Pillararene-Based Supramolecular Polymer

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Xuan Wu, Yong Chen, and Yu Liu

Contents

13.1 Introduction

As a new generation of macrocyclic host molecule, pillararene has attracted tremendous attention since its firstly being synthesized in 2008 [1] and advanced rapidly. Different with calixarene [2], which was meta-bridged phenolic macrocycles and

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X. Wu
College of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, China

Y. Chen · Y. Liu (✉)
College of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, China

Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin, China
e-mail: yuliu@nankai.edu.cn

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exhibited the vase-shape architecture, the pillararene was para-bridged hydroquinone units or their derivatives, which was pillar-shaped novel hosts (Fig. 1). According to the number of repeating units, this type of hosts was named as pillar[n]arene (*PnA*).

To enable this type of host molecules easy accessibility, three major strategies have thus been employed (Scheme 1) [3]. The first one is the Lewis acid-catalyzed condensation of 1,4-dialkoxybenzene and paraformaldehyde. The second one is the p-toluenesulfonic acid-catalyzed condensation of 1,4-dialkoxy-2,5-bis(alkoxymethyl) benzene. The last one is cyclooligomerization of 2,5-dialkoxybenzyl alcohols or 2,5-dialkoxybenzyl bromides catalyzed by an appropriate Lewis acid. Due to the relatively low yields of high-order pillar[n]arene ($n \geq 7$) [4], most researches have been focused on the *P5A*, *P6A*, and their derivatives. Based on these methods, a few modified strategies have been developed to synthesize functional unit modified pillar[n]arene to improve their binding affinity, thus resulting in the extensive application in both organic solution and aqueous solution [5]. Comparing to other macrocyclic host molecules, the pillar[n]arene presented some unique properties, such as totally symmetrical and relatively rigid structure, and versatile functionality, thus making them the promising candidates for applications in nanomaterials, molecular recognition, chemosensors, ion transport, supramolecular polymers, and so on [6].

Different from covalent polymers, supramolecular polymer was defined as polymers based on monomeric units held together by directional and reversible secondary interactions, resulting in polymeric properties in dilute and concentrated solutions, as well as in the bulk [7]. When the interaction between the monomers is generated by moderately strong, reversible noncovalent, but highly directional, forces that result in high-molecular-weight linear polymers under dilute conditions, the self-assembly is classified as a supramolecular polymerization. In supramolecular polymers, which are formed by the reversible association of bifunctional monomers, the average degree of polymerization (DP) is determined by the strength of the end group interaction [7b]. The degree of polymerization is obviously dependent on the concentration of the solution and the association constant, and a theoretical

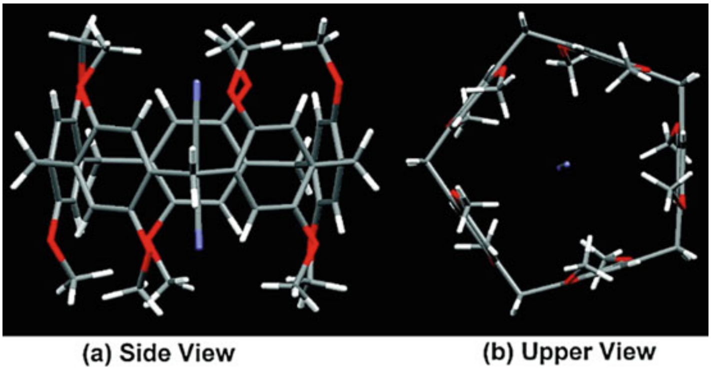
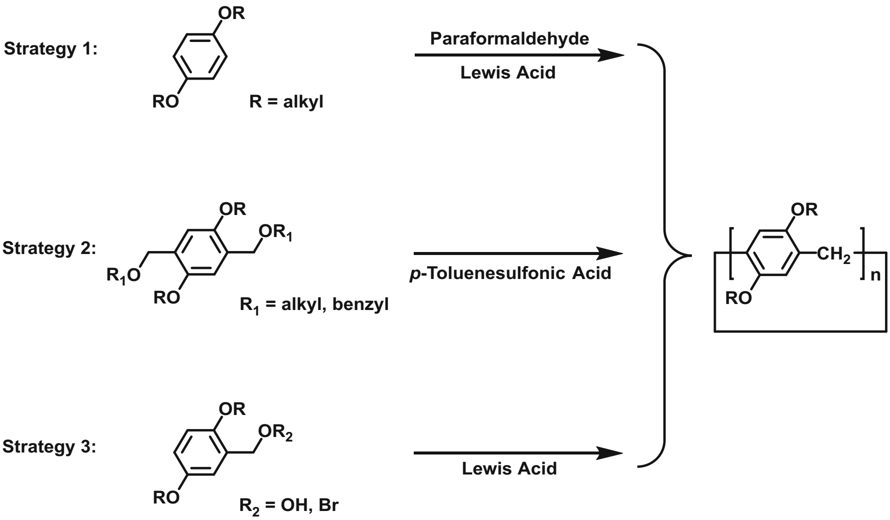


Fig. 1 Crystal structure of *DMP5A* from the side (**a**) and upper view (**b**). (Reprinted with permission from Ref. [1a]. Copyright © 2008 American Chemical Society)

relationship is given in Fig. 2. To obtain polymers with a high molecular weight, a high association constant between the repeating units is a prerequisite.

Therefore, various types of supramolecular polymers have been successfully constructed incorporation with noncovalent interaction, such as hydrogen bond, π-π interaction, hydrophobic interaction, metal-ligand binding, etc. Among these noncovalent interactions, host-guest interactions have also attracted great interest



Scheme 1 Three synthetic routes for pillar[n]arenes

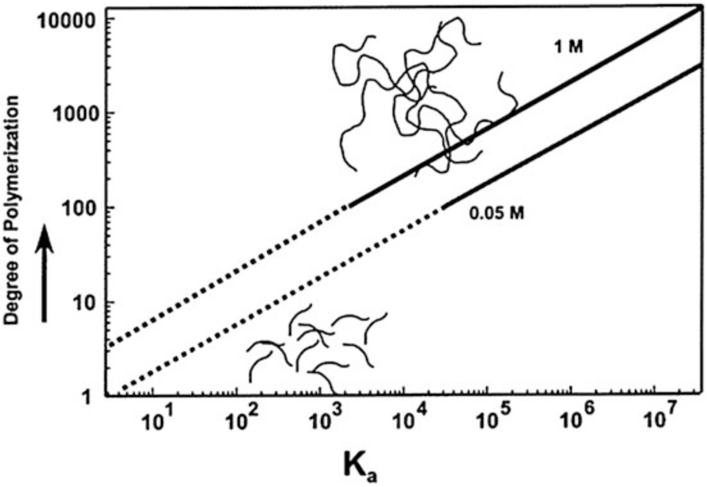


Fig. 2 Theoretical relationship between the association constant K_a and DP, using a simple isodesmic association function or “multistage open association” model. (Reprinted with permission from Ref. [7b]. Copyright 2001 © American Chemical Society)

because there are multiple and cooperative noncovalent interactions in the inclusion complexes of hosts and guests. In this chapter, the supramolecular polymer constructed by pillar[n]arene was summarized, as well as their potential application, which is mainly focused on the pillar[5]arene and pillar[6]arene. And we hope it can provide inspiration for the constructions of smart materials based on pillar[n]arenes.

13.2 Construction of Pillar[N]Arene-Based Supramolecular Polymer

13.2.1 Supramolecular Polymer Formed by Host-Guest Interaction

As a new generation of macrocyclic molecules, pillar[n]arene exhibited excellent host-guest properties due to their rigid structures, electron-rich cavities, and easy modification. Traditionally, the main driving forces to form the host-guest complexation were C-H•••π, C-H•••O, and cation•••π interaction. Based on these fundamental researches to explore the suitable guest molecules for this type host molecules, tremendous supramolecular polymers have also been successfully constructed.

Huang and coworkers reported the first example of pillar[5]arene-based supramolecular polymer (Fig. 3) [8]. Based on the discovery that the n-hexane was included in the cavity of the copillararene in the crystal structure, a long alkyl chain as the guest molecule was modified onto the pillar[5]arene through the typical [4 + 1] cycloaddidtion, thus affording the A-B-type monomers. It was discovered that this molecule could self-assemble into the linear supramolecular polymer through the host-guest interaction both in solid-state and solution phases. In the crystal structure, the octyl group of a copillararene deeply inserted into the electron-rich cavity of the adjacent copillararene and the monomers were arranged along an axis to form a head-to-tail linear supramolecular polymer.

The cationic molecules could also be encapsulated into the cavity of pillar[n]arenes for their electron-rich cavity [9]. Due to the different sizes of pillar[5]arene

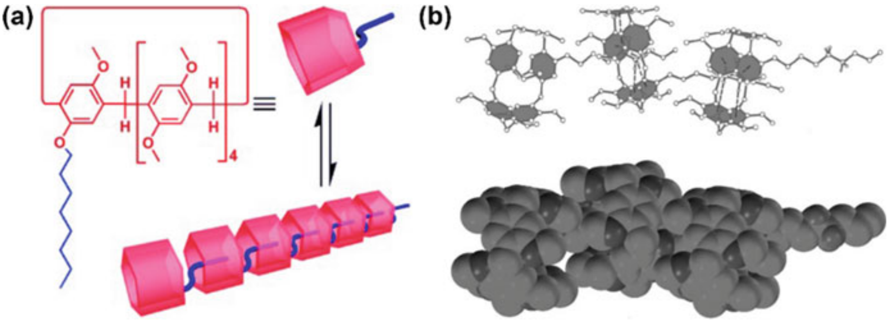


Fig. 3 (**a**) Schematic illustration of formation of supramolecular polymer reported by Huang and coworkers, (**b**) crystal structure of formed linear polymer. (Reprinted with permission from Ref. [8]. Copyright © 2011, John Wiley and Sons)

and pillar[6]arene, they exhibited different binding affinities with different guest molecules. Traditionally, the pillar[5]arene had a better binding ability with the secondary ammonium salt, while the bulky guest molecules, such as paraquat and positively charged DABCO derivatives, preferred to binding with pillar[6]arene (Fig. 4) [10]. Therefore, the same strategy with the previous research, the secondary ammonium salt was modified to the pillar[5]arene to form the A-B-type monomer, whose binding constant was determined to be $(2.40 \pm 0.20) \times 10^3\ M^{-1}$ in the chloroform. Driven by the strong host-guest interaction between these two motifs, the linear supramolecular polymer was formed. In addition, the obtained supramolecular polymer had anion responsiveness due to the ion-pair effect.

As well known, the decrease in the ion-pair interaction would increase the binding ability, and the inverse proposition was also correct [5c, 11]. Therefore, the addition of Cl^- into the polymer solution, the formed supramolecular polymer would disassemble for the formation of tight ion pairs between the secondary ammonium cation and halide anion. If the imidazole unit was incorporated into the pillar[5]arene, a pH-responsive supramolecular polymer could be successfully constructed, in which the difference in the binding constants between pillar[5]arene/imidazolium motif and pillar[5]arene/imidazole motif played the vital role, whose values were $(1.0 \pm 0.3) \times 10^4\ M^{-1}$ and $(2.3 \pm 0.2) \times 10^2\ M^{-1}$, respectively, in chloroform [12]. These results indicated the pH would affect the degree of polymerization of these molecules, which meant in the acidic solution the higher-molecular-weight supramolecular polymer would be formed than in the neutral solution, concluded by the theoretical relationship between the association constant and degree of polymerization.

Besides the single constituent to form the A-B-type supramolecular polymer, the hybrid polymers could be formed by adding another host molecule. Along with this line, Wang and coworkers synthesize a novel host molecules, in which the cryptand was fused into the pillar[5]arene, thus affording a host molecule with two cavities with different binding abilities (Fig. 5) [13]. From the fundamental research in the host-guest property, it was delighted to find that the cryptand cavity could selectively bind pyridinium cation and the pillar[5]arene cavity selectively bound the neutral guest with the cyano group at the end in an orthogonal manner. Therefore, the orthogonal supramolecular polymer could be successfully constructed by addition of two homoditopic guests with pyridinium cation and cyano group into the host solution.

13.2.2 Supramolecular Polymer Formed by Hydrogen Bonding and Halogen Bond

Hydrogen bond, as an extensively exited noncovalent interaction, has been one of the research hotspots and widely applied into molecular recognition, construction of foldamers and helix structures, crystal engineering, as well as the supramolecular polymer. Among all types of hydrogen bond structures, ureidopyrimidinone (UPy) has attracted tremendous attention due to the high binding constant ($10^7\ M^{-1}$ in chloroform), self-complementary structures, and easy access [7c]. Wang and coworkers firstly introduced this motif into the pillar[5]arene-based supramolecular

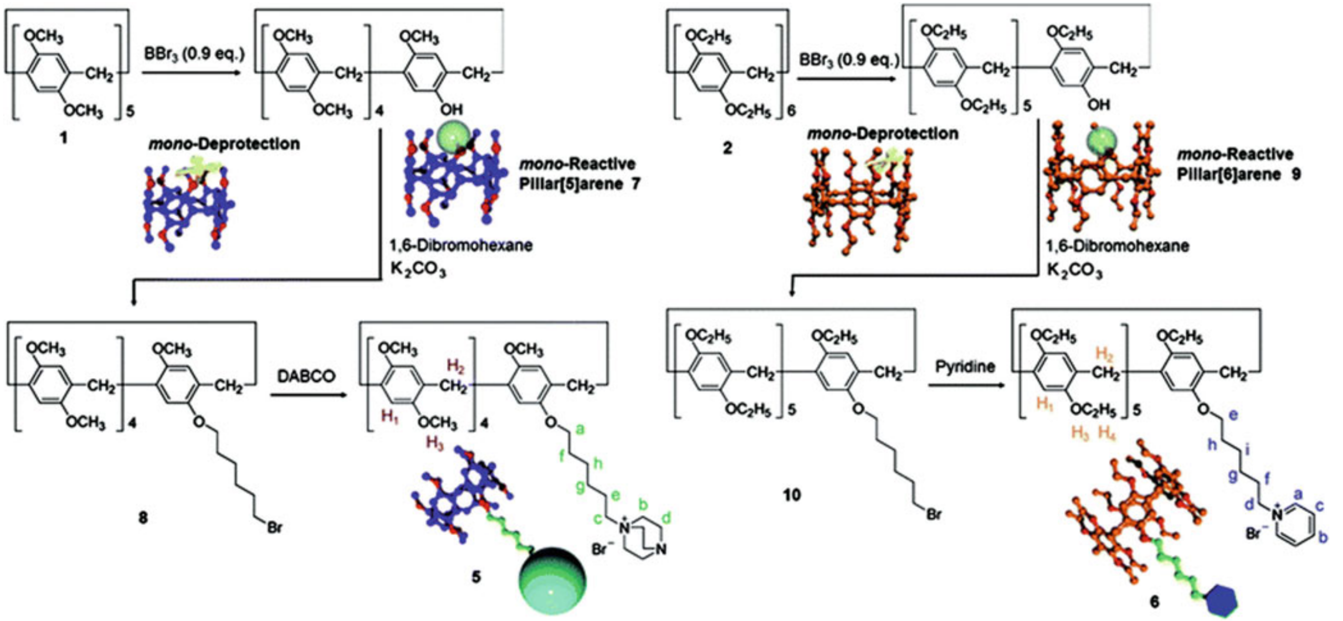


Fig. 4 Chemical structures of A-B-type supramolecular polymer reported by Ogoshi and coworkers. (Reprinted with permission from Ref. [10]. Copyright © 2012, Royal Society of Chemistry)

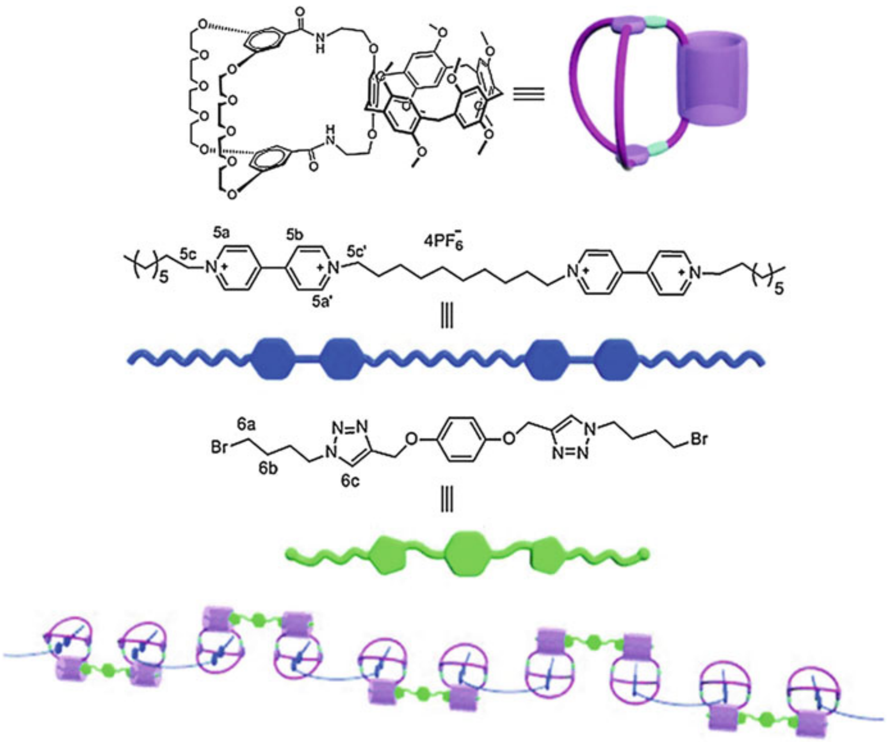


Fig. 5 Hybrid polymer constructed by Wang and coworkers. (Reprinted with permission from Ref. [13]. Copyright © 2015, Royal Society of Chemistry)

polymer systems (Fig. 6) [14]. Due to the self-complementary nature of UPy motif, a series of UPy interlocked rotaxanes has been successfully synthesized using the strategy of "diamine threading followed by endcapping with UPy units," in which the pseudorotaxane was firstly formed between the diamines and pillar[5]arenes followed by the endcapping reaction to form the UPy motif. In such novel dynamic polyrotaxanes, the UPy motifs particularly played quite important roles in the reversible formation of main-chain backbones of supramolecular polymers. The stepwise and one-pot strategies would provide a novel and efficient methodology for the smart design and construction of new types of higher-ordered architectures and sophisticated molecular devices.

Wang and coworkers also reported other types of supramolecular polymer by modifying the UPy motif on the side ring of pillar[5]arene to form the bifunctional UPy pillar[5]arene, which could self-assemble into the linear supramolecular polymer by hydrogen bonding [15]. In this self-assembly manner, the cavity of pillar[5]arene was not occupied by other guest molecules. Therefore, the addition of the corresponding guest molecules would produce different topological self-assembly manners. The polypseudorotaxane could be constructed by adding diamine into the pillar[5]arene polymer [15b], and the polymer network could be formed by the

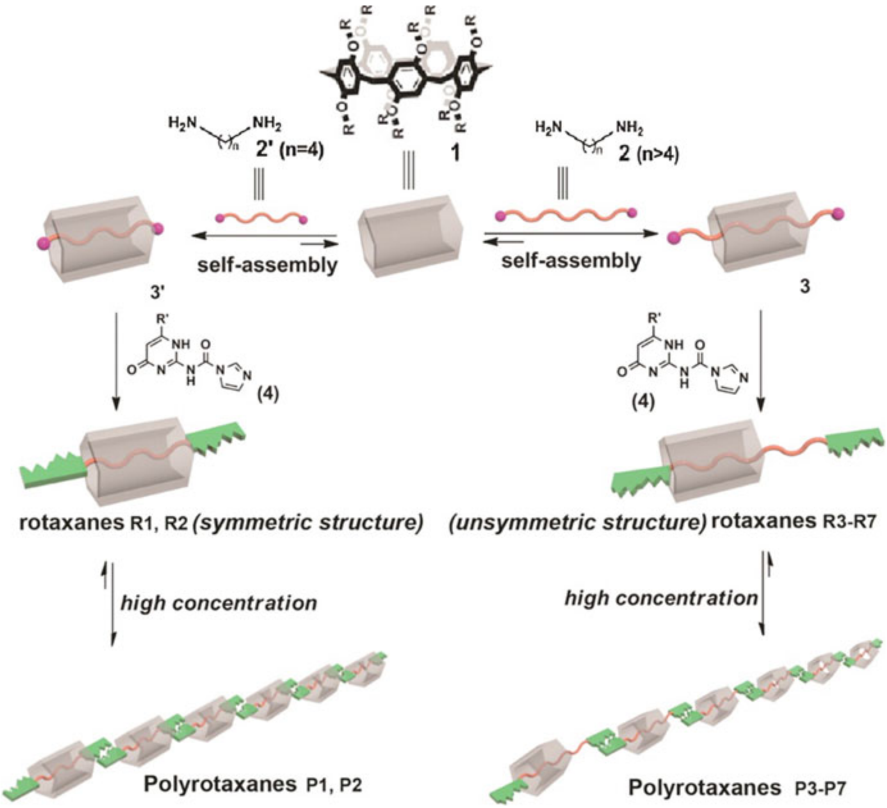


Fig. 6 Graphical representation of the construction of dynamic polyrotaxanes reported by Wang and coworkers. (Reprinted with permission from Ref. [14]. Copyright © 2012 American Chemical Society)

addition of homoditopic guest with pyridinium cation molecule [15a]. Besides the abovementioned self-complementary UPy-based supramolecular polymer, the supramolecular polymer could also be constructed between the monofunctional UPy pillar[5]arene by introducing another noncovalent interaction [15c]. Herein, an orthogonal supramolecular polymer was reported by Wang and coworkers by introducing the homoditopic guest with pyridinium cation molecule into the monofunctional pillar[5]arene. As well known, the host molecule could form a dimer in the solution due to the strong binding affinity of UPy motif, and the pyridinium unit could be encapsulated into the cavity of pillar[5]arene. Based on these results, the orthogonal supramolecular polymer was formed.

Halogen bond [16], similar to other noncovalent interaction, occurs when "there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity." Although it is the least exploited noncovalent interaction, it has been widely applied in liquid crystals, nonlinear optics, separation of isomers, catalysis, and anion binding. Researches also have been conducted on the fabrication of pillar[5]arene-based supramolecular polymers [17]. Huang and coworkers firstly introduced halogen bond into pillar[5]arene-based supramolecular polymer [17a]. A pillar[5]arene derivative bearing two pyridyl groups as the halogen bond acceptor was synthesized, which could form a linear supramolecular polymer backbone with 1,4-diiodotetrafluorobenzene (DITFB) in chloroform as well as in solid state (Fig. 7). With the supramolecular polymer backbone in hand, a linear side-chain supramolecular

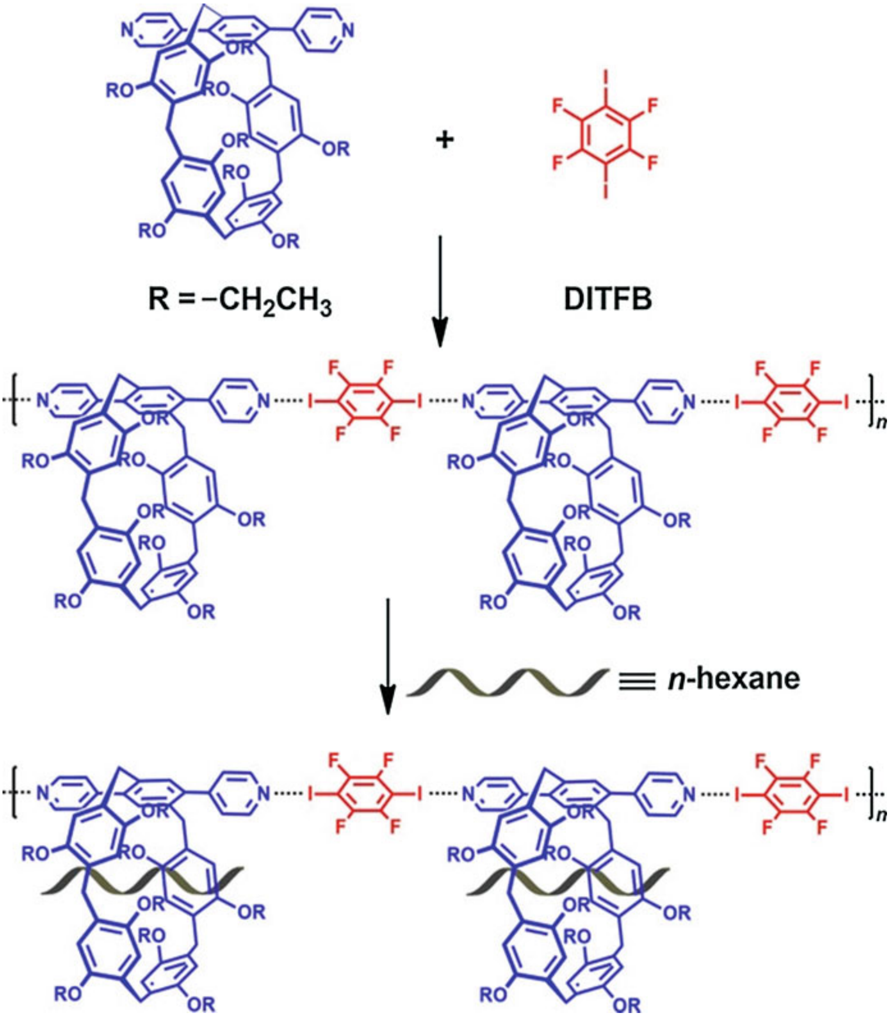


Fig. 7 Schematic representation of the formation of the supramolecular polymer backbone and the side-chain polypseudorotaxane. (Reprinted with permission from Ref. [17a]. Copyright © 2018, John Wiley and Sons)

polypseudorotaxane could be constructed by adding *n*-hexane. Moreover, the formation of polypseudorotaxane was certificated by X-ray crystal analysis. Połoński and coworkers reported two crystalline supramolecular polypseudorotaxanes constructed by combining permethylated pillar[5]arene as a macrocyclic wheel with 1,4-bis(1-imidazolyl)butane and 1,4-bis(iodoethynyl)benzene or 1,4-diiodo-1,3-butadiyne linked by C–I···N halogen bonds and creating a polyrotaxane axis [17b].

13.2.3 Supramolecular Polymer Formed by Metal-Ligand Binding

Mental-ligand binding is also another widely existed binding module in the nature, which gradually evolved to be a controllable and highly efficient methodology for the construction of supramolecular architectures with well-defined shapes and sizes. The moderate bond energy (15–50 kcal/mol) of metal-ligand bonds, as well as their directional and predictable features, endowed these supramolecular coordination complexes considerable stability yet reversibility [18].

Along with this line, a new 120° monofunctionalized pillar[5]arene dipyridyl donor and 180° linear di-Pt(II) acceptors with different lengths were selected and synthesized to construct the hexakis-pillar[5]arene metallacycles by Yang and coworkers (Fig. 8) [19]. Due to the well-defined structures of the hexamers, they

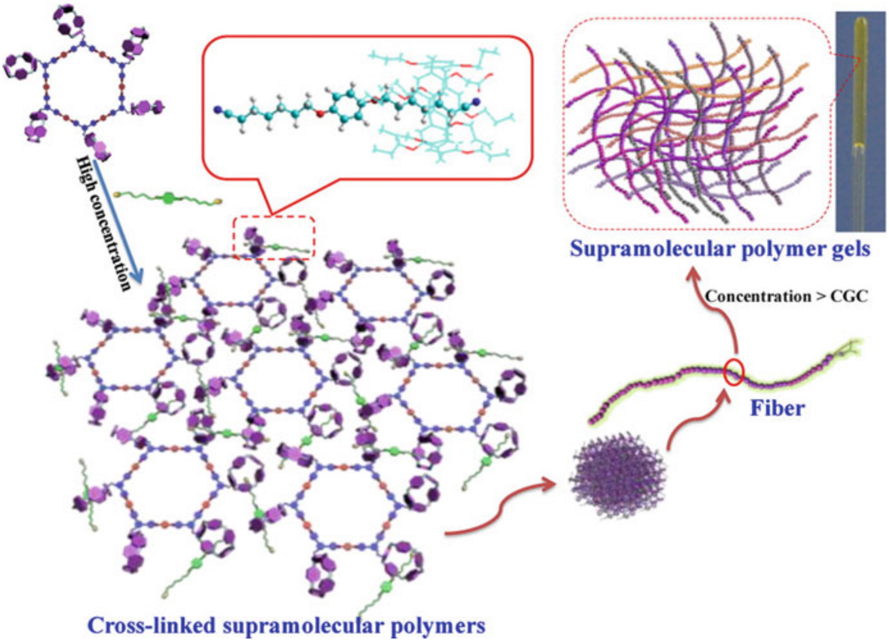


Fig. 8 Schematic representation of the formation of supramolecular polymer gels reported by Yang and coworkers. (Reprinted with permission from Ref. [19]. Copyright © 2014 American Chemical Society)

could act as the cores for the further construction of supramolecular polymer network after the addition of homoditopic guest molecules to form the host-guest complexation with pillar[5]arene. More importantly, by taking the advantages of the dynamic nature of metal-ligand bonds and host-guest interactions, reversible multiple stimuli-responsive gel-sol phase transition of such polymer gels was successfully realized, which could be destroyed by addition of TBABr and competitive guests and recovered by adding AgOTf to remove Br- and pillar[5]arene to remove competitive guests.

Wang and coworkers adopted "threading followed by coordination" method to synthesize coordination polymer [20]. Firstly, the guest molecule with the pyridine unit as the ending group was synthesized, which could form a stable 1:1 complexation with pillar[5]arene. Due to the introduction of pyridine motif, the complex could further coordinate with metal cation to form the supramolecular polymer. Therefore, the $Pd(OAc)_2$ was added to form the linear polymer for the 1:1 binding ratio between the pyridine guest and $Pd(OAc)_2$. Interestingly, due to the partial encapsulation of guest molecules by pillar[5]arene, the intramolecular hydrogen bonding would exist between the formed polyrotaxane backbones, leading to the further cross-linking to form the supramolecular gel.

Moreover, Shi and coworkers reported an orthogonal supramolecular polymer, in which the host-guest interaction, π···π stacking, and metal-ligand binding were introduced into this system (Fig. 9) [21]. Firstly, the terpyridine derivative with a long bromoalkyl chain was synthesized, which could form the 1:1 inclusion complex with pillar[5]arene by the recognition motif of bromoalkyl chain, as well as the 2:1 coordination compound with the Eu(III) ion by the terpyridine motif.

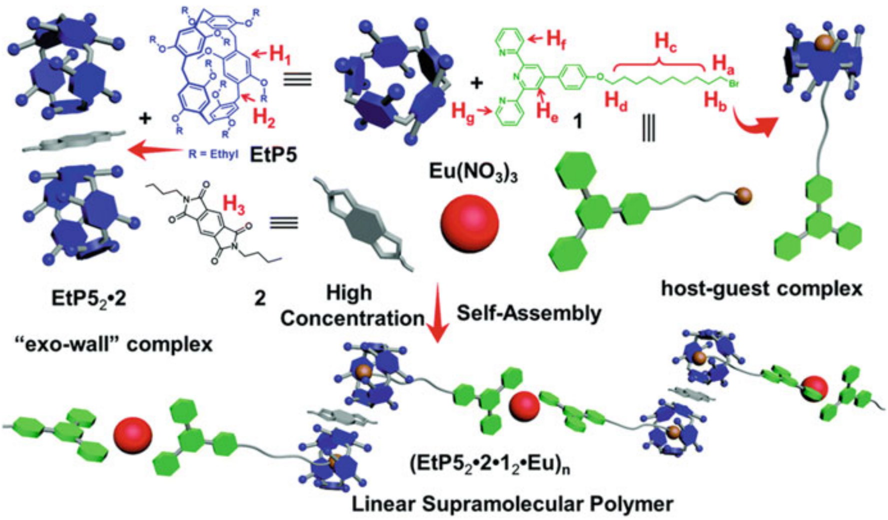


Fig. 9 The cartoon representation of the formation of a linear supramolecular polymer reported by Shi and coworkers. (Reprinted with permission from Ref. [21]. Copyright © 2017, Royal Society of Chemistry)

Then, the electron-poor molecule, N,N′-bis(n-butyl)pyromellitic diimide, was added to form an “exo-wall” complex with electron-rich pillar[5]arene due to the π•••π stacking, thus affording the linear Eu(III)-coordination fluorescent supramolecular polymer.

13.2.4 Supramolecular Polymer Constructed by Covalent Polymer

The researches on covalent polymer-based supramolecular polymer was firstly conducted by Harada and coworkers, in which the cyclodextrins were used as the host molecules to encapsulate the linear polymer, such as PPG, PEG, and PVA, to form the polypseudorotaxane [22]. This combination of macrocyclic molecules and covalent polymers could expand the application of traditional polymer and construct functional materials, such as self-healing materials, slipping materials, isolated molecular wires, etc. Pillar[n]arene, as a new generation of host molecules with excellent properties, could also be applied to construct this type of supramolecular polymers, and the researches were mainly focused on two parts, one is to form the main chain encapsulated polymers, and the other is the side-chain supramolecular polymers.

Similar with cyclodextrin-based main chain encapsulated polymers, Ogoshi and coworkers firstly reported the main chain polypseudorotaxane, by incorporating pillar[5]arene and viologen polymer (*VP-8*)) (Fig. 10) [23]. In this work, the inclusion complex was formed both in DMSO and the mixed solution of CH_3CN and acetone and results in the charge transfer complex while exhibiting different dynamic behaviors. In the CH_3CN and acetone system, the pillar[5]arene shuttling along the polymer axis was faster than the NMR time scale, concluded from NMR spectra. While in the DMSO solution, this shuttling movement was much slower than the NMR time scale. This dynamic behavior depended on the external temperature, at temperature above 60 °C, the shuttling movement of pillar[5]arene was faster than the NMR time scale, and pillar[5]arene molecules dethreaded from the viologen polymer chain at temperature above 110 °C. Moreover, the alkyl linker length between viologen motifs also affected the formation of supramolecular polymer; the shorter chain would decrease the potential to form inclusion complex. The adamantyl group was applied for the conversion of polypseudorotaxane to polyrotaxane as the stopping group, which exhibited excellent to stabilize the radical cation species due to the electron donors of pillar[5]arene molecules. Besides the viologen polymer, the polyaniline could also be concluded by pillar[5]arene for the strong reducing ability of the EB form in polyaniline. And tri(ethylene oxide) modified pillar[5]arene encapsulated polytetrahydrofuran to form the similar polyrotaxane.

Some researches are also conducted to synthesize conjugated polymer incorporated pillar[5]arene. The pioneering work was firstly conducted by Müllen and coworkers by using the Sonogashira polycondensation between the diyne modified pillar[5]arene and dihalo-aromatic compound to obtain the conjugated polymer with the number-average molecular weight at 16 kDa [24]. However,

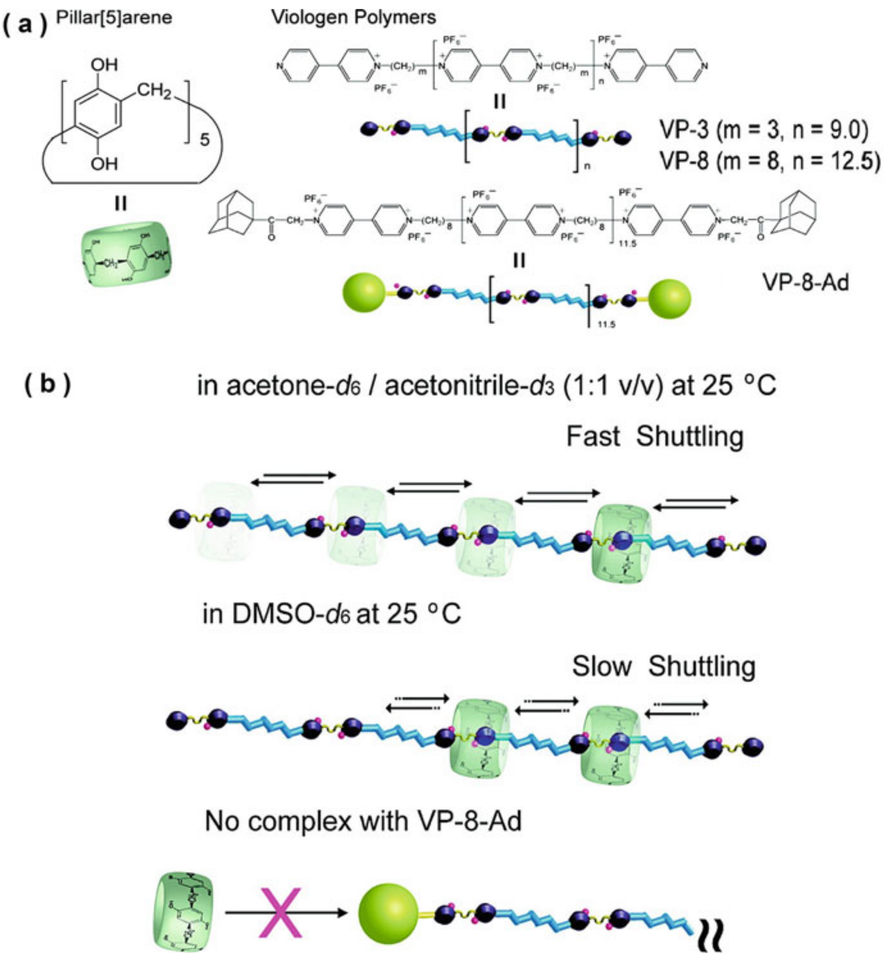
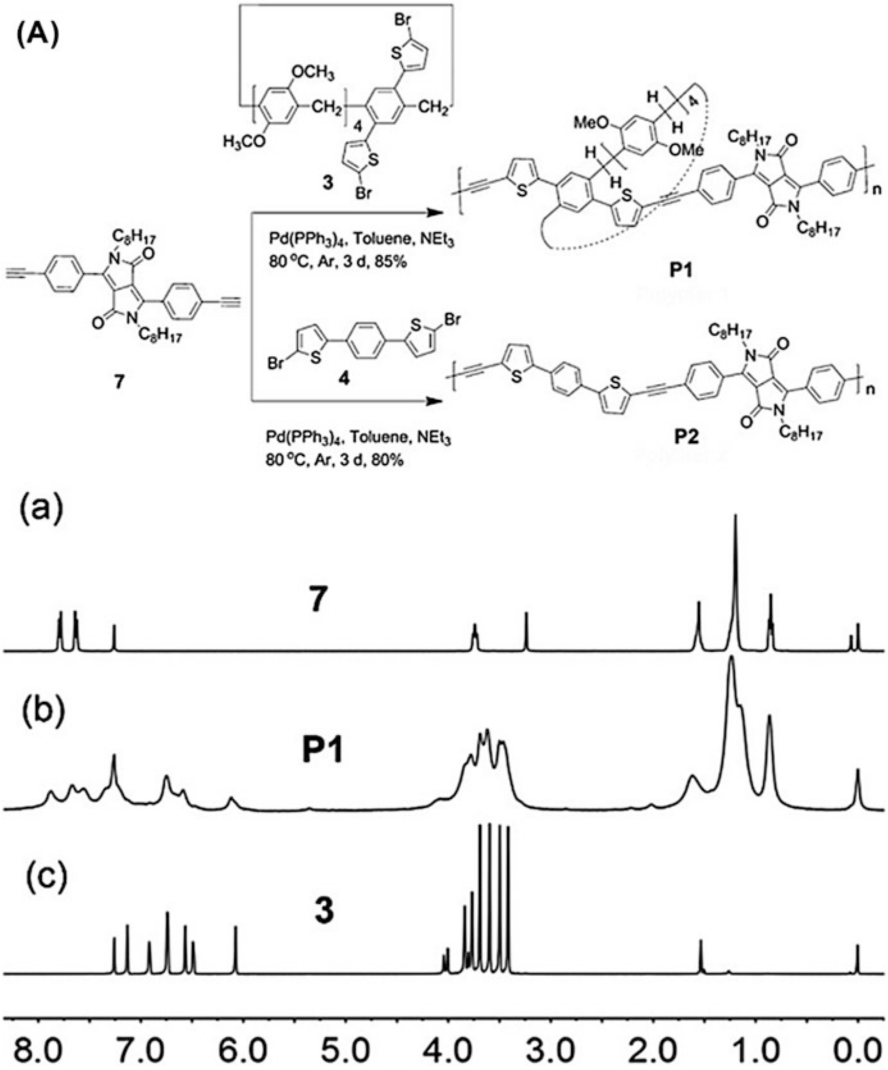


Fig. 10 (**a**) Chemical structures of pillar[5]arene and viologen polymers, (**b**) dynamic behavior of polypseudorotaxane reported by Ogoshi and coworkers. (Reprinted with permission from Ref. [23]. Copyright © 2010 American Chemical Society)

the further construction of polypseudorotaxane was not conducted. The Sonogashira polycondensation was also applied by Cao and coworkers to synthesize another pillar[5]arene incorporated conjugated polymer (*P1*) with the number-average molecular weight (Mn) about 13 kDa. After binding the homoditopic guest, the polypseudorotaxane was successfully constructed (Fig. 11) [25].

Besides the mentioned polymer, the side-chain supramolecular polymers have also been fabricated. Wang and coworkers successfully synthesized the side-chain functionalized polyphenylethynylene, whose linker was flexible alkyl chain. After the binding with pyridinium cation, the polypseudorotaxane could be formed with the decrease in fluorescence intensity, which could be recovered by addition of halide ion to destroy the polypseudorotaxane [26]. Moreover, the pillar[6]arene and ferrocene were also be modified to the side chain of different polymers, respectively. Due to the high binding affinity between pillar[6]arene and ferrocenium



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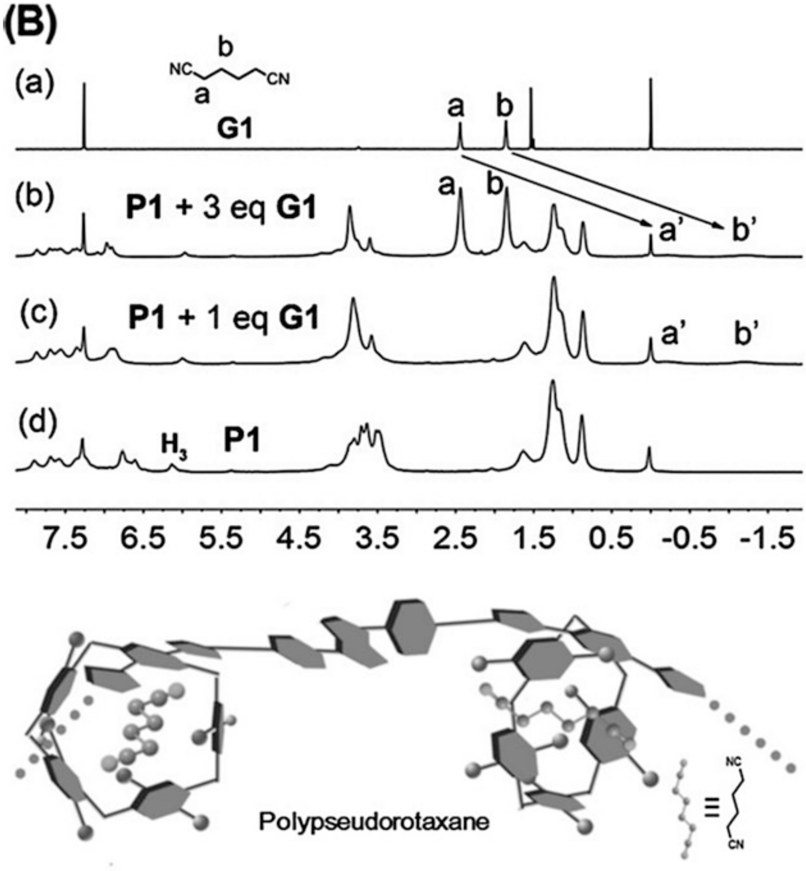

Fig. 11 (**A**) Synthesis of pillar[5]arene-based conjugated polymer, (**B**) formation of polypseudorotaxane. (Reprinted with permission from Ref. [25]. Copyright © 2017, John Wiley and Sons)

cation ($K = (2.0 \pm 0.1) \times 10^4\ M^{-1}$), the supramolecular cross-linked network could be formed after the addition of external redox reagent [27].

13.3 Function of Pillar[N]Arene-Based Supramolecular Polymer

As well known, supramolecular polymer was defined as polymers based on monomeric units held together by directional and reversible noncovalent interactions, which exhibited the dynamic nature upon the external stimuli, such as the temperature, pH, light, or competitive molecules. Therefore, with the careful design of pillar[n]arene-based supramolecular polymer, we could obtain the functional systems, which showed potential application in the chemical sensors, drug delivery systems, or other smart materials.

13.3.1 Chemical Sensors

Fluorescent sensors have attracted attention for both analytical sensing and optical imaging because of their high sensitivity, fast response time, and technical simplicity [28]. Once the analyte is recognized by the receptor, the fluorescence signal can be observed in the form of quenching, enhancement, or shift in the fluorescence maxima due to either electron transfer, charge transfer, or energy transfer processes. This allows on-site and real-time detection in an uncomplicated and inexpensive manner, providing qualitative and quantitative information.

Wang and coworkers reported a pillar[5]arene-modified conjugated host polymer (*M1*), using the polyphenylacetylene as the backbone (Fig. 12) [26]. Therefore, this polymer could form the side-chain supramolecular polymer with *n*-octylpyrazinium cation guest. Due to the strong charge transfer between the guest molecules and conjugated polymer, the fluorescence was quenched. After the addition of the halide anion (tetrabutylammonium salts), the fluorescence recovery could be observed due to the strong ion-pair interaction between *n*-octylpyrazinium cation and halide anion. The fluorescence enhancement of this system increased in the order of $I^- < Br^- < Cl^-$, and the differences in fluorescence intensity could be easily distinguished by naked eyes under UV light illumination, acting as the halide anion probe.

Wu and coworkers reported a thymine-substituted copillar[5]arene, which could coordinate with Hg^{2+} tightly through a $T{-}Hg^{2+}{-}T$ pairing to produce linear supramolecular polymer (Fig. 13) [29]. Moreover, a tetraphenylethylene (TPE) derivative was synthesized with a nitrile motif at the end of alkyl chain, which exhibited strong binding affinity with the pillar[5]arene. The copillar[5]arene and TPE derivative could only form the host-guest complex, which could not restrict the rotation of TPE motif, resulting in no fluorescence in the mixture solution. However, the addition of Hg^{2+} would lead to the formation of supramolecular network resulting from both the coordination interaction and the host-guest interaction, in which fluorescence of TPE would be on for restriction of TPE motif. Moreover, this system could selectively bind with Hg^{2+}, due to the unique coordination capacity of Hg^{2+} toward the thymine moieties, and shield the interference of other metal ions. Finally, the bonded Hg^{2+} could be removed by the addition of S^{2-}, resulting in the generation of HgS precipitate, to regenerate the sensor systems.

Lin and coworkers synthesized a bis-naphthalimide functionalized pillar[5]arene (*MP5*), in which the naphthalimide group could act as a $\pi \cdots \pi$ stacking site for the formation of linear supramolecular polymer as well as a fluorophore (Fig. 14) [30]. After the formation of the supramolecular polymer, it could further self-assemble into the stable π-gel, with strong aggregation-induced fluorescence in the cyclohexanol. Moreover, this supramolecular π-gel could successively sense Fe^{3+} as well as efficiently remove Fe^{3+} in water. The addition of Fe^{3+} into the gel would destroy the $\pi \cdots \pi$ stacking between the naphthalimide group and form the cation$\cdots\pi$ interaction, which could also maintain the structure of gels, while induce the quench in the fluorescence emission.

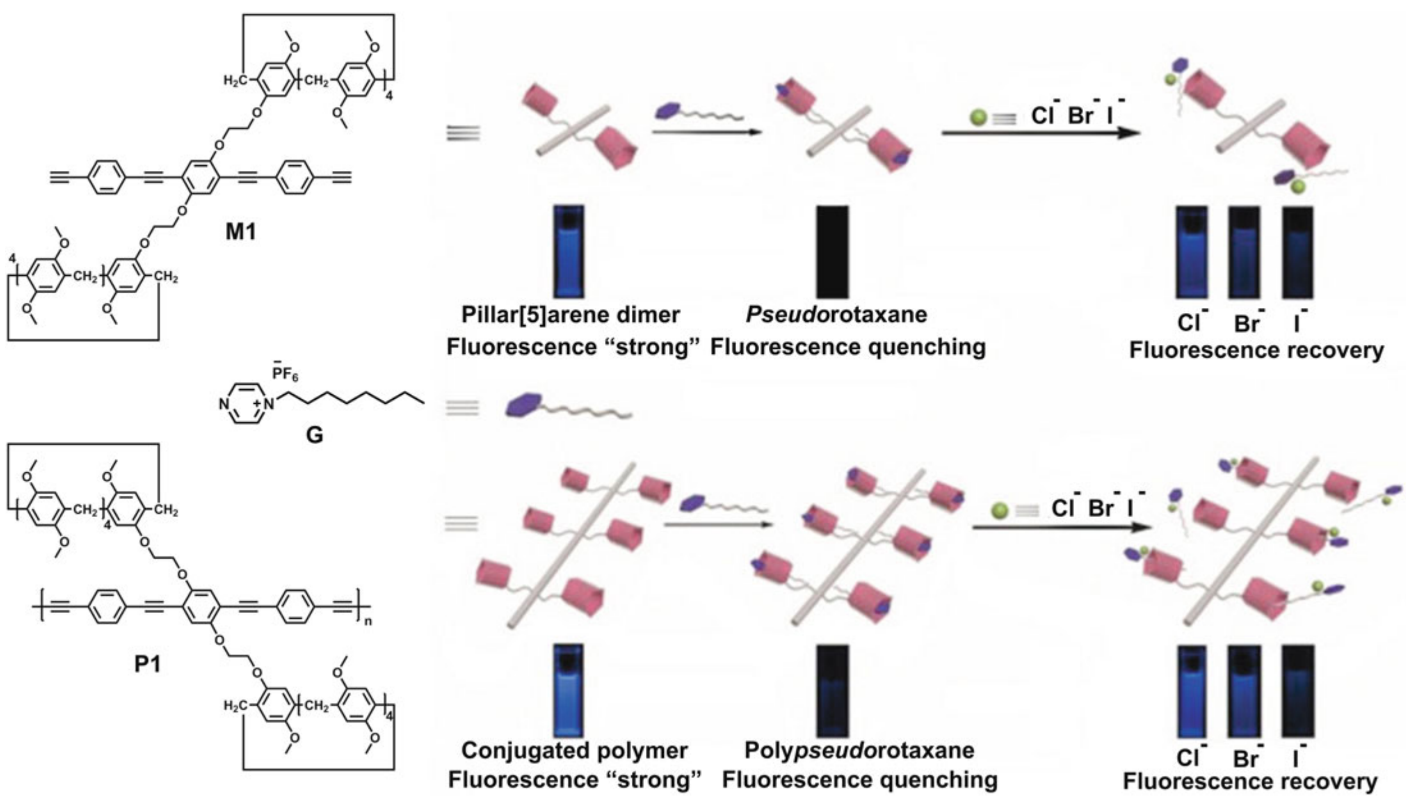

Fig. 12 Cartoon representation of the formation of pillar[5]arene-modified pseudorotaxane and polypseudorotaxanes system and their responsiveness to Cl^-, Br^-, and I^-. (Reprinted with permission from Ref. [26]. Copyright © 2013 Xiao-Yu Hu and Le-Yong Wang. Published by Elsevier B.V)

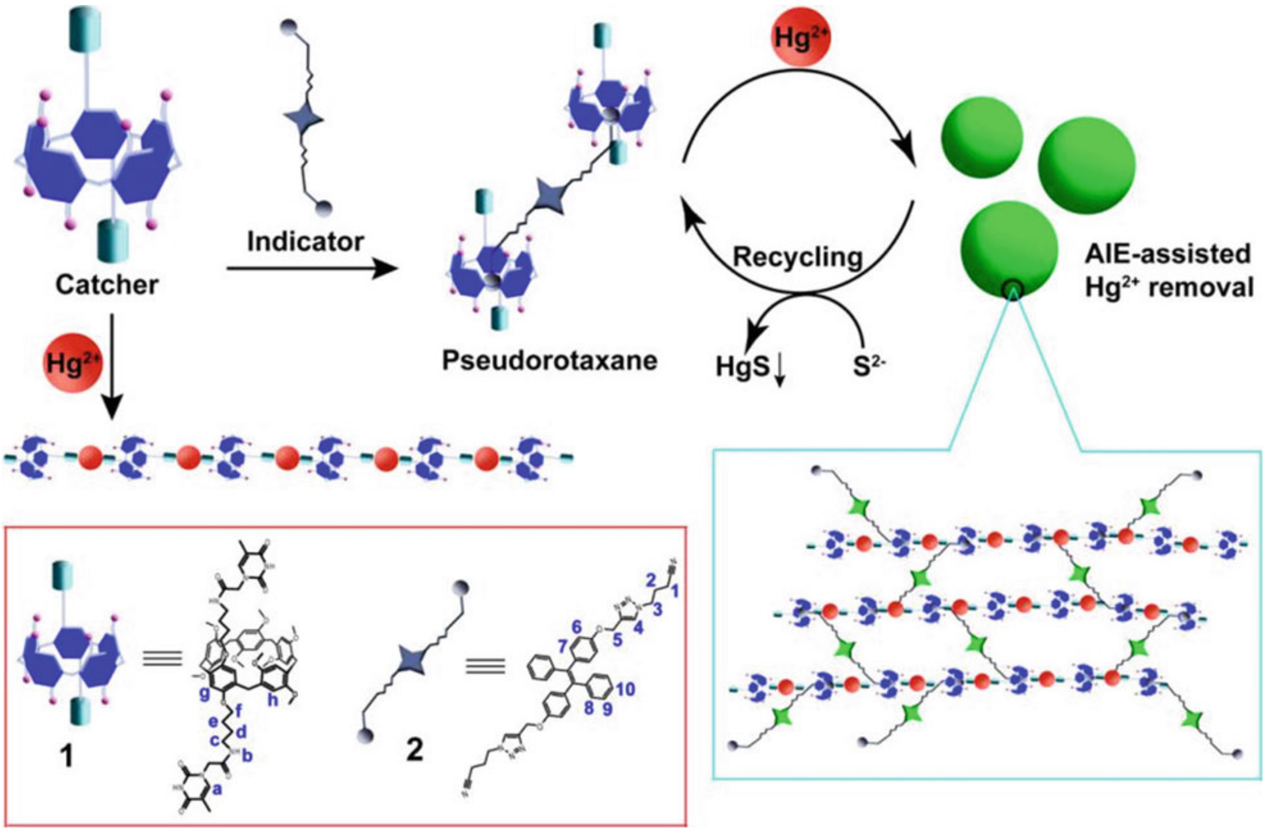

Fig. 13 Proposed strategy for the sensing and removal of Hg^{2+} based on the formation of supramolecular polymers. (Reprinted with permission from Ref. [29]. Copyright © 2017 American Chemical Society)

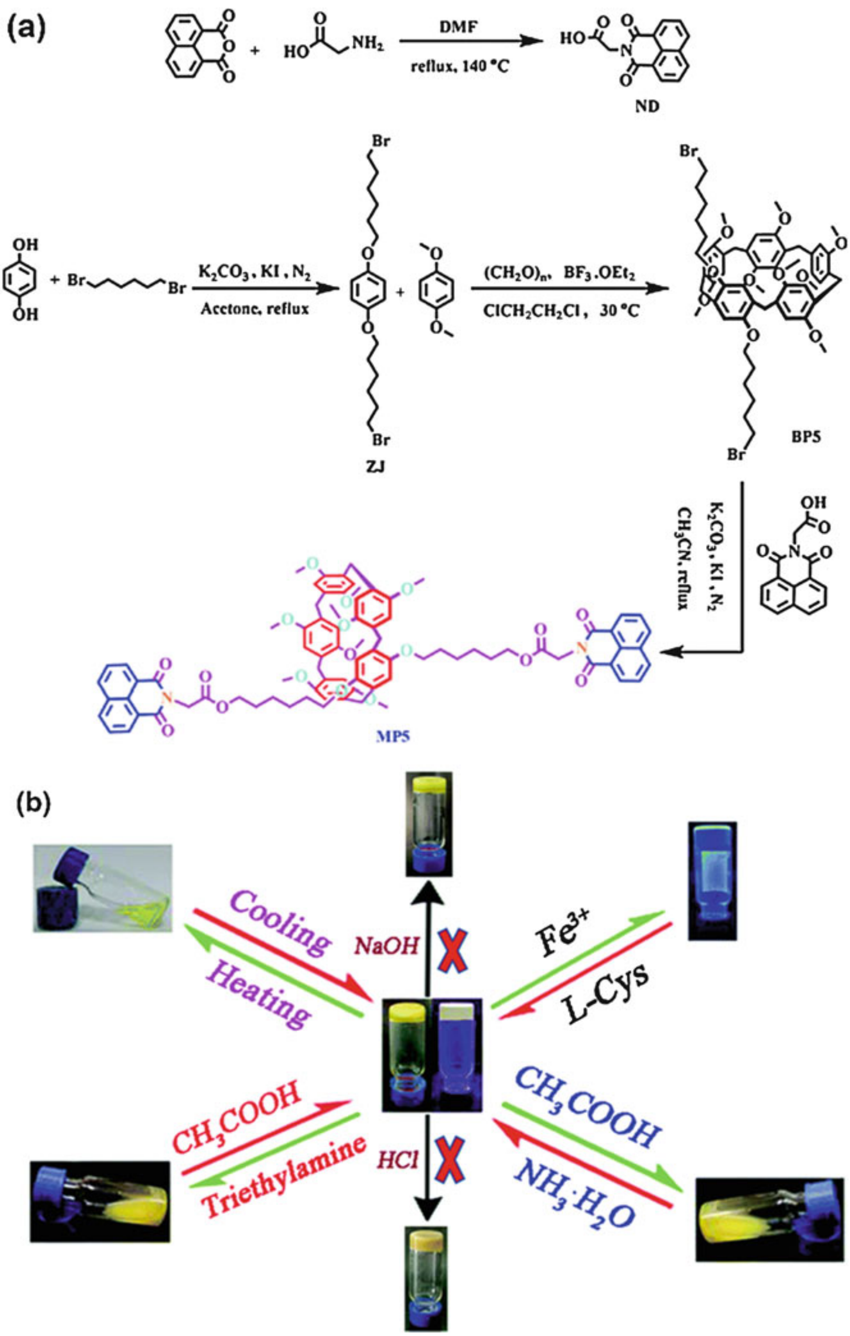

Fig. 14 (**a**) Synthesis of bis-naphthalimide functionalized pillar[5]arene (*MP5*), (**b**) external stimuli of pillar[5]arene-based gels. (Reprinted with permission from Ref. [30]. Copyright © 2018. Royal Society of Chemistry)

Compared with other reported fluorescent sensors for Fe^{3+}, this work showed a lower detection limit, which was 6.06×10^{-8} M. Meantime, the quenched fluorescence could be recovered by L-Cys, which acted as the competition of $\pi\cdots\pi$ stacking and cation$\cdots\pi$ interactions in the gel state.

Wei and coworkers reported a pillar[5]arene-based supramolecular organic framework for the detection of both metal ions and anionic molecules, in which two kinds of pillar[5]arene were incorporated (Fig. 15) [31]. Firstly, the bis-thioacetylhydrazine functionalized pillar[5]arene (*DPSH*) could self-assemble into linear supramolecular polymer through the hydrogen bond. Then this linear assembly could further bind the bis-bromohexane functionalized pillar[5] arene (*DPHB*) through the host-guest interaction, which result in the successful construction of supramolecular organic framework. This framework showed a fluorescent response for Fe^{3+}, Cr^{3+}, Hg^{2+}, and Cu^{2+} ions; the fluorescence emission of the framework was quenched. The lowest fluorescent response concentration of Fe^{3+}, Cr^{3+}, Cu^{2+}, and Hg^{2+} for the framework was determined in the range of 1.0×10^{-6} M to 1.0×10^{-7} M by fluorescent titrations. Moreover, the framework containing the metal cations could also be used as the fluorescence probe for the anionic molecules for the competitive binding with the metal ions. For example, to the framework solution containing Fe^{3+}, only the F^{-} and L-Cys could induce the emission of bright blue fluorescence at 456 nm. Other tested frameworks exhibited similar phenomena, the framework containing Hg^{2+} could selectively sense Br^{-}, and Cu-framework could selectively bind L-Cys. And the lowest fluorescent response concentrations were all determined to be in the range from 1.0×10^{-7} M to 1.0×10^{-8} M. This work showed a novel and efficient way for the development of multifunctional framework materials for multi-guests detection and recyclable separation.

13.3.2 Stimuli-Responsive Soft Materials

Gels are soft solids or solid-like materials that immobilize a large amount of solvent in a three-dimensional network held together by covalent bonds and noncovalent or topological interactions [32]. These materials are appealing to various applications owing to their compositional and structural versatility that allows introducing responsiveness to external stimuli.

Yang and coworkers prepared multiple stimuli-responsive supramolecular gels using metal-ligand bonds and host-guest interactions, in which discrete hexakis-pillar[5]arene metallacycles with different diameters were prepared by metal-ligand bonds between the di-pyridine modified pillar[5]arene and different linear di-Pt(II) acceptors [19]. Then the addition of ditopic guest containing nitrile motif, acting as the cross-linker, would result in the formation of cross-linked polymer, which further convert into the gels. These obtained supramolecular gels not only exhibited the thermal responsiveness but also exhibited responsibility to halide ions as well as the competitive guest molecules. As well known, the metal-ligand bonds possessed relatively moderate bond energies, which could be destroyed by the competitive ligand. In this system, the gel to sol transition behavior was observed when bromide

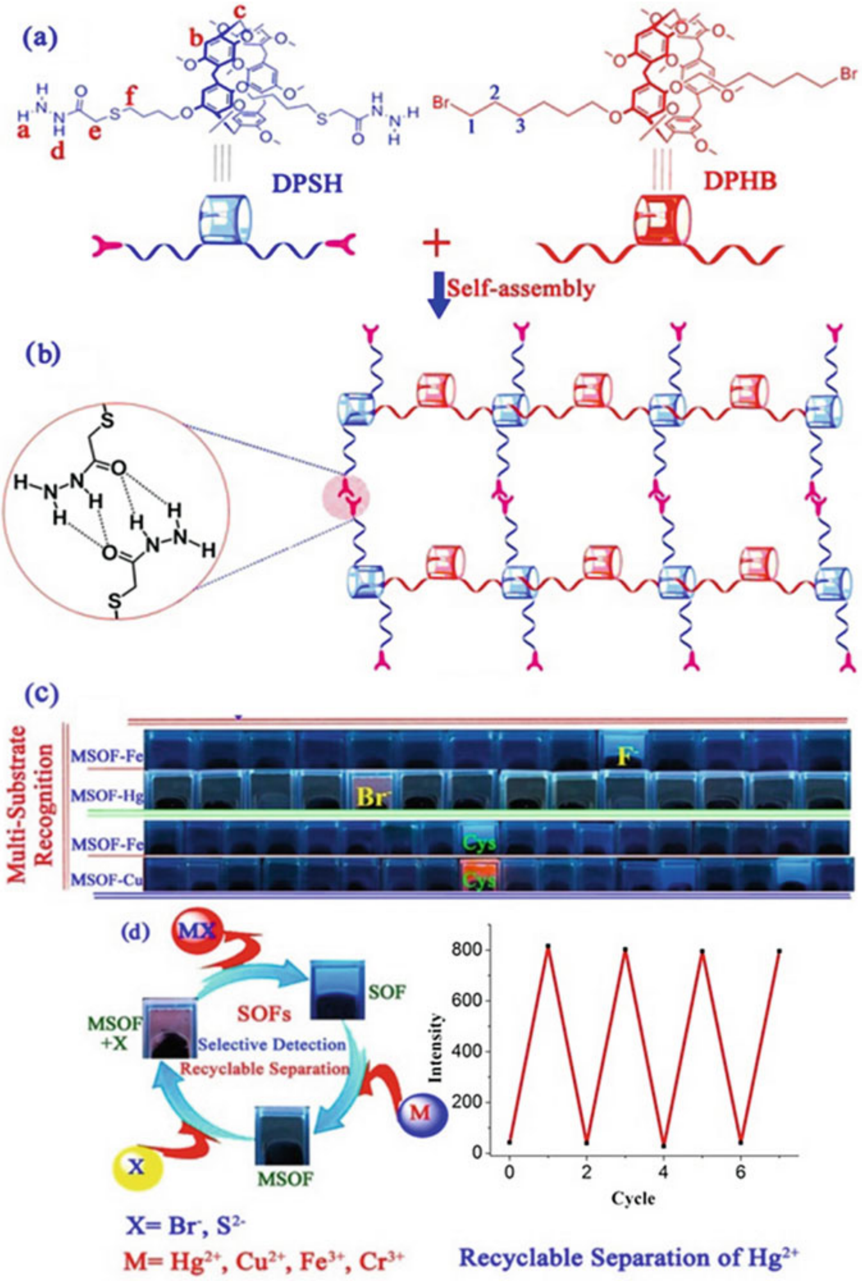

Fig. 15 (**a**) The chemical structures of *DPSH* and *DPHB*; (**b**) cartoon representation for the formation of the *SOF-THBP*; (**c**) multi-guest-response properties of *SOF-THBP* and metal-ions coordinated SOFs; (**d**) recyclable separation properties of *SOF-THBP*. (Reprinted with permission from Ref. [31]. Copyright © 2017, John Wiley and Sons)

anions were added, because the metal-ligand bonds were dissociated by the formation of Pt-Br complexes. The addition of AgOTf could remove the Br anion by formation of AgBr precipitate, thus resulting in the reformation of the discrete hexakis-pillar[5]arene metallacycles. Moreover, the competitive guest, 1,4-dicyanobutane, could also induce the gel-sol transition by destroying the host-guest interaction between the ditopic guest and the metallacycles. And the addition of the native pillar[5]arene to include the competitive guest would lead to the recovery of supramolecular gels.

Wang and coworkers reported rotaxane-based stimuli-responsive supramolecular gels, in which the pseudorotaxane could be formed by the ditopic guest containing the pyridine as the ending motifs and pillar[5]arene (Fig. 16) [20]. After the addition of $Pd(OAc)_2$, the metalla-supramolecular polymer could be formed with the rotaxane as the main backbone. Thanks to the intermolecular hydrogen between the guest molecules, the supramolecular gels could be obtained in a high concentration. Due to the dynamic nature of hydrogen bond, this gel exhibited responsiveness to the external temperature as well as the concentration of the gelators. Moreover, the gel to sol transition could also be achieved by the addition of PPh_3 to destroy the previous metal-ligand bonds. However, due to the occurrence of precipitate, the reverse sol to gel transition could not be achieved.

Yang and coworkers reported a stimuli-responsive blue fluorescent supramolecular gel based on the pillar[5]arene-modified TPE derivatives and corresponding guest molecules [33]. Firstly, they successfully synthesized the pillar[5]arene-modified TPE derivatives (*H1*) and the ditopic guest molecules (*G2*) containing the nitrile motifs (Fig. 17a) [33a]. Similar to the above gel formation process, the 2D supramolecular polymer could be generated by mixing the host and guest molecules, which could further aggregate into gels. The formation of large-scaled supramolecular polymer could restrict the rotation of TPE motif, affording the strong blue fluorescence emission. This fluorescent supramolecular gel exhibited responsiveness to the temperature and solvent. The increase in the temperature destroys not only the host-guest interaction but also the aggregation manners, leading to the destruction of supramolecular gels and the decrease in the fluorescence intensity. Moreover, they also explored the influence of alkyl chain length on the formation of stimuli-responsive supramolecular gels (Fig. 17b) [33b]. Two sets of pillar[5]arene-modified TPE derivatives (*SH* and *LH*) and neutral guests (*SG* and *LG*) with three binding sites were synthesized; the only difference in these molecules was the alkyl chain length, which could both form the supramolecular polymer by simply mixing corresponding host and guest molecules. However, only the set with long alkyl chain could form the supramolecular gels, resulting from the flexible structure induced looser supramolecular networks to include solvent molecules. And this supramolecular gel also exhibited external stimuli to the change in temperature.

Zhang and coworkers synthesized a copillar[5]arene derivative containing one 1,4-bis(hexadecyl)benzene unit, which could form the supramolecular gels in the CH_3CN solution, driven by the $C\text{-}H\cdots\pi$ interaction and the van der Waals forces [34]. This gel showed the aggregation-induced enhanced emission at 450 nm. The addition of the electron poor competitive guest molecule, hexadecylpyridinium chloride,

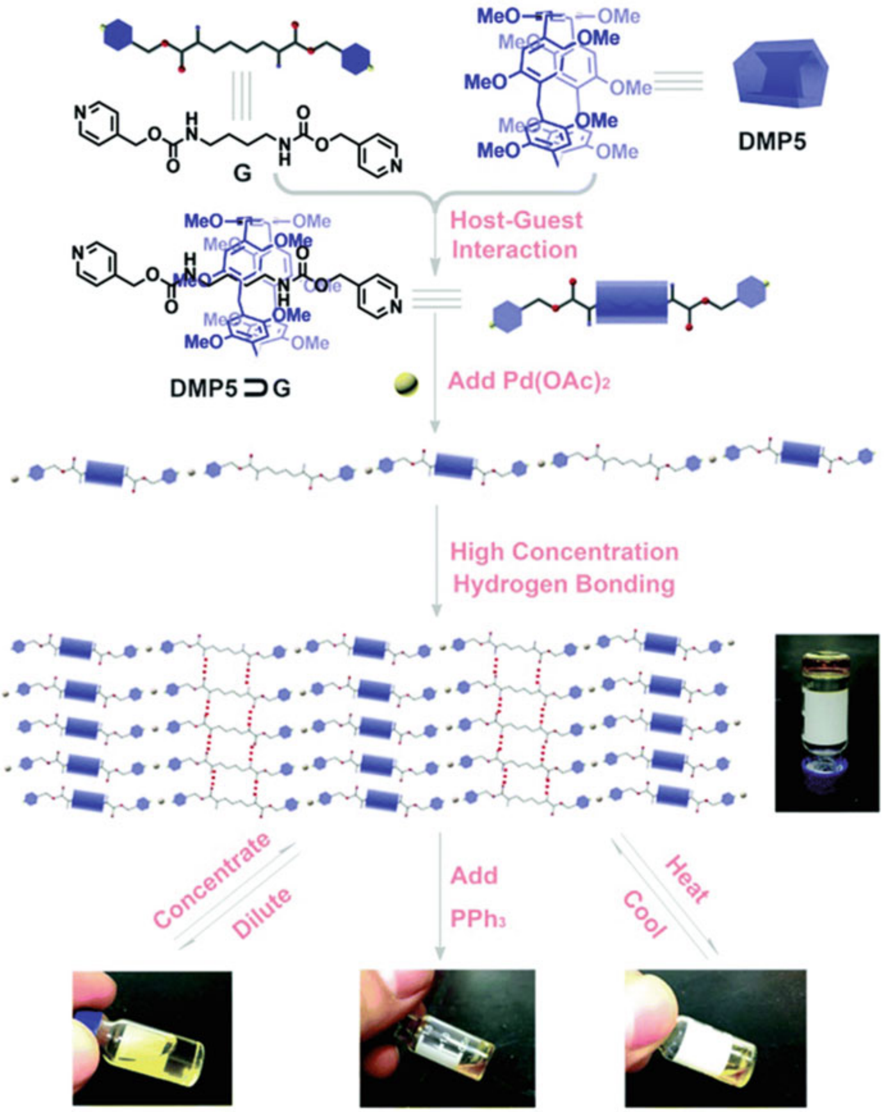

Fig. 16 Schematic of the formation of polyrotaxanes and sol-gel transformation reported by Wang and coworkers. (Reprinted with permission from Ref. [20]. Copyright © 2016. Royal Society of Chemistry)

would result in the destruction of the linear supramolecular polymer by the formation of host-guest complexation. Moreover, due to the strong charge transfer from the electron-rich pillar[5]arene and electron-poor guest molecule, the fluorescence could be quenched. The external temperature could also induce the reversible sol-gel transition, as well as the reversible change in the fluorescence emission.

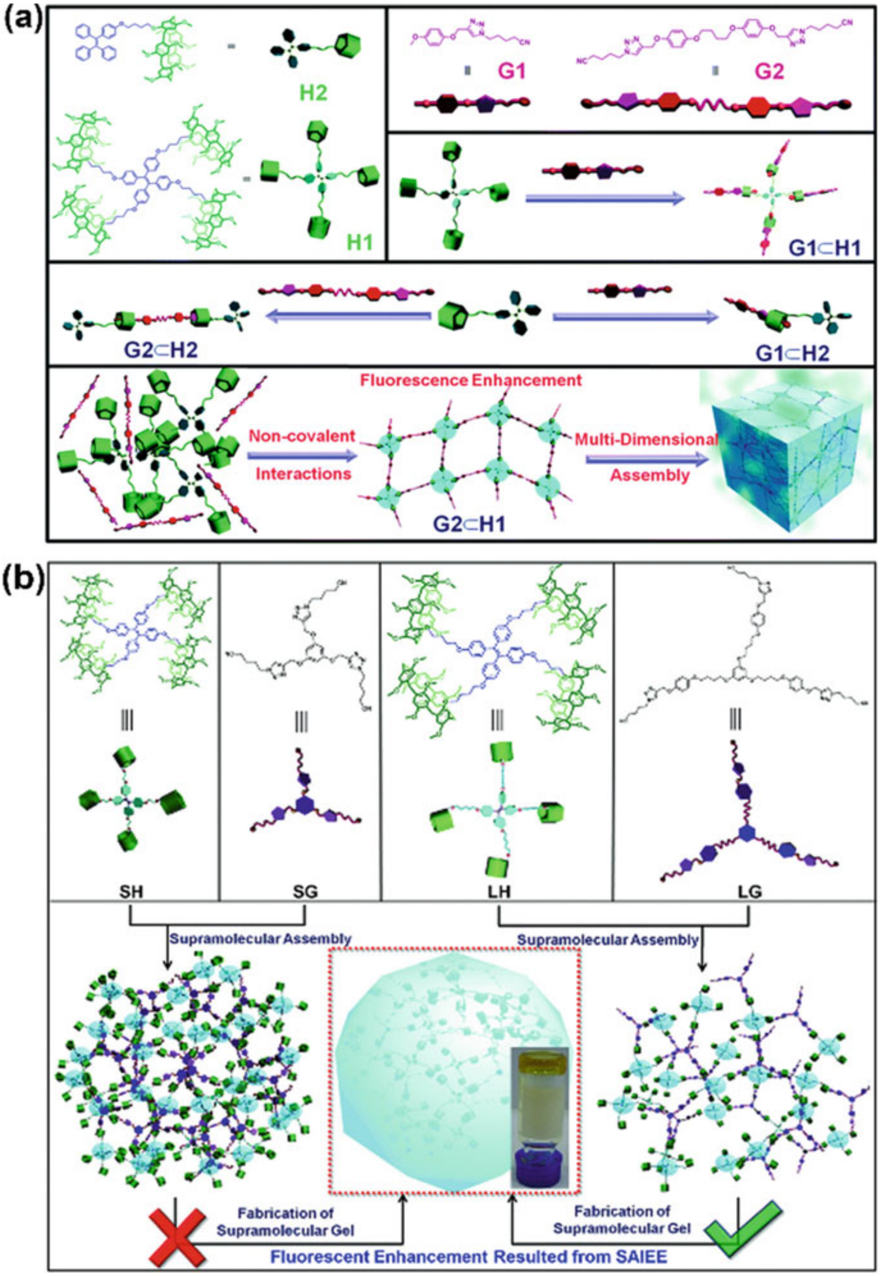

Fig. 17 (**a**) Schematic illustration of the construction of fluorescent supramolecular polymers. (Reprinted with permission from Ref. [33a.] Copyright © 2014. Royal Society of Chemistry). (**b**) Schematic illustration of the chemical structures of *SH*, *SG*, *LH*, and *LG* and fabrication of supramolecular assemblies of *SG*⊂*SH* and supramolecular gel of *LG*⊂*LH*. (Reprinted with permission from Ref. [33b]. Copyright © 2018, John Wiley and Sons)

Researches also have been conducted on the polymer-based supramolecular gels, in which the cross-linked network was constructed by the host-guest interaction between the pillar[n]arene and corresponding guests. Wang and coworkers constructed a redox-responsive gel based on copolymers containing pillar[6]arene moieties and ferrocene derivatives (Fig. 18) [27]. Herein, the copolymers containing pillar[6]arene moieties and ferrocene derivatives were prepared. No supramolecular gels were formed by mixing these two polymers in an organic solvent because no complexes were formed between the ferrocenes and pillar[6]arenes moieties. However, the addition of an oxidant to the mixture triggered the formation of a supramolecular gel because the ferrocenes were converted to ferrocenium cations, which could be included by pillar[6]arene, resulting in the formation of cross-linked network. Moreover, this gel to sol transition could be achieved by the addition of competitive host (native pillar[6]arene) and competitive guest (cobaltocenium hexafluorophosphate), which could destroy the formed stable inclusion complex, leading to the destruction of supramolecular gels.

Liao and coworkers constructed another type of polymer-based supramolecular gels (Fig. 19) [35]. Firstly, they synthesized a copolymer with pendant pillar[5]arene via free radical polymerization. Herein, a ditopic guest molecule with the pyridinium cation was synthesized for the cross-linker, which was different with the previous research by using the copolymer containing the guest molecules. The supramolecular polymeric gel based on the pyridinium-pillar[5]arene motif was fabricated readily by mixing the bifunctionalized guest with the copolymer. On the basis of the competition of host-guest interactions, such a gel could be transformed to sol by addition of competitive host (native pillar[5]arene) or guest molecules (butanedinitrile). Besides host-guest interactions, ordered stacking of pillararenes played an important role in construction of this supramolecular gel, which could realize the gel-sol transition by increasing temperature and the reverse process by decreasing temperature.

13.3.3 Application for the Nano-carrier

With the development of supramolecular chemistry, supramolecular delivery systems are providing incredible opportunities for biomedicine, especially for the diagnosis and treatment of diseases, due to the dynamic nature of noncovalent interaction leading to the diversification of delivery systems [36]. The combination of macrocyclic molecules and the covalent polymers could provide more external stimuli responsiveness than the traditional polymeric drug delivery systems.

Inspired by biodegradable and biocompatible polyglutamic acid, Wang and coworkers synthesized a butyl-ammonium group functionalized polymer (*polymer 3*) with the biotin moiety as the targeted unit (Fig. 20) [37]. Due to the host-guest interaction between butyl-ammonium group and the anionic pillar[5]arene (*WP5*), the side-chain supramolecular polymer could be obtained, which could further self-assemble into vesicles thanks to the electrostatic interaction and hydrophobic effect. Furthermore, this hollow assembly could encapsulate the hydrophilic anticancer drug mitoxantrone (MTZ). And the release of the encapsulated MTZ could be

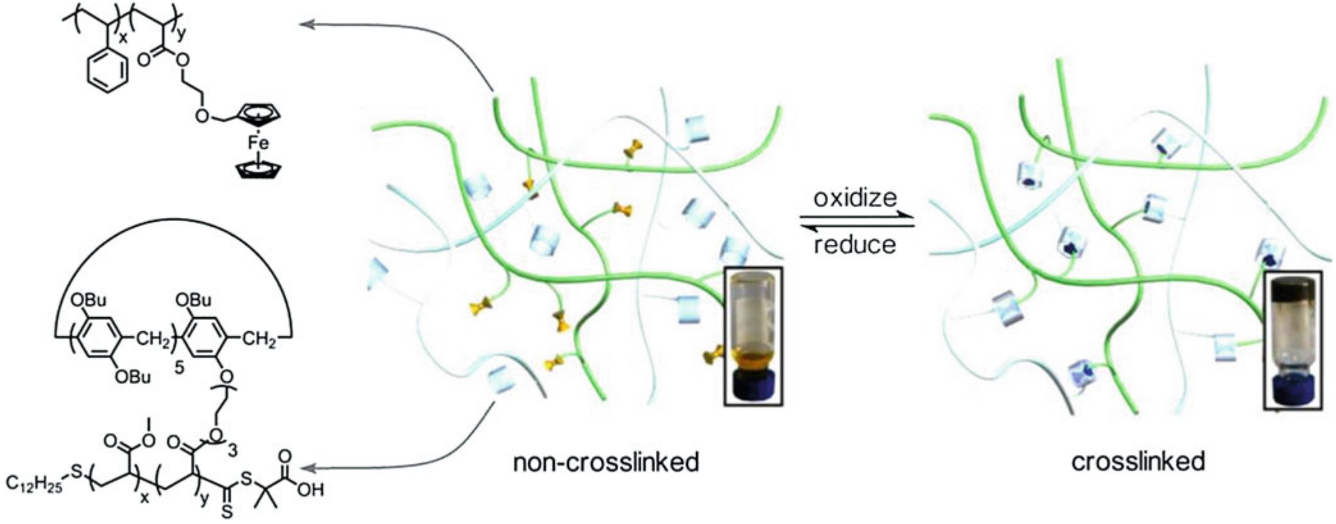

Fig. 18 Schematic illustration of pillar[6]arene-based redox-responsive gels reported by Wang and coworkers. (Reprinted with permission from Ref. [27]. Copyright © 2015, American Chemical Society)

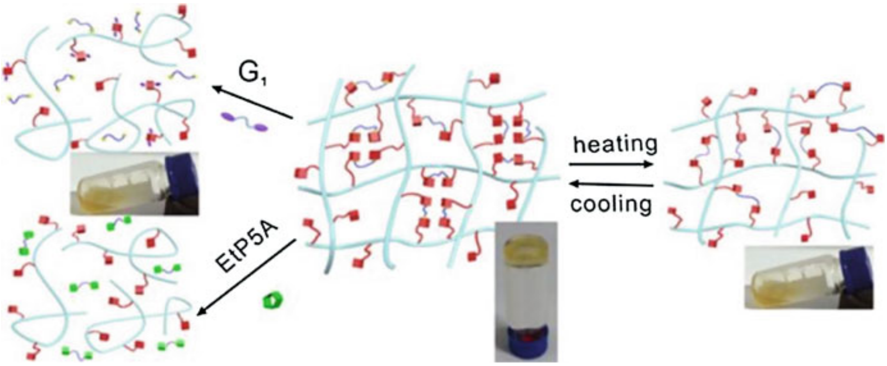

Fig. 19 Schematic illustration of dynamic gels reported by Liao and coworkers. (Reprinted with permission from Ref. [35]. Copyright © 2016, American Chemical Society)

achieved in the cancer cell environment, resulting in the death of cancer cells. Moreover, the MTZ-loaded vesicles with targeting biotin ligands could not only improve the anticancer efficiency of MTZ but also effectively reduce the undesirable cytotoxicity toward normal cells. This method to construct polymetric nano-carriers based on host-guest complexation with covalent polymer showed great advantages in comparison to traditional polymers; tedious synthesis is often required.

Huang and coworkers reported a dual-responsive nano-carrier based on azobenzene-containing random copolymer (*3*) and tri(ethylene oxide) modified pillar[7]arene (*WP7*) (Fig. 21) [38]. In this system, the azobenzene unit could be included into the cavity of pillar[7]arene, leading to the formation of poly-pseudorotaxane. Due to the introduction of pillar[7]arene, the amphipathy of the copolymer was changed, thus resulting in the formation of vesicles, which could encapsulate the model drug (calcein). Because of the thermoresponsiveness of tri (ethylene oxide) modified pillar[7]arene and photoresponsiveness of the azobenzene unit, the reversible transformations between solid nanospheres based on the self-assembly of the polymer backbone and vesicles based on the self-assembly of the supra-amphiphilic polypseudorotaxane are achieved by adjusting the solution temperature or UV-visible light irradiation. Therefore, the controlled release of the encapsulated cargoes could be achieved by both light and temperature. The same research group also conducted research on the **p**illararene-based amphiphilic supramolecular diblock polymer-based on the host-guest recognition between a water-soluble pillar[5]arene and a viologen salt. The efficient encapsulation and release of anticancer drug (doxorubicin hydrochloride) could be realized for the efficient cancer therapy.

Liu and coworkers synthesized a novel lateral-modified pillar[5]arene derivative through bromination reaction at methylene bridge of the dimethoxypillar[5]arene, which could form the covalent polymer with cystamine dihydrochloride, exhibiting highly stable nanostructures, and possess very thin shells composed of lateral covalent cross-linked pillar[5]arenes (Fig. 22) [39]. By taking advantages of the structural features of the nanocapsule shell that composed of host macromolecules,

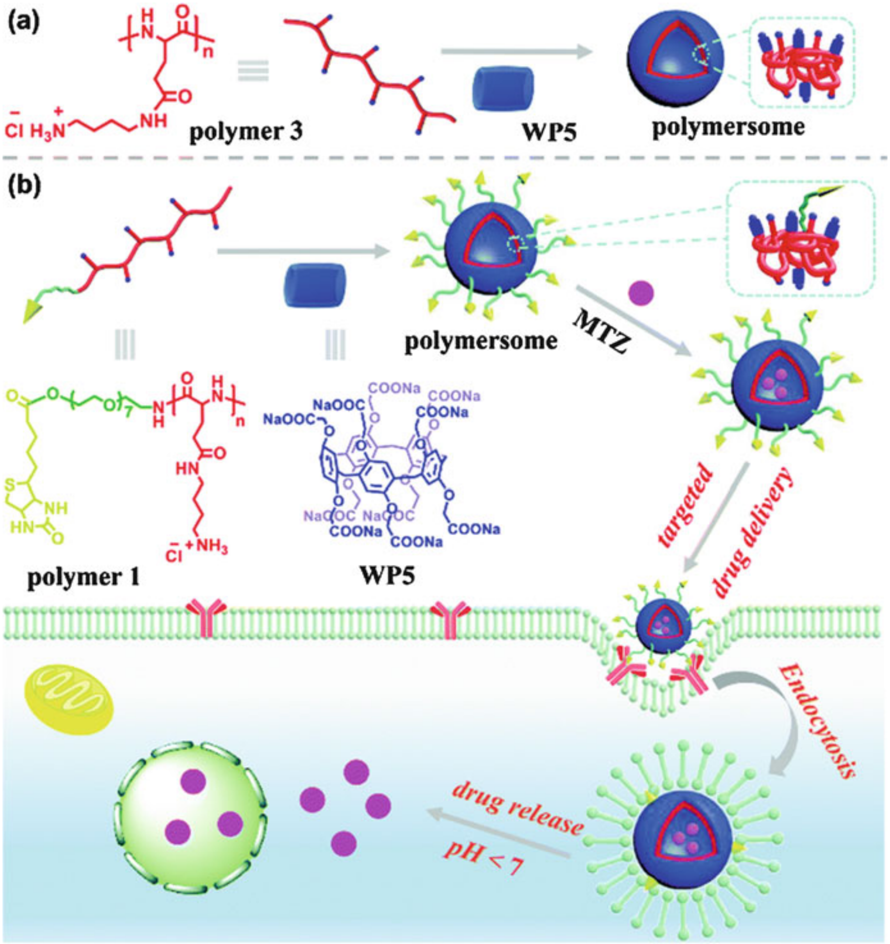

Fig. 20 Schematic illustration of (**a**) the strategy for the construction of supramolecular polymersomes and (**b**) the fabrication of supramolecular polymersomes and their applications in targeted drug delivery. (Reprinted with permission from Ref. [37]. Copyright © 2014. Royal Society of Chemistry)

the tumor-penetrating peptide with the binding site with pillar[5]arene was introduced to construct the supramolecular polymer-based nano-carriers by host-guest manner, thus successfully developing it as a new target smart vehicle for efficient drug delivery.

Huang and coworker synthesized a TPE and bipyridinium derivative modified brush copolymer (*PTPE*), which could form the side-chain supramolecular polymer with biotin-modified pillar[5]arene (*P5-PEG-Biotin*) due to the inclusion bipyridinium unit into the cavity of pillar[5]arene (Fig. 23) [40]. Furthermore, this supramolecular polymer could self-assemble into nanoparticles resulting in the

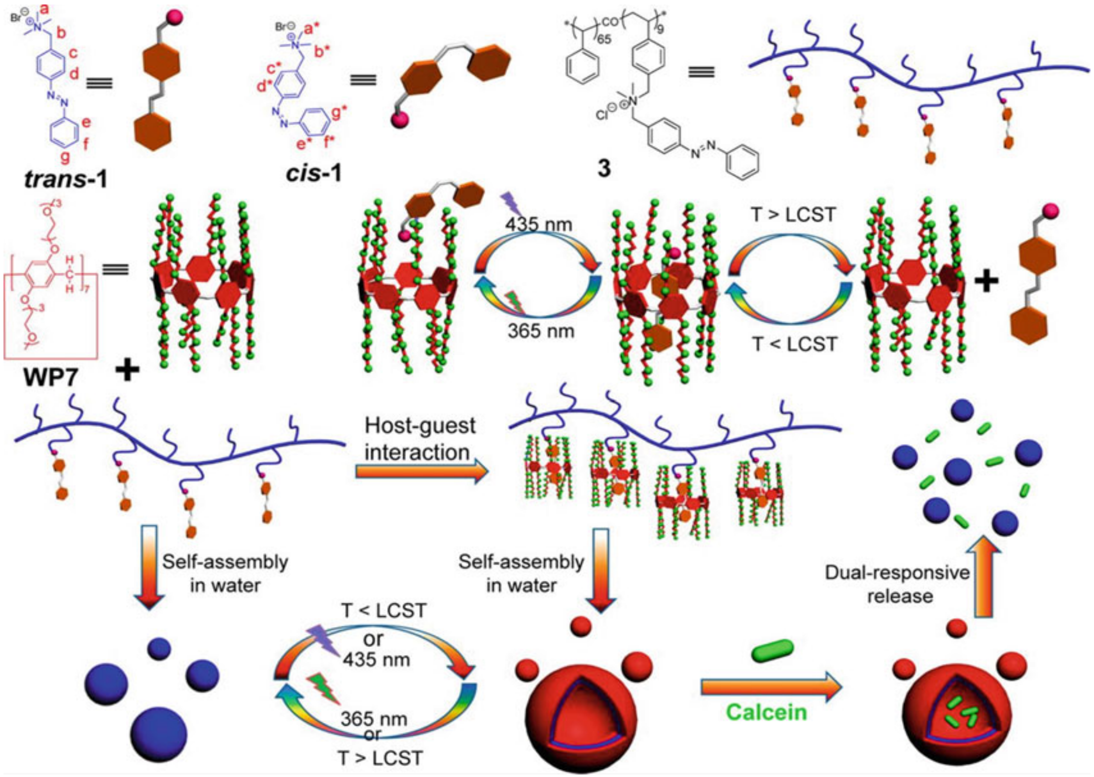

Fig. 21 Illustration of the dual-responsive controlled assembly and disassembly of supramolecular vesicles and the process of dual-responsive release of calcein molecules. (Reprinted with permission from Ref. [38]. Copyright © 2015, American Chemical Society)

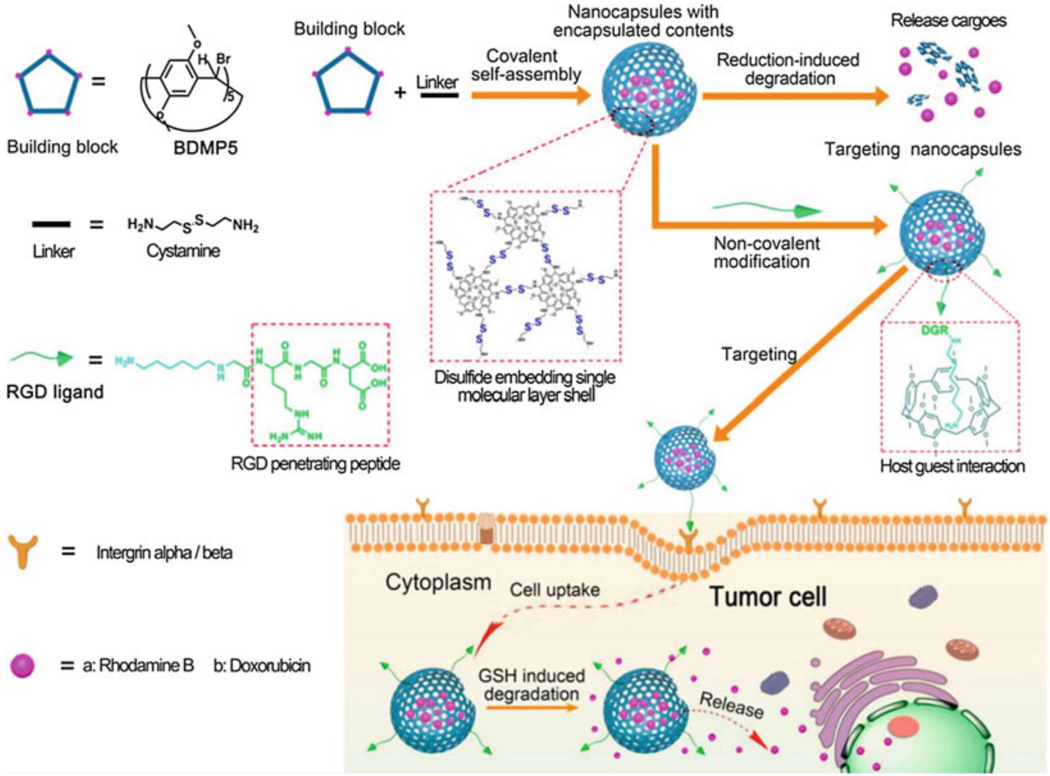

Fig. 22 Designing of reductive-responsive pillar[5]arene-based single molecular layer polymer nanocapsules for targeting anticancer drug delivery. (Reprinted with permission from Ref. [39]. Copyright © 2018, American Chemical Society)

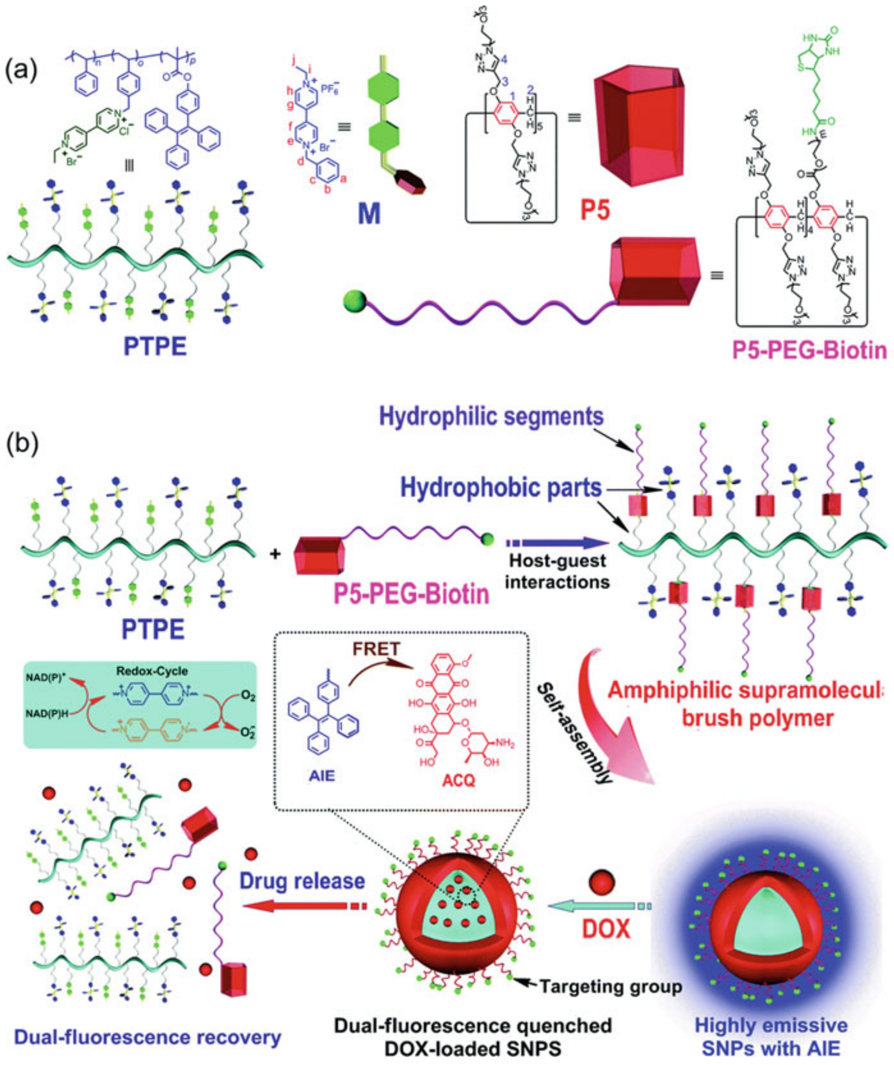

Fig. 23 (**a**) Chemical structures and cartoon representations of *M*, *P5*, *P5-PEG-Biotin*, and *PTPE*. (**b**) Schematic illustration of the formation of SNPs self-assembled from the amphiphilic supramolecular brush copolymer *P5-PEG-Biotin*. *PTPE* and their use as drug delivery vehicles. (Reprinted with permission from Ref. [40]. Copyright © 2014. Royal Society of Chemistry)

enhanced fluorescence emission of TPE moiety at 471 nm, and due to the well overlap between the emission spectrum of TPE and the absorption spectrum of DOX, indicating that TPE could act as a fluorescent donor for DOX, the DOX was successfully loaded into the formed nanoparticles to form a self-imaging drug delivery system. This dynamic FRET system exhibited some advantage in the potential clinical therapy. When the DOX was released in the cancer cells, the energy transfer process would be broken, resulting in a variation in the fluorescence signal, which could be used to track the process of translocation, drug release, and excretion of the nanomedicine.

13.3.4 Application for Optical Materials

Fluorescent material is an important kind of smart material, which can be applied in fluorescent sensors, optoelectronics, probes, biomedicine imaging, and light-emitting diodes [41]. Among the various fluorescent materials, fluorescent supramolecular polymers are very interesting as the fluorescent nature of the chromophores can be controllably regulated by polymerization process of supramolecular polymers.

Yang and coworkers reported the switchable optical waveguide microfibers based on fluorescent supramolecular polymer for the first time (Fig. 24) [42]. Firstly, the pillar[5]arene-based supramolecular polymer was constructed by mixing the bispillar[5]arene host and diphenylanthracene-derived guest with ditopic binding sites. And the supramolecular polymeric microfibers were prepared easily from the viscous solution. This obtained microfibers could act as an active optical waveguide material with long propagation distance (400 μm) and low optical propagation loss (0.01 dB/μm), which was much longer than the most reported organic micro−/nanocrystalline waveguide materials, providing a chance to investigate the long-distance light propagation. Moreover, the ternary supramolecular microfibers could be obtained by the addition of dithienylethene-based guest molecular. Due to the overlap between the emission band of diphenylanthracene and the absorption band of dithienylethene in the closed form, the switchable optical waveguide system could be successfully constructed, in which the clear blue emission was detected at the other tip, indicating the light propagation of this microfiber, while after the irradiation, the light propagation of the microfiber was inhibited, ascribing to the energy transfer from the diphenylanthracene units to the dithienylethene units.

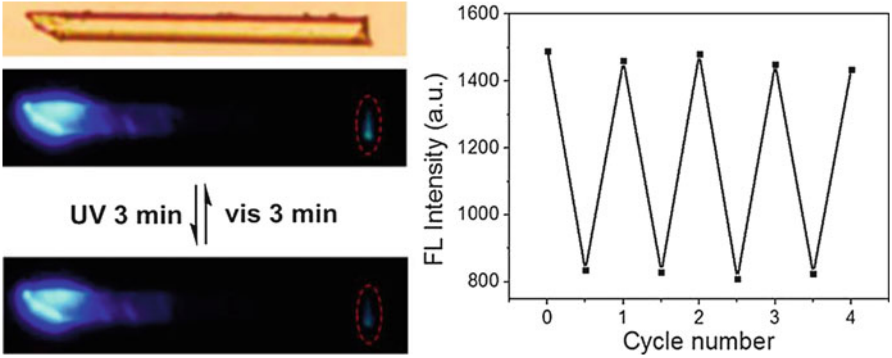

Fig. 24 Switchable optical waveguide microfibers reported by Yang and coworkers. (Reprinted with permission from Ref. [42]. Copyright © 2018, American Chemical Society)

Wang and coworkers reported a FRET-capable supramolecular polymers based on a boron-dipyrromethene (BODIPY)-bridged pillar[5]arene dimer with BODIPY guests for mimicking the light-harvesting system of natural photosynthesis [43]. Herein, two guest molecules were synthesized with bis-binding sites and tri-binding sites for pillar[5]arene, thus constructing the AA/BB-type and A_2/B_3-type supramolecular polymers. Due to the overlap between the emission band of host molecules and the absorption band of guest molecules, the fluorescence (or Förster) resonance energy transfer (FRET) could be occurred, and the transfer efficiency was calculated to be 51% and 63%, respectively. This was the first example of pillar[5]arene-based supramolecular polymers for mimicking the light-harvesting system.

Tian and coworkers reported an emission-tunable supramolecular polymer by changing metal ion types or using mixed metal ions (Fig. 25) [44]. Firstly, the

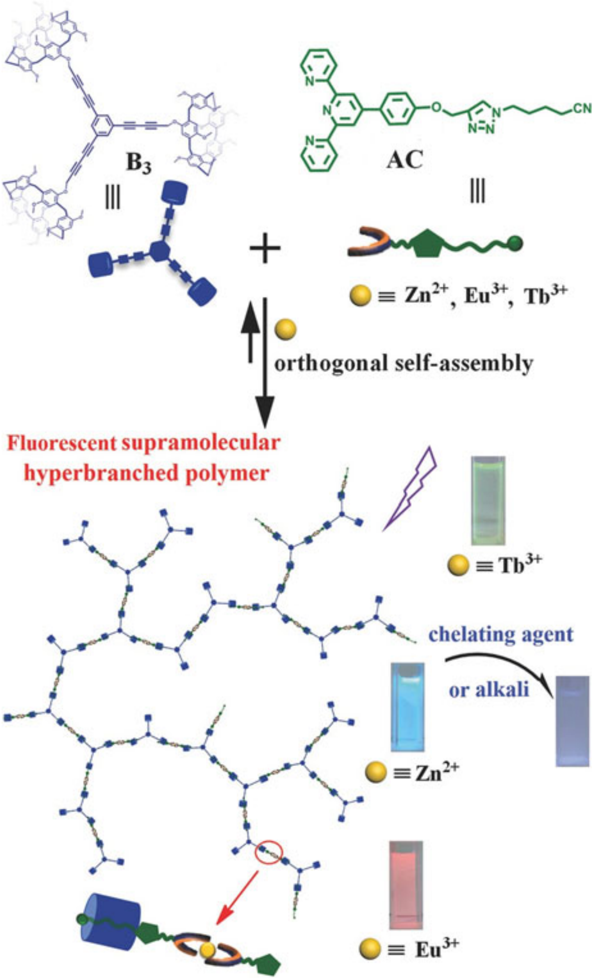

Fig. 25 Schematic depiction of the fluorescent supramolecular hyperbranched polymer prepared from monomer B_3, *AC*, and metal ion by orthogonal self-assembly. (Reprinted with permission from Ref. [44]. Copyright © 2018, John Wiley and Sons)

homotritopic pillar[5]arene monomer (*B_3*) was synthesized, which comprised of three symmetrical pillar[5]arene groups linked by rigid alkynyl chains, as well as the heteroditopic building block (*AC*), which contained a terpyridyl ligand group and a triazole binding site. After the addition of metal ions, the hyperbranched polymer could be constructed by orthogonal self-assembly: pillararene-based host-guest interaction and metal-ligand bond. By simply altering the metal ions or the percentage of mixed metal ions, different emission colors could be observed. Moreover, the addition of competitive ligand could result in the quench in the fluorescence emission. This method would provide a convenient approach toward the construction of structure-tunable fluorescent supramolecular materials with different colors.

Moreover, Cao and coworkers also pioneeringly conducted researches on the OLED devices based on the AA/BB-type supramolecular polymers constructed by pillar[5]arene (Fig. 26) [45]. The monomers *H3* and *G3* were designed based on fluorene derivatives that lead to a blue emission. Another guest molecule *G4* was synthesized based on fluorene-co-benzothiadiazole derivatives with a green-emitting character as the dopant unit in the formed linear AA/BB-type supramolecular polymers. As a result of the efficient energy transfer caused by the exciton trapping on narrow band gap guest *G4*, by applying a doping strategy, the light-emitting color of the resulting polymers could be easily turned from blue to green. Meanwhile, photoluminescent efficiencies up to 81.6% were obtained. All the supramolecular polymers prepared in this work were utilized as the emissive layers (EMLs) in light-emitting devices, and a maximum luminance efficiency (LE) of nearly 5 cd A^{-1} was achieved.

13.3.5 Other Functional Materials

Thermal responsive materials have been widely researched due to their potential application in controlled drug release, molecular separation, and tissue culture substrates [46]. As well known, their lower critical solution temperature (LCST) was depended on their external environment. Along with line, Yu and coworkers constructed a side-chain supramolecular polymer by using the paraquat modified copolymer and water-soluble pillar[10]arene (*WP10*) [47]. After the formation of supramolecular polymer, the T_{CP} was improved by the gradual addition of *WP10*, caused by the increased electrostatic repulsion and steric hindrance arising from the introduction of *WP10*, which inhibited intra−/interpolymer aggregations in solution more effectively. Moreover, the addition of competitive guest molecule, 1,10-phenanthrolinium, would destroy the supramolecular polymer, resulting in the recovery of T_{CP} to the original value, reflected by the transparency of the solution.

This method to tune the transparency of solution would be applied as the smart window [48]. Wang and coworkers synthesized a supramolecular cross-linker polymer network by the host-guest interaction between the glycol-modified pillar[6]arene (*EGP6*) and the ferrocene groups [48b]. Due to the thermal responsiveness of *EGP6*, the transparency of the hydrogel could be reversibly tuned by the temperature. In the relatively high temperature, the hydrogel became turbid, thus regulating the input of solar energy for a more comfortable indoor environment. Moreover, by

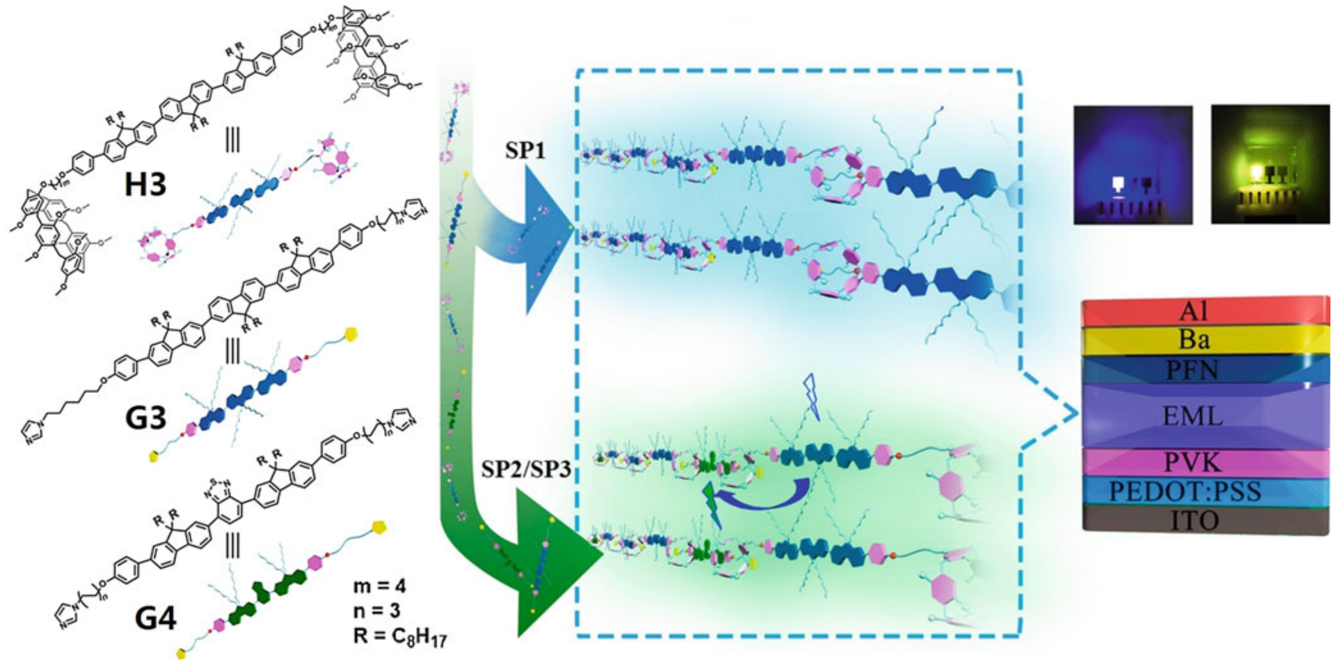

Fig. 26 The construction of supramolecular polymers with different emitting colors and model device structure reported by Cao and coworkers. (Reprinted with permission from Ref. [45]. Copyright © 2017, American Chemical Society)

addition of ATO nanoparticles, which could result in plasmonic heating induced by NIR absorption, the photoresponsive smart window was successfully constructed (Fig. 27) [48a].

The swelling-shrinking materials have been utilized as shape-memory polymers, artificial muscles, and actuators [49]. However, the swelling-shrinking transition of hydrogels was either in small degree or did not efficiently exhibit responsiveness to external multistimuli in these systems. Wang and coworkers report a smart hydrogel whose swelling ratio could be dramatically promoted by host-guest interaction based on water-soluble pillar[6]arene (*WP6*), and the well-swollen hydrogel showed good

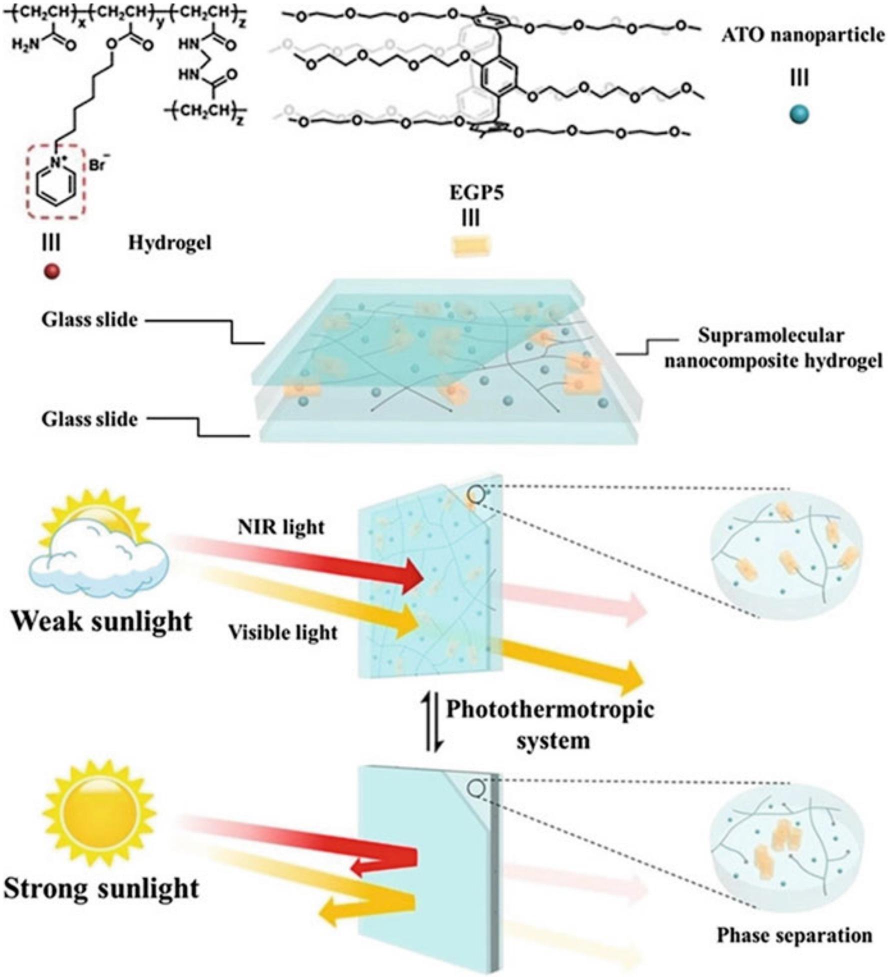

Fig. 27 Chemical structures and schematic illustration of sunlight-induced photo-thermochromic supramolecular nanocomposite hydrogel film for smart window reported by Wang and coworkers. (Reprinted with permission from Ref. [48a]. Copyright © 2018, John Wiley and Sons)

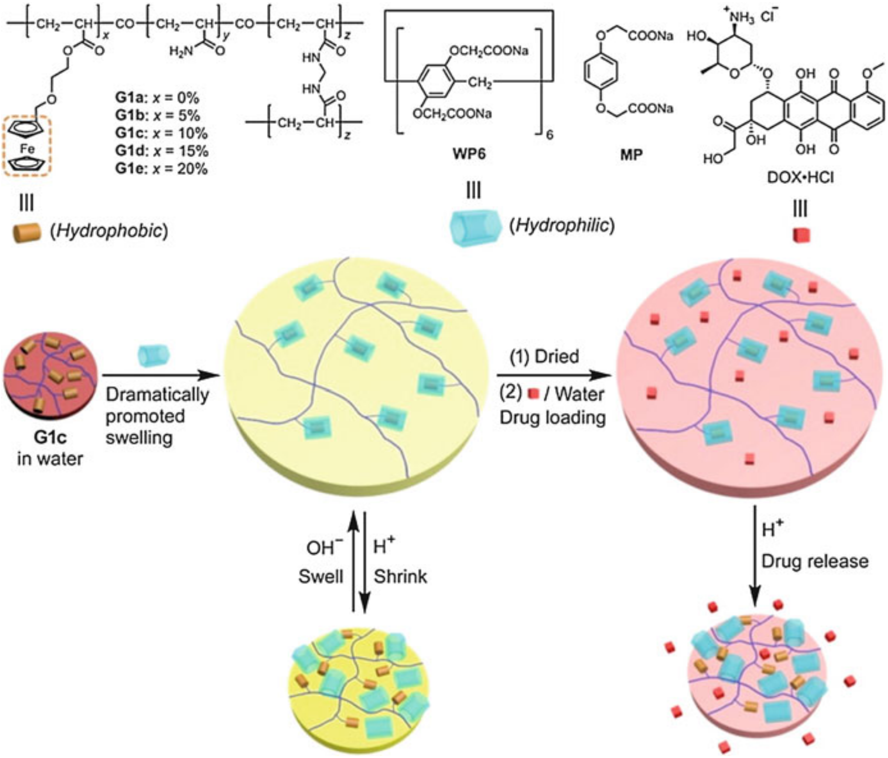

Fig. 28 Illustration of the dramatically promoted swelling by *WP6*-ferrocene host-guest interactions and subsequently pH-responsive swelling-shrinking transition and application in controlled drug (DOX·HCl) release. (Reprinted with permission from Ref. [50]. Copyright © 2016, American Chemical Society)

multistimuli responsive behaviors (Fig. 28) [50]. Firstly, the ferrocene group modified cross-linked polymer was synthesized, which exhibited little swollen ratio. After binding with *WP6*, formation of side-chain supramolecular cross-linked polymer, the swollen ratio was dramatically improved to more than 25 times. Moreover, in an acidic environment, the swelled hydrogel could shrink, and this process exhibited excellent reversibility. Taking advantage of this swelling-shrinking transition, the controlled uptake and release of DOX could be achieved, which might have potential application as controlled drug delivery systems.

13.4 Conclusion

In summary, the pillar[n]arene-based supramolecular polymer has attracted tremendous attention in the past decade. We could easily construct various pillararene-based supramolecular polymeric assemblies with various topologies and properties by employing the host-guest properties of pillararenes for their facile modification and intrinsically intriguing inclusion properties. Moreover, due to the dynamic nature of the noncovalent interaction between pillar[n]arene and corresponding guest molecules, these assemblies exhibited excellent responsiveness to external stimuli, such as pH, concentration, solvent polarity, temperature, photochemistry, and competitive components. Therefore, they might have potential application into the chemical sensors, stimuli-responsive materials, and optical materials.

However, compared to crown ethers, cyclodextrins, calixarenes, and cucurbiturils, it is still an immature project to build pillararene-based supramolecular polymers. There are a lot of challenges and opportunities in this emerging research field. Firstly, although various pillar[n]arene-based supramolecular polymer was successfully constructed, little efforts had been engaged in the research their properties and applications, especially in the energy and environment fields. Secondly, to date most researches were conducted in the organic solvent and mainly focused on the pillar[5]arene and pillar[6]arene, which would limit their potential application in the biological fields as well as the real life. Finally, how to combine the lab research with the industrial production was still the barrier to overcome.

References

1. (a) Cao D, Kou Y, Liang J, Chen Z, Wang L, Meier H (2009) A facile and efficient preparation of pillararenes and a pillarquinone. Angew Chem Int Ed 48:9721–9723; (b) Ogoshi T, Kanai S, Fujinami S, Yamagishi T-A, Nakamoto Y (2008) Para-bridged symmetrical pillar[5]arenes: their lewis acid catalyzed synthesis and host–guest property. J Am Chem Soc 130:5022–5023
2. (a) Guo D-S, Liu Y (2014) Supramolecular chemistry of p-sulfonatocalix[n]arenes and its biological applications. Acc Chem Res 47:1925–1934; (b) Zhao B-T, Zhang H-Y, Liu Y (2005) Progress on molecular self-assembly based on calixarene derivatives. Chin J Org Chem 25:913–925
3. (a) Ogoshi T, Hashizume M, Yamagishi T-A, Nakamoto Y (2010) Synthesis, conformational and host−guest properties of water-soluble pillar[5]arene. Chem Commun 46:3708–3710; (b) Chen Z, Cao D (2010) Synthesis of bis(4-bromo-2,5-dialkoxyphenyl)methane and its analogues. Chin J Org Chem 30:1742–1744; (c) Ma Y, Zhang Z, Ji X, Han C, He J, Abliz Z, Chen W, Huang F (2011) Preparation of pillar[n]arenes by cyclooligomerization of 2,5-dialkoxybenzyl alcohols or 2,5-dialkoxybenzyl bromides. Eur J Org Chem 2011:5331–5335
4. (a) Han C, Zhang Z, Chi X, Zhang M, Yu G, Huang F (2012) Synthesis of 1,4-bis(n-propoxy) pillar[7]arene and its host-guest chemistry. Acta Chim Sin 70:1775–1778; (b) Hu X-B, Chen Z, Chen L, Zhang L, Hou J-L, Li Z-T (2012) Pillar[n]arenes (n = 8–10) with two cavities: synthesis, structures and complexing properties. Chem Commun 48:10999–11001
5. (a) Li C, Han K, Li J, Zhang H, Ma J, Shu X, Chen Z, Weng L, Jia X (2011) Synthesis of pillar[5]arene dimers and their cooperative binding toward some neutral guests. Org Lett 14:42–45; (b) Li C, Ma J, Zhao L, Zhang Y, Yu Y, Shu X, Li J, Jia X (2013) Molecular selective binding of basic amino acids by a water-soluble pillar[5]arene. Chem Commun 49:1924–1926; (c) Ni M, Guan Y, Wu L, Deng C, Hu X, Jiang J, Lin C, Wang L (2012) Improved recognition of alkylammonium salts by ion pair recognition based on a novel heteroditopic pillar[5]arene receptor. Tetrahedron Lett 53:6409–6413
6. (a) Ogoshi T, Yamagishi T-A (2013) Pillararenes: versatile synthetic receptors for supramolecular chemistry. Eur J Org Chem 2013:2961–2975; (b) Wu X, Duan Q, Ni M, Hu X, Wang L

(2014) Recent advances of (pseudo) Rotaxanes constructed by pillar[n]arenes. Chin J Org Chem 34:437–449; (c) Xue M, Yang Y, Chi X, Zhang Z, Huang F (2012) Pillararenes, a new class of macrocycles for supramolecular chemistry. Acc Chem Res 45:1294–1308; (d) Zhang H, Zhao Y (2013) Pillararene-based assemblies: design principle, preparation and applications. Chem Eur J 19:16862–16879; (e) Li C (2014) Pillararene-based supramolecular polymers: from molecular recognition to polymeric aggregates. Chem Commun 50:12420–12433

7. (a) De Greef TFA, Smulders MMJ, Wolffs M, Schenning APHJ, Sijbesma RP, Meijer EW (2009) Supramolecular polymerization. Chem Rev 109:5687–5754; (b) Brunsveld L, Folmer BJB, Meijer EW, Sijbesma RP (2001) Supramolecular polymers. Chem Rev 101:4071–4098; (c) Sijbesma RP, Beijer FH, Brunsveld L, Folmer BJB, Hirschberg JHKK, Lange RFM, Lowe JKL, Meijer EW (1997) Reversible polymers formed from self-complementary monomers using quadruple hydrogen bonding. Science 278:1601–1604
8. Zhang Z, Luo Y, Chen J, Dong S, Yu Y, Ma Z, Huang F (2011) Formation of linear supramolecular polymers that is driven by C-H···π interactions in solution and in the solid state. Angew Chem Int Ed 50:1397–1401
9. (a) Han C, Yu G, Zheng B, Huang F (2012) Complexation between pillar[5]arenes and a secondary ammonium salt. Org Lett 14:1712–1715; (b) Li C, Shu X, Li J, Fan J, Chen Z, Weng L, Jia X (2012) Selective and effective binding of pillar[5,6]arenes toward secondary ammonium salts with a weakly coordinating Counteranion. Org Lett 14:4126–4129; (c) Li C, Xu Q, Li J, Yao F, Jia X (2010) Complex interactions of pillar[5]arene with paraquats and bis (pyridinium) derivatives. Org Biomol Chem 8:1568–1576; (d) Xia B, He J, Abliz Z, Yu Y, Huang F (2011) Synthesis of a pillar[5]arene dimer by co-oligomerization and its complexation with n-octyltrimethyl ammonium hexafluorophosphate. Tetrahedron Lett 52:4433–4436
10. Ogoshi T, Kayama H, Yamafuji D, Aoki T, Yamagishi T-A (2012) Supramolecular polymers with alternating pillar[5]arene and pillar[6]arene units from a highly selective multiple host-guest complexation system and monofunctionalized pillar[6]arene. Chem Sci 3:3221–3226
11. (a) Gao L, Dong S, Zheng B, Huang F (2013) Synthesis of a pillar[5]arene-based heteroditopic host and its complexation with n-octyltriethylammonium salts. Eur J Org Chem 2013:1209–1213; (b) Han C, Xia B, Chen J, Yu G, Zhang Z, Dong S, Hu B, Yu Y, Xue M (2013) A pillar[5]arene-based anion responsive supramolecular polymer. RSC Adv 3:16089–16094
12. Xia B, Zheng B, Han C, Dong S, Zhang M, Hu B, Yu Y, Huang F (2013) A novel pH-responsive supramolecular polymer constructed by pillar[5]arene-based host-guest interactions. Polym Chem 4:2019–2024
13. Wang Q, Cheng M, Zhao Y, Wu L, Jiang J, Wang L, Pan Y (2015) A pillar[5]arene-fused cryptand: from orthogonal self-assembly to supramolecular polymer. Chem Commun 51:3623–3626
14. Hu X-Y, Wu X, Duan Q, Xiao T, Lin C, Wang L (2012) Novel pillar[5]arene-based dynamic polyrotaxanes interlocked by the quadruple hydrogen bonding ureidopyrimidinone motif. Org Lett 14:4826–4829
15. (a) Hu X-Y, Wu X, Wang S, Chen D, Xia W, Lin C, Pan Y, Wang L (2013) Pillar[5]arene-based supramolecular polypseudorotaxane polymer networks constructed by orthogonal self-assembly. Polym Chem 4:4292–4297; (b) Hu X-Y, Zhang P, Wu X, Xia W, Xiao T, Jiang J, Lin C, Wang L (2012) Pillar[5]arene-based supramolecular polypseudorotaxanes constructed from quadruple hydrogen bonding. Polym Chem 3:3060–3063; (c) Guan Y, Ni M, Hu X, Xiao T, Xiong S, Lin C, Wang L (2012) Pillar[5]arene-based polymeric architectures constructed by orthogonal supramolecular interactions. Chem Commun 48:8529–8531
16. Cavallo G, Metrangolo P, Milani R, Pilati T, Priimagi A, Resnati G, Terraneo G (2016) The halogen bond. Chem Rev 116:2478–2601
17. (a) Liu P, Li Z, Shi B, Liu J, Zhu H, Huang F (2018) Formation of linear side-chain polypseudorotaxane with supramolecular polymer backbone through neutral halogen bonds and pillar[5]arene-based host–guest interactions. Chem Eur J 24:4264–4267; (b) Eichstaedt K, Wicher B, Gdaniec M, Polonski T (2016) Halogen bonded polypseudorotaxanes based on a pillar[5]arene host. CrystEngComm 18:5807–5810

18. (a) Schmidtendorf M, Pape T, Hahn FE (2012) Stepwise preparation of a molecular square from NR,NR- and NH,O-substituted dicarbene building blocks. Angew Chem Int Ed 51:2195–2198; (b) Yoshizawa M, Tamura M, Fujita M (2006) Diels-alder in aqueous molecular hosts: unusual regioselectivity and efficient catalysis. Science 312:251–254
19. Li Z-Y, Zhang Y, Zhang C-W, Chen L-J, Wang C, Tan H, Yu Y, Li X, Yang H-B (2014) Cross-linked supramolecular polymer gels constructed from discrete multi-pillar[5]arene metallacycles and their multiple stimuli-responsive behavior. J Am Chem Soc 136:8577–8589
20. Wu X, Yu Y, Gao L, Hu X-Y, Wang L (2016) Stimuli-responsive supramolecular gel constructed by pillar[5]arene-based pseudo[2]rotaxanes via orthogonal metal–ligand coordination and hydrogen bonding interaction. Org Chem Front 3:966–970
21. Shangguan L, Xing H, Mondal JH, Shi B (2017) Novel rare earth fluorescent supramolecular polymeric assemblies constructed by orthogonal pillar[5]arene-based molecular recognition, Eu (III)-coordination and π-π donor-acceptor interactions. Chem Commun 53:889–892
22. (a) Harada A, Hashidzume A, Yamaguchi H, Takashima Y (2009) Polymeric rotaxanes. Chem Rev 109:5974–6023; (b) Harada A, Takashima Y, Nakahata M (2014) Supramolecular polymeric materials via cyclodextrin–guest interactions. Acc Chem Res 47:2128–2140
23. Ogoshi T, Nishida Y, Yamagishi T-A, Nakamoto Y (2010) Polypseudorotaxane constructed from pillar[5]arene and viologen polymer. Macromolecules 43:3145–3147
24. Ma Y, Chen L, Li C, Müllen K (2016) A fishing rod-like conjugated polymer bearing pillar[5] arenes. Chem Commun 52:6662–6664
25. Cui W, Tang H, Xu L, Wang L, Meier H, Cao D (2017) Pillar[5]arene-diketopyrrolopyrrole fluorescent copolymer: a promising recognition and adsorption material for adiponitrile by selective formation of a conjugated polypseudorotaxane. Macromol Rapid Commun 38: 1700161
26. Sun S, Shi J-B, Dong Y-P, Lin C, Hu X-Y, Wang L-Y (2013) A pillar[5]arene-based side-chain Pseudorotaxanes and polypseudorotaxanes as novel fluorescent sensors for the selective detection of halogen ions. Chin Chem Lett 24:987–992
27. Xia W, Ni M, Yao C, Wang X, Chen D, Lin C, Hu X-Y, Wang L (2015) Responsive gel-like supramolecular network based on pillar[6]arene–ferrocenium recognition motifs in polymeric matrix. Macromolecules 48:4403–4409
28. (a) Kim HN, Guo Z, Zhu W, Yoon J, Tian H (2011) Recent progress on polymer-based fluorescent and colorimetric chemosensors. Chem Soc Rev 40:79–93; (b) Zhou Y, Xu Z, Yoon J (2011) Fluorescent and colorimetric chemosensors for detection of nucleotides, FAD and NADH: highlighted research during 2004–2010. Chem Soc Rev 40:2222–2235
29. Cheng H-B, Li Z, Huang Y-D, Liu L, Wu H-C (2017) Pillararene-based aggregation-induced-emission-active supramolecular system for simultaneous detection and removal of mercury(II) in water. ACS Appl Mater Interfaces 9:11889–11894
30. Zhang Y-M, Li Y-F, Zhong K-P, Qu W-J, Yao H, Wei T-B, Lin Q (2018) A bis-naphthalimide functionalized pillar[5]arene-based supramolecular π-gel acts as a multi-stimuli-responsive material. New J Chem 42:16167–16173
31. Lin Q, Fan Y-Q, Mao P-P, Liu L, Liu J, Zhang Y-M, Yao H, Wei T-B (2018) Pillar[5]arene-based supramolecular organic framework with multi-guest detection and recyclable separation properties. Chem-Eur J 24:777–783
32. (a) Raghavan SR, Douglas JF (2012) The conundrum of gel formation by molecular nanofibers, wormlike micelles, and filamentous proteins: gelation without cross-links? Soft Matter 8:8539–8546; (b) Strandman S, Zhu XX (2016) Self-healing supramolecular hydrogels based on reversible physical interactions. Gels 2:16
33. (a) Song N, Chen D-X, Qiu Y-C, Yang X-Y, Xu B, Tian W, Yang Y-W (2014) Stimuli-responsive blue fluorescent supramolecular polymers based on a pillar[5]arene tetramer. Chem Commun 50:8231–8234; (b) Song N, Lou X-Y, Hou W, Wang C-Y, Wang Y, Yang Y-W (2018) Pillararene-based fluorescent supramolecular systems: the key role of chain length in gelation. Macromol Rapid Commun 39:1800593
34. Wei T, Li H, Zhu Y, Lu T, Shi B, Lin Q, Yao H, Zhang Y (2015) Copillar[5]arene-based supramolecular polymer gel: controlling stimuli–response properties through a novel strategy with surfactant. RSC Adv 5:60273–60278

35. Chang J, Zhao Q, Kang L, Li H, Xie M, Liao X (2016) Multiresponsive supramolecular gel based on pillararene-containing polymers. Macromolecules 49:2814–2820
36. Webber MJ, Langer R (2017) Drug delivery by supramolecular design. Chem Soc Rev 46:6600–6620
37. Guo S, Liang T, Song Y, Cheng M, Hu X-Y, Zhu J-J, Wang L (2017) Supramolecular Polymersomes constructed from water-soluble pillar[5]arene and cationic poly(glutamamide)s and their applications in targeted anticancer drug delivery. Polym Chem 8:5718–5725
38. Chi X, Ji X, Xia D, Huang F (2015) A dual-responsive supra-amphiphilic polypseudorotaxane constructed from a water-soluble pillar[7]arene and an azobenzene-containing random copolymer. J Am Chem Soc 137:1440–1443
39. Fu S, Zhang Y, Guan S, Huang Q, Wang R, Tian R, Zang M, Qiao S, Zhang X, Liu S, Fan X, Li X, Luo Q, Hou C, Xu J, Dong Z, Liu J (2018) Reductive-responsive, single-molecular-layer polymer nanocapsules prepared by lateral-functionalized pillar[5]arenes for targeting anticancer drug delivery. ACS Appl Mater Interfaces 10:14281–14286
40. Yu G, Zhao R, Wu D, Zhang F, Shao L, Zhou J, Yang J, Tang G, Chen X, Huang F (2016) Pillar[5]arene-based amphiphilic supramolecular brush copolymers: fabrication, controllable self-assembly and application in self-imaging targeted drug delivery. Polym Chem 7:6178–6188
41. (a) Jiang K, Sun S, Zhang L, Lu Y, Wu A, Cai C, Lin H (2015) Red, green, and blue luminescence by carbon dots: full-color emission tuning and multicolor cellular imaging. Angew Chem Int Ed 54:5360–5363; (b) Zhu X-H, Peng J, Cao Y, Roncali J (2011) Solution-Processable single-material molecular emitters for organic light-emitting devices. Chem Soc Rev 40:3509–3524
42. Sun C-L, Gao Z, Teng K-X, Niu L-Y, Chen Y-Z, Zhao YS, Yang Q-Z (2018) Supramolecular polymer-based fluorescent microfibers for switchable optical waveguides. ACS Appl Mater Interfaces 10:26526–26532
43. Meng L-B, Li D, Xiong S, Hu X-Y, Wang L, Li G (2015) FRET-capable supramolecular polymers based on a BODIPY-bridged pillar[5]arene dimer with BODIPY guests for mimicking the light-harvesting system of natural photosynthesis. Chem Commun 51:4643–4646
44. Li H, Chen W, Xu F, Fan X, Liang T, Qi X, Tian W (2018) A color-tunable fluorescent supramolecular Hyperbranched polymer constructed by pillar[5]arene-based host–guest recognition and metal ion coordination interaction. Macromol Rapid Commun 39:1800053
45. Yang X, Cai W, Dong S, Zhang K, Zhang J, Huang F, Huang F, Cao Y (2017) Fluorescent supramolecular polymers based on pillar[5]arene for OLED device fabrication. ACS Macro Lett 6:647–651
46. (a) Wang F, Klaikherd A, Thayumanavan S (2011) Temperature sensitivity trends and multi-stimuli sensitive behavior in amphiphilic oligomers. J Am Chem Soc 133:13496–13503; (b) Betancourt JE, Rivera JM (2009) Nonpolymeric thermosensitive supramolecules. J Am Chem Soc 131:16666–16668
47. Yu G, Zhou J, Chi X (2015) Pillar[10]arene-based size-selective host–guest complexation and its application in tuning the LCST behavior of a thermoresponsive polymer. Macromol Rapid Commun 36:23–30
48. (a) Xu Z, Wang S, Hu X-Y, Jiang J, Sun X, Wang L (2018) Sunlight-induced photo-thermochromic supramolecular nanocomposite hydrogel film for energy-saving smart window. Sol RRL 2:1800204; (b) Wang S, Xu Z, Wang T, Xiao T, Hu X-Y, Shen Y-Z, Wang L (2018) Warm/cool-tone switchable thermochromic material for smart windows by orthogonally integrating properties of pillar[6]arene and ferrocene. Nat Commun 9:1737
49. (a) Peters O, Ritter H (2013) Supramolecular controlled water uptake of macroscopic materials by a cyclodextrin-induced hydrophobic-to-hydrophilic transition. Angew Chem Int Ed 52:8961–8963; (b) Miyamae K, Nakahata M, Takashima Y, Harada A (2015) Self-healing, expansion–contraction, and shape-memory properties of a preorganized supramolecular hydrogel through host–guest interactions. Angew Chem Int Ed 54:8984–8987
50. Ni M, Zhang N, Xia W, Wu X, Yao C, Liu X, Hu X-Y, Lin C, Wang L (2016) Dramatically promoted swelling of a hydrogel by pillar[6]arene–ferrocene complexation with multistimuli responsiveness. J Am Chem Soc 138:6643–6649