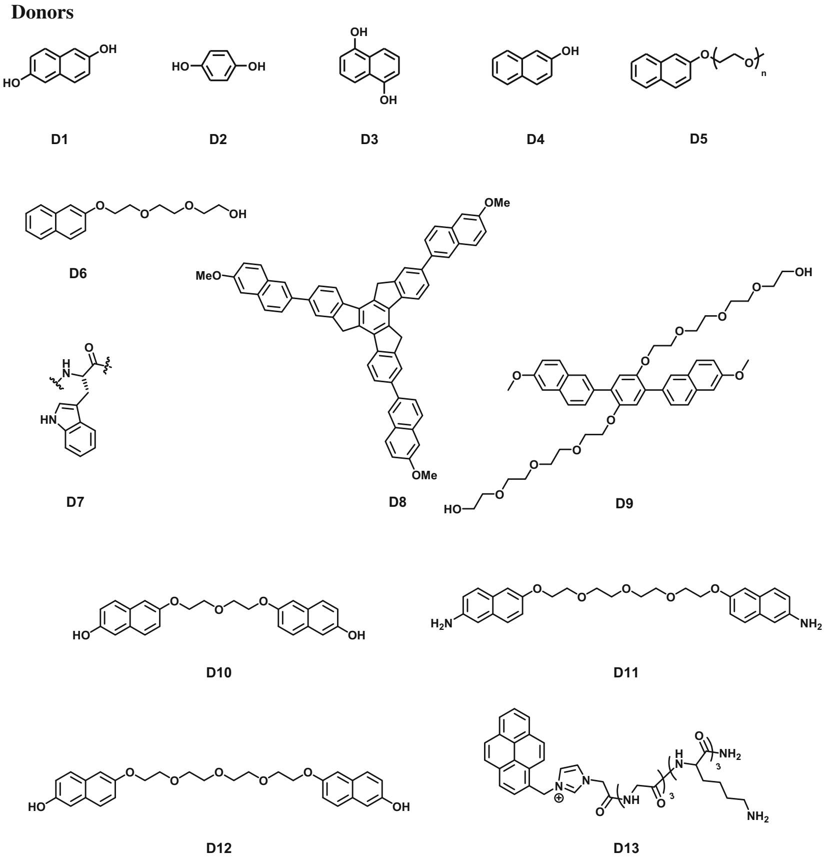

Fig. 6 Structures of monomers of CT heteroternary

developed via CB[8]-mediated, respectively [69–71]. Scherman et al. [72, 73] facilitated reversible cross-linking of multivalent copolymers based on the host-stabilized CT interaction, offering a versatile method for preparation of smart, self-healing, and controlled supramolecular hydrogels. More interesting, the authors utilized atomic force microscopy-based single-molecule force spectroscopy to investigate the binding forces involved in the heteroternary of MV^{2+}/CB[8]/naphthol. Such studies bring many opportunities to understanding of host-guest supramolecular complex information as well as the property-structure relationship [74].

Li, Zhao, and other groups [75–77] constructed single-layer two-dimensional SOF via the 1:1:1 ternary complex based on host-stabilized CT interaction (Fig. 8). Compared with previous 2D SOF construction strategy using homoternary of rigid building blocks, the heteroternary extends the variety of 2D soft nanomaterials, providing a novel approach to fabricate 2D supramolecular materials with diversified topologies and intriguing properties.

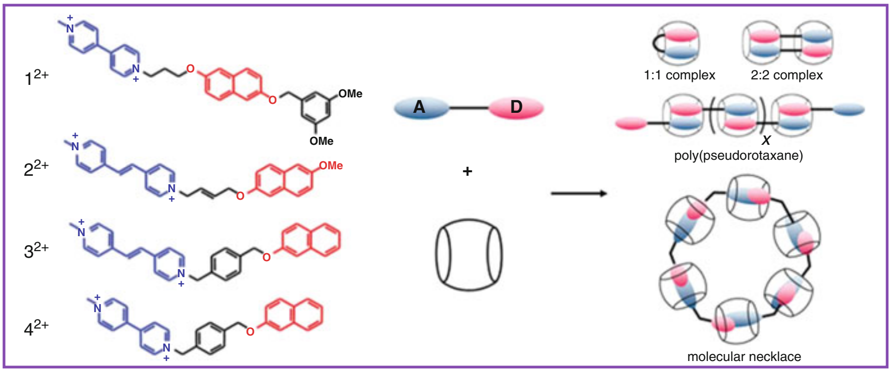

Fig. 7 Possible supramolecular assemblies built with CB[8] and D-A molecules containing both electron-donor and electron-acceptor units connected by a suitable linker [68]. (Copyright © 2007, Royal Society of Chemistry)

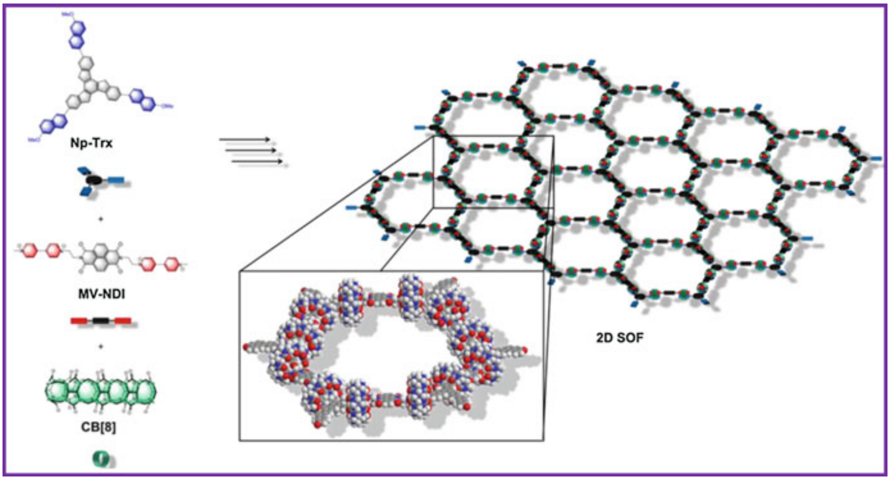

Fig. 8 Hexagonal superstructure 2D SOF promoted by CB[8] host-stabilized CT interaction [75]. (Copyright © 2015, American Chemical Society)

Since then, more and more CT pairs have been found out. In 2010, Zhang et al. [78] proposed a “dimer in dimer” strategy to fabricate supramolecular polymer by an ABBA-type monomer through multiple CT interaction (Fig. 9). The monomer contained two viologen moieties as electron acceptors and two anthracene moieties as electron donors. Moreover, butylidene acted as the short spacer, which was inhibited the formation of 1:1 cyclic complex efficiently. Furthermore, the authors found that the anthracene could have higher affinity with MV-CB[8] than naphthalene or tryptophan due to the geometric structure and electron property. The multiple host-stabilized CT interactions possessing a high binding constant and orientation

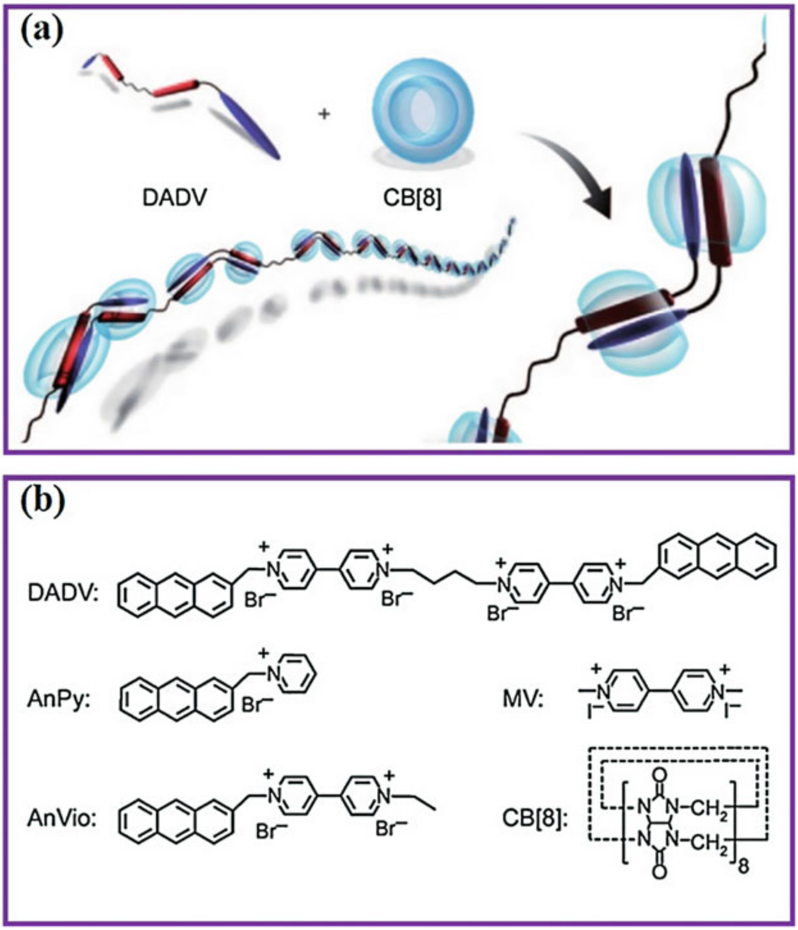

Fig. 9 (**a**) Formation of the supramolecular polymer based on multiple host-stabilized charge-transfer interactions. (**b**) Structure of monomers [78]. (Copyright © 2010, John Wiley and Sons)

selectivity can be employed as the powerful driving force to fabricate various supramolecular polymers.

Some significant CT pairs have been demonstrated by Scherman group, such as pyrene and its derivatives as electron donors and the viologen units as the electron acceptors or perylene bis(anhydride) derivatives as both electron donors and acceptors and MV^{2+} and N,N′-dimethyldipyridyliumethylene or dibenzofuran, azobenzene, biphenyl, and anthracene as the second guests, respectively [79–81].

Light is a clean and controlled resource and can be applied in a remote manner as well as offers precise control over wavelength. Therefore, photosensitive host-guest complexes are very fascinating among supramolecular stimuli-responsive systems. In 2012, Scherman et al. [38] demonstrated CB[8]-mediated heteroternary complexation with viologen and azobenzene derivatives as functional guests in water, exhibiting a various platform for the orthogonal stimuli-responsive supramolecular systems. The authors also designed the photocontrolled CB[8]-mediated supramolecular polymer based on azobenzene-containing monomers. It was uncommon that the CB[8] polymers were characterized both in solution and in the solid state (Fig. 10A, B) [82]. Afterward, a series of smart and ingenious light-responsive supramolecular assemblies [83] have been developed and applied in many materials fields, including microscale flow control devices (Fig. 10C) and visible light-regulated supramolecular polymer based on fluorinated azobenzene (FAB) incorporated monomer [84].

29.2.3 Other Models of CB[8]-Based Supramolecular Polymers

29.2.3.1 Metal Coordination

For construction of supramolecular polymers with high molecular weight, other non-covalent interactions, such as hydrogen-bonding and metal coordination, are requisite. In 2013, Zhang et al. [85] designed a heteroditopic molecule bearing both naphthalene moiety and terpyridine moiety, which could bond with CB[8] in 2:1 motif and metal ion Fe^{2+}, respectively, to fabricate a hybrid supramolecular polymer. Masson group [86, 87] prepared a series of dynamic oligomers taking advantage of coulombic interactions between a metal (Fe or Ir) and CB[8] mediated by an organic ligand with terpyridine, in which CB[8] acted as a “soft” and non-covalent linker. The dynamic oligomers undergoing social self-sorting with alternating Fe and Ir metallic cores are rare.

In 2015, our group [88] designed a water-soluble supramolecular polypseudorotaxane based on the host-guest interaction of CB[8] and $Ru(bpy)_3$ bearing two naphthalene imidazolium (Fig. 11). UV-vis spectroscopy and fluorescence spectroscopy were employed to study the binding mode, where naphthalene moieties were encapsulated in the cavity of CB[8]. DOSY, AFM, and DLS results also illustrated the formation of supramolecular polymer. More interestingly, the linear supramolecular polymer exhibits DNA condensation, which can be used as an inhibitor for DNA cleavage enzymes. Meanwhile, the linear supramolecular polymer also represents excellent fluorescent properties and traces the translocation of DNA into 293T cells efficiently, which is a potential application in pharmaceutical chemistry and biological technology fields.

29.2.3.2 Cooperation with Other Macrocyclic Molecules

It is well known that macrocyclic hosts could form various host-guest complexes, due to their diverse binding selectivity and distinguishable inclusion affinities to diverse substrates. It can be seen that introduction of different macrocyclic hosts in one supramolecular system can enrich the functionality and stimuli-responsiveness. In 2012, our group [89] reported the CB[8]-modulated supramolecular assembly, which achieved the interesting topological conversion from cyclic oligomers to linear polymers (Fig. 12). In this method, a binary supramolecular assembly was fabricated by bipyridinium derivative (HBV^{4+}) and bis(*p*-sulfonatocalix[4]arenes) (bisSC4A) firstly. And then, a ternary supramolecular polymer participated by CB [8] was fabricated through the bisSC4A and [2]pseudorotaxane HBV^{4+}/CB[8].

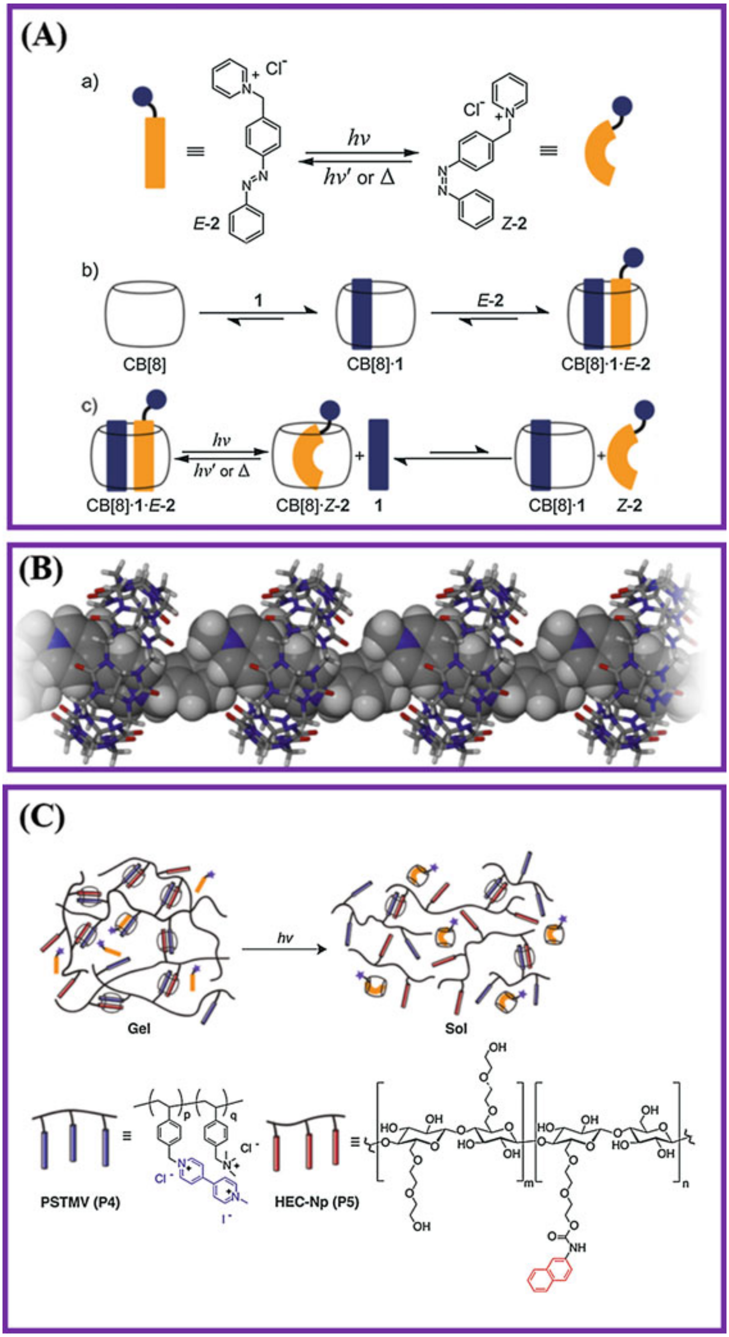

Fig. 10 (**A**) Azobenzene derivatives with/without viologen in the cavity of CB[8] before and after UV irradiation. (**B**) Side view of the X-ray crystal structure of CB[8] supramolecular polymer [82] (Copyright © 2013, American Chemical Society). (**C**) Photoinduced gel-to-sol transition of the HEC polymer network [83]. (Copyright © 2015, Royal Society of Chemistry)

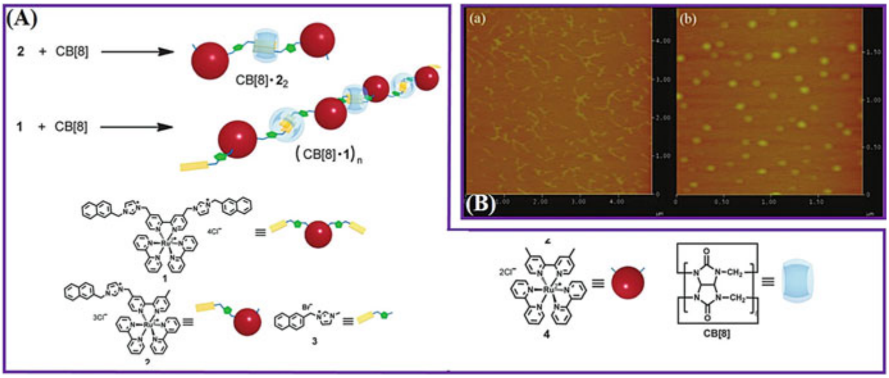

Fig. 11 (**A**) Formation of supramolecular polymer with Ru coordination. (**B**) AFM images of the DNA condensation effect of the supramolecular polymer [88]. (Copyright © 2015, Royal Society of Chemistry)

Furthermore, CB[8] not only tuned the topological conversion but also promoted the redox-responsive assembly/disassembly property, proving an alternative method for constructing smart supramolecular materials with diverse structures and self-mending capability.

Cyclodextrins (CDs), a class of cyclic oligosaccharides, are widely used in supramolecular chemistry, due to the outstanding water solubility, low toxicity, as well as environment friendliness. Recently, our group [90] designed supramolecular polymer based on the combination of CB[8]-stabilized CT interactions and CD-adamantane host-guest interactions (Fig. 13a). A naphthol-modified β-CD (Np-β-CD) and an adamantane-viologen ditopic guest were mixed to obtain a host-guest complex with a preorientational donor-acceptor pair, which inhibited the oligomeric cyclic complex in the further polymerization by addition of CB[8]. Moreover, this kind of supramolecular polymer possesses several inherent advantages: (1) the satisfactory binding abilities toward various neutral/ionic substrates due to combining different macrocyclic molecules and (2) the introduction of strong CT interaction, along with the affinity of the CD-adamantane pair, jointly leading to high degree of polymerization. Another multistimuli-responsive supramolecular assembly was successfully constructed by inclusion complexation of α-CD with azobenzene and the host-stabilized CT interaction of naphthalene and a bispyridinium guest with CB[8] in water (Fig. 13b) [91]. Interestingly, the supramolecular nanostructure can be efficiently modulated by external stimuli, including temperature, UV-/visible light irradiation, and chemical redox, benefiting from the photoinduced isomerization of the azophenyl group and the chemical reduction of bispyridinium moiety. The incorporation the multistimuli-responsive functional units into the supramolecular assembled entities can fabricate more sophisticated and advanced molecular materials with new functionality, good reproducibility, and easier operability.

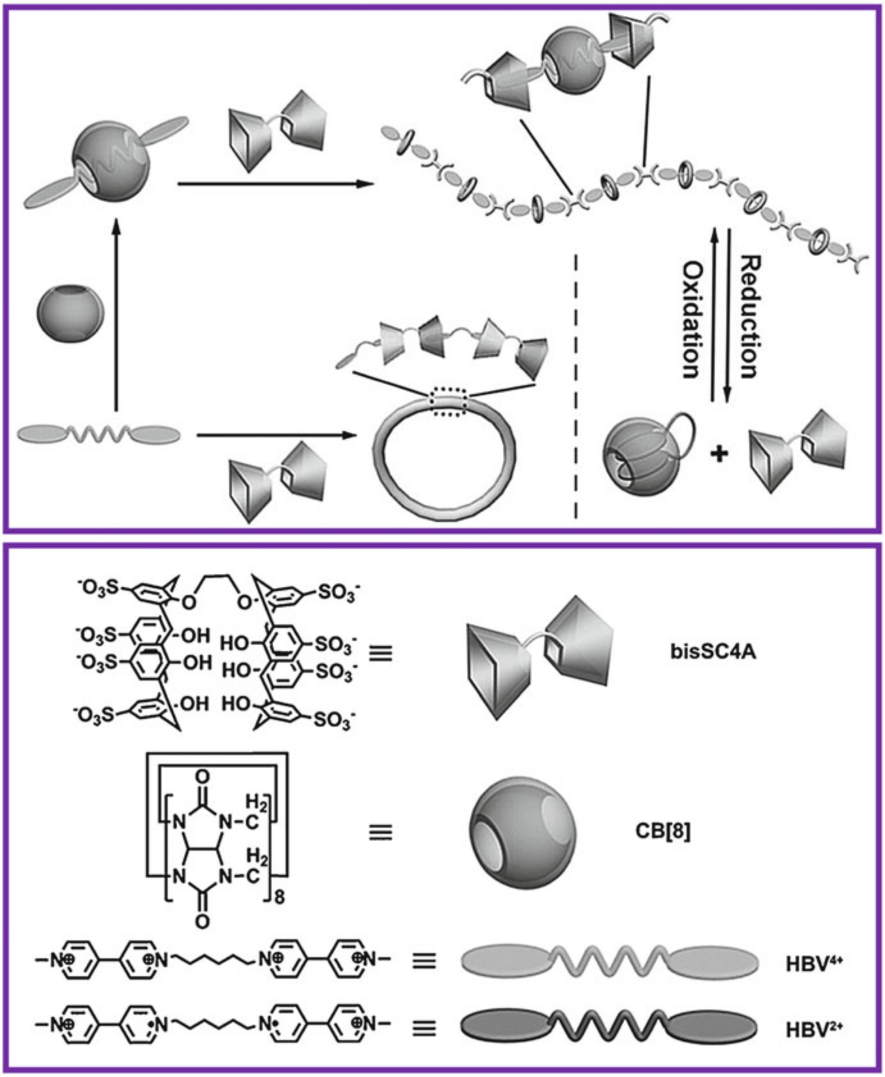

Fig. 12 CB[8]/bisSC4A cooperated supramolecular polymer and the redox stimulus response [89]. (Copyright © 2012, John Wiley and Sons)

Zhang et al. [92] fabricated a novel supramolecular polymer through supramolecular polymerization of supramonomers, which were obtained by mixing CB [8] and Phe-Gly-Gly linked with azobenzene group in 1:2 ratio. Then the supramolecular polymerization occurred when bis-β-CD was added in a molar ratio of 1:1 through host-guest complexation between azobenzene group and β-cyclodextrin.

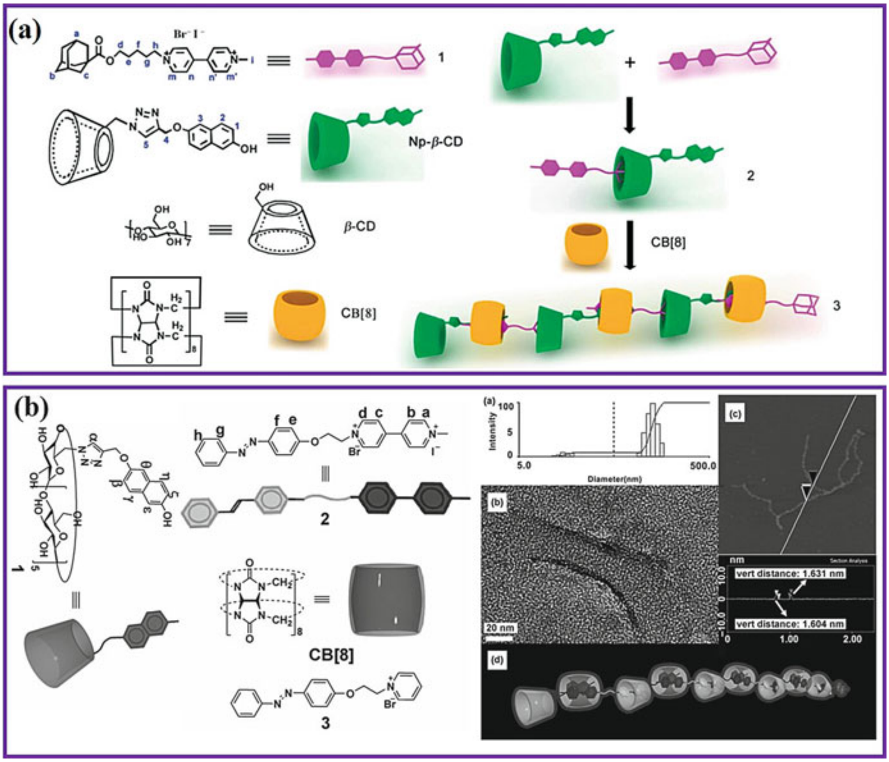

Fig. 13 Formation of multistimuli-responsive supramolecular polymers based on CB[8]/CD cooperation [90, 91]. (Copyright © 2013, Royal Society of Chemistry; Copyright © 2014, John Wiley and Sons)

This work can enrich the methodology of fabricating supramolecular polymers on account that various non-covalent interactions can be in management of the formation of supramonomers and the supramolecular polymerization. In 2014, the authors and co-workers [93] reported another method to construct supramolecular polymerization through self-sorting, that is, molecules were endowed with the ability to selectively and specifically form complexes with their own recognition units within a complex mixture. They designed and synthesized a bifunctional monomer containing *p*-phenylene and naphthalene moieties, in which the *p*-phenylene group could be selective recognized by CB[7], and the naphthalene groups complexed with CB[8] in 2:1 ratio. It was vital to adjust the amount of CB[7], which controlled the supramolecular polymerization process. This line of research will expand the field of supramolecular polymer chemistry with important advances toward the realization of molecular weight and structural control.

29.3 Applications

CB[8]-based supramolecular polymers possess not only convenient preparation but also reversible stimuli-responsive. Therefore, various functional and advanced materials have been developed in the past decades. In the following part, we will briefly introduce the recent progresses on functions and applications of CB[8]-based supramolecular polymers.

29.3.1 Supramolecular Hydrogel

Recently, supramolecular polymeric hydrogel has attracted much attention on account of the mechanical properties benefiting from the polymeric building blocks and the stimuli responsivity as well as inherent process ability based on the supramolecular units used in cross-linking. Sherman group developed a series of supramolecular hydrogels with the cross-link density being controlled by CB[8] host-guest complexation.

29.3.1.1 Supramolecular Cross-Linked Network

It is very important to tune the solution viscosity of aqueous systems in many applications, such as controlled drug delivery, self-healing materials, and regenerative medicine. Scherman et al. [72] designed a system for the construction of three-dimensional supramolecular cross-linked polymeric materials based on the strong yet reversible CB[8] stabilized charge-transfer interaction. Different types of multivalent side-chain functional polymers bearing either electron-rich naphthoxy or

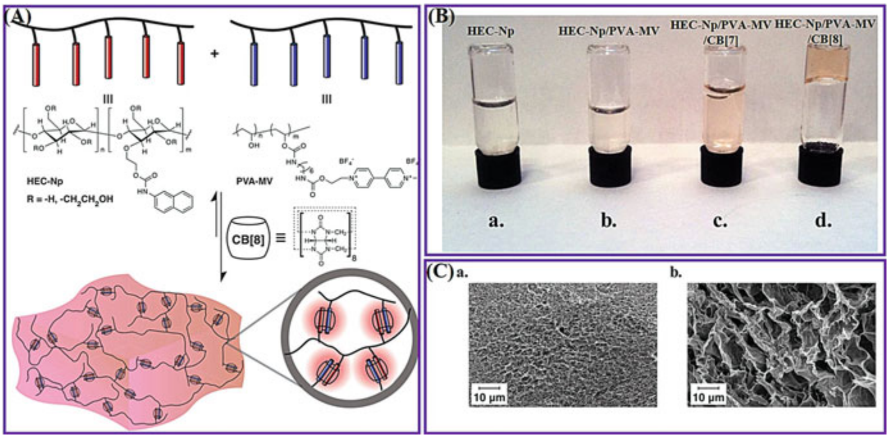

Fig. 14 (**A**) Formation of a supramolecular hydrogel. (**B**) Inverted vial tests of the hydrogel from the mixture of HEC-Np (0.5 wt %). (**C**) SEM images of cryo-dried and lyophilized samples of (a) HEC-Np (0.5 wt %)/PVA-MV (0.05 wt %)/CB[8] (1 equiv) and (b) HEC-Np (0.5 wt %)/PVA-MV (0.1 wt %)/CB[8] (1 equiv) [73]. (Copyright © 2012, American Chemical Society)

electron-acceptor viologen were prepared through radical polymerization. And then the dynamic supramolecular hydrogels were observed as a result of the formation of 1:1:1 ternary complexation mediated by CB[8]. Furthermore, the supramolecular hydrogels exhibited thermal reversibility and subsequent facile modulation of microstructure upon adjustment of the dosage CB[8] and heat treatment. Afterward, high water content hydrogels (up to 99.7%, water by weight) were built based on cellulosic derivatives (HEC-Np) and commodity polymers (PVA-MV) [73]. Significantly, these hydrogels represented multiple responsiveness toward external stimuli, such as temperature, chemical potential, and competing guests (Fig. 14). The simplicity of their preparation and the availability from inexpensive renewable resources enable these materials great potential in the further application, especially in a variety of important biomedical and industrial applications.

The same authors also demonstrated the other charge-transfer pairs mediated by CB[8] in the process of supramolecular cross-link networks. [94] Pyrenyl (Pyr), dibenzofuranyl (DBF), and 2-naphthyl (Np), functionalized multivalent random copolymers, were prepared (Fig. 15). On the other hand, post-polymerization conjugation of a methyl viologen species to commercially available poly (vinyl alcohol) (PVA-MV) and copolymerization of a methyl viologen functional monomer with a water-soluble comonomer (P(StAM-r-StMV)) also were synthesized. More

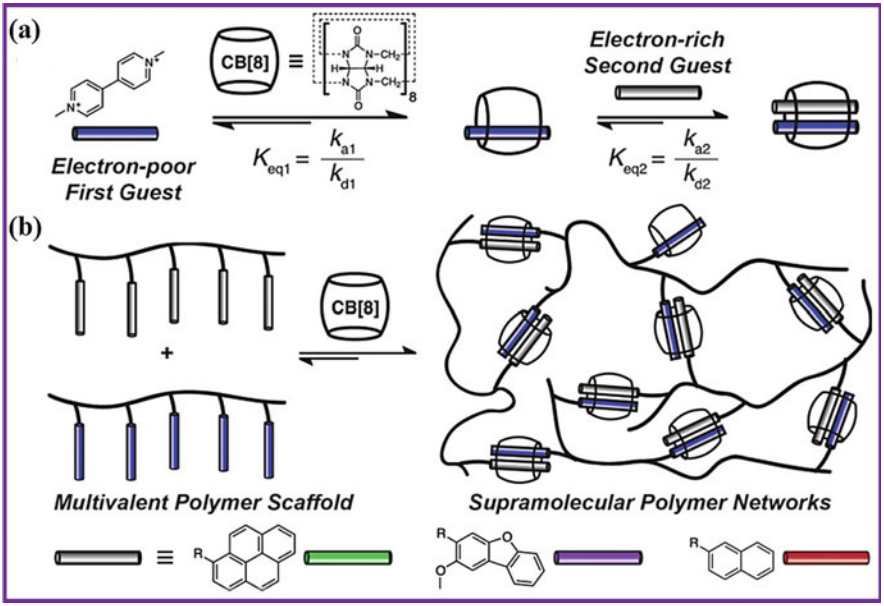

Fig. 15 Probing the role of supramolecular dynamics in CB[8]-based supramolecular gel. (**a**) Schematic representation of the two-step binding of cucurbit[8]uril with dimethyl viologen and a suitable second guest. (**b**) Multivalent side-chain functional polymers bearing good guests for ternary complex formation with CB[8] form supramolecular hydrogels upon addition of the host molecule [94]. (Copyright © 2014, John Wiley and Sons)

interestingly, they investigated the association and dissociation kinetic rates of the second guest-functional copolymers binding to the first guest complex of monovalent small-molecule dimethyl viologen and CB[8] complex by means of stopped-flow experiments. The impact of guest molecules on the macroscopic properties of the corresponding hydrogels was elucidated by independent characterization of the molecular kinetics and thermodynamics of the binding of these guest moieties. That is, the energetic barrier to dissociation determines the mechanical strength, whereas that to association does the capacity of the materials to self-heal. Therefore, a deep analysis of the role of supramolecular dynamics and the importance of the energetic barrier for dissociation in determining bulk material properties was illuminated. CB [8] binding motif has been proved an effective and powerful in the supramolecular cross-linked materials.

As shown in Fig. 16, our group [95] successfully designed a supramolecular hydrogel based on CB[8] and a tetraphenylethylene (TPE) derivative bearing four

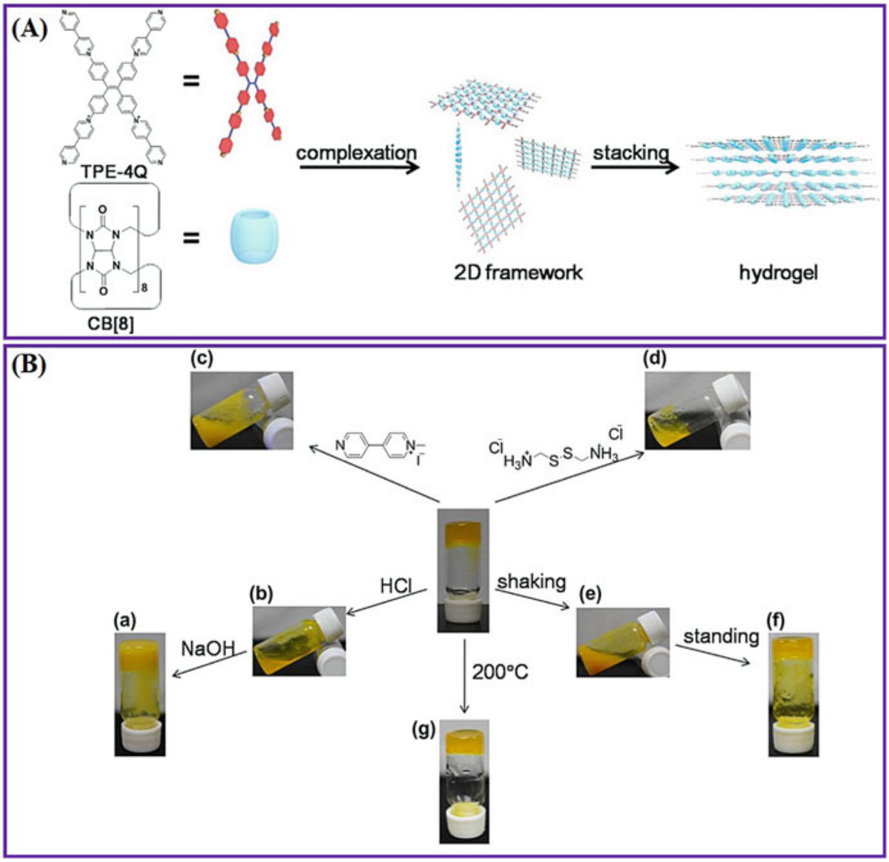

Fig. 16 (**A**) Formation of supramolecular hydrogel. (**B**) Multistimuli responsiveness of the supramolecular hydrogel [95]. (Rights managed by Taylor & Francis)

monocharged viologen (TPE-4Q) via formation of homoternary complexation. The obtained hydrogel exhibited bright orange fluorescence due to the TPE structure. It is worth noting that the hydrogel is highly thermostable even at 200 °C, which enables the hydrogel potential wide application in the real world. In addition, the supramolecular hydrogel could be modulated to process assembly/disassembly by external stimuli, such as pH, mechanical force, and competitive guests. Moreover, the hydrogel could specifically absorb π-conjugated anionic dyes in water with high adsorption efficiency, due to the π-stacking interaction with TPE backbones and electrostatic interaction with the monocharged viologen sites, which might be applied in various fields, e.g., wastewater treatment and environmental surveillance.

29.3.1.2 Photo-stimuli Supramolecular Hydrogel

The dynamic nature of complex materials gives rise to remarkable superiority in potential application, especially photo-stimuli, showing controllability, adjustability, and cleanability. Scherman group [96] reported CB[8]-mediated photo-stimuli activated supramolecular hydrogel in corporation of viologen and azobenzene-functional guests (Fig. 17). In order to gain the mesoscale self-assembling, a new class of hydrophilic CB[8]-threaded highly branched polyrotaxanes (HBP-CB[8]) were synthesized through a semi-batch reversible RAFT. Specifically, a bisfunctional viologen monomer, styrene-violeogen-styrene (St-Vi^{2+}-St), was employed both as a cross-linker and as a first guest for CB[8] and then copolymerized with N-hydroxyethyl acrylamide

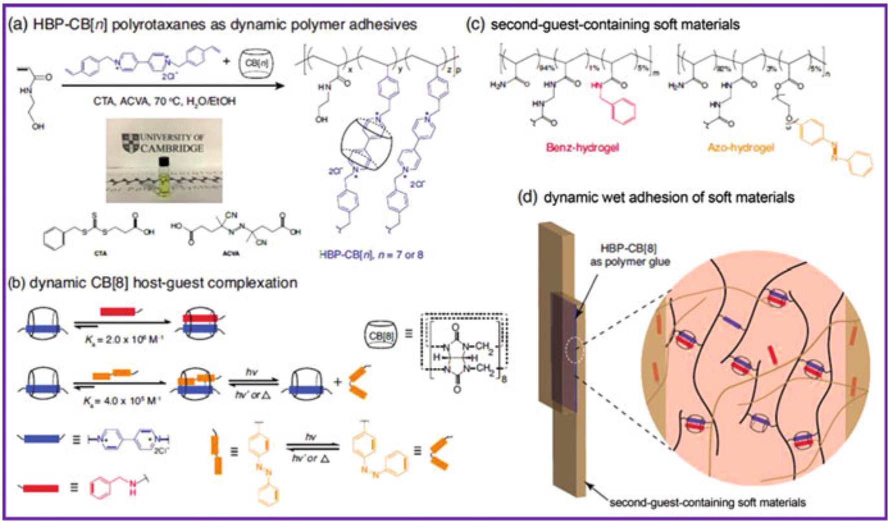

Fig. 17 (**a**) Synthesis of the HBP-CB[n]polyrotaxanes through a semi-batch RAFT polymerization in the presence of CB[n]. (**b**) Stepwise formation of the heteroternary complexes among CB[8], viologen, and a second guest such as Benz and Azo. (**c**) Chemical compositions of the hydrogel networks containing either Benz or Azo as second guests. (**d**) Schematic of the dynamic interfacial gluing of two hydrogels with HBP-CB[8] polyrotaxane as adhesive [96]. (Copyright © 2018, John Wiley and Sons)

(HEAm), resulting in the highly branched polyrotaxanes (HBP-CB[8]) with CB [8] mechanically locked onto the HBP-CB[8] backbones. To achieve the macroscopic adhesion of synthetic soft materials with HBP-CB[8], other two hydrogels containing benzylamine (Benz) and azobenzene (Azo) as the second guests were tailored. Notably, due to the photoinduced isomerization of azobenzene moieties, the macroscopic adhesion of the two hydrogels (HBP-CB[8] and azo-hydrogel) displayed reversible association/dissociation through photo-irradiation. The strategy provides photo-tunable interfacial adhesion for on-demand control over the dynamic interfacial affinity, which might promise potential in tissue repair, wound dressings, and elastic issue sealing without the need for suturing.

29.3.1.3 Self-Healing Supramolecular Hydrogel

Recently progress on highly tough and stretchable polymer networks has highlighted the very important self-healing intrinsic property, which will enable the construction of various structures and new materials with improved durability and functionalities. Scherman et al. [19] presented a new class of aqueous dual network, which incorporated both a small amount of non-covalent CB[8]-mediated homoternary supramolecular assembly (2.5 mol%) and a trace amount of covalent cross-linking (0.05 mol%), closely mimicking titin's structure/function model (Fig. 18). Firstly, a supramolecular cross-linker was constructed via a polymerizable guest (1-benzyl-3-vinylimidazolium) and CB[8] in a 2:1 manner ($K_{a1} = 4.21 \times 10^7\ M^{-1}$, $K_{a2} = 4.25 \times 10^5\ M^{-1}$). Subsequently, the non-covalent supramolecular assembly was polymerized with a trace amount of chemical cross-linker *N,N′*-methylenebisacrylamide (MBA, 2 mol% of the non-covalent CB[8] cross-links) and a hydrophilic monomer acrylamide; thus, an aqueous dual network was achieved. The dual network sample exhibited remarkable mechanical strength (hold 500× its own weight without failure), a high stretch ability up to 24× its original length before fracture. Furthermore, the self-healing property was tested by cyclic tensile: demonstrating significant quasi-plastic deformation and pronounced hysteresis, for which the supramolecular interactions played a critical role. In order to illustrate directly the dual network' ability to dissipate energy, the authors performed a drop ball test. When a metal ball (16 g, diameter of 2 cm, drop height of 45 cm) was dropped onto the dual network film, a large deformation was observed. Delightedly, the ball stretched it extensively before bouncing back, upon hitting the film. Three fundamental mechanical properties, including strength, toughness, and elasticity (self-recovery), are all-in-one within the dual network supramolecular system. The dual network fabrication provided a powerful and facile strategy for the construction of biomimetic supramolecular materials and promising application in artificial muscles, cartilage replacement and tissue engineering, wearable electronic devices, and microactuators.

The same group [20] described another supramolecular polymer network as well through in situ copolymerization of acrylamide and functional monomers, which could be involved in the cavity of CB[8]. Just a small-amount dynamic CB [8]-mediated non-covalent cross-link (2.5 mol%), together with high molecular weight, resulted in extremely stretchable and tough supramolecular polymer

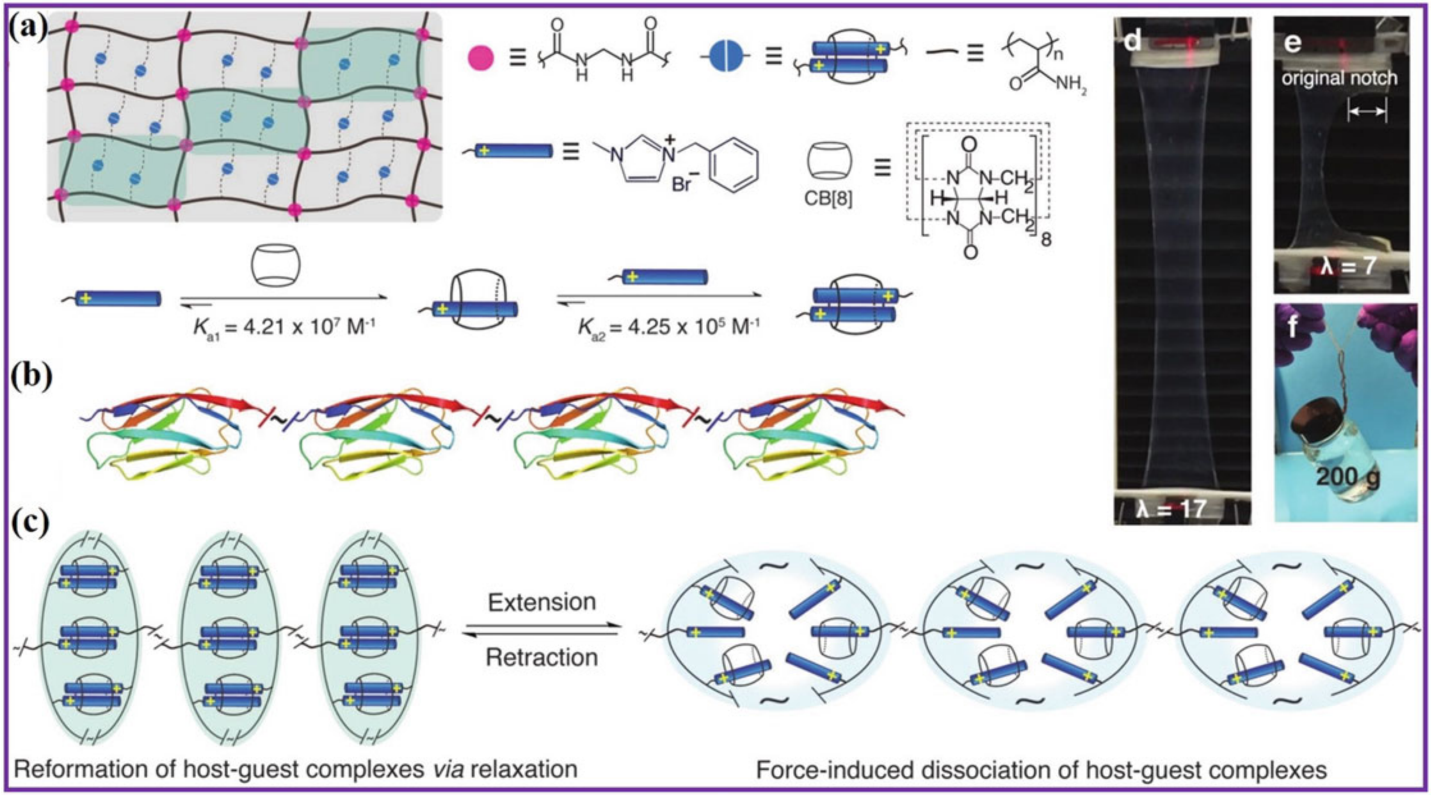

Fig. 18 The design concept of a biomimetic supramolecular network: (**a**) schematic illustration of a modular dual network composed of non-covalent supramolecular. (**b**) A typical modular section of titin structure. (**c**) Schematic illustration of a dual network containing multiple loops held by the CB[8] host-

network, with outstanding self-healing capability at room temperature. It has to say that the dynamic CB[8] host-guest interactions promote the networks' toughness through crack bridging by polymer chain entanglement and sliding; meanwhile, the energy dissipation by reversible and simultaneous association/dissociation of the host-guest complexes is also enhanced. The modulus and stress of the hydrogel decreased in the tensile measurement immediately after the cyclic tensile test at a strain of 8×, and then the sample recovered all of the initial mechanical properties in a period of 30 min. More interestingly, the mobile ions within the hydrogel enable the percolation of conductive pathways with higher resistivity comparing with other electronic conductors. The kind of supramolecular hydrogel improved the practicability of tough hydrogels for promising applications, including biomaterials, sensors, as well as wearable electronic devices.

29.3.2 Stimulus-Responsive Supramolecular Nanoparticles

Formation of well-defined architectures in supramolecular chemistry via specific non-covalent interactions is one of the most important research branches. Nanoparticles (NPs), which possess unique size-dependent properties, have attracted much attention in the biomedical application fields, such as drug delivery. The stimuli-responsive self-assembly supramolecular nanoparticles based on CB [8] have been greatly developed by the Huskens group. As shown in Fig. 19, this group designed and demonstrated dual-responsive supramolecular nanoparticles (SNPs) based on the CB[8]-mediated CT ternary host-guest complexation with methyl viologen polymer and mono- and multivalent azobenzene functionalized molecules, in which the SNP could be controlled switch assembly/disassembly reversibly in multiple cycles by the photo-switching of Azo and irreversibly by the chemical reduction of the MV units [97]. Thus, a novel kind of supramolecular nanoparticles had been created with controllable particle sizes, in which the size-controlled self-assembly of the particles could be observed by tuning the mixing ratios of mono- and multivalent Azo, multivalent MV-PEI, and CB[8], involved in the formation of the ternary complex. More interestingly, the authors utilized the SNP system as an AND operator in logic terms. That is, only when the Azo moiety in the *trans* form as well as the MV moiety in the dicationic state the SNPs were formed. Changing either of them led to inhibition of the particle formation process. Furthermore, the dual responsive character and its reversibility make the kind of SNPs system as a potential platform for the functional material engineering.

Fig. 18 (continued) guest complexation. (**d**) Photographs of a unnotched dual network sample (dimension: 40 mm (L) × 1 mm (W) × 1.5 mm (T)) upon stretching to a strain of 17× (**e**) and a notched sample (notch size 20 mm) to a strain of 7×. (**f**) Image demonstrating the capability of a dual network sample (40 mm (L) × 2 mm (W) × 1.5 mm (T)) sustaining a weight of 200 g [19]. (Copyright © 2017, John Wiley and Sons)

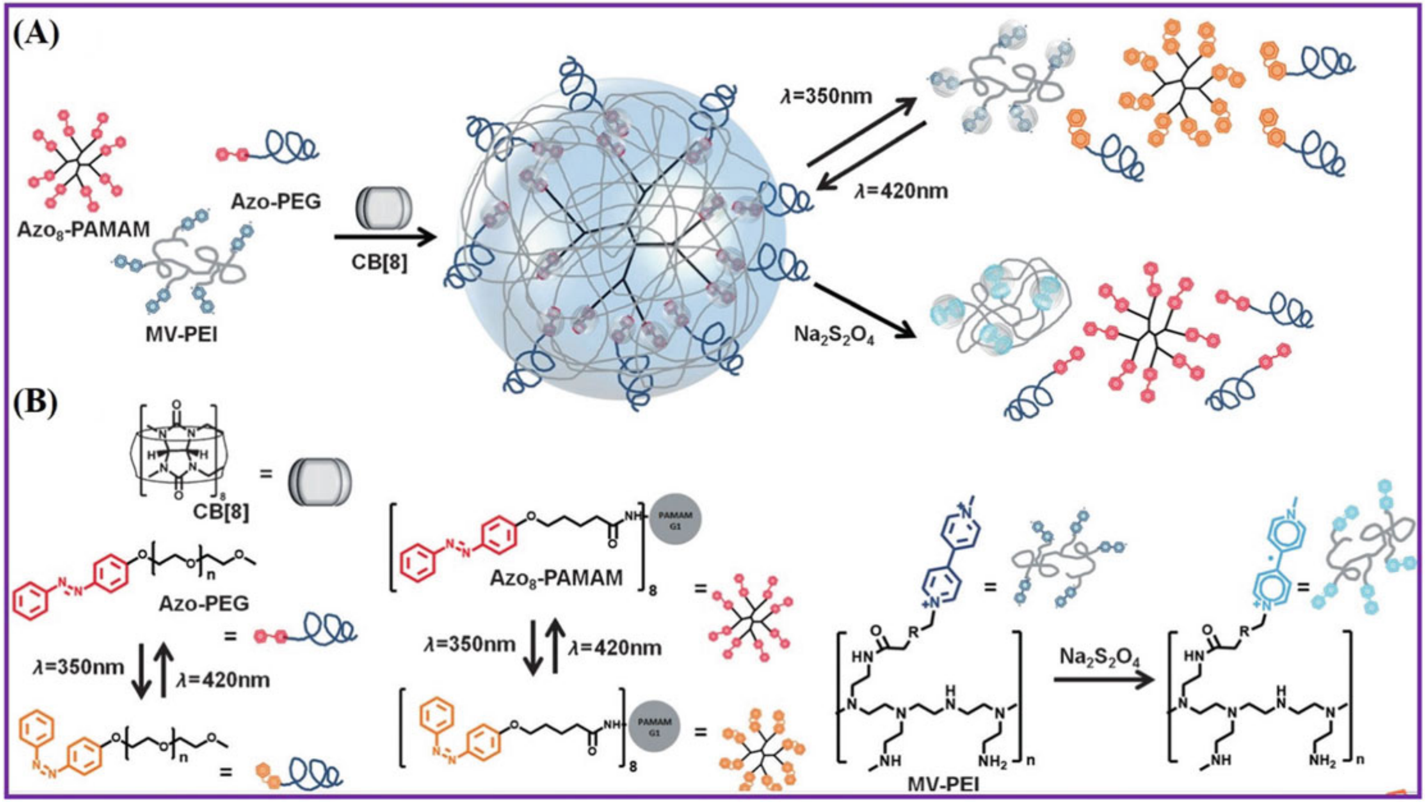

Fig. 19 Supramolecular nanoparticle (SNP) self-assembly and triggered disassembly mediated by formation and disruption of the ternary complex [97]. (Copyright © 2014, John Wiley and Sons)

Afterward, this group fabricated zwitterionic supramolecular nanoparticles (ZSNPs) from appropriately functional mono- and multivalent components [98]. Different from the previous system, this work used the monovalent, small-molecule, non-fouling Azo-carboxybetaine analog (Azo-Zwit) as the shell-forming component, which is much shorter than the typically used polymeric PEG molecules. Surprisingly, the ZSNPs could stain outstanding stability not only in water but also in PBS (pH 7.4) at ionic strengths ranging from 0 to 700 mM, even in the PBS containing BSA. MV polymer and Azo dendrimer could assemble to form the core of the SNPs in the presence of CB[8] through CT interactions; meanwhile, the Azo-Zwit was involved to constitute the shell of the ZSNPs to confirm the stability. The ZSNPs exhibited light-triggered disassembly without comment, as a result of photoisomerization of Azo. More interestingly, the ZSNPs occurred simultaneous aggregation at the intermediate pH values 6.2 and 6.8, which corresponds with the extracellular pH observed in tumor tissue. In a word, the aggregation mechanism of the ZSNPs seemed to be more universal, which might potentially be used to design self-assembling materials with good application prospects in biomedical fields.

29.3.3 Luminescent Materials

29.3.3.1 Tunable Luminescent Materials

Light-emitting materials especially that can be tuned simply offer widespread potential application in optoelectronic devices, fluorescent sensors, as well as imaging agents. Water-soluble luminescent materials are great challenge because of the limited solubility of the organic chromophores. On the other hand, the supramolecular assembly has been proved to a convenient method to fabricated smart photo-functional materials. Recently, Tao and co-workers [99] demonstrated a novel supramolecular approach based on a linear π system of oligo(*p*-phenylenevinylene) (OPV) dye and CB[8] via host-guest interaction which greatly decreased the synthetic steps and required constituent elements to produce the system with runnable and dynamical photophysical properties (Fig. 20). Moreover, the color of emissions was tunable, including cyan, yellow, green, and white light, with the increased fluorescence lifetime and quantum yield due to the electronic distributions of the chromophore guest included in the hydrophobic cavity of CB[8]. The results provided a facile and promising strategy for the development of the construction of smart and tunable luminescent materials.

29.3.3.2 CB[8] Highly Enhanced Fluorescence

Cyanostilbenes, possessing excellent optical, electrical, and self-assembly properties, are great potential for the various applications in organic materials. Park et al. [100] designed a supramolecular polymer with highly enhanced fluorescence based on CB[8] as host and an appropriate cyanostilbene derivative (Py^+-CN-MBE) as the guest molecule. The Py^+-CN-MBE was chosen as the chromophore due to the following features: (1) the exhibited J-aggregation, (2) its water-solubleness, (3) the strong binding affinity to CB[8], and (4) the stable SP formation by induced

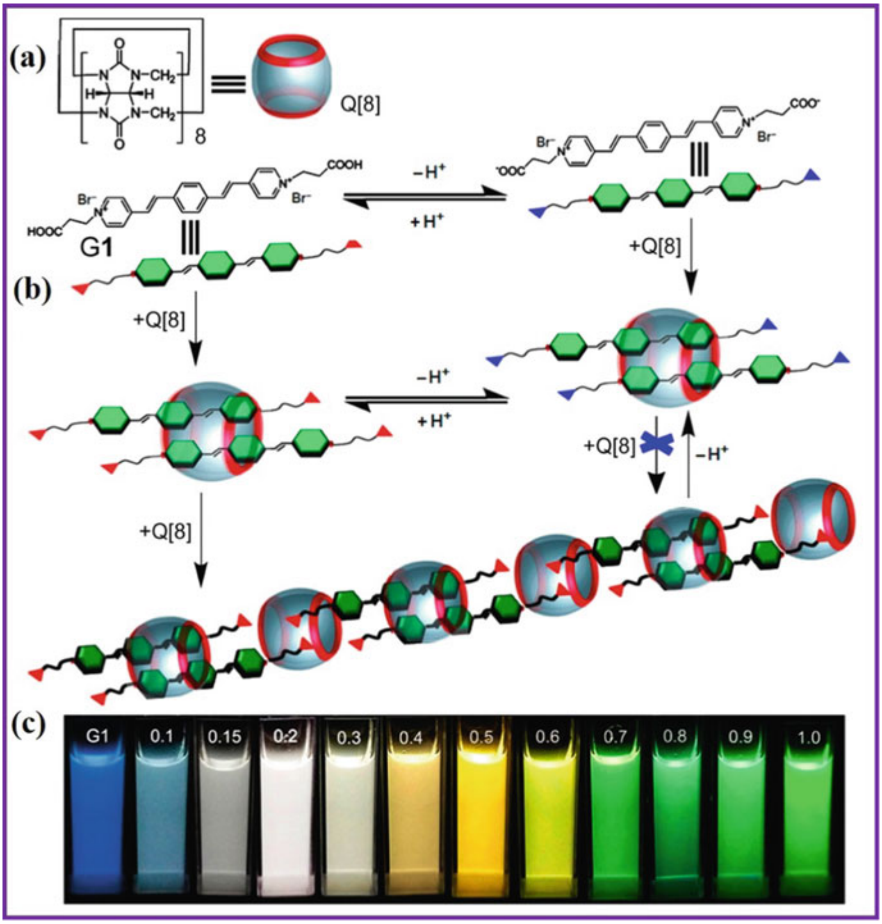

Fig. 20 Representation of the CB[8]-based supramolecular polymer approach for fabricating smart luminescent materials [99]. (Copyright © 2016, American Chemical Society)

with CB[8]. Surprisingly, in the fluorescence quantum yields of ≈ 0% in the monomer state of the cyanostilbene derivative, however, up to 91% of fluorescence quantum yields was obtained in the CB[8]-induced supramolecular polymer state. The authors employed detailed experiments and computational analysis to demonstrate the intriguing photophysical properties of the supramolecular polymer. Furthermore, the supramolecular polymer paves a novel way toward the functional water-soluble fluorescent supramolecular polymer materials.

29.3.3.3 Light-Harvesting Fluorescent System

There exist widely light-harvesting systems in nature, so the study on the wonderful formation to make energy conversion has attracted much attention. Park and co-workers [101] demonstrated a novel system of light-harvesting supramolecular block copolymers (SBCPs) in water using the finely color-tuned supramolecular homopolymers (SHPs) comprising CB[8] host and different cyanostilbene guests (named B, G, Y, and R) with emitting blue, green, yellow, and red fluorescence. Firstly, a series of different fluorescent CB[8]-based SHPs were synthesized and characterized to develop the best D/A pair of the further light-harvesting system. From the result of c_{SHP} and time-resolved polarized PL measurements, the authors proposed the most probable mechanism of the cyanostilbene/CB[8] supramolecular polymerization process in water is that the 1D SHPs were firstly formed and further transformed into 3D SHP nanobundles. Afterward, the CB[8]-based light-harvesting SBCP system was conveniently constructed by a simple procedure mixing B@CB [8] SHP and R@CB[8] SHP in water via a dynamic guest exchange reaction. The novel strategy of light-harvesting SBCPs is promisingly useful for eco-friendly or biological applications, such as light-driven fuel productions and therapeutic treatments.

29.3.3.4 Near-Infrared Emission Materials and Cell Imaging

Cell imaging, especially organelle-targeted, based on supramolecular self-assemblies with fluorescence has attracted much attention in recent years. Near-infrared (NIR) fluorescent (650–900 nm) is widely used in cell imaging due to the slight photodamage on biological, deep tissue penetration as well as the minimum interference from biomolecule autofluorescence. Recently, our group [102] reported a two-stage mediated NIR emissive supramolecular assembly for lysosome-targeted cell imaging (Fig. 21). An anthracyl pyridinium derivative (ENDT) was designed and synthesized as an organic dye with weak fluorescence emission at 625 nm. The ENDT could form complexes with CB[8] in a sled n:n binding motif with J-aggregates. The binary supramolecular polymer assembled into nanorods with a near-infrared fluorescence emission (655 nm) and fluorescence enhancement as the first stage. Afterward, the binary supramolecular polymer interacted with lower-rim dodecyl-modified sulfonatocalix[4]arene (SC4AD) to form nanoparticles for further fluorescence enhancement as the second stage. Significantly, the ternary supramolecular assembly can be applied in NIR lysosome-targeted cell imaging, according to the co-staining experiment with Lyso Tracker Blue. The study proved a novel method to construction supramolecular assemblies through dual macrocycles cooperation for functional and advance materials creation.

29.3.4 Biological Materials

Supramolecular polymers exhibit an attractive choice for construction of novel multifunctional materials in biology fields. The CB[8] ternary complex system provides more stable binding units in water and can be utilized to prepare various supramolecular nanostructures via non-covalent route, which assemble into vesicles and can encapsulate/release biologically active factors.

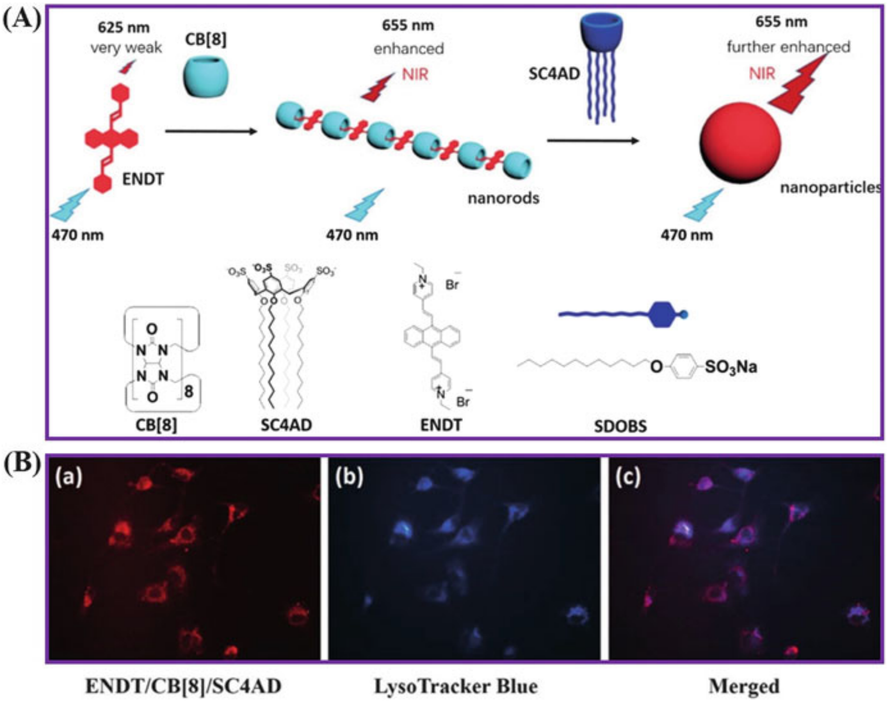

Fig. 21 (**A**) Formation of NIR fluorescent supramolecular assemblies. (**B**) Confocal fluorescence images of A549 cells co-stained with ENDT/CB[8]/SC4AD and Lyso Tracker Blue [102]. (Copyright © 2018, John Wiley and Sons)

29.3.4.1 Triggered Insulin Release

Diabetes mellitus (DM) is a metabolic disease which results from a person not to produce sufficient insulin or not to respond well to insulin produced in the body. Type I DM on the account of the body's failure to produce insulin leads to the patient requiring frequent injections of the hormone. It is a great challenge to develop efficient platform that can be able to release insulin in a triggered manner, thus reducing the patient inconvenience and discomfort of the frequent injections. Scherman et al. [103] designed and synthesized a supramolecular double-hydrophilic block copolymers (DHBCs) instead of traditional difficult block copolymers in a non-covalent manner through CB[8] ternary complexation (Fig. 22). The supramolecular DHBCs self-assembled into micelles at physiological temperature and can be used to encapsulated as well as release insulin. Furthermore, the system sensitively and selectively responded to temperature, glucose, and a competitive guest, allowing releasing insulin at different rates depending on the specific requirements. The novel supramolecular insulin nanocarrier will lead to a new generation of stimuli-responsive drug delivery vehicles for insulin therapies and the treatment of diabetes.

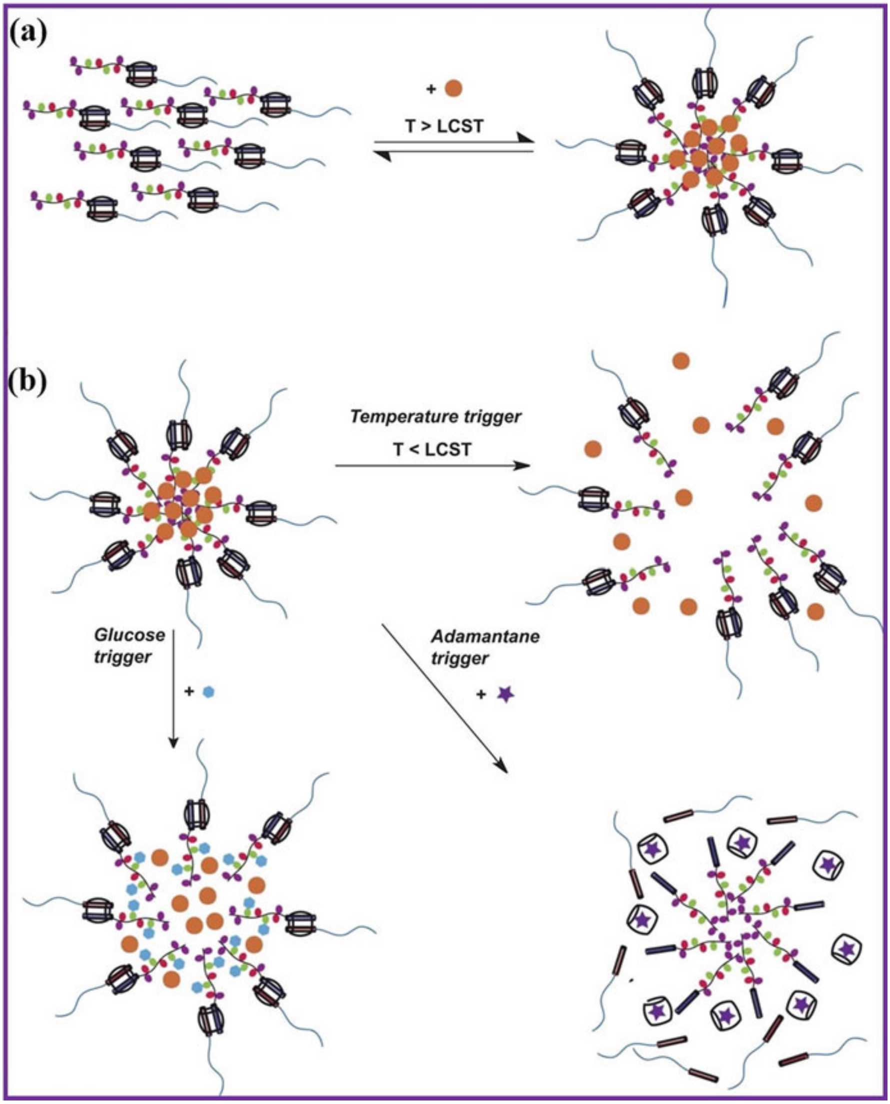

Fig. 22 (**a**) The formation of the micelles by raising the temperature of the system above the LCST. (**b**) The effect of different triggers on the micelle morphology [103]. (Copyright © 2012, Royal Society of Chemistry)

29.3.4.2 Doxorubicin (DOX) Release

DOX is an anthracycline antibiotic used widely in cancer chemotherapy for the treatment of broad range of cancers, such as many types of carcinoma, hematological malignancies, and soft tissue sarcomas. However, the high toxicity is DOX's major drawback, which limits the clinical applications. Incorporating the drug in micelles or other carriers is necessary. Scherman group reported a triply triggered DOX release from supramolecular nanocontainers on the basic of the previous study (Fig. 23) [104]. A supramolecular double-hydrophilic block copolymer (DHBC) was fabricated by CB[8] “handcuff” of naphthalene-terminated poly(dimethylaminoethylmethacrylate) (PDMAEMA) and methylviologen terminated poly(*N*-isopropylacrylamide) (PNIPAM-

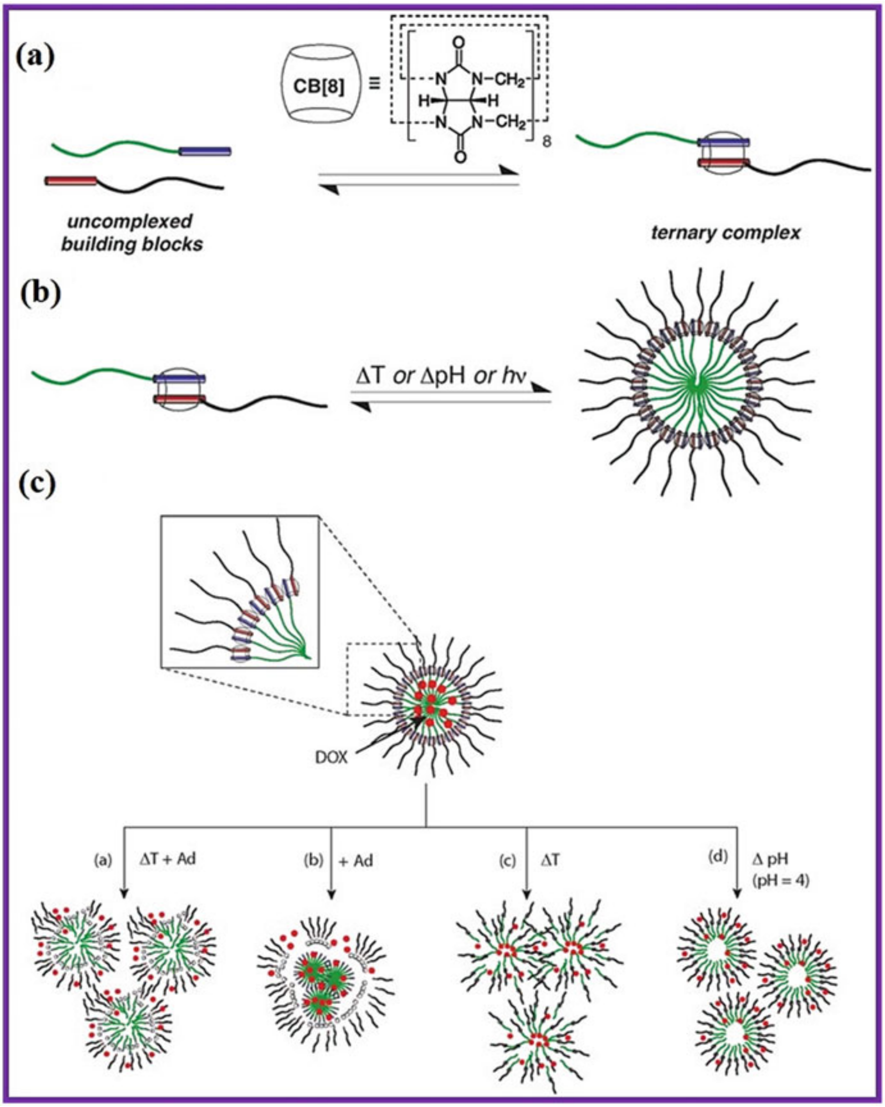

Fig. 23 Hierarchical self-assembly of the supramolecular entity under different conditions and its subsequent mode of drug release after being exposed to different triggers [104]. (Copyright © 2012, American Chemical Society)

MV). Thus, the system could be responsive to multiple external triggers including temperature, pH, and the competitive guest. Afterward, DOX-loaded DHBC micelle was prepared through a solvent evaporation method. Delightedly, the DHBC micelle system represented a significant reduction in the viability of HeLa cells upon triggered release of DOX from the supramolecular nanocontainers, which was more intelligent than the covalent analog. The DHBC system paved the novel way to develop the unique and clinically applicable therapies.

29.3.4.3 Biocompatible Polymeric System

The artificial extracellular matrix (ECM) is a template on which cell can adhere and proliferate to regenerate the tissue. It is a great challenge task to design and prepare the biomaterials, reproducing the in vivo environment of tissues by providing a surface that resembles the native ECM. Das and Ukil [105] applied a multiple cross-linking strategy combining with the host-guest chemistry of CB[8] to fabricate a peptide-based supramolecular polymer (Fig. 24). Multiple cross-links occurred in the process: covalent linkage through disulfide bond formation, supramolecular linkage mediated by CB[8] homoternary complexation, as well the peptide-based polymer decorated with cell-adhesive RGDS sequence. Surprisingly, the size of the polymer can be tuned by changing the sequence of cross-linking. And the pendent RGDS sequence at the surfaces of the peptide-based supramolecular polymer allowed to the polymer be applied for efficient adhesion and proliferation of RAW264.7 murine macrophages. Thus, the multiple cross-linking strategy provides novel method to prepare artificial ECM.

29.3.5 Other Applications

29.3.5.1 Supramolecular Microcapsule

Up to date, a few approaches have been provided to prepare polymeric nanocarriers. As one of the most important methods, microfluidic techniques have been developed for revolution of formation of microscale droplets, allowing for high monodispersity in

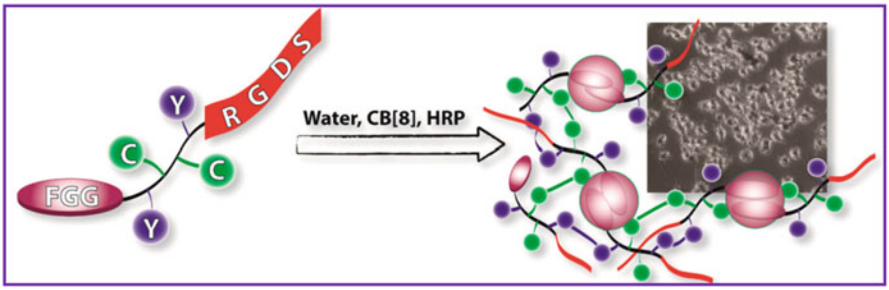

Fig. 24 Formation of biocompatible polymeric systems with efficient cell adhesion and proliferation property by multiple cross-linking of a small peptide [105]. (Copyright © 2018, American Chemical Society)

both size and composition, reproducibility, material efficiency, as well as the high-throughput manipulation and analysis. In 2014, Scherman and co-workers [106] reported the self-assembly of complementary-functionalized hydrophilic and hydrophobic copolymers which can be controlled co-assembly at the interface of water-chloroform utilizing microfluidic techniques. Taking advantage of CB[8] ternary host-guest complex, the water-soluble poly(HEMA-co-StMV-co-FOA) (containing 20 mol % of MV^{2+} group) and the hydrophobic poly (MMA-co-AA-co-HEMA) (with naphthalene isocyanate) can be cross-linked to form a supramolecular polymeric skin at the interface of the microdroplet. Ingeniously, the authors marked the two functional polymers by fluorescein and rhodamine, respectively, in order to observe the detail nanostructure of microcapsule shell for further study the significance of the supramolecular heteroternary complexation. Furthermore, a dendritic polymer, poly(EGDMA-co-DMAEMA-co-HEMA-co-Azo) containing UV-responsive azobenzene units, was designed and synthesized, which exploited the multilayer microcapsule for both cargo encapsulation and subsequent release with external stimuli. The system provides novel strategy for drug delivery, as well as acoustic, electronic, optical, and magnetic materials. Importantly, the supramolecular assembly interfacially of bilayer microcapsules afford a platform for quantitatively investigating the mechanism and kinetics of self-assembly at liquid-liquid or soft matter interfaces, which is of great meaningful in biological systems. Based on this pioneering work, a series of interesting supramolecular polymer systems within a droplet microfluidic platform were demonstrated which are potentially applied in developing site-specific delivery vector, drug release, bio-sensing, as well as high-throughput analysis.

29.3.5.2 Surface Engineering

Surface engineering plays a great role in the fabrication of widespread industrial product, including aeroplanes, wooden furniture, and medical instruments. The modification of surfaces using supramolecular polymers has been explored to tune the surface properties such as wettability, corrosion resistance, and biocompatibility of various materials. Hybrid raspberry-like colloids (HRCs) displayed attractive hierarchical structure with a large core particle decorated with smaller corona particles, containing both organic and inorganic components. Comparing with the traditional synthetic procedure, the supramolecular methods may be straightforward and convenient for preparation functional colloids. Scherman et al. [107] reported a feasible route to construct HRCs, in which a polymeric nanoparticles assembled onto a silica surface through CB[8] ternary complexation (Fig. 25). The authors chose 4-hydroxyazobenzene-functionalized silica microspheres (Azo-silica core) as the core of the HRCs. Meanwhile, MV-functionalized polymeric nanoparticles (MV-NP corona) were employed as the corona nanoparticles. Interestingly, the non-covalent nature of CB[8]-mediated host-guest interaction allowed the supramolecular HRCs a novel property of reversible assembly/disassembly controlled by light. The facile approach provided a platform to prepare HRCs with structural

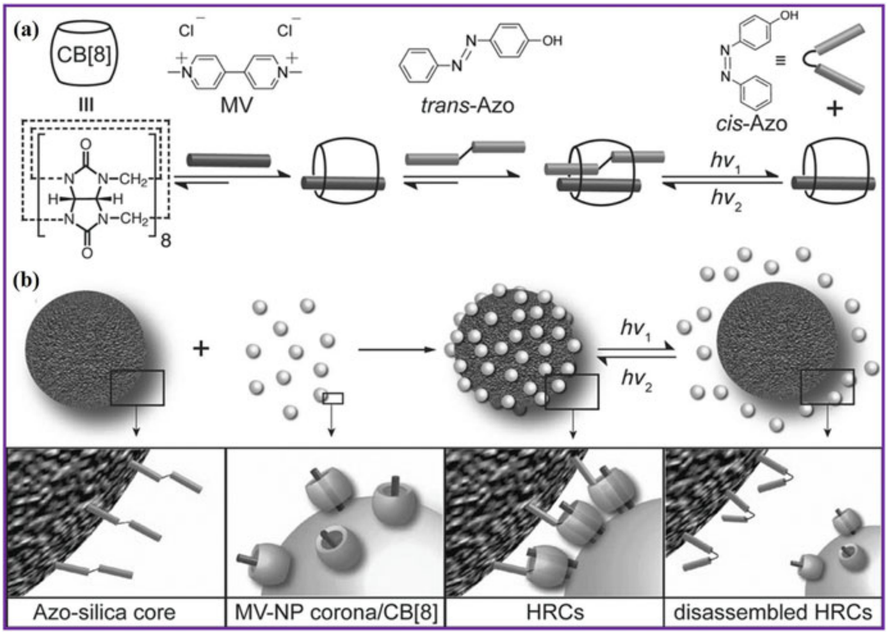

Fig. 25 (**a**) Stepwise formation and light-driven reversible disassembly of the ternary complex. (**b**) HRCs obtained by the formation of ternary complexes and light-driven reversible disassembly of the HRCs [107]. (Copyright © 2014, John Wiley and Sons)

advantages for potential applications such as cargo loading and delivery as well as compartmentalized catalysis.

29.3.5.3 Polymer Modified

CB[8]-mediated host-stabilized charge-transfer (HSCT) complex has been widely used in construction of various supramolecular structures, which could further self-assemble into nano-objects. Recently, Chen and Jiang [108] realized cyclization of linear polymer via CB[8] HSCT supramolecular method based on a thermoresponsive poly(N-isopropylacrylamide) (PNIPAM) with naphthalene (Np) ends and viologen dimer (Fig. 26). Moreover, the authors investigated the stability of the HSCT interaction by raising the experimental temperature gradually, causing a dramatic change of the surrounding of the complex form hydrophilic to hydrophobic. In this process, the HSCT interaction decreased with charged CB[8] complex disassembly, that is, the Np end groups escaped from the CB[8] cavities. Furthermore, VT-^{1}H NMR showed that the dissociation of HSCT interaction was found totally reversible. Compared to the linear counterpart, the dynamic cyclic PNIPAM leaded higher LCST and smaller aggregates, which could allow various conformations in functional polymers.

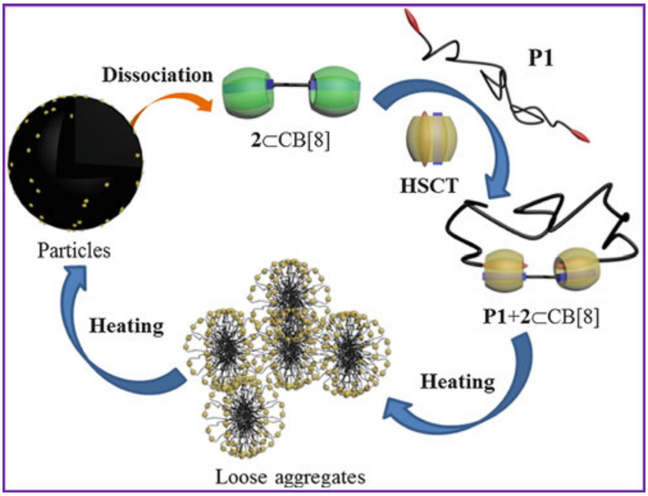

Fig. 26 Formation and dissociation of the assembly of cyclization PNIPAM [108]. (Copyright © 2016, American Chemical Society)

29.4 Conclusion

In summary, the construction of CB[8]-based supramolecular polymers has attracted wide attention of supramolecular chemists. The main types of non-covalent interaction are the CB[8]-mediated 1:2 homoternary and 1:1:1 heteroternary host-guest complexation through cation-dipole interactions, hydrophobic forces, and optimization of host-guest packing coefficients. In addition, the synergistic effects with other macrocyclic host molecules as well as metal cooperation also play vital roles in the fabrication of CB[8]-based supramolecular polymers. Significantly, it is still very important and meaningful to design and synthesize various and functional supramolecular polymers taking advantage of non-covalent interactions.

The past researches have witnessed a great harvest in CB[8]-based supramolecular polymers and their further application in developing advanced materials, including supramolecular hydrogel, stimulus-responsive supramolecular nanoparticles, luminescent materials, biological materials, supramolecular microcapsules, etc. On the other hand, although plenty of excellent works have been reported, controllable and effective construction of CB[8]-based supramolecular polymers remains a challenge. More detail mechanism about the formation of CB [8]-based supramolecular polymers with existing and characterization techniques is necessary. With the fast development, we believe that more and more exciting findings and potentials of CB[8]-based supramolecular polymers systems and their application will be discovered and explored in the near future.

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