



# Photoresponsive Supramolecular Polymers Based on Host-Guest Interactions

# 16

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## Contents

16.1	Introduction	452
16.2	Photoresponsive Supramolecular Polymers Based on Cyclodextrin (CDs)	453
16.2.1	CD-Based Polymer Networks and Hydrogels	453
16.2.2	CD-Based Polymer Self-Assemblies and Vesicles	458
16.3	Photoresponsive Supramolecular Polymers Based on Cucurbituril (CBs)	459
16.3.1	Adjustable Dynamic Photophysical Properties Based on CB	460
16.3.2	Supramolecular Polymer with Photoisomerism Based on CB	460
16.3.3	Controllable Supramolecular Polymerization Based on CB	463
16.4	Photoresponsive Supramolecular Polymers Based on Crown Ether	464
16.4.1	Networks and Hydrogels of Supramolecular Polymer Based on Crown Ether	465
16.4.2	Conjugated Polymer Network and Its Disassembly Induced by Different Signals	466
16.5	Photoresponsive Supramolecular Polymers Based on Calixarene	467
16.5.1	Supramolecular Polymer with Photoisomerism Based on Calixarene	468
16.5.2	Networks and Self-Assemblies of Supramolecular Polymer Based on Calixarene	468
16.6	Photoresponsive Supramolecular Polymers Based on Pillararene	470
16.6.1	Cross-Linked Polymer Networks Based on Pillararene	470
16.6.2	Supramolecular Polymer with Photoisomerism Based on Pillararene	471
16.6.3	Supramolecular Polymer with Two Guest Monomers Based on Pillararene	475
16.7	Conclusions	479
16.8	Cross-References	480
	References	480

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## 16.1 Introduction

Owing to their potential applications in the fields of optics, biology, and medicine, supramolecular materials are drawing more and more attention from researchers. Supramolecular polymers are constructed from monomer components, small supramolecular systems, or polymers that are repeatedly linked by such reversible noncovalent interactions as hydrogen bonds,  $\pi$ - $\pi$  stacking, hydrophobic effects, host-guest interaction, and electrostatic interactions [1]. Since the noncovalent interactions are reversible, supramolecular polymers tend to make differences to external factors, such as pH changes, chemical and electrochemical redox, light stimulation, temperature/concentration changes, enzyme stimuli, etc. and accompanied by assembly conformation or property changes.

The host-guest interaction is the driving force of the host-guest complex, which involves the synergy of a variety of noncovalent bonds, such as hydrophobic interactions, hydrogen bonds, ionic bonds, van der Waals forces, and electrostatic interactions. Since the discovery of cryptands and crown ethers by Lehn, Cram, and Pedersen, the host-guest system has greatly contributed to the development of supramolecular chemistry. As the name suggests, the host-guest system consists mainly of two components: the host and the guest, which form the supramolecular inclusion. The host molecule usually contains a cavity that specifically recognizes the guest molecule. The host-guest function has characteristic selectivity, because the subject has various restrictions on the object, such as size, shape, charge, and polarity. In the development of supramolecular chemistry, the control and regulation of molecular recognition based on host-guest interaction in supramolecular polymers has attracted a lot of attention [2]. The mechanism of polymerization and the nature of the polymer are determined by the strength and nature of the host-guest units.

The host molecules involved in the preparation of supramolecular polymers based on host-guest systems are typically crown ethers, cyclodextrins, cucurbiturils, calixarenes, and column aromatics. And the guest molecules are generally organic compounds that can enter the bulky cavity. In the following, we will outline the development of photoresponsive supramolecular polymers in this field according to the classification of the host molecules.

Organic materials have many advantages such as good regulation, rich color, smart molecular design, low cost, and toxicity compared with inorganic materials. The combination of supramolecular chemistry to construct highly efficient luminescent materials not only simplifies the preparation process but also imparts good stimuli responsiveness and reversibility to these materials through noncovalent attachment. The noncovalently guided assembly-disassembly process can affect the aggregation and energy transfer between the fluorophores [3], thus regulate the luminescence behavior of the materials. Therefore, luminescent systems constructed concerning supramolecular systems are generally capable of responding to external stimuli such as pH, temperature, solvent polarity, light radiation, redox, etc. accompanied by reversible conformation and structural transformation. In recent years, materials with tunable luminescence properties have been demonstrated their

potential applications in many fields, such as optoelectronic devices, fluorescence sensing, and imaging agents [4]. Due to the introduction of many functional units [5], reports on supramolecular polymers will be further explored because of its luminescent properties.

Herein, we discussed an overview of the photoresponsive supramolecular systems induced by the host–guest interaction. The host–guest recognition is an important noncovalent bonding using hosts such as CD, CB, crown ether, calixarene, and pillararene to encapsulate the guests in the constructed supramolecular system. Furthermore, the guest unit undergoes a reversible structure or conformation difference under specific light stimulation, resulting in the corresponding changes of the supramolecular polymer. In this chapter, we introduce the photoresponsive supramolecular systems according to the different types of hosts and make summaries and outlooks on its functions and applications.

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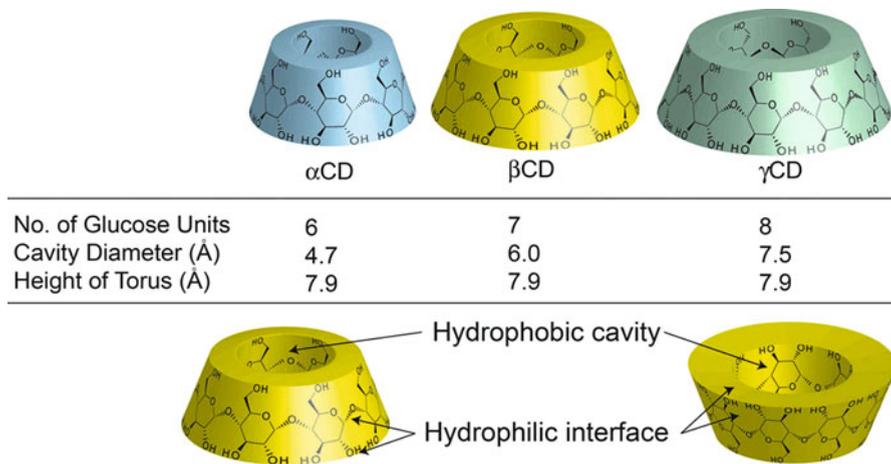
## 16.2 Photoresponsive Supramolecular Polymers Based on Cyclodextrin (CDs)

CDs are a class of widely used supramolecular macrocyclic host molecules, which are cyclic oligomers composed of  $\alpha$ -(1-4)-glycosidically linked glucopyranose units. In the structure of the CD, there is a hydrophilic surface and a hydrophobic cavity, and its hydrophobic cavity can form an inclusion in water with a series of organic molecules. Because of this unique advantage of CD, scientists have linked it to the phosphorescent emission of organic molecules. Reports on CD-induced room temperature phosphorescence (CD-RTP) were first published in the early 1980s [6]. In 2011, we also reported a RTP addressing pseudorotaxane induced by the inclusion of  $\beta$ -CD and  $\alpha$ -BrNp. After that, we constructed a supramolecular hydrogel system capable of rapidly self-healing and room temperature phosphorescence based on the action of  $\beta$ -CD and  $\alpha$ -BrNp [7].

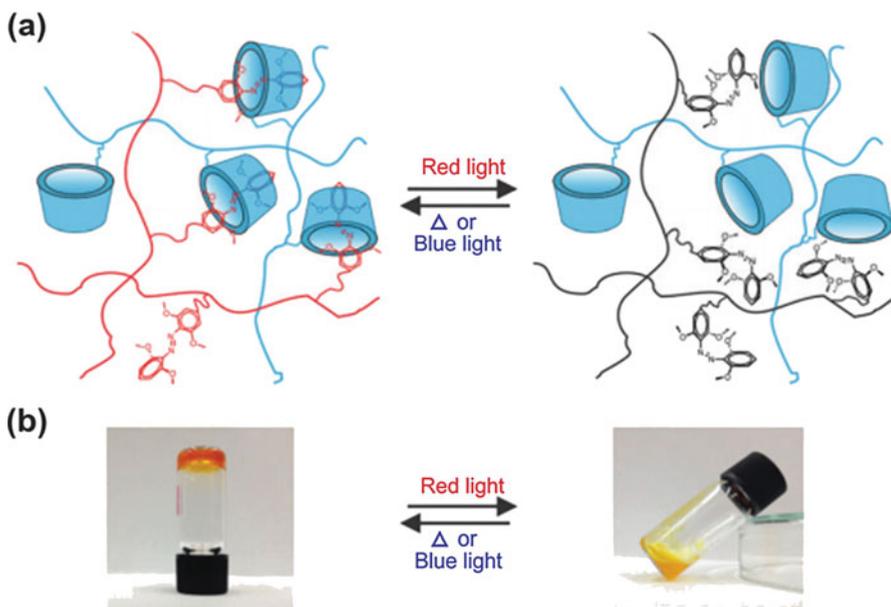
For a supramolecular system based on the action of the host and guest, the host molecule can be selected based on the size of the cavity of the macrocyclic molecule. The cavity size of the  $\gamma$ -CD molecule is 0.75 nm, which is much larger than that of  $\alpha$ -CD and  $\beta$ -CD. The structures and related properties of CDs are shown in Fig. 1.

### 16.2.1 CD-Based Polymer Networks and Hydrogels

Many photoresponsive supramolecular polymer systems in side-chain are based on cyclodextrin because of its high solubility and protective effect on the optical signal. Herein, we introduce the cyclodextrins interacted with the corresponding object to achieve light response control. In 2015, Wu et al. [8] reported a novel supramolecular complex which is formed by tetra-ortho-methoxy-substituted azobenzene (mAzo) and  $\beta$ -cyclodextrin ( $\beta$ -CD), shown in Fig. 2. They synthesized a mAzo-functionalized polymer and a  $\beta$ -CD-functionalized polymer and obtained the supramolecular hydrogels by mixing the two polymers. The supramolecular

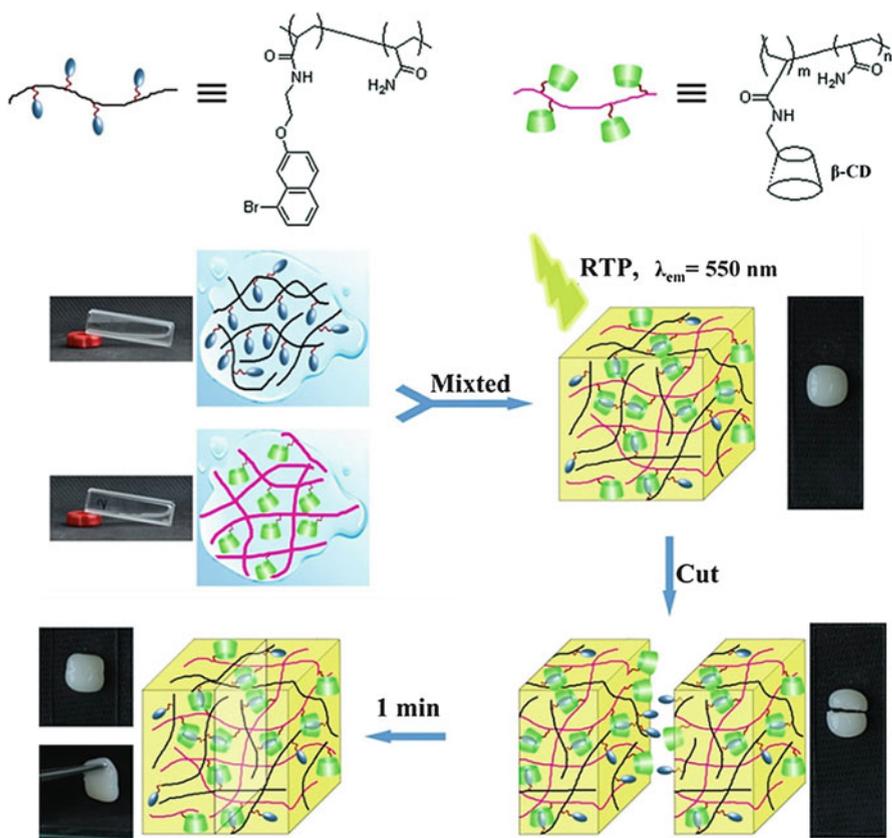


**Fig. 1** Chemical structures, approximate geometric dimensions, and physical properties of cyclodextrins. (Reprinted with permission from Ref. [6]. Copyright (2014) American Chemical Society)



**Fig. 2** Schematic model (a) and photographs (b) of the reversible sol-gel transition of the PAA-mAzo/PAA- $\beta$ -CD mixture. (Reprinted with permission from Ref. [8]. Copyright (2015) Royal Society of Chemistry)

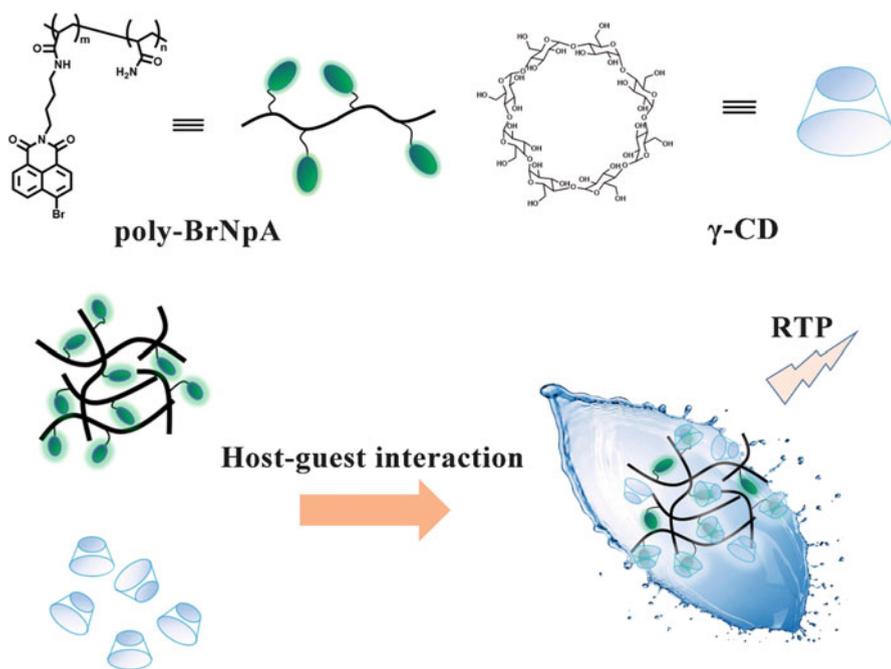
hydrogel was used as a protein carrier which could precisely control the release of the protein by red light. More interestingly, the author also demonstrated that the red-light-responsive supramolecules showed more advantages compared with the conventional UV-responsive supramolecules in controllable aspects.



**Fig. 3** Construction of the supramolecular polymeric hydrogel by host-guest interaction between host-guest polymers and its rapidly self-healing property. (Reprinted with permission from Ref. [9]. Copyright (2014) John Wiley and Sons)

Ma et al. (2014) [9] synthesized two water-soluble side-chain polymers with polymer monomers containing  $\beta$ -cyclodextrin and  $\alpha$ -bromonaphthalene, seen in Fig. 3. Based on the host-guest interaction, the hydrogel material can be simply prepared by the mechanical mixing of the  $\beta$ -cyclodextrin host polymer and the  $\alpha$ -bromonaphthalene guest polymer. Meanwhile, the hydrogel material is available of rapidly self-healing within 1 min in the natural environment, and owing to the inclusion interaction in this supramolecular system, the supramolecular polymer has strong phosphorescence emission at room temperature.

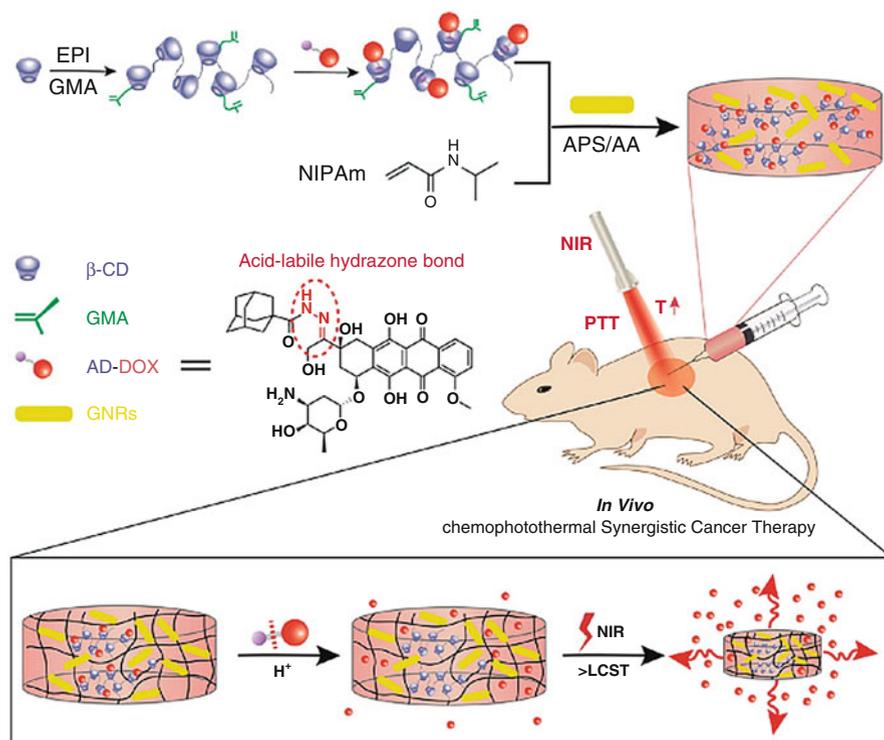
Later, Ma et al. (2016) [10] developed another poly-BrNpA/ $\gamma$ -CD system based on the host-guest recognition between  $\gamma$ -CD and the BrNpA moiety, which could emit a RTP signal in aqueous solution, as shown in Fig. 4. As a new CD-RTP system, its emission could be controlled by the photoisomerization of the Azo unit of poly-Azo in aqueous solution. Moreover, a pure organic RTP hydrogel based on the poly-BrNpA/ $\gamma$ -CD system was also constructed. This study may help to enrich the strategies to construct CD-RTP systems and pave the way for chemists in designing new RTP materials.



**Fig. 4** Schematic representation of the CD-RTP system via host-guest interaction between poly-BrNpA and  $\gamma$ -CD. (Reprinted with permission from Ref. [10]. Copyright (2016) Royal Society of Chemistry)

Xu et al. (2015) [11] reported a new kind of drug carrier constructed by supramolecular polymers. Due that the prolonged ultraviolet (UV) exposure is harmful to cells and UV light has limited tissue penetration ability, this system offers a solution using a magnetic field to aggregate microcapsules to an accurate area and then release the drug upon UV light. The grafted  $\beta$ -CD of CD-g-DexO and AD-PASP will be broken down in an acidic tumor environment, leading to the release of drugs to the certain location. This research of the drug carrier is expectedly designed as multimodal functional imaging probe for treatment of cancer.

Zhao et al. (2017) [12] incorporated gold nanorods (GNRs) into the hydrogel networks formed by the copolymerization of *N*-isopropylacrylamide (NIPAm) and methacrylated poly- $\beta$ -cyclodextrin (MPCD)-based macromere to fabricate an injectable and near-infrared (NIR)/pH responsive poly(NIPAm-co-MPCD)/GNRs nanocomposite hydrogel, which could serve as a long-acting implant for chemophotothermal synergistic cancer therapy, shown in Fig. 5. The nanocomposite hydrogel showed superior mechanical and swelling properties, gelation characteristics, and excellent NIR-responsive property. A hydrophobic acid-labile adamantane-modified doxorubicin (AD-DOX) prodrug was loaded into the hydrogel efficiently by host-guest interaction. The nanocomposite hydrogel exhibited a manner of sustained



**Fig. 5** Schematic illustration of the formation of injectable, NIR/pH-responsive nanocomposite hydrogel, and chemophotothermal synergistic cancer therapy as a long-acting implant. (Reprinted with permission from Ref. [12]. Copyright (2017) American Chemical Society)

drug release and could sustain the slow and steady release of DOX for more than 1 month. The pH-responsive release of DOX from the nanocomposite hydrogel was observed owing to the cleavage of acid-labile hydrazone bond between DOX and the adamantyl group in acidic environment. NIR irradiation could accelerate the release of DOX from the networks, which was controlled by the collapse of the hydrogel networks induced by photothermal effect of GNRs. The *in vitro* cytotoxicity test demonstrated the excellent biocompatibility and photothermal effect of the nanocomposite hydrogel. Moreover, the *in situ*-forming hydrogel showed promising tissue biocompatibility in the mouse model study. The *in vivo* antitumor test demonstrated the capacity of the nanocomposite hydrogel for chemophotothermal synergistic therapy with reduced adverse effects owing to the prolonged drug retention in the tumor region and efficient photothermal effect. Therefore, this injectable and NIR/pH-responsive nanocomposite hydrogel exhibited great potential as a long-term drug delivery platform for chemophotothermal synergistic cancer therapy.

### 16.2.2 CD-Based Polymer Self-Assemblies and Vesicles

Due to the excellent chemical stability and remarkable biocompatibility, nano-diamonds (NDs) have received widespread research attention by the biomedical field. The excellent water dispersibility of NDs has significant importance for biomedical applications. Therefore, surface modification of NDs with hydrophilic polymers has been extensively investigated over the past few decades. Zhang et al. (2018) [13] synthesized  $\beta$ -CD containing hyperbranched polymer functionalized ND (ND- $\beta$ -CD-HPG) composites with high water dispersibility via supramolecular chemistry based on the host-guest interaction between  $\beta$ -CD and adamantane (Ad). The hydroxyl groups of NDs first reacted with 1, 1-adamantanecarbonyl chloride to obtain ND-Ad, which was further functionalized with  $\beta$ -CD containing hyperbranched polymers to form the final ND- $\beta$ -CD-HPG composites. The successful preparation of ND- $\beta$ -CD-HPG composites was confirmed by several characterization techniques. Furthermore, the loading and release of the anticancer agent doxorubicin hydrochloride (DOX) on ND- $\beta$ -CD-HPG composites was also examined to explore its potential in drug delivery. When compared with traditional methods of surface modification of NDs, this method was convenient, fast, and efficient. We demonstrated that ND- $\beta$ -CD-HPG composites have great water dispersibility, low toxicity, high drug-loading capacity, and controlled drug-release behavior. Based on these characteristics, ND- $\beta$ -CD-HPG composites are expected to have high potential for biomedical applications.

Jiang et al. (2018) [14] prepared an oligo(ethylene glycol)-based amphiphilic star polymer containing fluorescent coumarin as end groups and dual tertiary amine as center. This polymer could self-assemble into vesicles in the aqueous solution. The crosslinking pattern in the hydrophobic membrane of the vesicles could form noncovalent crosslinking by adding  $\gamma$ -CD into the solution, and the formed 2/1 host-guest inclusion between  $\gamma$ -CD and coumarin groups led to a higher sensitivity and faster disassembly speed of the vesicles by injecting  $\text{CO}_2$ ; while after 365 nm light irradiation, the formed coumarin dimers acting as crosslinking point gave a more stable hydrophobic membrane and less sensitive to  $\text{CO}_2$ . The work reported here gives a notable polymer system that the  $\text{CO}_2$ -responsive behaviors can be easily tuned by controlling the crosslinking pattern, bearing a great promise in the areas including latexes, surfaces, sensors, carriers, and so on.

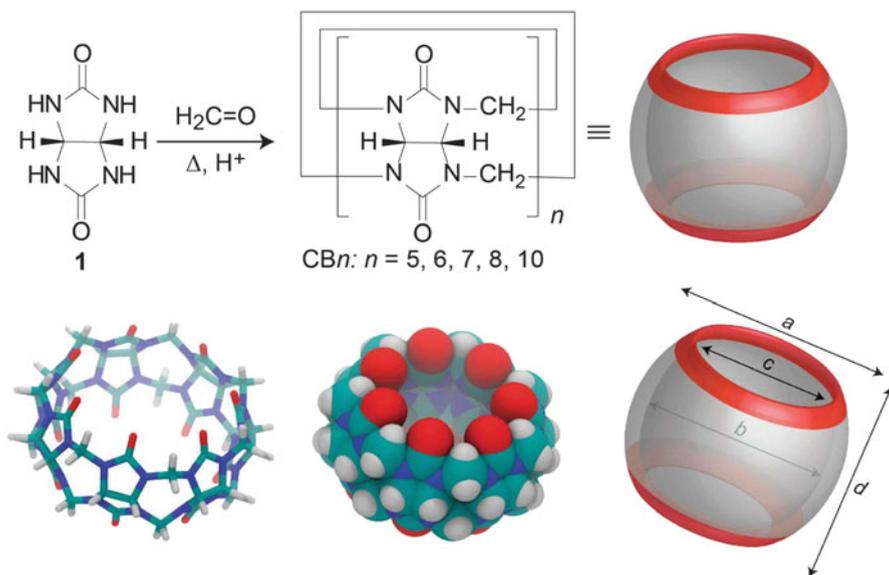
Zhang et al. (2014) [15] reported a fabrication of photoresponsive block-controlable supramolecular polymer which was constructed through host-guest interactions. This supramolecular polymer based on the assembly of two homopolymers according to the host-guest recognition between CDs and Ad/Azo moieties in aqueous solution is a kind of triblock polymer. Upon alternating irradiation of UV/visible light, this triblock polymer can reversibly transform into supramolecular diblock polymers with the change in morphology between the self-assembly and disassembly. In addition, this supramolecular polymer showed potential applications in stimuli-responsive drug delivery systems.

Yuan et al. (2017) [16] prepared a kind of functional (PCL-CD)<sub>16</sub>/Azo-PDMAEMA supramolecular aggregates with tunable morphologies based

on the IC between the dendritic host polymer and the linear guest polymer. The morphologies of the aggregates could be adjusted by changing the molar ratio of (PCL-CD)16: Azo-PDMAEMA in the supramolecules. The supramolecular aggregates changed from nanorods to nanowires, and then to spherical micelles when the (PCL-CD)16:Azo-PDMAEMA molar ratio was changed from 1:1 to 1:8 and 1:16, respectively. Benefitting from the UV-response of  $\beta$ -CD/Azo IC, the supramolecular aggregates demonstrated UV responsive properties. Upon UV light irradiation, the morphologies of the aggregates became irregular and agglomeration occurred. Meanwhile, because of the thermoresponsive PDMAEMA, the supramolecular aggregates showed thermoresponsive properties. When the temperature was increased, the aggregates changed into smaller aggregates and then aggregated with each other upon further heating. Therefore, the supramolecular aggregates with tunable morphologies were UV- and thermoresponsive. These functional nano-materials have potential applications in nanotechnology and biomedicine.

### 16.3 Photoresponsive Supramolecular Polymers Based on Cucurbituril (CBs)

CBs represent another class of cyclic host molecules. As shown in Fig. 6, they are macrocyclic oligomers of methylene-bridged glycolurils, which are named after the shape of the zucchini of the genus Cucurbita. They are called cucurbit[n]



**Fig. 6** (Top) Synthesis of CB[n] homologues and (bottom) different representations of CB[7] structure. (Reprinted with permission from Ref. [17]. Copyright (2015) Royal Society of Chemistry)

uril (CB[n]) depending on the number of units of glycoluril. They contain a hydrophobic cavity lining the urea carbonyl and can enclose a series of neutral or positively charged guests with very high binding constants, providing an opportunity for the development of new supramolecular polymers. The first member of this circular family is hexamer CB[6], and since then CB[n] has evolved to include smaller or larger homologs (CB[5]-CB[10]). In this family, CB[6] and CB[8] have poor water solubility, while CB[5] and CB[7] have moderate solubility. In this regard, Mock, J. Fraser Stoddart, Kimoon Kim, Lyle Isaacs, etc. have done a lot of exploratory work [17].

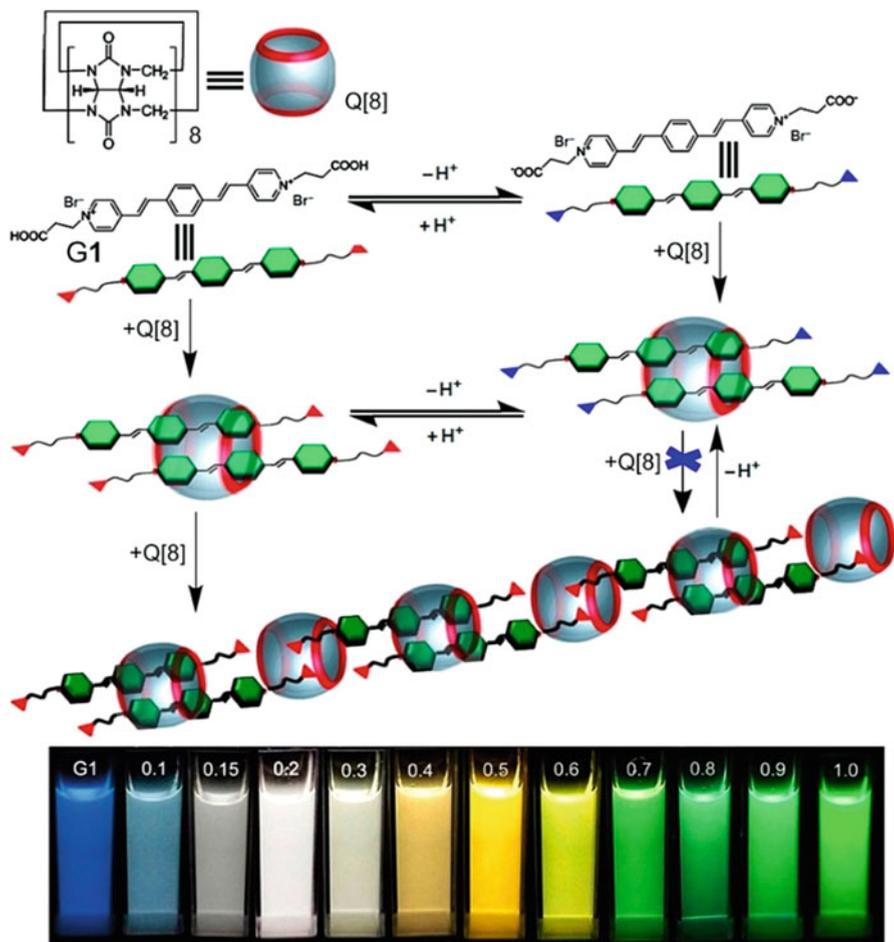
However, due to the difficulty in the modification of CBs, supramolecular polymers based on CB[5], CB[6], and CB[7] are rarely reported. The particularity of CB[8] is that its larger cavity can entrap two specific guest molecules. Therefore, in the CB family, CB[8] is the most promising host molecule for the construction of supramolecular polymers. However, limited by the poor water solubility (<1 mM) of CB[8], in most cases, dimerization and oligomerization cyclization dominate in diluted aqueous solutions compared to linear polymerization.

### 16.3.1 Adjustable Dynamic Photophysical Properties Based on CB

In 2016, Tao et al. (2016) [18] reported a class of supramolecular methods based on host-guest function, which greatly reduced the synthesis steps to construct a system with adjustable dynamic photophysical properties. As shown in Fig. 7, due to the new electron distribution of the chromophore guest molecule in the CB[8] rigid hydrophobic cavity, the luminescent color of the system can achieve blue-green, yellow, green, and white changes by simply adding the host molecule in the aqueous solution, accompanied by an increase in fluorescence lifetime and quantum yield. This work realizes the stimuli response adjustment of color in a single solution combined with a single organic fluorescent object and a single body, which provides a new idea for the development of new luminescent materials.

### 16.3.2 Supramolecular Polymer with Photoisomerism Based on CB

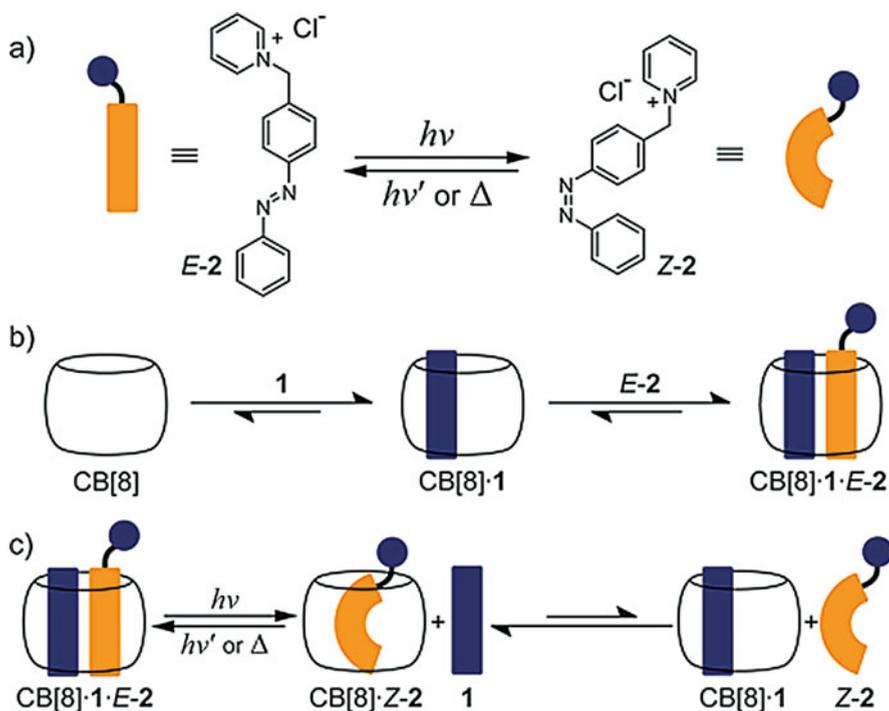
Scherman et al. (2013) [19] displayed control over the stoichiometry of a series of CB [8] complexes through photoirradiation. The E-Z isomerism of azobenzene-containing guest molecules for CB[8] was modified in the presence of the macrocycle, Fig. 8. A remarkable stabilization of the Z-azobenzene moieties of guests 2-4 was achieved by CB[8] complexation. Host-guest complexes that can be remotely switched between highly thermostable photostationary states in aqueous media are valuable molecular systems in biological and materials sciences and are also of interest in information storage technologies and for the construction of molecular machinery. Furthermore, guests 3 and 4 in the presence of CB[8] can form supramolecular polymers, which were characterized both in solution and, for the first time, in the solid state and whose structures can be externally controlled by light irradiation.



**Fig. 7** Schematic representation of the CB[8]-based approach for fabricating smart luminescent materials. (Reprinted with permission from Ref. [18]. Copyright (2015) American Chemical Society)

Ma et al. (2015) [20] constructed a rigid aqueous phase supramolecular polymer, using the CB[8] urea as the host and the 4,4'-bipyridyl group conjugated at both ends of the azobenzene as the guest, seen in Fig. 9. Since the CB[8] macrocycle could contain two 4,4'-bipyridyl groups at the same time, the host and guest system was packed in a 1:1 ratio. Owing to the photoisomerism of azobenzene, the supramolecular polymer would respond under the light of specific wavelengths (254 and 365 nm), and the linear/nonlinear reversible regulation of its morphology would be realized.

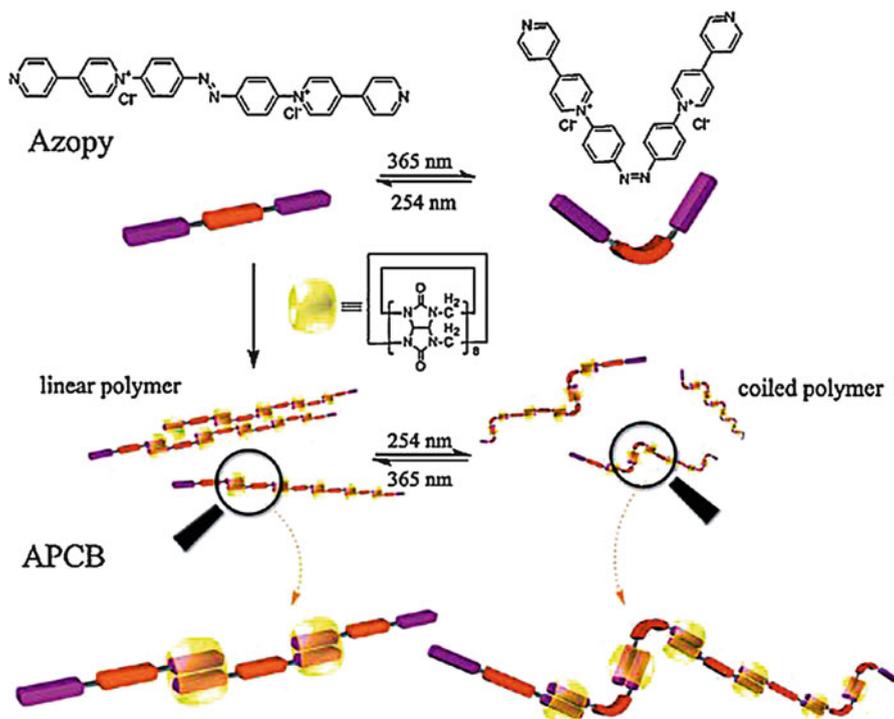
Scherman et al. (2017) [21] reported a light and chemical responsive supramolecular hyperbranched-like polymer (SHP) with 1:1:1 heteroternary complex between methyl viologen (MV), azobenzene, and CB[8], which could



**Fig. 8** (a) Isomerization of **2**; (b) stepwise formation of CB[8]·1·E-2; (c) isomerization of **2** in the presence of CB[8] and **1** and equilibrium after UV irradiation of CB[8]·1·E-2. (Reprinted with permission from Ref. [19]. Copyright (2013) American Chemical Society)

reversibly achieve the conversion between (Z)-B3-CB[8] and (E)-B3-CB[8] upon exposure to blue light or heat. SHP created an extended physically crosslinked supramolecular network which can be formed at the interface of a droplet, thus it could be further explored as surfactant in the future.

Zhang et al. (2018) [22] demonstrated the fabrication of water-soluble cucurbit[8]uril (CB[8])-mediated supramolecular polymers by connecting the fluorinated azobenzene (FAB)-containing monomers through host-enhanced heteroternary  $\pi$ - $\pi$  stacking interactions. Benefiting from the unique visible-light-induced E  $\rightarrow$  Z photoisomerization of the FAB photochromophores, the encapsulation behaviors between the CB[8] macrocycle and the monomers can be regulated upon visible light irradiation, resulting in the depolymerization of such CB[8]-mediated supramolecular polymers. This CB[8]-based hybrid recognition motif was expected to be served as molecular trafficking system, which may find widespread applications such as drug delivery and release, photopharmacology, and so on. The use of visible light as external stimulus provided well remote spatiotemporal controllability, together with the advantages of mild aqueous conditions at room temperature. The development of such unique visible-light-regulated CB[8]-mediated supramolecular polymers as well as the related hybrid host-guest systems was highly valuable in the construction of biocompatible smart materials.

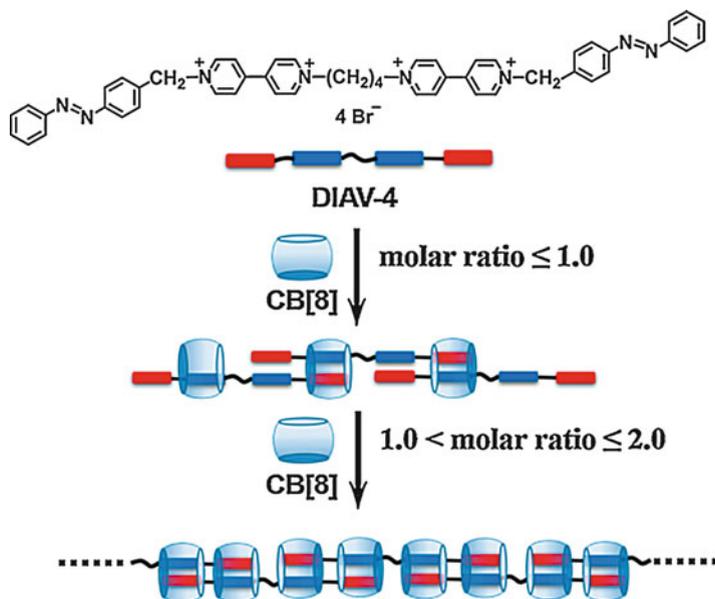


**Fig. 9** Schematic representation for the construction of the supramolecular polymer APCB via host-guest interaction between Azopy and CB[8]. (Reprinted with permission from Ref. [20]. Copyright (2015) Elsevier)

### 16.3.3 Controllable Supramolecular Polymerization Based on CB

Zhang et al. (2015) [23] developed a new method for controllable supramolecular polymerization based on ABBA type monomer and CB[8] monomer through host-guest interaction and photochemistry, Fig. 10. The molecular weight and polydispersity of supramolecular polymers could be well controlled by tuning the molar ratio of these host and guest monomers or by tuning the isomer ratio of azobenzene groups in the guest monomers upon the competitive irradiation of lights. This was somehow like a dissipative supramolecular polymerization through the transfer of matter and energy. In addition to the CB[8], other host molecules such as cyclodextrin, crown ethers, calixarene, pillar[n]arenes, and even other noncovalent interaction systems are supposed to be available by employing this methodology. Therefore, it was anticipated that this line of research provides a general methodology for controllable supramolecular polymerization.

Zhang et al. (2016) [24] reported a new method of controllable supramolecular polymerization, taking advantage of host-enhanced photodimerization, seen in Fig. 11. The low-molecular-weight supramolecular oligomers were formed by

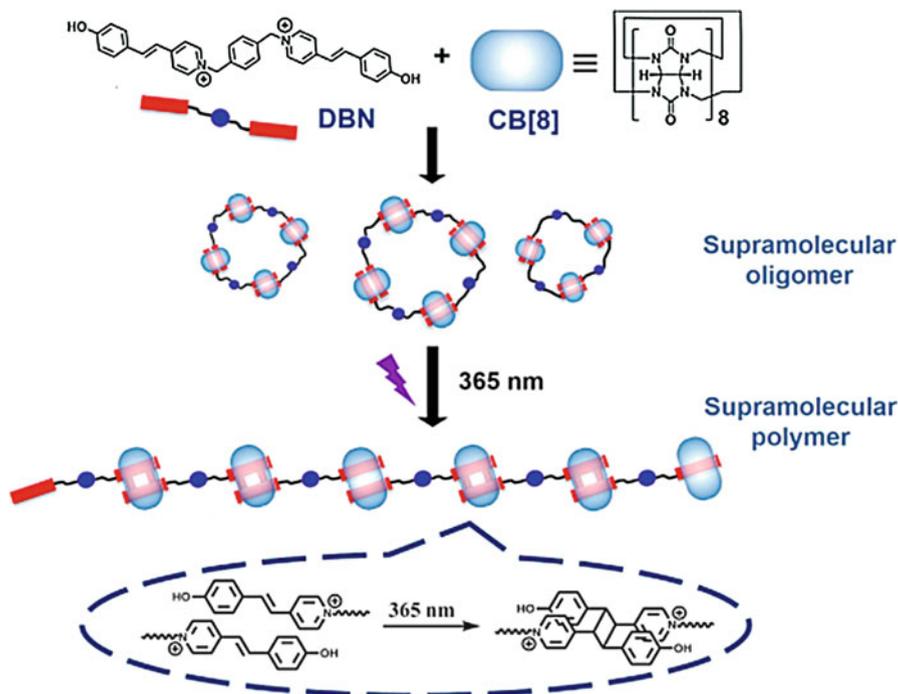


**Fig. 10** Schematic representation of controllable supramolecular polymerization by tuning the molar ratio of CB[8]/DIAV-4. (Reprinted with permission from Ref. [23]. Copyright (2015) American Chemical Society)

noncovalent complexation between cucurbit[8]urils (CB[8]) and the bifunctional monomers (DBN) with Brooker's merocyanine moiety (MOED) on either end. Interestingly, when irradiated with UV light, the supramolecular oligomers could transform into supramolecular polymers with high molecular weight. The molecular weight of supramolecular polymers could be controlled by varying the irradiation time. In addition, it is available to transfer the solution process to liquid-solid interface, fabricating thin films by the interfacial supramolecular polymerization promoted by UV irradiation. It is highly anticipated that this work can enrich the methods on the modulation of supramolecular polymerization.

## 16.4 Photoresponsive Supramolecular Polymers Based on Crown Ether

A crown ether is a cyclic compound composed of a plurality of ether groups. As the first generation of synthetic macrocyclic bodies, crown ether marks the birth of supramolecular chemistry. The host-guest interaction between the crown ether and the guest molecule, usually the secondary ammonium salt and the paraquat derivative, is a secondary interaction that can be used to construct smart materials to simulate natural systems. In the past few decades, crown ethers like 18-crown-6 (18C6), diphenyl-24-crown-8 (DB24C8), double-form benzene-26-



**Fig. 11** Schematic illustration of light-promoted supramolecular polymerization of DBN@CB[8]. (Reprinted with permission from Ref. [24]. Copyright (2016) American Chemical Society)

crown-8 (BMP26C8), and double-form benzene-32-crown-10 crown ethers (BMP32C10) are used to construct topologies such as molecular machines [25] and supramolecular polymers [26]. In order to expand the applications of molecular recognition based on crown ethers, many researchers have begun to challenge the development of crown ethers, like preparing organic white light-emitting materials.

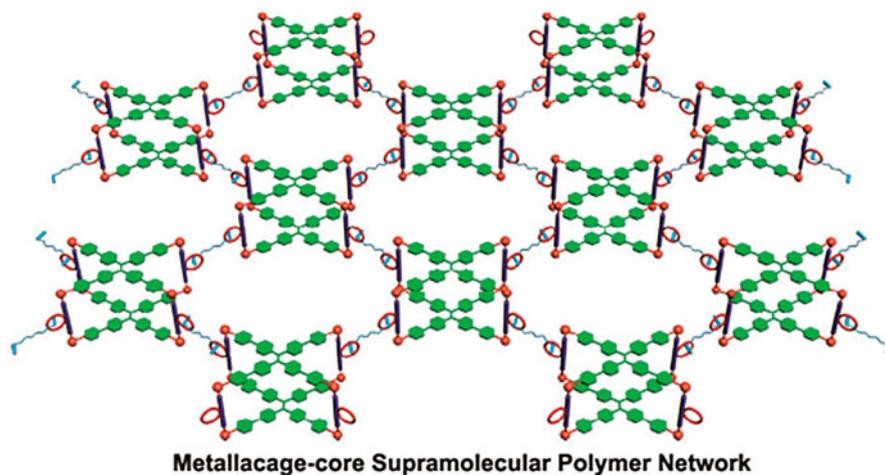
#### 16.4.1 Networks and Hydrogels of Supramolecular Polymer Based on Crown Ether

Photoresponsive supramolecular polymer systems based on crown ethers are rarely reported in recent years. Huang et al. (2015) [27] reported novel supramolecular polymers by utilizing the host-guest interaction with dependent photoresponse and self-healing property. A conjugated polymer **1** and the guest component **2** were used for the fabrication of the polymer network which could be disassembled by the inducement of different signals. The conjugated polymer in its assembled state showed a weak fluorescence, while it was enhanced in the presence of potassium ion, chloride ion, pH increase, and heating.

### 16.4.2 Conjugated Polymer Network and Its Disassembly Induced by Different Signals

Stang et al. (2018) [28] reported the preparation of a multifunctional metallacage-core supramolecular gel by orthogonal metal coordination and host-guest interaction, shown in Fig. 12. This work introduced a tetragonal prismatic cage with four appended 21-crown-7 (21C7) moieties in its pillar parts, which was first prepared via the metal-coordination-driven self-assembly of *cis*-Pt(PtEt<sub>3</sub>)<sub>2</sub>(OTf)<sub>2</sub>, tetraphenylethene (TPE)-based sodium benzoate ligands and linear dipyridyl ligands. Moreover, further addition of a bisammonium linker to the cage delivered a supramolecular polymer network via the host-guest interaction between the 21C7 moieties and ammonium salts, which formed a supramolecular gel at relatively higher concentrations. Due to the incorporation of a TPE derivative as the fluorophore, the gel shows emission properties. Multiple stimuli responsiveness and good self-healing properties were also observed because of the dynamic metal coordination and host-guest interaction used to stabilize the whole network structure. The studies described not only enrich the functionalization of fluorescent metallacages via elegant ligand design but also provide a way to prepare stimuli-responsive and self-healing supramolecular gels as robust and smart materials.

Lee et al. (2016) [29] synthesized rotaxane-type hyperbranched polymers for the first time from A<sub>2</sub>B type semi-rotaxane monomers formed in situ via complexation of bis(*m*-phenylene)-32-crown-10 dimethanol and two paraquat *x*-*n*-alkylenecarboxylic acid derivatives with tris(*p*-*t*-butylphenyl)methylphenylalkylene stoppers. The molecular size increases upon formation of the hyperbranched polymers are confirmed by dynamic light scattering and by viscometry. As with covalent hyperbranched polymers, a number of potential applications exist; the



**Fig. 12** Schematic description of the multifunctional metallacage-core supramolecular gel. (Reprinted with permission from Ref. [28]. Copyright (2018) American Chemical Society)

unique mechanically linked character and the presence of uncomplexed host and guest moieties foreshadow the use of such systems for their responses to external stimuli with the added benefit of providing molecular recognition sites useful as delivery vehicles. Use of other host-guest motifs to form the semi-rotaxane A<sub>2</sub>B monomers is possible and complementary systems with higher binding constants will enable efficient syntheses of high molecular weight, mechanically linked hyper-branched polymers.

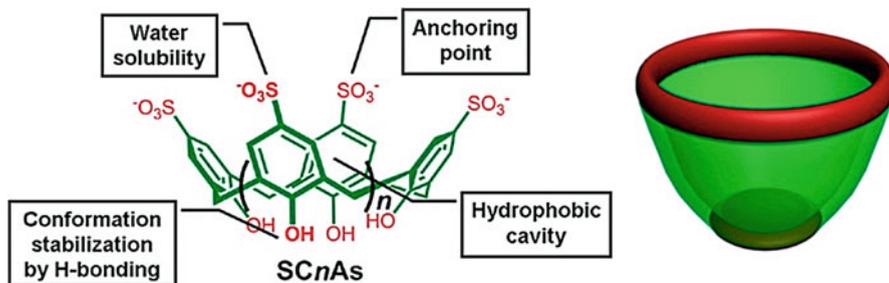
Liu et al. (2016) [30] successfully constructed a crown ether-based supramolecular gel with a three-dimensional network structure via a hierarchical induced assembly strategy. Therein, the coordination linkage of bis(terpyridyl)dibenzo-24-crown-8 (**1**) with Zn<sup>2+</sup> produces the 1/Zn<sup>2+</sup> supramolecular polymer as the primary assembly. Then, the anthryl-dibenzylammonium guest **2** was grafted to the 1/Zn<sup>2+</sup> supramolecular polymer via the noncovalent association of dibenzylammonium moieties on guests with the dibenzo-24-crown-8 rings on supramolecular polymer. Furthermore, the supramolecular polymer with anthryl grafts underwent a photo-induced secondary assembly to produce the supramolecular gel, which could be reversibly disassembled by a thermoinduced dissociation of anthracene dimers. These photo/thermo-induced hierarchical assembly/disassembly behaviors will provide a potential way to construct degradable hierarchical supramolecular assemblies employing environment-friendly external stimuli, such as light and heat, as controlling method.

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## 16.5 Photoresponsive Supramolecular Polymers Based on Calixarene

Calixarenes are macrocyclic molecules composed of 2- and 6-positions of methylene-linked phenolic units and are a class of widely studied organic supramolecular hosts. Because it is easy to be modified, its possibilities for development are unlimited. The encapsulation ability of the unmodified calixarene cavity is not as good as the crown ether, cyclodextrin, and cucurbituril mentioned above, so extensive chemical modification of calixarene is necessary to achieve sufficient inclusion.

Sulfonated calix[n]arenes (*p*-sulfonatocalix [n] arenes, SCnAs,  $n = 4-8$ , Fig. 13) were first reported by Shinkai et al. (1984) [31], which is a class of outstanding water-soluble calixarene derivatives. The calixarene derivative has a strong binding ability to a guest in aqueous solution. Advantages that sulfonated calix[n] arenes possess as a host are as follows [32]: first, it can be easily obtained by direct sulfonation of the upper edge of the calixarene in a relatively satisfactory yield; second, it has high water solubility. Compared with organic solvents, it can be more effectively encapsulated with the guest by hydrophobic and  $\pi$ - $\pi$  stacking in water; third, the upper edge of the sulfonic acid group provides a connection point as a  $\pi$ -rich electron cavity. It acts as a complementary combination; therefore, it has strong binding ability and high selectivity with a series of organic cations. Finally, it is biocompatible.



**Fig. 13** Structure of SCnAs ( $n = 4-8$ ). (Reprinted with permission from [32]. Copyright (2014) American Chemical Society)

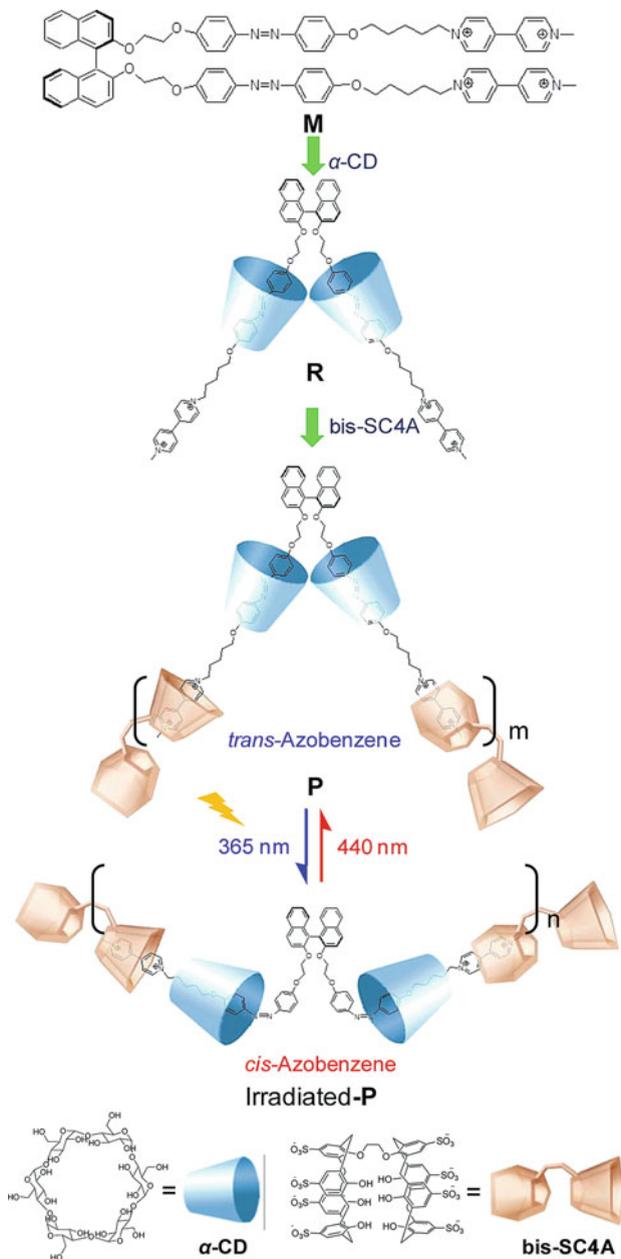
### 16.5.1 Supramolecular Polymer with Photoisomerism Based on Calixarene

According to the host–guest recognition, Ma et al. (2014) [33] prepared a supramolecular polymer formed by sulfonated biphenyl[4]arene and dithiophene ethylene derivatives. In this supramolecular complex, the resulting polymer exhibits significant color changes and morphological changes at different wavelengths of light. In advance, it can achieve a variety of functions by combining different functional units, which is an important develop direction of supramolecular polymer.

Tian et al. (2013) [34] successfully constructed a novel light-driven, linear, helical, chiral supramolecular polymer in water by noncovalent host–guest molecular recognition between the calixarene bis-SC4A and the pseudorotaxane **R** containing an axially chiral 1,1'-binaphthyl unit and two  $\alpha$ -CD-included azobenzene arms terminated with 4,4'-bipyridinium units, shown in Fig. 14. More interestingly, dynamically self-assembled, light-driven, single-helical supramolecular polymer molecules with lengths of hundreds of nanometers to micrometers in water were for the first time observed in the native state using cryo-TEM measurements. Preliminary molecular modeling was performed to substantiate this photoresponsive supramolecular structure. This work provides an exciting impetus for building controllable supramolecular polymers with tailored functionalities.

### 16.5.2 Networks and Self-Assemblies of Supramolecular Polymer Based on Calixarene

Pappalardo et al. (2016) [35] synthesized a poly(*p*-phenyleneethynylene) polymer (PCF [5]), bearing two  $\pi$ -rich cone-like calix[5]arene cavities (assembling cores) attached to a rigid *p*-phenyleneethynylene spacer by a Pd-catalyzed cross-coupling reaction. UV-vis absorption and fluorescence spectroscopies combined with dynamic light scattering measurements provided evidence for the self-assembly of PCF [5](homopolytopic host molecule) with a complementary  $C_{60}$  fulleropyrrolidine ( $C_{60}$ -Pyr) guest in solution, in the construction of a supramolecular polymer



**Fig. 14** Molecular structures of monomers **M**,  $\alpha$ -CD, and bis-SC4A and a schematic description of the self-assembly process for forming  $\alpha$ -CD-based pseudo[3]rotaxane **R**, the supramolecular polymer **P** with azobenzene in the *trans* configuration, and the corresponding UV-irradiated **P** containing *cis*-azobenzene (Br<sup>-</sup>, I<sup>-</sup>, and Na<sup>+</sup> ions have been omitted for clarity). (Reprinted with permission from [34]. Copyright (2013) American Chemical Society)

network. Atomic force microscopy analysis of PCF[5]/C<sub>60</sub>-Pyr highlighted the formation of a bicontinuous network consisting of a uniform distribution of prominent structures, within a polymeric background forming a biphasic structure.

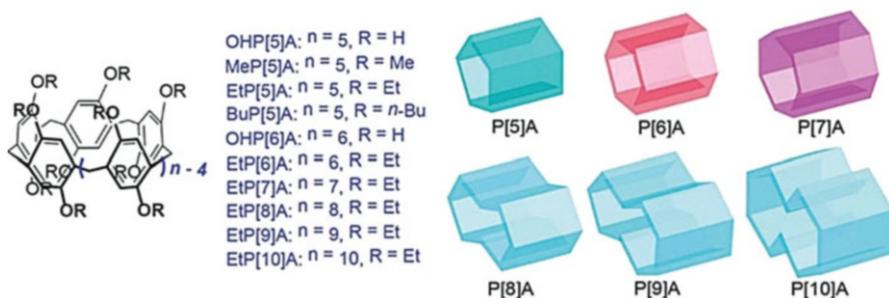
Haino et al. (2014) [36] described a facile process for fabricating fullerene polymers driven by host–guest interactions between calix[5]arene and C<sub>60</sub>. The formation and structures of the supramolecular polymers and networks were carefully examined using a variety of spectroscopic techniques. During the experiments, the dimensions of the supramolecular polymers were controlled by the rational design of the monomer components. Although each of the monomers was connected via noncovalent interactions, supramolecular polymers belong to the class of polymers in terms of macroscopic properties. The designability of supramolecular polymers can open up new possibilities for molecular organization in nanospace.

## 16.6 Photoresponsive Supramolecular Polymers Based on Pillararene

Pillararenes, a novel class of macrocyclic molecules, were first reported by Ogoshi et al. (2008) [37]. They are formed by the 2, 5 positions of methylene-bridged hydroquinone. Unlike the traditional cup-aroma basket structure, it has a symmetrical columnar structure with typical characteristics [38]: first, with simple preparation and flexible modification, it can be easily dissolved in organic solvents and can also be dissolved in water by modification. In addition, there are six synthons that have been synthesized up to now (Fig. 15). Second, the symmetric columnar structure has a unique advantage in the construction of supramolecular polymers. Third, the relatively rigid and  $\pi$ -rich electron cavities can be combined with a series of objects.

### 16.6.1 Cross-Linked Polymer Networks Based on Pillararene

Based on the reversible [4 + 4] cycloaddition reaction of anthracene and the host–guest binding between column[5]arene and imidazole, Yang et al. (2013)



**Fig. 15** Chemical structures of typical pillar[n]arenes host molecules. (Reprinted with permission from [38]. Copyright (2014) Royal Society of Chemistry)

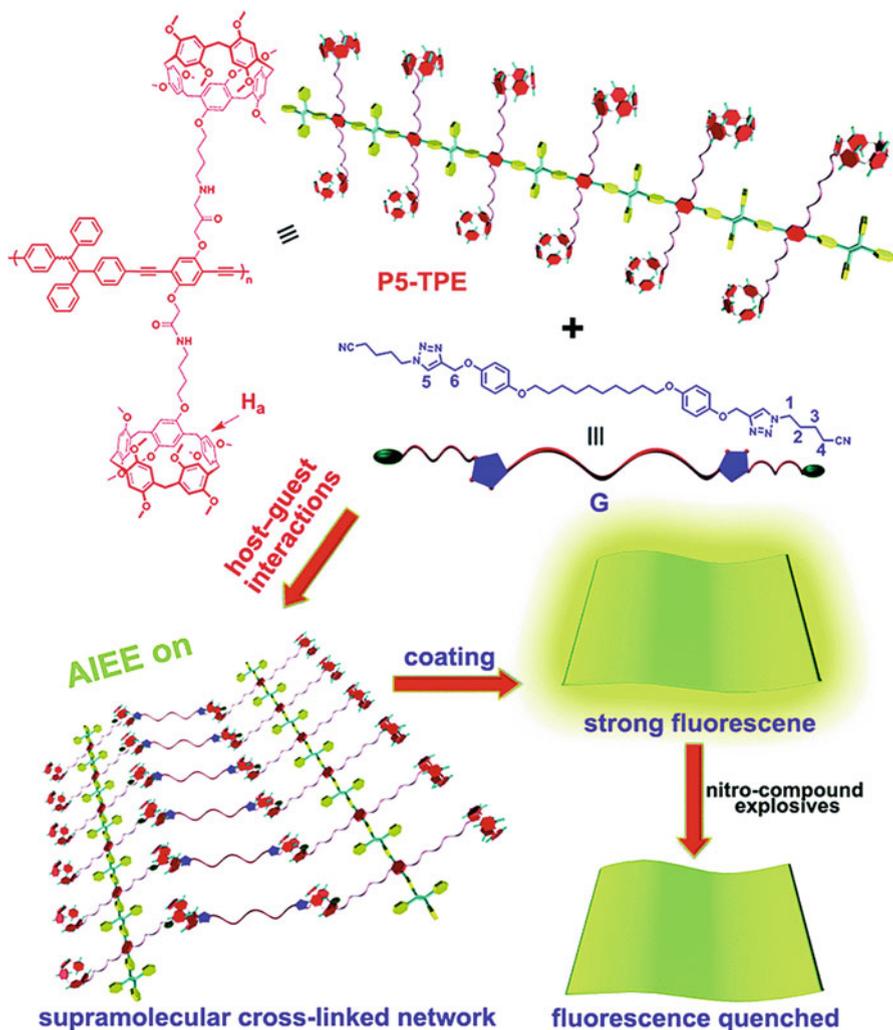
[39] designed a supramolecular polymer with light/heat double stimulus response SP7. Short-time heating (1 min) of the supramolecular polymer solution will only lead to decomposition of the host and guest complexes. However, prolonged heating (1 day) and recooling will result in the depolymerization of anthracene dimer units. The depolymerization of the unit, which forms an oligomer, can be restored to its original supramolecular state by cooling or light irradiation, but it is to be noted that the transition time of the polymer to the monomer is too long to achieve effective light control.

Huang et al. (2018) [40] constructed a novel fluorescent supramolecular cross-linked polymer network with aggregation-induced enhanced emission (AIEE) properties via pillar[5]arene-based host-guest recognition, seen in Fig. 16. The crosslinking and decrosslinking processes of the supramolecular polymer network could be controlled by external stimuli including temperature and addition of competitive guests, consequently leading to changes in fluorescence intensity. Moreover, the fluorescent supramolecular polymer network could be further used for the detection of nitrocompound explosives, exhibiting its practical application in our daily life. This work is the combination of supramolecular chemistry and conjugated polymer science and the co-built supramolecular network system may pave a new way to develop novel multifunctional fluorescent materials in the future.

Yao et al. (2015) [41] constructed a kind of fluorescent supramolecular polymer driven by pillararene-based molecular recognition and metal coordination, shown in Fig. 17. The phase transitions of the fluorescent supramolecular polymer could be realized by subsequent alteration of heating and cooling, and the fluorescent supramolecular polymer showed base-stimulus responsive property. This supramolecular polymer has concentration controllable fluorescence emissions. Moreover, a thin film of the fluorescent supramolecular polymer was prepared, which was confirmed to be a convenient test kit for detecting OH anions. This work may be of high importance for developing novel functional fluorescent materials and molecular devices in the future.

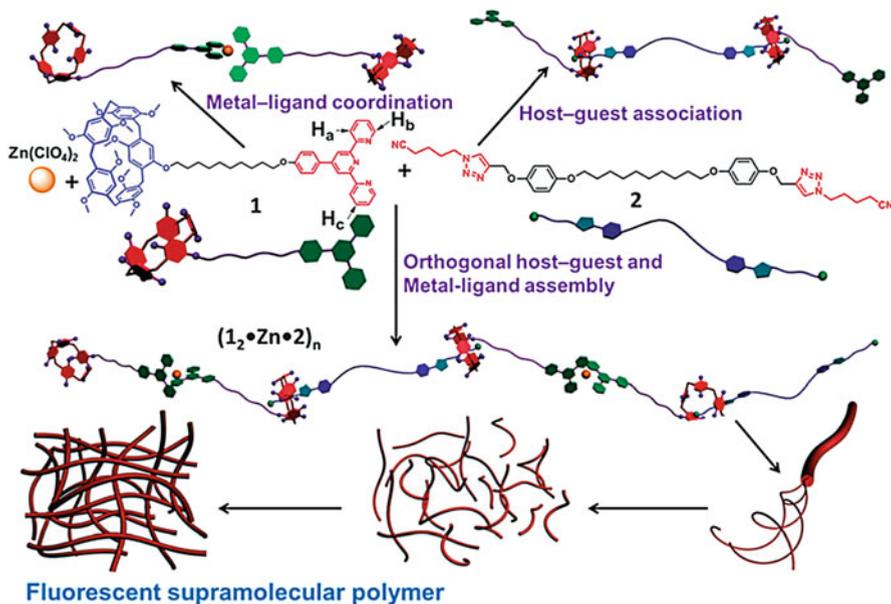
### 16.6.2 Supramolecular Polymer with Photoisomerism Based on Pillararene

The construction of supramolecular systems with azobenzene as bridging agent has recently set off a boom. Yu et al. (2014) [42] represented a linear supramolecular polymer and a supramolecular polymer network, and both of them were based on the host-guest interactions with photoresponsive characteristics. The linear supramolecular polymer was fabricated from self-assembly of an azobenzene moiety acting as a molecular bridge, pillar[5]arene dimer and a bisammonium salt. The supramolecular polymer network was constructed by the secondary ammonium salt which exhibited the recognition of molecular motif. The presence of the host-guest complexation made it possible of the reversible transitions between polymer-oligomer and polymer-monomer upon UV irradiation and PH changes.



**Fig. 16** Chemical structures of P5-TPE and G and illustration of the formation of an aggregation-induced enhanced emission (AIEE) fluorescent supramolecular polymer network and detection of nitro-compound explosives. (Reprinted with permission from [40]. Copyright (2018) Royal Society of Chemistry)

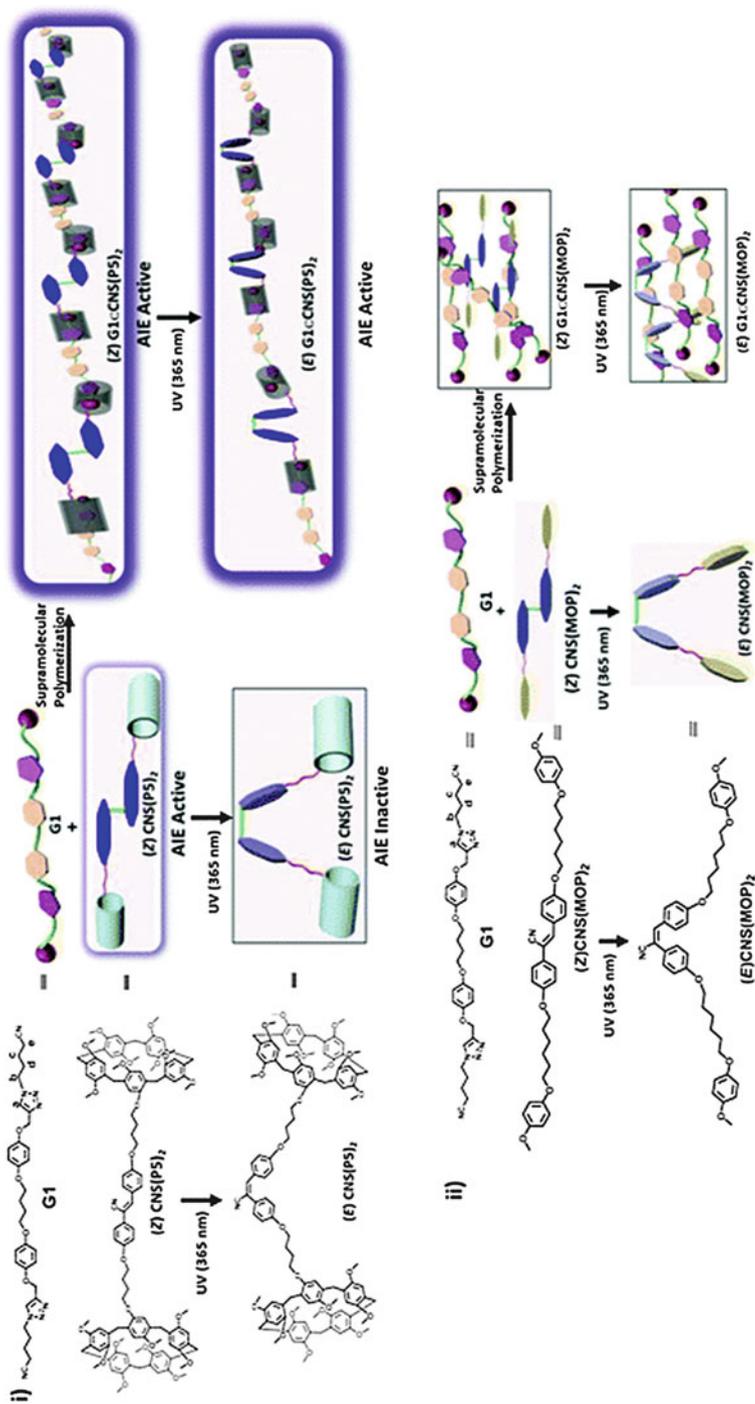
Gong et al. (2017) [43] successfully achieved a new AA-type homo-ditopic cyanostilbene-linked bis-pillar[5]arene by cost-effective Knoevenagel condensation, seen in Fig. 18. In this work, supramolecular polymerization-enabled, configuration-independent aggregation-induced emission (AIE) systems of cyanostilbene was achieved through host-guest interaction between pillar[5]arene and nitrile triazole guests. Interestingly, control-host and control-guest



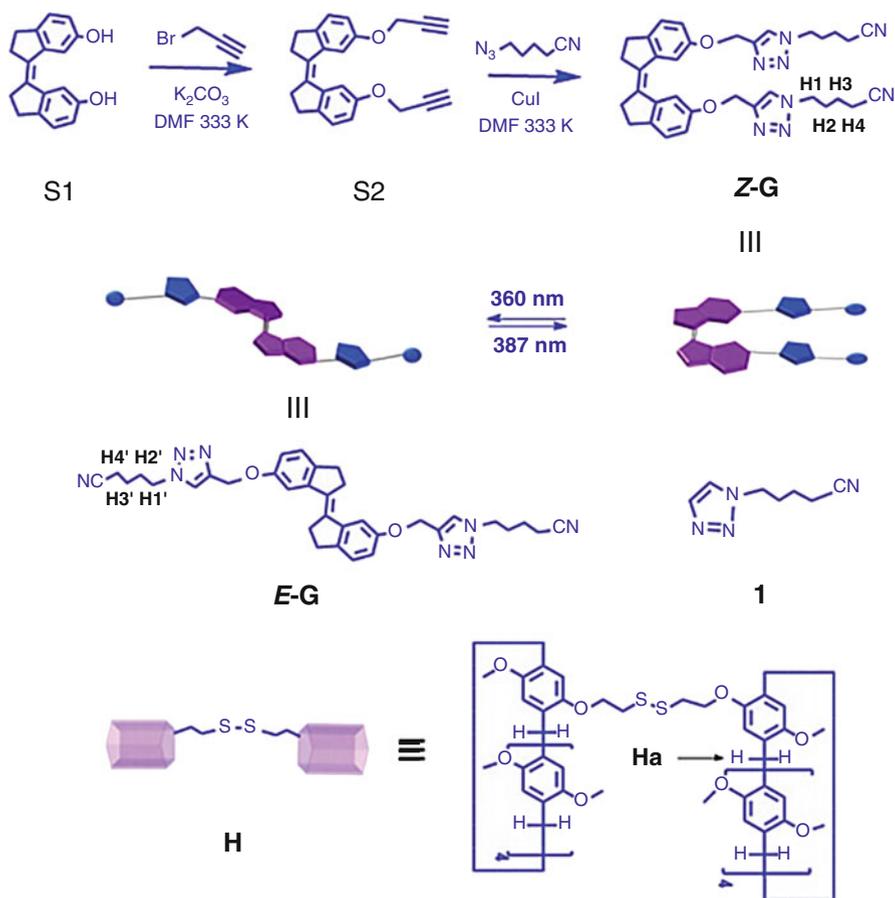
**Fig. 17** Cartoon representation of the formation of the fluorescent supramolecular polymer based on orthogonal host–guest association and metal ion coordination. (Reprinted with permission from [41]. Copyright (2015) Royal Society of Chemistry)

lost its AIE upon photoisomerization due to the absence of host–guest interaction.  $^1\text{H}$  NMR, DOSY NMR, and fluorescence studies of the supramolecular polymers before and after UV irradiation clearly indicated the significant role of photostable host–guest interaction in enhancing and retaining AIE. In addition, strong host–guest interaction played a key role in retaining the polymeric assembly and AIE, which is an interesting finding. The current study provides a new strategy to preserve the AIE activity of photoresponsive cyanostilbene derivatives.

Yang et al. (2017) [44] reported the facile preparation of photoresponsive supramolecular polymers by the assembly of stiff-stilbene-based guests (**Z-G**/**E-G**) and a bispillar[5]arene (**H**), seen in Fig. 19. The 1:1 mixture of **Z-G** and **H** assembled into oligomers at 5–150 mM. In contrast, the 1:1 mixture of **E-G** and **H** assembled into AA/BB-type supramolecular polymers following a ring-chain polymerization mechanism. The assembly behavior between the host and guest molecules was regulated by the photoisomerization of the stiff stilbene units in guest molecules. The formation and disassembly of the AA/BB supramolecular polymer were reversible by alternating irradiation between 387 nm and 360 nm light. The light responsive pillar [5]arenes based AA/BB-type supramolecular polymers may have potential applications in biomaterials.



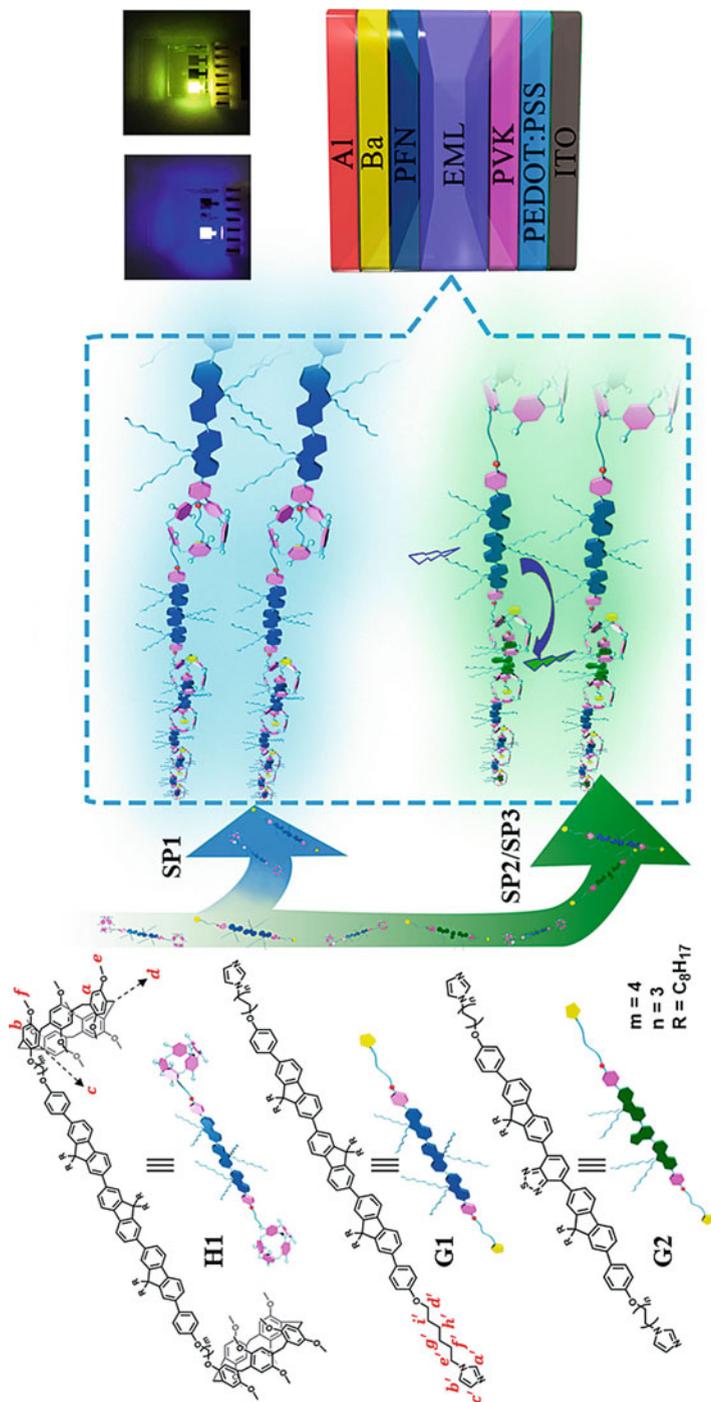
**Fig. 18** Schematic representations of supramolecular polymerization and photoisomerization in (i)  $(Z)CNS(P5)_2$  and  $G1C(Z)CNS(P5)_2$  and (ii)  $(Z)CNS(MOP)_2$  and  $G1C(Z)CNS(MOP)_2$ . (Reprinted with permission from [43]. Copyright (2017) Royal Society of Chemistry)



**Fig. 19** Chemical structures of the pillar[5]arene dimer (**H**) and the guest molecules (**Z-G** and **E-G**). (Reprinted with permission from [44]. Copyright (2017) Royal Society of Chemistry)

### 16.6.3 Supramolecular Polymer with Two Guest Monomers Based on Pillararene

Huang et al. (2017) [45] prepared new fluorescent pillar[5]arene supramolecular polymers based on host monomer **H1** and two neutral guest monomers **G1** and **G2**, seen in Fig. 20. Linear supramolecular polymers with fluorescent character for OLED fabrication were successfully prepared and confirmed by multiple methods. As the doping strategy was successfully applied in these SPs, SP1 and SP2-3 exhibited blue-emitting and green-emitting, respectively, as expected. The efficient energy transfer caused by the exciton trapping on narrow band gap guest **G2** led to an improvement on the PL efficiencies. Furthermore, the first OLED device utilizing pillar[5]arene-based supramolecular polymers as the emissive layer. Maximum LEs for SP1, SP2, and SP3 were achieved at 0.62, 3.88, and 4.88  $cd A^{-1}$ , respectively,

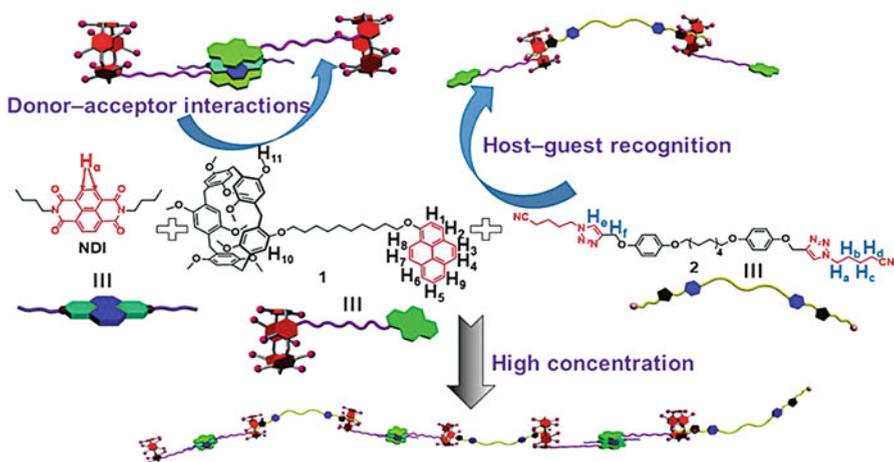


**Fig. 20** Chemical structures of **H1**, **G1**, and **G2**, the construction of supramolecular polymers with different emitting colors, and model device structure fabricated in this work. (Reprinted with permission from [45]. Copyright (2017) American Chemical Society)

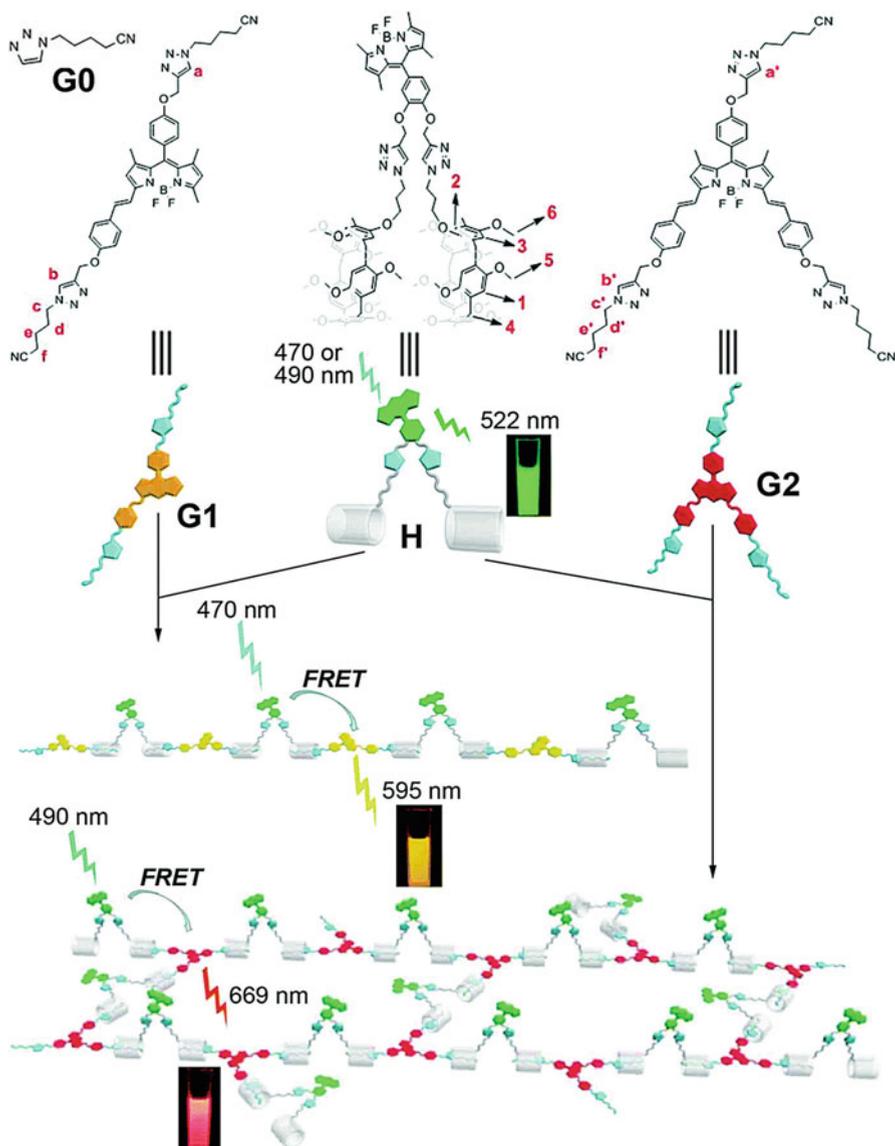
which were comparable efficiencies to those of analogous conventional conjugated polymers, indicating that pillar[n]arenes could be an ideal choice for supramolecular polymer-based optoelectronic applications. This study inspired us to take a deeper insight on pillar[n]arene-based polymers and further illuminate their applications in organic semiconductor area.

Shi et al. (2016) [46] successfully prepared a neutral linear supramolecular polymer using donor–acceptor interactions and pillar[5]arene-based molecular recognition in a hierarchical orthogonal fashion, seen in Fig. 21. Through  $^1\text{H}$  NMR, DOSY, and specific viscosity, they found that the monomer concentration exerts a significant impact on the formation of the supramolecular polymer. Moreover, rod-like fibers were drawn from a high concentration solution of the monomers, which provided direct evidence for the formation of a linear supramolecular polymer. Interestingly, the supramolecular polymer shows reversible glue-sol phase transitions upon heating and cooling. Considering the favorable properties induced by donor–acceptor interactions and host–guest molecular recognition, this pillararene-based supramolecular polymer may be of high importance for developing supramolecular materials with more complex structures and functions in the future.

Wang et al. (2015) [47] successfully prepared a BODIPY-bridged pillar[5]arene dimer **H** and two BODIPY derivative guests **G1** and **G2** to construct AA/BB-type and A2/B3-type FRET-capable supramolecular polymers for mimicking the photosynthetic light-harvesting system, shown in Fig. 22. Both assemblies exhibited very strong absorption in a broad region from 300 to 700 nm. Due to the high complexation stability of the host–guest pair, they showed efficient FRET effects and the transfer efficiencies were 51% for G1CH and 63% for G2CH, which were comparable with previous artificial models. This is the first example



**Fig. 21** Chemical structures of **1**, **NDI** and **2**. Cartoon representation of the formation of the linear supramolecular polymer. (Reprinted with permission from [46]. Copyright (2016) Royal Society of Chemistry)



**Fig. 22** Chemical structures of H, G1, G2, and G0 and the cartoon representation of the construction of two kinds of FRET-capable functional supramolecular polymers. (Reprinted with permission from [47]. Copyright (2015) Royal Society of Chemistry)

of pillar[5]arene-based supramolecular assemblies for mimicking the light harvesting system. Therefore, this work not only provided a novel model for fabricating artificial light-harvesting systems but also extended the potential applications of pillararenes in the field of optoelectronic materials.

Yang et al. (2018) [48] presented the successful fabrication of a new family of AIE cross-linked supramolecular polymer through hierarchical self-assembly involving coordination and host-guest interaction. From a newly synthesized dipyrindyl donor **G1** containing a TPE scaffold and two nitrile units, a rhomboidal metallacycle **G2** with four nitrile units was smoothly obtained. A pillar[5]arene dimer **H** was also successfully obtained to play as a linker. Subsequently, driven by the host-guest interaction between rhomboidal metallacycle **G2** and pillar[5]arene dimer **H**, a new family of AIE cross-linked supramolecular polymer was obtained. Interestingly, such fluorescent supramolecular polymer exhibited dual-stimuli responsive behaviors to halide and competitive guest. Thus this research enriches the family of supramolecular polymer with multiple functionalities, which may find potential applications in the fields of molecular sensors and biological imaging in the future.

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## 16.7 Conclusions

The overview we discussed here is surrounded with the photoresponsive supramolecular polymer systems constructed via the host-guest interaction, using hosts including CD, CB, crown ether, calixarene, and pillararene, to encapsulate the guests in the constructed supramolecular polymer systems. Furthermore, guest units undergo different reversible structures or conformations under specific light stimulation, resulting in the corresponding changes of the supramolecular polymer. As far as we can see, photoresponsive supramolecular polymer is one of the hotspots of supramolecular chemistry in recent years. Since the photoresponsive supramolecular polymer combines the properties of supramolecular polymer, photoisomerization unit, and light absorption unit, it has extra advantages like long-range responsiveness, low toxicity, and so on. The changing of specific light not only can achieve the reversible regulation of supramolecular polymer structure and its assembly morphology but also will effectively expand its applications in tissue engineering, drug carrier, and chemical conversion. At the same time, it has important academic significance to seek simple and effective means to achieve the transformations between supramolecular polymer and covalent polymer [49]. According to the recent published research, the wavelength of most incident lights are still concentrated in the ultraviolet and visible areas, therefore the ability to introduce near infrared components into the polymer will greatly expand its application in biochemistry. Nowadays, self-assembly supramolecular assembled by thermal equilibrium has been progressively approaching the kinetic-driven system, which has proved more potential value in the development of supramolecular chemistry. In addition, the challenge to be solved is finding more effective and universal methods to precisely dominate the supramolecular polymers, such as the control of the size and dimension of supramolecular polymer [50].

## 16.8 Cross-References

### ► Functional Rotaxanes

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