

## Functional Supramolecular Polymeric Networks: The Marriage of Covalent Polymers and Macrocycle-Based Host–Guest Interactions

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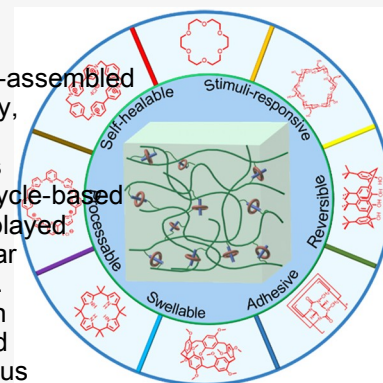
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**ABSTRACT:** Covalent polymers connected by non-covalent interactions constitute a fascinating set of materials known as supramolecular polymeric networks (SPNs). A key feature of SPNs is that the underlying covalent polymers endow the resulting self-assembled materials with features such as structural and mechanical integrity, good processability, recyclability, stimuli-responsiveness, self-healing, and shape memory, that are not recapitulated in the case of classic covalent polymer systems. The unique nature of SPNs derives from the controlled marriage of traditional covalent polymers and macrocycle-based host–guest interactions. As a consequence, supramolecular polymeric networks have played important roles in a number of diverse fields including polymer science, supramolecular chemistry, materials science, biomedical materials, and information storage technology. This Review summarizes advances made in the area of functional SPNs with a focus on original literature reports appearing in the past five years. The treatment is organized according to the key macrocycle-based host–guest interactions used to produce various SPNs. The role of the underlying polymer backbones is also discussed.



### CONTENTS

1. Introduction B
2. Supramolecular Polymeric Networks Constructed by Combining Covalent Polymers with Crown Ether-Based Host–Guest Interactions C
  - 2.1. Benzo-21-Crown-7/Dialkylammonium Salt Recognition Motifs C
  - 2.2. Dibenzo-24-Crown-8/Dibenzylammonium Salt Recognition Motifs E
  - 2.3. Dibenzo-24-Crown-8/Pyridinium-Modified Cyclic Tertiary Ammonium Salt Recognition Motifs H
  - 2.4. Comparisons between Supramolecular Polymeric Networks Constructed by Crown Ether-Based Host–Guest Recognition Motifs H
3. Supramolecular Polymeric Networks Constructed via the Combination of Covalent Polymers and Cyclodextrin-Based Host–Guest Interactions H
  - 3.1.  $\alpha$ -Cyclodextrin/Azobenzene Host–Guest Recognition Motifs H
  - 3.2.  $\alpha$ -Cyclodextrin/Polyethylene Glycol Host–Guest Recognition Motifs J
  - 3.3.  $\beta$ -Cyclodextrin/Adamantane Host–Guest Recognition Motifs K
  - 3.4.  $\beta$ -Cyclodextrin/Azobenzene Host–Guest Recognition Motifs N
  - 3.5.  $\beta$ -Cyclodextrin/Ferrocene Host–Guest Recognition Motifs O

- 3.6.  $\beta$ -CD/Cholesterol Host–Guest Recognition Motifs Q
- 3.7.  $\beta$ -Cyclodextrin/Cholic Acid Host–Guest Recognition Motifs Q
- 3.8.  $\beta$ -Cyclodextrin/Dansyl Group Host–Guest Recognition Motifs Q
- 3.9.  $\beta$ -Cyclodextrin/Phenolphthalein Host–Guest Recognition Motifs Q
- 3.10.  $\beta$ -Cyclodextrin/Reduced Methyl Viologen Host–Guest Recognition Motifs R
- 3.11.  $\beta$ -Cyclodextrin/Polypropylene Glycol Host–Guest Recognition Motifs R
- 3.12.  $\beta$ -Cyclodextrin/N-Isopropylacrylamide Host–Guest Recognition Motifs R
- 3.13.  $\gamma$ -Cyclodextrin/Polyethylene Glycol Host–Guest Recognition Motifs S
- 3.14.  $\gamma$ -Cyclodextrin/Adamantane or Fluoroalkane Host–Guest Recognition Motifs T
- 3.15.  $\gamma$ -Cyclodextrin/Tetraaniline and Polyethylene Glycol Host–Guest Recognition Motifs U

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3.16. Comparisons between Supramolecular Polymeric Networks Constructed by Cyclodextrin-Based Host–Guest Recognition Motifs	V
4. Supramolecular Polymeric Networks Constructed from Covalent Polymers That Exploit Calix[n]arene-Based Host–Guest Interactions	V
4.1. Calix[4]arene/Methyl Viologen Host–Guest Recognition Motifs	V
4.2. Calix[5]arene/1,10-Decanediyldiammonium Salt Host–Guest Recognition Motifs	X
5. Supramolecular Polymeric Networks Constructed through the Combination of Covalent Polymers and Cucurbit[n]uril-Based Host–Guest Interactions	X
5.1. Cucurbit[7]uril/Adamantane Host–Guest Recognition Motifs	Y
5.2. Cucurbit[8]uril/Phenylalanine Host–Guest Recognition Motifs	Y
5.3. Cucurbit[8]uril/1-Benzyl-3-vinylimidazolium Bromide Host–Guest Recognition Motifs	Y
5.4. Cucurbit[8]uril/Methyl Viologen and Naphthalene Host–Guest Recognition Motifs	Z
5.5. Cucurbit[8]uril/Tripeptide Phe–Gly–Gly Ester Derivative Host–Guest Recognition Motifs	AA
5.6. Cucurbit[8]uril/Methyl Viologen and Benzyl Amide or Azobenzene Host–Guest Recognition Motifs	AA
5.7. Comparisons between Supramolecular Polymeric Networks Constructed by Cucurbit[n]uril-Based Host–Guest Recognition Motifs	AB
6. Supramolecular Polymeric Networks Constructed via the Combination of Covalent Polymers and Pillar[n]arene-Based Host–Guest Interactions	AC
6.1. Pillar[6]arene/Ferrocenium Salt Host–Guest Recognition Motifs	AC
6.2. Pillar[5]arene/Pyridinium Salt Host–Guest Recognition Motifs	AD
6.3. Pillar[5]arene/Cyanoalkane Host–Guest Recognition Motifs	AD
6.4. Pillar[5]arene/Trimethylammonium Salt Host–Guest Recognition Motifs	AG
6.5. Comparisons between Supramolecular Polymeric Networks Constructed by Pillar[n]arene-Based Host–Guest Recognition Motifs	AH
7. Supramolecular Polymeric Networks Constructed through the Combination of Covalent Polymers and Other Macrocyclic-Based Host–Guest Interactions	AH
7.1. Calix[4]pyrrole/Anion Host–Guest Recognition Motifs	AH
7.2. Tetracationic Imidazolium Macrocyclic/Anion Host–Guest Recognition Motifs	AI
7.3. Cyclobis(paraquat-p-phenylene)/Naphthalene Host–Guest Recognition Motifs	AJ
8. Comparisons between Supramolecular Polymeric Networks Constructed by Means of Different Non-covalent Interactions	AJ
8.1. Macrocyclic-Based Host–Guest Interactions	AJ
8.2. Other Kinds of Non-covalent Interactions	AK
9. Conclusions and Future Perspectives	AK
Author Information	AL
Corresponding Authors	AL

Author	AL
Notes	AL
Biographies	AL
Acknowledgments	AM
Abbreviations	AM
References	AN

## 1. INTRODUCTION

Supramolecular polymeric networks (SPNs) are covalent polymers cross-linked by non-covalent interactions.<sup>1–4</sup> Compared to covalent bond cross-linked polymer networks, SPNs have appeal in terms of ease of recycling, experimental adaptability, and their ability to undergo self-healing after damage.<sup>1,5–9</sup> Due to the reversibility and stimuli-responsiveness endowed by their constituent non-covalent interactions, SPNs have attracted attention as smart materials in a number of fields, including in the construction of inter alia self-healing materials, drug delivery systems, memory retention materials, systems with high adhesion, and polymer-based electrolytes.<sup>10–25</sup>

It is important to appreciate that SPNs do not rely solely on non-covalent interactions; rather, they are based on covalent polymers. This feature of SPNs means they are predicated on materials that have long been subject to industrialized production and which have good mechanical and thermal integrity, as well as an established history of use across a number of fields.<sup>26,27</sup> Moreover, changing the monomers used to produce the polymer backbone creates systems with different properties that can be used to address different needs. For example, thiophene-, poly(p-phenylenevinylene)-, or acene-based conjugated polymers can be applied to the preparation of organic photovoltaic devices, such as organic field-effect transistors, organic light-emitting diodes, and organic solar cells.<sup>28</sup> Poly(N-isopropylacrylamide) (PNIPAM), with lower critical solution temperatures (LCSTs), has found application in thermal-responsive materials and proved useful in controlling surface wettability, effecting gene delivery, and producing nanoreactors.<sup>29–31</sup> Polymers containing gas-sensitive molecules, such as diethylamine (CO<sub>2</sub>-sensitive), o-phenylenediamine (NO-sensitive), or o-azidomethylbenzoate (H<sub>2</sub>S-sensitive) groups, have allowed for the construction of gas-responsive materials that in turn, have been used to fabricate microgels, control self-assembly, and produce sensors.<sup>32</sup> Photo-sensitive moieties such as azobenzene (Az), spiropyrans, anthracene, and 2-nitroresorcinol derivatives, can provide polymers with photo-responsive properties that are playing important roles in the fields of photo-healing, light-regulated supramolecular engineering, and photo-chemotherapy.<sup>33–40</sup> Separately, polymers containing biologically important molecules are attracting attention in various medically relevant fields, including theranostics and nanomedicine. These platforms have also led to the generation of enzyme-responsive hydrogels. Not surprisingly, an effort has been made to import the beneficial features of these functionalized covalent polymers into the realm of SPNs.

Key to creating SPNs is control over non-covalent interactions, such as hydrogen bonding,<sup>12,47–54</sup> host–guest recognition,<sup>55–63</sup> metal coordination,<sup>64–67</sup> π–π donor–acceptor effects,<sup>68–70</sup> cation–π interactions,<sup>71</sup> electrostatic binding,<sup>72</sup> salt bridges,<sup>73</sup> and halogen bonding.<sup>24,74</sup> Taken in concert, these recognition effects provide SPNs with good processability, recyclability, stimuli-responsiveness, self-healing, and shape memory. Among various types of non-covalent interactions,

macrocycle-based host-guest recognition has received the greatest attention, perhaps due to the unique properties and tunability the underlying binding imparts to the resulting complexes. Macrocycle-based host-guest interactions typically rely on a number of effects, including charge transfer interactions, electrostatic interactions, and hydrophobic interactions.<sup>75,76</sup> Also attractive is the fact that the host or guest molecules involved in macrocycle-based host-guest interactions can often be decorated with functional groups. In the context of SPNs, this can allow regulation of the properties of the resulting self-assembled systems. Independent of direct functionalization, macrocycle-based host-guest interactions can impart various stimuli-responsive functions, allowing triggering by light, redox effects, pH, and temperature, as well as exposure to anions and cations. Therefore, macrocycle-based host-guest interactions have been widely used to construct functional SPNs.<sup>3,27,84–86</sup> To date, much of the focus has involved five classic series of macrocycles, namely crown ethers, cyclodextrins (CDs), calix[n]arenes, cucurbit[n]urils (CB[n]s), and pillar[n]arenes.<sup>80,87–99</sup> In recent years, however, several other macrocycles, including a tetracationic imidazolium macrocycle, cyclobis(paraquat-p-phenylene) (CBPQT<sup>4+</sup>), and calix[4]pyrroles (C4Ps) have begun to be explored in the context of preparing supramolecular polymeric materials.<sup>100–106</sup>

The marriage of covalent polymers and macrocycle-based host-guest interactions provides SPNs with a number of desirable properties, including good mechanical strength, structural stability, diverse functionality provided by the covalent polymers as well as dynamic and responsive features made possible by the underlying host-guest interactions. As a result, SPNs are providing a new frontier for materials-related research. They are also driving advances in both polymer science and supramolecular chemistry. In this Review, we summarize recent advances in functional SPNs, species we define as covalent polymers cross-linked by various macrocycle-based host-guest interactions. For the sake of organization, SPNs will be discussed according to the type of hosts involved.

## 2. SUPRAMOLECULAR POLYMERIC NETWORKS CONSTRUCTED BY COMBINING COVALENT POLYMERS WITH CROWN ETHER-BASED HOST-GUEST INTERACTIONS

Crown ether, the first generation of macrocyclic hosts, have been widely used to fabricate various supramolecular architectures.<sup>88,107,108</sup> Indeed, countless host-guest recognition systems based on crown ethers have been reported. Classic pairings include, for example, benzo-18-crown-6 (B18C6)/primary alkylammonium salts (B21C7)/dialkylammonium salts (DAAS) (Figure 1),<sup>109</sup> dibenzo-24-crown-8 (DB24C8)/dibenzylammonium salts (DBAS) (Figure 1),<sup>116–120</sup> DB24CB/pyridinium-modified cyclic tertiary am-

monium salts (PCTAS) (Figure 1),<sup>121</sup> bis(m-phenylene)-32-crown-10 (BMP32C10)/methylviologen (MV<sup>2+</sup>),<sup>55,122–125</sup> and bis(p-phenylene)-34-crown-10 (BPP34C10)/MV<sup>2+</sup>.<sup>126</sup>

Among these host-guest recognition systems, B21C7/DAAS and DB24C8/DBAS were applied early on to create SPNs. For example, in 2009, Huang, Liu, and co-workers reported a supramolecular polymer gel based on a DB24C8-terminated four-arm star poly(caprolactone) and a DBAS-terminated two-arm poly(caprolactone).<sup>127</sup> Due to the inherent thermal-sensitive nature of the supramolecular interactions and the pH-responsiveness of the deprotonation/protonation process for DBAS, DB24C8/DBAS recognition is endowed with dual thermal- and pH-responsiveness, providing the corresponding gel with analogous stimuli-responsive properties. In 2012, Huang and co-workers reported an interesting self-healing supramolecular polymer gel that was obtained by cross-linking poly(methyl methacrylate) (PMMA) via DB24C8/DBAS host-guest interactions.<sup>128</sup> In 2012, Wang and co-workers reported a multi-responsive SPN based on the host-guest interactions between a DAAS-functionalized polystyrene and a complementary homoditopic B21C7 cross-linker.<sup>29</sup> More recently, SPNs based on host-guest recognition motifs consisting of either B21C7/DAAS, DB24C8/DBAS, and DB24C8/PCTAS pairs have been reported (Figure 1). Collectively, these contributions have served to underscore the potential benefits associated with using crown ether-based host-guest interactions to create SPNs.

### 2.1. Benzo-21-Crown-7/Dialkylammonium Salt Recognition Motifs

Mechanically interlocked structures, such as catenanes and rotaxanes, are attractive building blocks for the preparation of supramolecular architectures. These now-canonical structures are characterized by degrees of freedom that are restrained in at least one dimension; however, they still permit effective translation or rotation depending on the system in question.<sup>130–132</sup> The incorporation of mechanically interlocked structures into bulk materials thus offers the potential of transforming specific molecular motions into macroscopic scale changes. This property, in turn, can lead to materials with special dynamic properties or unique mechanical features. Xing and co-workers reported a SPN that takes advantage of interactions between a catenane-based B21C7 cross-linker and a DAAS-grafted polymer. As shown in Figure 2, the two B21C7 host units were linked by the [2]catenane moiety to generate cross-linker 1. Then, polymer 2 was cross-linked by 1 in CHCl<sub>3</sub> to form SPN 3. Compared with a traditional covalent bond-connected homoditopic B21C7 cross-linked polymer, SPN 3 displayed much better viscoelastic properties. In addition,

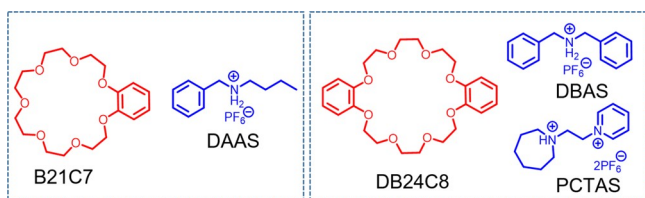


Figure 1. Chemical structures of B21C7 and DB24C8 and their complementary guests, DAAS, DBAS, and PCTAS.

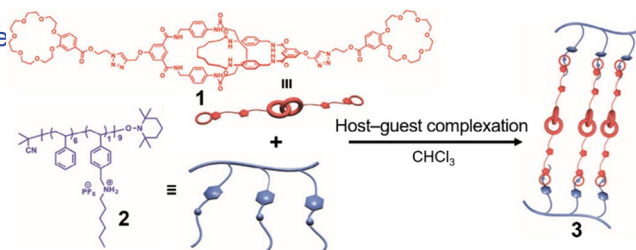


Figure 2. Formation of SPN 3 from the catenane-based B21C7 cross-linker 1 and the DAAS-functionalized polymer 2. Reproduced with permission from ref 137. Copyright 2018 The Royal Society of Chemistry.



SPN 3 was found to form a supramolecular polymer gel at high monomer concentration. The critical gelation concentration (CGC) at 298 K was determined to be 45 mM in 1 and 10 mM in 2. The gel itself displayed thermo-pH-, and chemoresponsive sol-gel transition behavior; presumably, these desirable features reflect the multi-responsive nature of the B21C7/DAAS host-guest interaction.

Polymer blends consisting of two or more polymers have been widely applied in various fields, including as electrochemical transistors, adhesives, and biomimetic materials. This applicability reflects the enhancements in the overall physical and chemical features relative to the original individual components.<sup>138–141</sup>

Of particular appeal are polymer blends that are cross-linked through non-covalent interactions since such systems often display adaptability in response to changes in their external environment.<sup>11,142–144</sup> Xue and co-workers reported a poly(methyl acrylate)/polystyrene (PMA/PS) blend.<sup>145</sup> As shown in Figure 3, polymer 4 is a PMA polymer

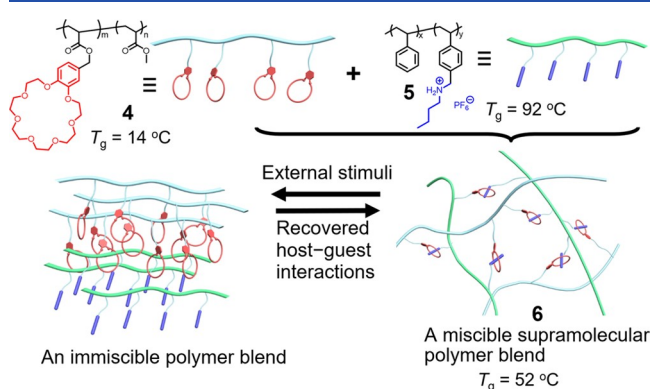


Figure 3. Schematic showing the formation of the miscible supramolecular polymer blend 6 from polymers 4 and 5, and the adaptability of this material to changes in the external environment.

with pendent B21C7 units, while polymer 5 is a PS polymer with pendent DAAS moieties. Driven by B21C7/DAAS host-guest interactions, the two components of the blend interact with one another, resulting in the formation of a miscible polymer blend 6. In this system, a mixture of 4 and 5 displays only one glass-transition temperature, namely 52 °C; this value is between the  $T_g$  values for 4 (14 °C) and 5 (92 °C). This finding was taken as evidence of successful polymer blending. In addition, this system was found to recover its original form after being damaged by various environmental factors, highlighting its potential utility.

Many supramolecular polymer gels are predicated on a single type of non-covalent interaction, such as metal coordination, hydrogen bonding, or host-guest complexation, respectively, that serves to abet cross-linking.<sup>3,146–148</sup> However, the use of supramolecular cross-linkers that support more than one kind of supramolecular interaction is attractive. In principle, this approach can be used to retain the integrity of the polymer network while allowing for useful responses to a broader range of stimuli.<sup>149</sup> Specifically, such gels can exhibit macroscopic expansion-contraction behavior when exposed to appropriate external stimuli without undergoing a gel-sol transition. This is because one cross-linker can be used to maintain the gel while the other can be used to change the cross-linking density of the gel.<sup>63,150–153</sup>

An example of a double supramolecular cross-linked polymeric gel exhibiting macroscopic expansion and contraction behavior and multi-stimulus response features (9) was reported by Huang, Zimmerman, and co-workers.<sup>154</sup> As shown in Figure 4, this system was built up from polymer 7, which consists of a PS backbone bearing pendent 2,7-diamido-1,8-naphthyridine (DAN) and DAAS groups. A second polymer 8, consisting of a poly(butylmethacrylate) (PBMA) backbone that bears deaza-uguanosine (DeUG) and B21C7 subunits, was also prepared. When these two polymeric precursors were mixed, a doubly cross-linked supramolecular polymer gel 9 was produced that is presumably stabilized via a combination of B21C7/DAAS-based

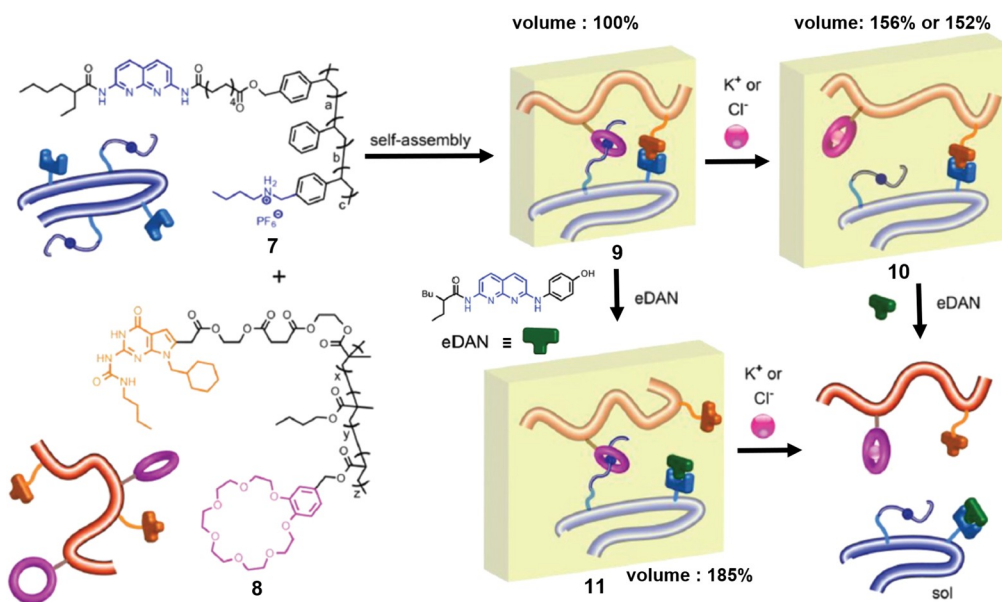


Figure 4. Cartoon representations of polymers 7 and 8 and illustration of the stimuli-responsiveness of the double supramolecular cross-linked polymer gel 9 that forms when they are mixed. Also shown are the expanded single supramolecular cross-linked networks 10 and 11 that can be generated from 9 by exposure to appropriate stimuli. Reproduced with permission from ref 154. Copyright 2015 The Royal Society of Chemistry.



host-guest complexation and DAN/DeUG quadruple hydrogen-bonding interactions<sup>159</sup>, orthogonal molecular recognition modalities were used to maintain the gel state and alter the cross-linking density of the gel. These latter alternations were induced by means of external stimuli, including treating with  $K^+$ ,  $Cl^-$ , and the competitive guest eDAN. Upon addition of  $K^+$  or  $Cl^-$ , an expanded single SPN, 10, formed with the volume of the gel increasing from 100% to 156% or 152%. Upon addition of eDAN, a different expanded single SPN, 11, is formed with the volume of the gel increasing from 100% to 185%. However, the addition of both  $KCl$  and eDAN led to a gel-sol transition, presumably because both molecular recognition motifs were effectively precluded. The net result is a gel system (i) that displays expansion-contraction behavior without undergoing a gel-sol transition and (ii) whose fundamental features could be modulated by exposure to an appropriate external stimulus.

Fluorescent SPNs are an important class of smart soft materials that have been proved useful in optoelectronics and fluorescence sensing among other application areas.<sup>155</sup> One of the inherent properties of conventional organic fluorogen-based fluorescent supramolecular polymers is that the high effective local concentration of the appended fluorophores can lead to aggregation-based quenching. The incorporation of aggregation-induced emission (AIE) fluorogens into supramolecular polymeric materials is seen as a way to overcome these inherent limitations.<sup>157,158</sup> Huang and co-workers reported a fluorescent supramolecular cross-linked polymer gel that exploits crown ether-based host-guest interactions while incorporating AIE-active tetraphenylethylene (TPE) moieties.<sup>159</sup> Here, the DAAS-containing PS polymer 5 and a TPE-modified B21C7 tetramer 12 were mixed in  $CHCl_3$  to create the fluorescent supramolecular cross-linked polymer gel 13. The stability of this system was ascribed to a combination of host-guest effects and aggregation of the TPE moieties (cf. Figure 5). Reversible gel-sol transitions could be induced in this system, a finding attributed to the reversible recognition and stimuli-response features provided by the B21C7/DAAS host-guest combination. These transformations could be followed by monitoring changes in the fluorescence emission intensity.

## 2.2. Dibenzo-24-Crown-8/Dibenzylammonium Salt Recognition Motifs

In recent years, fluorescent sensors based on SPNs have attracted considerable attention due to their high selectivity and sensitivity. This has proved especially true for polymeric backbone-based fluorescent conjugated polymers.<sup>160,161</sup> As prepared, conjugated polymers typically exhibit a strong fluorescence emission. After being cross-linked by means of non-covalent interactions, they generally display weak or quenched fluorescence, making them attractive as potential "turn on" fluorescent sensors.<sup>162,163</sup> Huang and co-workers reported a SPN cross-linked by means of host-guest interactions between the pendent DB24C8 units of poly(p-phenylene-ethynylene) (PPE)-based polymer 14 and a homoditopic DBAS dimer 15 (Figure 6). The SPN obtained in this way (16) exhibited weak fluorescence compared to the conjugated polymer 14, result ascribed to the aggregation of the polymer main chains. This weak fluorescence intensity could be enhanced by the stimulus-induced destruction of the cross-linked network structure. Stimuli that proved effective for this purpose were found to include potassium cations, chloride anions, increases in pH, and heating. Given this diversity of

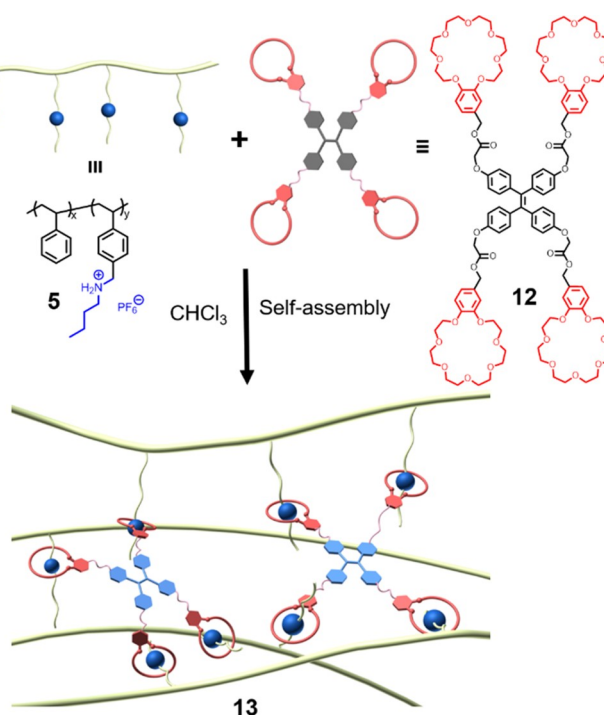


Figure 5. Schematic representation of the PS polymer 5 bearing pendent DAAS moieties, B21C7-based tetramer 12, and the fluorescent supramolecular cross-linked polymer gel 13.

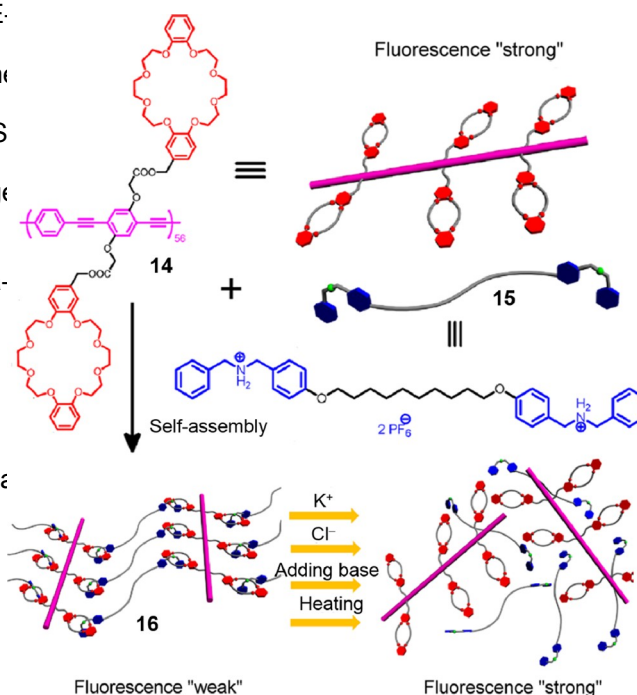


Figure 6. Cartoon representation of the DB24C8-containing polymer 14 and the homoditopic DBAS dimer 15. Also shown in schematic fashion is the formation of the supramolecular conjugated polymeric network 16 and its disassembly promoted by different chemical and physical stimuli. Reproduced with permission from ref 164. Copyright 2013 American Chemical Society.

response-inducing inputs, it was suggested that network 16 could serve as a multi-substrate fluorescent sensor that would prove effective both in  $CH_3OH/CH_3CN$  (1:1, v/v) solution and in thin films.

The use of mechanically interlocked structures to prepare SPNs has attracted considerable interest within the community due to the excellent stability and dynamic features of the resulting SPNs.<sup>133,165–168</sup> Rotaxane cross-linked polymers (RCPs) exhibit unique properties that include an ability to stabilize mechanically tough bulk elastomers and hydrogels.<sup>169–173</sup> Takata and co-workers reported a series of RCPs based on the DB24C8/DBAS recognition motifs. For example, as shown in Figure 7, radical polymerization of n-butyl acrylate

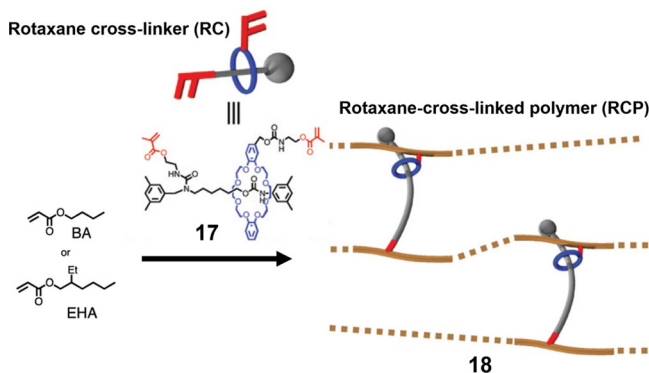


Figure 7. Chemical structure of RC 17 and schematic illustration of the RCPs 18 produced via the polymerization of vinyl monomers in the presence of 17. Reproduced with permission from ref 174. Copyright 2017 The Royal Society of Chemistry.

(BA) or 2-ethylhexyl acrylate (EHA) in the presence of 0.5 mol % of the rotaxane cross-linker (RC) 17 gives rise to the [2]rotaxane cross-linked SPN 18 characterized by a high level of toughness.<sup>174</sup> RC 17 was prepared from a DB24C8/DBAS rotaxane by treatment with 2-isocyanatoethyl methacrylate. The mechanical properties of network 18 are enhanced relative to related covalently cross-linked polymers.

To study how variations in the chemical structure of the RC can affect the properties of RCPs, Takata and co-workers prepared a series of RCs with different axle lengths and used them to produce various SPNs.<sup>175</sup> It was revealed that the swelling ratios of the RCPs were directly proportional to the lengths of the RCs. On this basis it was inferred that the intermotions inherent in the RCPs could serve to equalize the local uniformity that is typically found in cross-linked polymers.

Polymeric materials can be downsized to the colloidal scale. This significantly simplifies the manufacturing of bulk materials and makes them amenable for use in unconventional applications.<sup>176,177</sup> To obtain films based on polymer microspheres with outstanding mechanical properties, mini-emulsion polymerization processing of the microspheres is typically required. This post-polymerization processing adds steps to the overall process and can serve as an impediment to practical applications.<sup>178</sup>

Suzuki and co-workers reported elastomer microspheres cross-linked with rotaxanes and showed that the resulting systems afforded mechanically strong and flexible films upon evaporation of water from the initial microsphere dispersions thus obviating the need for any additional post-polymerization reactions.<sup>178</sup>

As shown in Figure 8, the mini-emulsion polymerization of RC 17 and vinyl monomers BA and MMA gave rise to rotaxane-cross-linked elastomer microspheres of generalized structure 19. Microsphere dispersions consisting of a copolymer of approximately 40 mol% BA and 60 mol% MMA showed the best results. In addition, microspheres with low levels of cross-

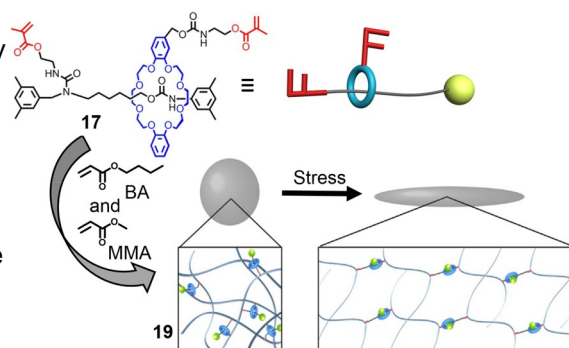


Figure 8. Chemical structure of RC 17 and schematic illustration of the rotaxane cross-linked elastomer microspheres 19 and associated films obtained following polymerization and evaporation of solvent. Reproduced with permission from ref 78. Copyright 2017 John Wiley and Sons.

linking by RC 17 (e.g., 0.05 mol%) exhibited increased strength and fracture strain.

An ability to undergo self-healing is a salient feature of biological materials and is a key to wound recovery and the natural repair of cracks in skin and bone. These remarkable attributes have inspired efforts to develop hydrogels endowed with self-healing capabilities.<sup>179,180</sup> An added incentive to prepare such systems comes from an appreciation that classic, polymeric materials, based on covalent bonds, typically lack this self-healing capacity. It is now recognized that dynamic non-covalent interactions can be used to produce polymeric materials that respond to external stimuli while maintaining stability and functionality; they are thus ideally suited for fabricating self-healing materials.<sup>90,181,182</sup> Chen and co-workers reported a self-healing supramolecular polymer gel stabilized by host–guest interactions between a DB24C8-based cross-linker and a copolymer containing the DBAS moieties shown in Figure 9, the DBAS-containing poly(ethyl acrylate) (PEA)-

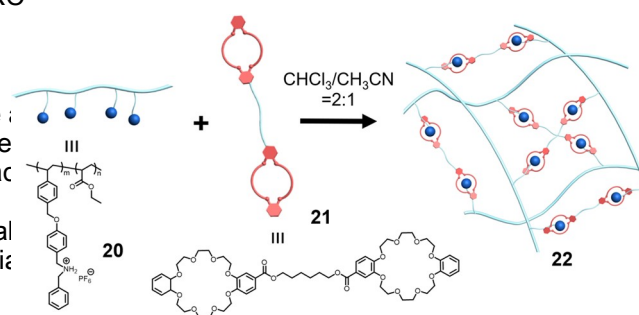


Figure 9. Schematic illustration of the DBAS-containing copolymer 20, the DB24C8 dimer 21, and the resulting self-healing supramolecular polymer gel 22.

The DB24C8 dimer 21 and the resulting self-healing supramolecular polymer gel 22. The DB24C8 dimer 21 and the resulting self-healing supramolecular polymer gel 22. The DB24C8 dimer 21 and the resulting self-healing supramolecular polymer gel 22.

Non-covalent interactions have been exploited to prepare homoditopic supramolecular dimers that can be used as cross-linkers to fabricate SPNs. The resulting SPNs typically benefit from simplified syntheses while displaying an ability to respond to a variety of stimuli. For instance, Yin and co-workers reported a fluorescent SPN (26) based on a DB24C8 supramolecular dimer and a DBAS-grafted polymer. The preparation is

shown in schematic form in Figure 10. One component is polymer 23, which comprises a PS backbone bearing both

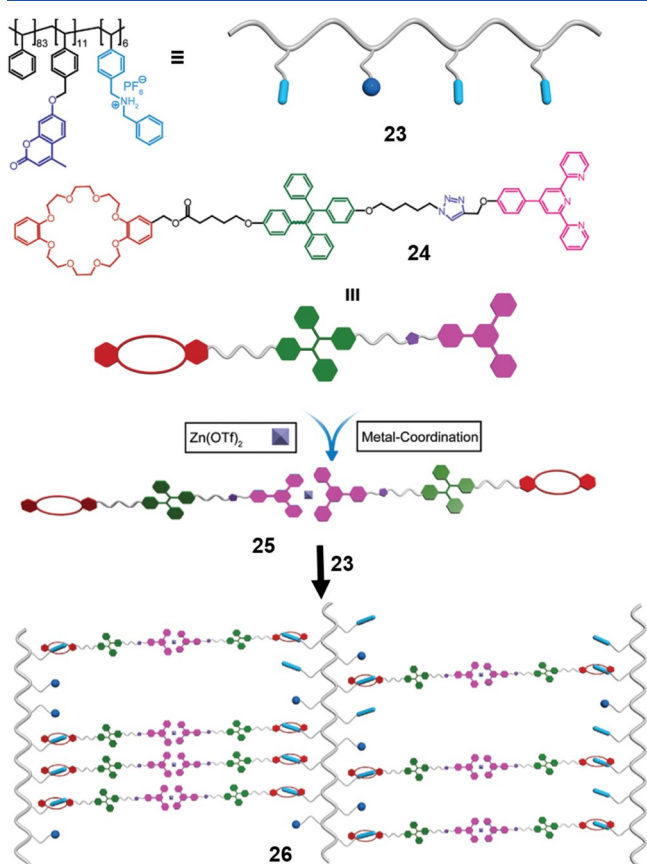


Figure 10. Cartoon representation of 23, 24, the supramolecular dimer 25 formed from 24 and  $\text{Zn}(\text{OTf})_2$ , and the resulting SPN 26. Reproduced with permission from ref 184. Copyright 2018 The Royal Society of Chemistry.

pendant coumarin and DBAS groups. Another component is compound 24; it contains DB24C8, terpyridine, and TPE groups. In concert, these precursors were used to prepare the supramolecular dimer 25 via  $\text{Zn}^{2+}$  cation complexation. The presence of two fluorophore subunits, namely TPE and coumarin, endowed the resulting SPN 26, with ratiometric fluorescence sensing capability for  $\text{Cl}^-$ ,  $\text{Et}_3\text{N}$ , and cyclen. In addition, SPN 26 was found to form a supramolecular polymeric gel at high concentrations. It also displayed stimuli-responsive gel-sol transitions and good self-healing properties.

The use of macrocyclic hosts as “molecular glue” to connect polymer chains containing guest units via host-guest interactions provides a convenient means of preparing SPNs.<sup>129,185</sup> Chen and co-workers reported two kinds of DB24C8-based dimer hosts, 27 and 28, that could be used as molecular glue to cross-link DBAS-containing PMA-based copolymer 29-1 and PEA-based copolymer 29-2 so as to produce the cross-linked SPN 30 in  $\text{CHCl}_3/\text{CH}_3\text{CN}$  (1:1, v/v) and 31 in  $\text{CHCl}_3$  respectively (Figure 11).<sup>186,187</sup> SPN 30 forms a colorless and transparent supramolecular polymer gel at high concentrations. This gel displayed reversible responsiveness to a variety of stimuli, as well as intrinsic self-healing capability. SPN 31 was found to form a supramolecular polymer gel when fully cross-linked yet retain a well-defined porous structure. Its mechanical properties could be modulated by treating with

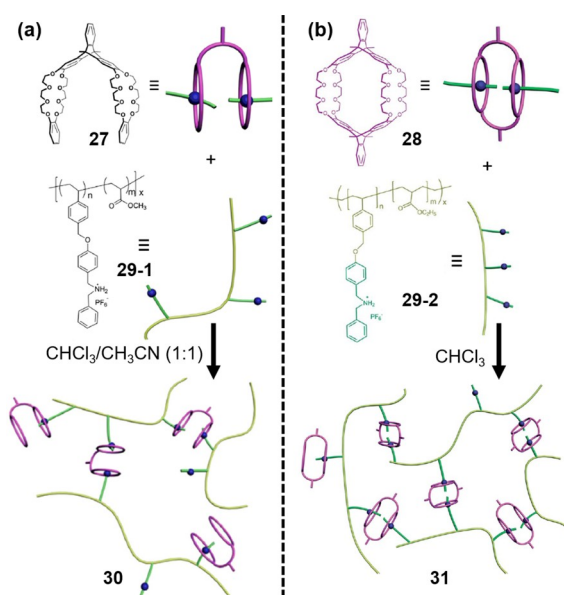


Figure 11. (a) Cartoon representations of host 27, polymer 29-1, and the supramolecular polymer gel 30 whose formation they permit. Reproduced with permission from ref 186. Copyright 2013 Elsevier. (b) Cartoon representations of host 28, copolymer 29-2, and supramolecular polymer gel 31. Reproduced with permission from ref 187. Copyright 2013 The Royal Society of Chemistry.

different levels of host 28. SPN 31 was also found to undergo reversible acid/base- and thermo-induced gel-sol transitions; this process allowed it to be employed for the encapsulation and controlled release of squaraine dyes.

One of the more efficient approaches to preparing SPNs involves the use of polymers, wherein host and guest recognition units are present as pendant groups.<sup>145,188</sup> The resulting SPNs often display good mechanical properties and control over the cross-linking density.<sup>189</sup> Ikeda and co-workers reported a SPN generated from two polymers functionalized with DB24C8 and DBAS units as side groups, respectively.<sup>190</sup> As shown in Figure 12, polymers 32 and 33, decorated in this way, could be prepared from glycidyl azide polymers via azide-alkyne Huisgen cycloaddition. Upon mixing, SPN 34 is formed, which was found to exist as an organogel above a concentration of 3 wt% in  $\text{CHCl}_3$  or 1,1,2,2-tetrachloroethane, presumably as the result of the host-guest cross-linking between the DB24C8

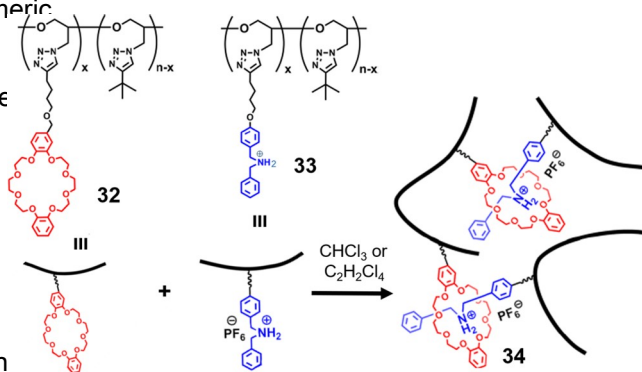


Figure 12. Schematic views of the DB24C8-containing polymer 32, the DBAS-containing polymer 33, and the SPN 34 they can be used to create. Reproduced with permission from ref 190. Copyright 2013 American Chemical Society.



and DBAS subunits. The estimated number of effective cross-links led the authors to suggest that not all of the binding sites function as cross-links. Nevertheless, gel 34 displayed high elasticity, a finding ascribed to the constituent high-molecular-weight flexible glycidyl polymers 32 and 33 with many binding sites and the dynamic nature of the supramolecular cross-links. Gel 34 was also found to respond to a variety of chemical stimuli and display self-healing features. Furthermore, fluorescence correlation spectroscopic analyses showed that within gel 34, the diffusion coefficient of a low-molecular-weight fluorescence tracer is near to that in an ostensibly analogous covalently linked gel.

### 2.3. Dibenzo-24-Crown-8/Pyridinium-Modified Cyclic Tertiary Ammonium Salt Recognition Motifs

The majority of SPNs based on covalent polymers and host-guest interactions reported to date have been prepared by cross-linking polymers bearing host or guest units as appended side groups. The use of polymers with host or guest units within the main chain provides a different strategy to fabricate SPNs. Tiburcio and co-workers reported that the complementary ditopic PCTAS guest 35 could be used in conjunction with the DB24C8-containing polymer 36 to produce SPN 37.<sup>191</sup> As shown in Figure 13, predicative studies revealed that the

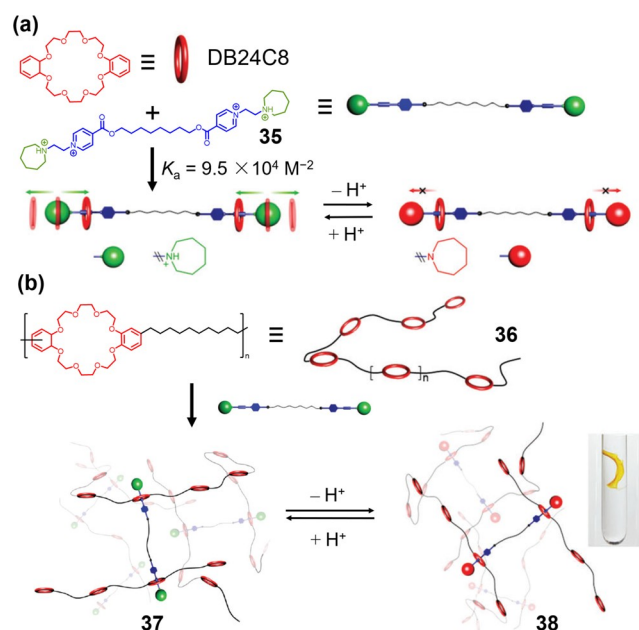


Figure 13. (a) Chemical structures of guest 35 and its deprotonated form. Also shown are schematic views of the transformation between the [3]pseudorotaxane and [3]rotaxane species produced from DB24C8 and 35. (b) Chemical structure of polymer 36 and schematic representations of SPNs 37 and 38. Reproduced with permission from ref 191. Copyright 2016 The Royal Society of Chemistry.

DB24C8 host can accommodate PCTAS guest 35 with an association constant,  $K_a$ , of  $9.5 \times 10^4 \text{ M}^{-2}$  in nitromethane to form a [3]pseudorotaxane. After deprotonation, this [3]pseudorotaxane transformed into a mechanically interlocked [3]rotaxane. This basic host-guest interaction, allowed SPN 37 to be produced by mixing the DB24C8-containing polymer 36 with the PCTAS dimer 35 in nitromethane. SPN 37 showed good solvent and temperature responsiveness when studied in solution or as gels and films. Deprotonation of 35 served to convert SPN 37 into the corresponding mechanically locked

SPN 38. The authors thus proposed that SPN 37 could be protected from external stimuli by mechanically locking its structure through rotaxane formation.

### 2.4. Comparisons between Supramolecular Polymeric Networks Constructed by Crown Ether-Based Host-Guest Recognition Motifs

To date, PS and polyacrylate (PA) have been the most widely used covalent polymeric backbones for SPN preparation. This has permitted a number of molecular designs to be tested with the resulting functions deriving not just from the host-guest interactions but also from the underlying polymer backbones. It has also allowed differences resulting from the specific backbone choice to be inferred. Some of the key features of crown ether-based SPNs, which in aggregate permit this kind of analysis, are summarized in Table 1.

## 8. SUPRAMOLECULAR POLYMERIC NETWORKS CONSTRUCTED VIA THE COMBINATION OF COVALENT POLYMERS AND CYCLODEXTRIN-BASED HOST-GUEST INTERACTIONS

CDs, cyclic oligosaccharides, are arguably the most widely used water-soluble hosts.<sup>192–196</sup> CDs containing between 6 and 8 glucose units are readily available. These CDs are toroidal in shape and possess both hydrophilic exteriors and relatively hydrophobic cavities. They have been demonstrated as binding guests containing a variety of functional groups, including Azo,<sup>197–200</sup> polyethylene glycol (PEG),<sup>201,202</sup> polypropylene glycol (PPG),<sup>203</sup> reduced methylogelogen (MV),<sup>204</sup> adamantane (Ad),<sup>205,206</sup> ferrocene (Fc),<sup>207,208</sup> cholesterol,<sup>209,210</sup> cholic acid,<sup>211</sup> dansyl,<sup>212</sup> phenolphthalein,<sup>213</sup> NIPAM,<sup>214</sup> and tetraaniline<sup>215</sup> functionalities (Figure 14). The resulting host-guest systems provide excellent platforms for constructing a range of supramolecular polymeric materials in aqueous media.<sup>87,92,188,194,198,216–234</sup> Differences in the stimuli-responsive properties of the underlying host-guest recognition motifs endow the resulting supramolecular polymeric materials with versatility in terms of their external stimuli-responsiveness; this feature, in turn, has made these systems of interest across a number of fields.<sup>194,197,206,225–233</sup> Representative SPNs that contain covalent polymeric backbones and which exploit CD-based host-guest interactions are highlighted in this section. Some of the rationales underlying their preparation are also discussed.

### 3.1. $\alpha$ -Cyclodextrin/Azobenzene Host-Guest Recognition Motifs

The sliding motion of myosin and actin filaments has inspired the development of artificial molecular muscles.<sup>133</sup> Linked constructs with built-in host-guest subunits that can self-assemble to form so-called [c2]daisy chains have emerged as useful building blocks for the fabrication of artificial molecular muscles because they often display sliding actuation that can be controlled by different stimuli.<sup>234–237</sup> Harada and co-workers reported photo-responsive wet- and dry-type molecular actuators, hydrogels and xerogels, respectively, comprising [c2]daisy chains based on the  $\alpha$ -CD/Azo recognition motif.<sup>238</sup> As shown in Figure 15, actuators 39 and 40 (one to be produced by mixing the DB24C8-containing polymer 36 with the PCTAS dimer 35 in nitromethane) were prepared based on an  $\alpha$ -CD/Azo [c2]daisy chain strategy. Light-induced actuation, leading to sliding motion within the [c2]daisy chain, allowed transformation between the limiting forms 39 and 40. The hydrogel/xerogel 41 was then obtained in aqueous solution by

Table 1. SPNs Based on Crown Ether-Based Host–Guest Recognition Motifs Classified by the Underlying Covalent Polymers

molecular recognition figure number	cross-linking motif	SPN	ref
Polystyrene (PS)			
B21C7/DAAS	Figure 2 B21C7-based [2]catenane 1 with DAAS-decorated PS polymer 2	3	137
	Figure 3 B21C7-grafted PMA 4 with DAAS-containing PS 5	6	145
	Figure 4 DAN- and DAAS-containing PS polymer 7 and DeUG- and B21C7-decorating PBMA polymer 8	11	154
	Figure 5 DAAS-containing PS 5 with TPE-based B21C7 tetramer 12	13	159
	Figure 10 DBAS- and coumarin-containing PS polymer 23 with DB24C8 dimer 25	26	184
Polyacrylate (PA)			
B21C7/DAAS	Figure 3 B21C7-grafted PMA 4 with DAAS-containing PS 5	6	145
	Figure 4 DAN- and DAAS-containing PS polymer 7 and DeUG- and B21C7-decorating PBMA polymer 8	11	154
DB24C8/DBAS	Figure 7 RC 17 with BA or EHA after polymerization	18	174
	Figure 8 RC 17 with BA and MMA after polymerization	19	178
	Figure 9 DBAS-containing PEA-based copolymer 20 with homoditopic DB24C8 dimer 21	22	183
	Figure 11a DB24CB-based dimer hosts 27 with DBAS-containing PMA copolymer 29-1	30	186
	Figure 11b DB24CB-based dimer hosts 28 with DBAS-containing PEA copolymer 29-2	31	187

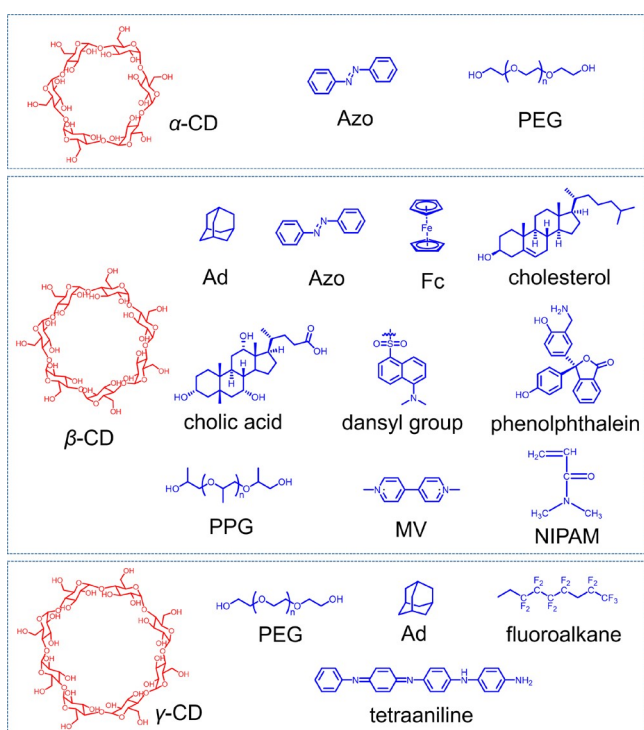


Figure 14. Chemical structures of CDs and various guests.

the polycondensation reaction between 39 and succinimidyl ester group-modified TetraPEG. Similarly, UV light irradiation was found to induce molecular motion and cause the hydrogel xerogel 41 to bend toward the light source. The xerogel form, which was obtained under dry conditions, was found to convert very quickly (bending 7°/sec); this motion was ca. 10 800 times faster than what was seen for the hydrogel (7° over the course of 3 h). These researchers also noted that the xerogel form could be used as a crane arm to lift an object under conditions of UV light irradiation, thus demonstrating an ability to carry out mechanical work.

Harada and co-workers also exploited the α-CD/Azo recognition motif to create a photo-responsive topologically cross-linked polymer hydrogel actuator based on a [2]-rotaxane.<sup>239</sup> As shown in Figure 16, the lysine-modified α-CD 42 and the Azo-containing guest 43 form the [2]pseudorotaxane 44 with a  $K_d$  value of  $(8.7 \pm 1.7) \times 10^{-4} \text{ M}^{-1}$  in water. Adding a

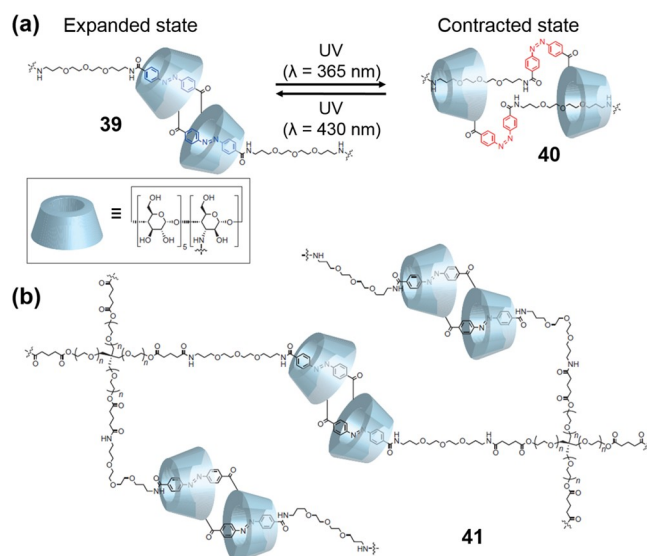


Figure 15. (a) Chemical structures and photoisomerization scheme for actuators 39 and 40 (one compound; two limiting forms). (b) Chemical structure of hydrogel/xerogel 41 that is based on a four-armed polyethylene glycol (PEG) core. Reproduced with permission from ref 238. Copyright 2016 Springer Nature.

succinimidyl-modified PEG and lutidine to 44 was found to produce the self-standing poly([2]rotaxane) hydrogel. In this latter construction, the lysine-modified α-CD units connected to the PEG chains serve not only to thread the rings but also as end-capping moieties. Hydrogel 45 exhibited excellent extension capability as revealed by tensile experiments. Presumably, this extension ability reflects the stress distribution provided by sliding motions within the rotaxane-containing cross-links. Hydrogel 45 could be reversibly converted into a deformed state (denoted as 46) in aqueous media by alternatively irradiating with UV and visible light. Interestingly, the dried material (xerogel form) showed a faster response than the hydrogel. The xerogel could be stretched and the resulting material was found to bend toward a light source upon irradiation with UV light. Thus, as true for 41, the xerogel derived from 45 could be used to convert formally light energy into mechanical work.

Photo-responsive hydrogels have seen application in a number of areas, such as drug delivery, shape retaining memory

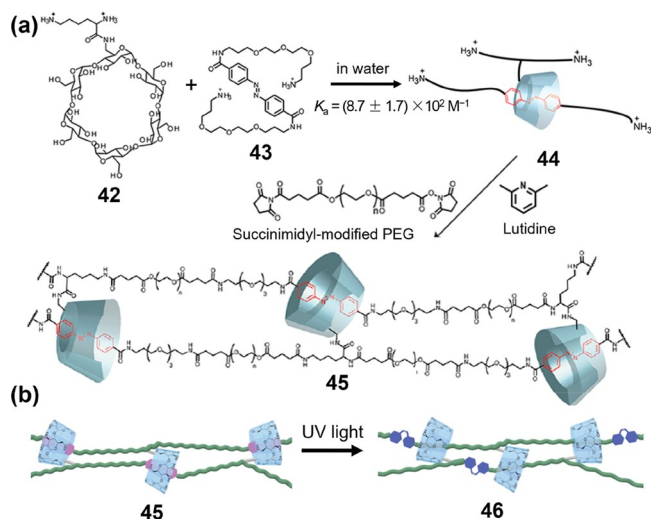


Figure 16. Chemical structures of the host 42, guest 43, pseudorotaxane 44 and the rotaxane-containing cross-linked SPN 45. (b) Schematic illustration of the photo-induced transition from 45 to a deformed state 46. Reproduced with permission from ref 249. Copyright 2018 American Chemical Society.

materials development and analyte detection, due to the particular advantages afforded associated with using light as a stimulus.<sup>19,240–242</sup> However, the specific use of light to mediate the conductivity of hydrogels by modulating ionic migration remains a challenge. This is particularly true in the absence of additional additives. In an effort to address this challenge, Harada and co-workers developed an ion-conducting supramolecular

hydrogel with reversible photoconductive properties. This was done by incorporating Azo-containing substituents,  $\alpha$ -CD moieties, and an ionic liquid-like imidazolium salt within a hydrogel matrix.<sup>243</sup> As shown in Figure 17, this hydrogel 50 and 51; same bulk material but different forms could be prepared from the  $\alpha$ -CD, Azo, and imidazolium monomers 47–49. The mobile ions of the ionic liquid-like species in 49 form a weaker host–guest complex with  $\alpha$ -CD than does the trans form of the Azo derivative. As a consequence, photo-induced trans–cis isomerization of the Azo subunit serves to switch the host–guest interactions. This isomerization process affects the concentration of mobile (free) anions and the effective conductivity of the hydrogel. The net result is a light-mediated reversible transformation between 50 and 51. These define the low- and high-resistance states of the hydrogel, respectively. Hydrogel 50 was used to construct a logic gate that can be used to switch remotely and reversibly an electric circuit either on or off via light irradiation. As shown in Figure 17, there are two limiting pathways within this construct. When the hydrogel is in its low-resistance form, 50, a high voltage serves to switch on the green light through the green-light logic circuit. In contrast, when the hydrogel is in its high-resistance form, 51, application of a low voltage serves to illuminate the red light through the corresponding red-light logic circuit.

### 3.2. $\alpha$ -Cyclodextrin/Polyethylene Glycol Host–Guest Recognition Motifs

PEG chains can typically thread CD rings to form polyrotaxanes. When the CD rings are covalently bonded to polymer chains, this threading may be used to create polymeric networks wherein free movement along the PEG chains is retained. This feature, in turn, results in the presence of multiple pulley-like motifs that serve to lower external tension exerted on the

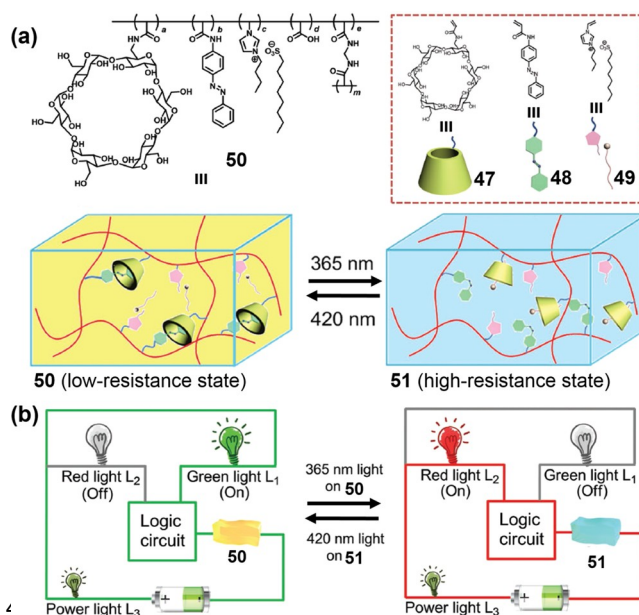


Figure 17. (a) Chemical structures and schematic representations of monomers 47, 48, and 49, as well as hydrogels 50 and 51. Also shown is a diagram highlighting the guest exchange that can be induced within hydrogel 50 under conditions of 365 or 420 nm photo-irradiation. (b) Schematic illustrating the incorporation of hydrogels 50 and 51 in a logic gate circuit and reversible switching on and off of red or green lights upon photo-illumination with 365 or 420 nm light, respectively. Reproduced with permission from ref 243. Copyright 2019 John Wiley and Sons.

polymer. Choi and co-workers demonstrated the utility of their  $\alpha$ -CD/PEG polyrotaxane constructs by preparing silicon microparticle (SiMP) anodes.<sup>244</sup> As shown in Figure 18, polyacrylic acid (PAA) was modified with  $\alpha$ -CD to form the  $\alpha$ -CD-containing PA 52. In conjunction with the PEG derivative 53, PA 52 was found to impart extraordinary stretchability and elasticity to the resulting polyrotaxane-cross-linked SPN 54. This approach was found to overcome the volume expansion-related problems that would otherwise be expected to be seen for SiMP anodes when subject to repeated charge–discharge cycles. As a result, even pulverized Si particles remain coalesced and do not disintegrate during repeated charge–discharge cycles due to the sliding of the  $\alpha$ -CD within the polyrotaxane. In contrast, a simple linear PAA binder without the polyrotaxanes derived from 52 and 53 was found to produce patchy solid electrolyte interphase (SEI) layers during use. This linear binder was considered suboptimal because it did not perform as well as the polyrotaxane binder.

As noted previously, self-healing is an important feature of many biological and artificial materials.<sup>179,245–248</sup> There are four approaches that have been used to design and prepare self-healing materials:<sup>11,245</sup> (1) using encapsulated-monomer approach,<sup>249,250</sup> (2) exploiting irreversible bonds,<sup>251</sup> (3) making use of reversible dynamic covalent bond formation;<sup>247</sup> and (4) taking advantage of supramolecular interactions.<sup>252,253</sup>

Supramolecular approaches and dynamic covalent bond formation have been exploited by Harada and co-workers to create hydrogels capable of self-healing in both the wet and semi-dry states.<sup>254</sup> Specifically, these researchers reported a self-healing SPN constructed from a  $\alpha$ -CD/PEG polyrotaxane and a poly(AAM-co-4-vinylphenylboronic acid) polymeric chain cross-linked with boronate linkages. As shown in Figure 19,



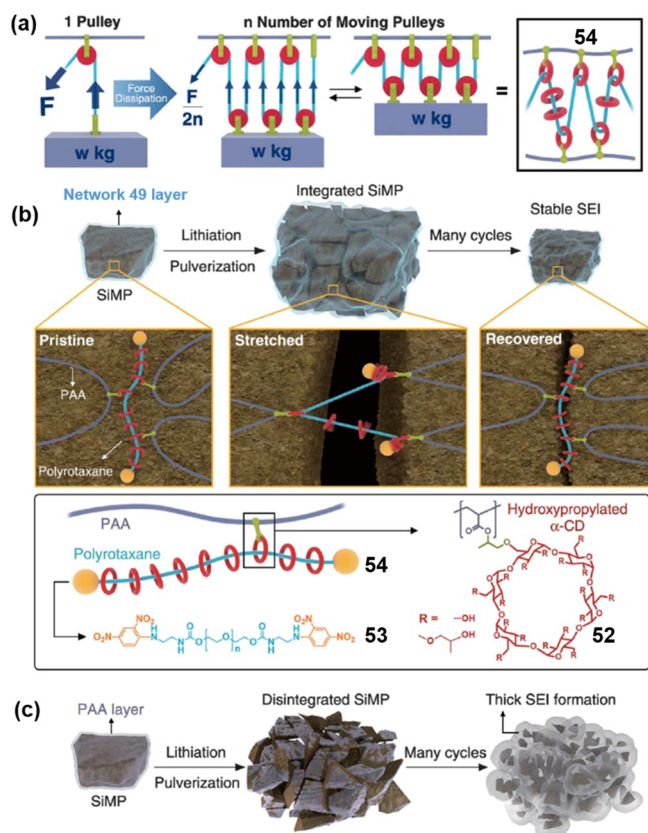


Figure 18. Proposed stress dissipation mechanism for SiMP anodes bearing polyrotaxane 54. (a) Illustration of the pulley principle used to facilitate the lifting of an object. (b) Graphical representation of how SiMPs serve to dissipate stress during repeated volume changes. Also shown are the chemical structures of PAA and the constituent threading and ring species, 52 and 53. (c) Schematic illustration of the pulverization of the PAA-SiMP electrode seen during cycling and layer growth. Reproduced with permission from ref 244. Copyright 2017 The American Association for the Advancement of Science.

the polyrotaxane 55 could be prepared wherein a 2-hydroxypropyl-modified  $\alpha$ -CD provides the wheels, PEG chains act as the axles, and the Ad groups serve as the stoppers. Dynamic covalent bonds between the boronic acid and the diol components then led to formation of gel 56. To allow for effective comparisons, several control polymers were prepared. These included three gels, gel 57, which consisted of polyrotaxane 55 and a poly(AAM-co-acrylate) copolymer cross-linked by covalent bonds, gel 59 consisting of the polysaccharide 58 cross-linked by dynamic boronate linkages, and gel 59a covalently cross-linked version of 59 inferred from mechanical property tests, the relaxation time of the polymer networks within gel 56 is longer than those of the comparison samples. Gel 56 was found to exhibit 100% self-healing in the gel state. Moreover, films made from gel 56 showed efficient self-healing in the semi-dry state. In contrast, the control samples, including the covalently bonded gels 57 and 60, proved incapable of self-healing when studied as gels. Gel 57a showed insufficient self-healing as films and 60 showed no self-healing as films. In the case of the dynamic covalently linked gel 59 only ~20% healing was observed in the gel state and insufficient healing was seen in the film state. Self-healing property of 56 was ascribed to two factors. One was the mobility of the  $\alpha$ -CD wheels along the axle in polyrotaxane 55; the other

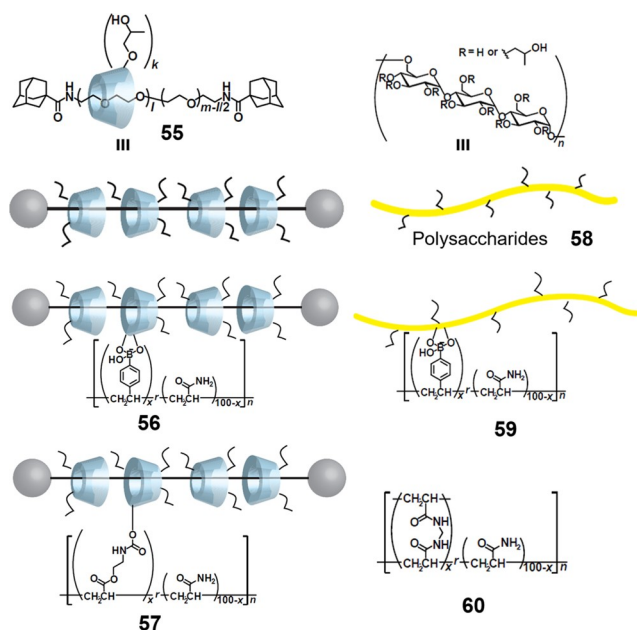


Figure 19. Schematic representation of polyrotaxane-linked polymers: polyrotaxane 56 incorporating dynamic covalent bonds, polyrotaxane 57 containing covalent bonds, polysaccharide 58, dynamic covalent cross-linked polymer 59, and covalent polymer 60. Reproduced with permission from ref 245. Copyright 2016 Elsevier.

was the dynamic interactions between the phenylboronic units within 56 and the hydroxyl groups on 55.

The high swelling and stress-relaxing features of RCPs have made them attractive for use as inter alia SiMP node binders and self-healing coatings.<sup>244,254</sup> CD-based rotaxanes, which have the advantage of being easily prepared in water,<sup>255,256</sup> are convenient building blocks to construct RCPs. Kata and co-workers reported two SPNs constructed from  $\alpha$ -CD dimer- and trimer-based rotaxanes. As shown in Figure 20, the  $\alpha$ -CD dimer 61 and trimer 62 were threaded by methacrylate-type PEG-based macromonomers 63 to form the vinylic supramolecular cross-linkers 64 and 65, respectively, in 0.1 M NaOH. RCPs 66 and 67 were then obtained via the photo-induced radical polymerization of N,N-dimethylacrylamide (DMAAM) with cross-linkers 64 and 65, respectively, in 0.1 M NaOH. The swelling ratios of RCPs 66 and 67 in water and organic solvents was affected by the size of the vinylic supramolecular cross-linkers. At low concentrations of 64 and 65, small cross-linkers were formed. This resulted in a lower cross-link density and a higher swelling ratio. In contrast, at higher concentrations of 64 and 65, higher cross-link densities and lower swelling ratios were observed.

### 3.3. $\beta$ -Cyclodextrin/Adamantane Host-Guest Recognition Motifs

Harada and co-workers reported a hydrogel material cross-linked by  $\beta$ -CD/Ad host-guest interactions, and demonstrated its potential for regulating in dynamic fashion cell-substrate interactions.<sup>258</sup> As shown in Figure 21, the side chains of  $\gamma$ -amino acid (AAM) monomers were modified with  $\beta$ -CD host and an Ad guest to form monomers 68 and 69, respectively. Monomers 68 and 69 were mixed in water at 90 °C for 3–4 h. After cooling, the host-guest complex 70 formed. By optimizing the ratio between the monomers, namely pure AAM (matrix) monomers 68 and 69, it proved possible to create a cross-linked hydrogel, 71, after UV irradiation-induced polymerization using

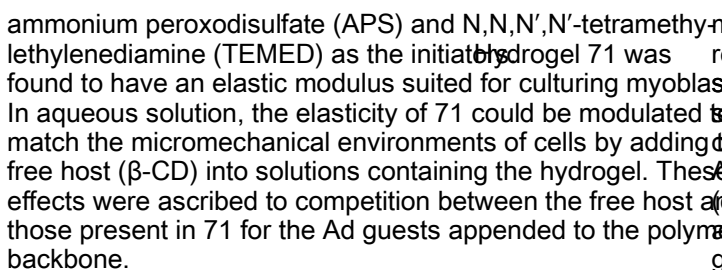


Figure 22. (a) Chemical structures of gels 72, 73, 74, and 75. (b) Schematic illustration of the adhesion between gels 72 and 73 that stabilizes gel 76. Reproduced with permission from ref 262. Copyright 2015 American Chemical Society.

Aggregate-based self-assembled polymers driven by supramolecular interactions have attracted considerable interest in recent decades.<sup>27,84,263–265</sup> Polyphosphazenes, which possess a backbone of alternating phosphorus and nitrogen atoms with two side groups linked to each phosphorus, are a unique class of organic-inorganic hybrid polymers of interest in this context.<sup>266</sup> Allcock and co-workers reported the self-assembly of poly(organophosphazene) structures based on host-guest interactions between  $\beta$ -CD and Ad.<sup>267</sup> As shown in Figure 2A, Ad groups were attached to the main-chain terminus of



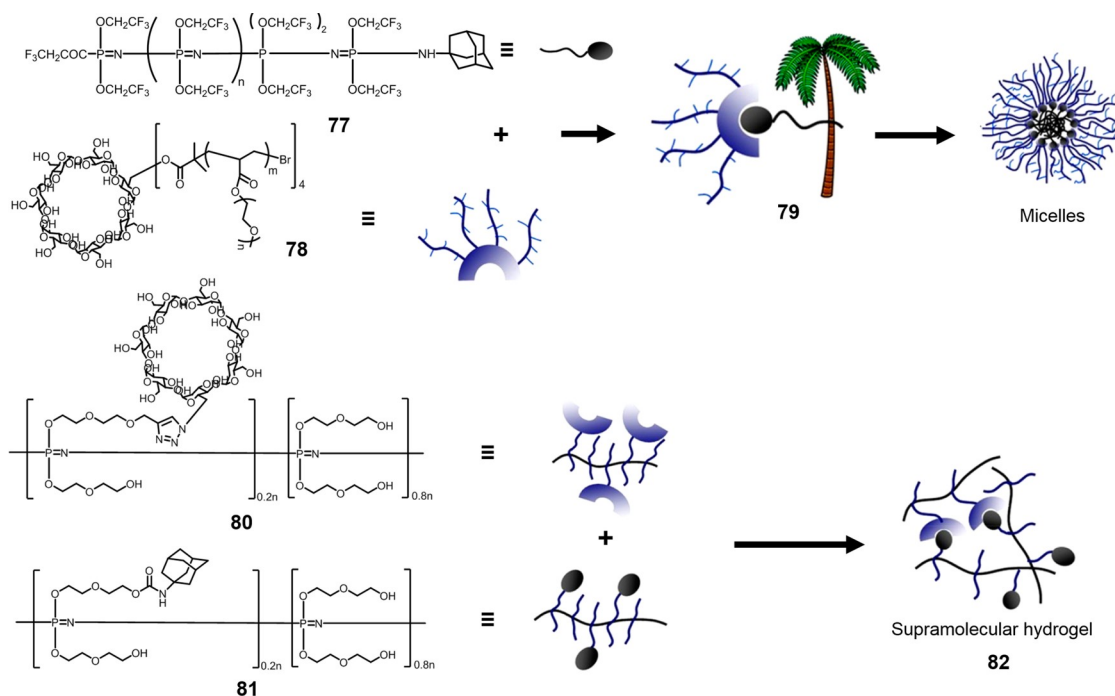


Figure 23. Chemical structures of polymers 77, 80, and 81. Also shown in schematic form are the amphiphilic palm tree-like pseudo-block copolymer 79, the self-assembled micelles it supports, and the supramolecular gel 82 produced from 80 and 81. Reproduced with permission 267. Copyright 2014 American Chemical Society.

polyphosphazene to give the hydrophobic polymer 77. After mixing with the hydrophilic branched star polymer 78 bearing  $\beta$ -CD end groups, the amphiphilic palm-tree-like pseudo-block copolymer 79 was formed. Amphiphilic copolymer 79 was found to self-assemble into micelles in water.  $\beta$ -CD and Ad were also linked to the side chains of the polyphosphazenes to create polymers 80 and 81, respectively. The supramolecular cross-linked gel 82 was then obtained as the result of host-guest interactions. Both this gel and the self-assembled micelles formed from 79 were found to dissociate when treated with  $\beta$ -CD.

Many biomaterials are complex composites assembled from weakly associated components. Often these materials display unique mechanical properties. This continues to inspire the design and preparation of synthetic functional materials. In fact, intrigued by animal muscles, which are both mechanically robust and stretchable materials with self-healing capacity, Zhang and co-workers prepared a tough self-healing elastomer based on  $\beta$ -CD/Ad host-guest interactions. As shown in Figure 24, ( $\pm$ )-epichlorohydrin cross-linked poly( $\beta$ -CD) 83 and hydroxyethyl methacrylate (HEMA)-modified Ad 84 could be mixed to form the host-guest complex 85. Polymerization of the presence of  $\alpha$ -hydroxyethylacrylate (HEA) then gave the double network elastomer 86. The first network within 86 is a classic elastomer matrix, namely poly(HEMA-co-HEA), cross-linked by strong hydrogen bonding. The second network is based on the host-guest interactions between Ad and 83 with the copolymer. The resulting double network elastomer 86 displayed high strength and elasticity. In addition, when cut or broken, elastomer 86 was found to self-heal under ambient conditions.

Injectable hydrogels are promising materials for biomedical applications such as tissue engineering and drug delivery. Interest in such systems reflects their multiple advantages, including biocompatibility, controllable degradation, and tunable

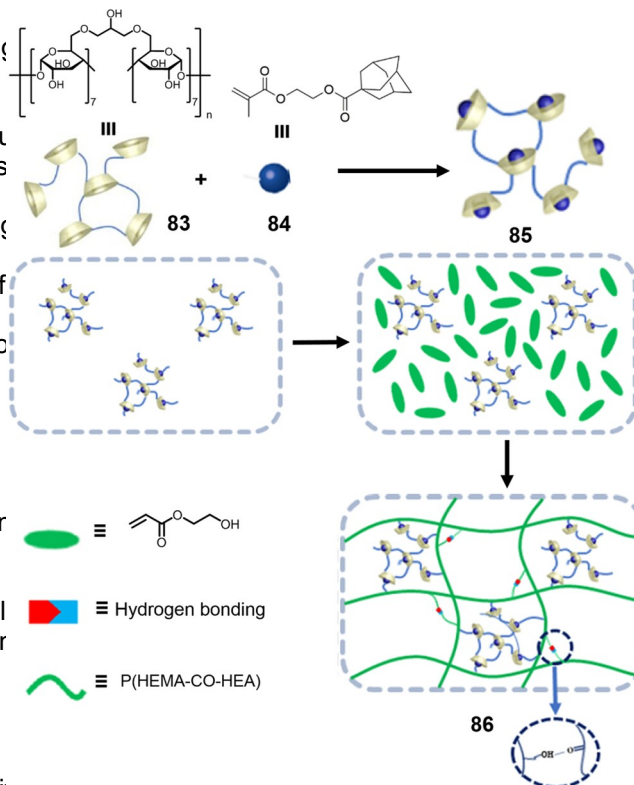


Figure 24. Structures of poly( $\beta$ -CD) 83 and HEMA-modified Ad 84. Also shown in schematic form is the host-guest complex 85 formed from 83 and 84 as well as the double network 86 produced through these interactions in conjunction with hydrogen bonding. Reproduced with permission from ref 270. Copyright 2019 American Chemical Society.



mechanical properties, environmental responsiveness, high water content, and minimal propensity to migrate into or “invade” surrounding tissues.<sup>271,272</sup> Hydrogels that can be made less viscous as the result of so-called shear-thinning but the heal upon removal of the shear stress are particularly attractive for biomedical applications. This is because they may be injected easily but then regain a more robust form.<sup>273</sup> Park and co-workers reported an injectable shear-thinning hydrogel with improved mechanical strength based on  $\beta$ -CD/Ad host-guest recognition and thermo-gelling at 37 °C.<sup>274</sup> As shown in Figure 25, the tetronic-Ad conjugate 87 was found to self-assemble

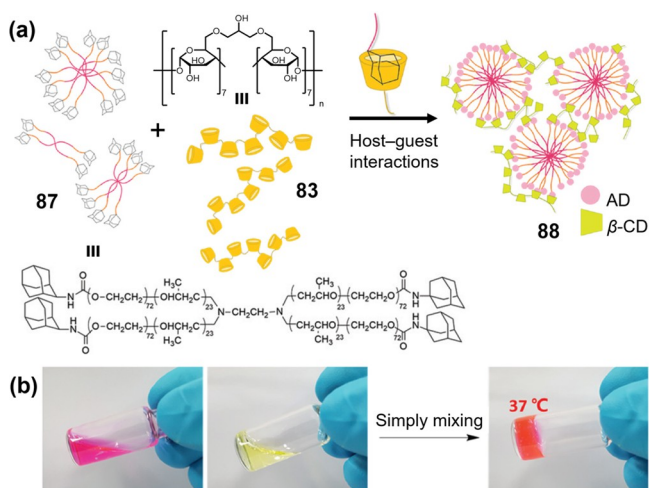


Figure 25. (a) Schematic illustration showing the formation of hydrogel 88 produced from the combination of the tetronic-Ad conjugate 87 and poly( $\beta$ -CD) 83. (b) Vial tilting test involving 87 at 20 wt% (left), 83 at 20 wt% (middle), and hydrogel 88 (right). Reproduced with permission from ref 274. Copyright 2019 The Royal Society of Chemistry.

micelles at 37 °C. These micelles could be cross-linked by treating with poly( $\beta$ -CD) 83 to form the injectable shear-thinning hydrogel 88. A vial tilting test revealed that both 87 and 83 were flowable liquids, whereas hydrogel 88 was a stable gel. However, gel 88 displayed both useful shear-thinning behavior and rapid recovery property. In addition, it was injectable into Dulbecco's phosphate-buffered saline (DPBS) at 37 °C using a 26G needle. It also allowed for the pH-responsive release of doxorubicin hydrochloride (DOX). In addition, the hydrogel system showed biocompatibility and DOX released from the gel exhibited an anticancer effect.

Other attributes of hydrogels, including their excellent biocompatibility, degradability, cellular response ability to interact with biological scaffolds, and low immune rejection rates make them attractive as biomaterials for tissue engineering.<sup>275,276</sup> However, disadvantages of classic hydrogels, as low mechanical strength, low stability, lack of self-healing, and poor 3D-printability have hindered their development in this context.<sup>277</sup> To advance the potential application of hydrogels in tissue engineering, Shi and co-workers developed a 3D-printable, self-healing, and mechanically reinforced hydrogel that contains both non-covalent and covalent networks.<sup>278</sup> As shown in Figure 26, the Ad-modified acryloylated tetraethylene glycol 89 and the  $\beta$ -CD-functionalized 2-isocyanatoethyl acrylate 90 could be mixed to form a three-armed host-guest complex 91. After UV light-induced polymerization with methacryloyl gelatin using 2-hydroxy-4'-(2-hydroxyethoxy)-2-

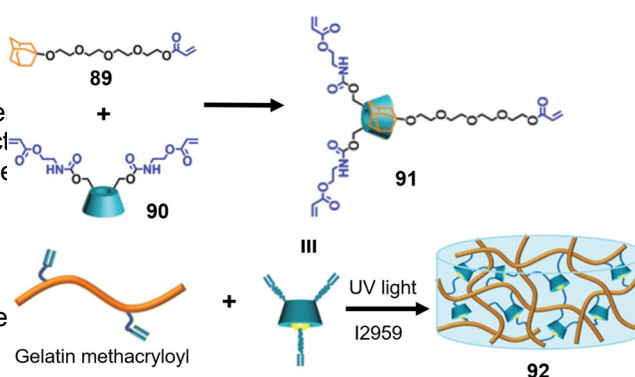


Figure 26. Structures of the Ad-modified acryloylated tetra-ethylene glycol 89,  $\beta$ -CD-functionalized 2-isocyanatoethyl acrylate 90, and the host-guest complex 91 formed upon their mixing. Also shown is a schematic illustration of the cross-linked hydrogel network 92 formed from 91 upon polymerizing in the presence of a gelatin methacryloyl precursor. Reproduced with permission from ref 278. Copyright 2019 The Royal Society of Chemistry.

methylpropiophenone (12959) as the initiator, a double-networked hydrogel (92) was obtained. Hydrogel 92 is stabilized in part through non-covalent  $\beta$ -CD/Ad host-guest interactions that allow for self-healing as well as through covalent bonds, which serve to maintain the shape of the hydrogel. In fact, hydrogel 92 proved robust and displayed good elasticity, fatigue resistance, and reproducible self-healing features. The compression modulus of 92 was found to be 525% larger than that of pure gelatin methacryloyl hydrogel, thus reaching the level of most human soft tissues. Hydrogel 92 could also be used to print 3D scaffolds with homogeneous porous structures that displayed good biocompatibility and histocompatibility.

The non-covalent interactions that underlie dynamic polymers, assemblies, and networks<sup>278,279</sup> tend to create materials with heterogeneity that can support formation of adaptive and evolved structures.<sup>280</sup> In the case of hydrogels, heterogeneity may influence their efficiency in the context of, for example, their drug release profiles and interactions with cells.<sup>281</sup> Therefore, efforts are being devoted to bridging the knowledge gap between polymeric self-assembly and the resulting supramolecular microstructures as an important step along these lines was taken by Burdick and co-workers, who reported the evolution of heterogeneity in supramolecular hydrogels formed through  $\beta$ -CD/Ad host-guest interactions. In this study  $\beta$ -CD and Ad groups were linked to the side chains of hyaluronic acid to form polymers 93 and 94, respectively (Figure 27). Upon mixing, the cross-linked hydrogel 95 was obtained. In time, hierarchical assembly occurs to produce highly porous microstructures. Micromechanical analyses revealed that the pores contained only low concentrations of dissociated polymers, presumably as the result of stochastic erosion without formation of a solid hydrogel. The porosity was seen to evolve in temporal fashion to give materials with both greater void fractions (up to  $93.3 \pm 2.4\%$ ) and pore diameters that were increased by up to 3 orders of magnitude. This tunability led to suggestions that these scaffolds might be of interest in the context of cellular studies and potential biomedical applications.

### 3.4. $\beta$ -Cyclodextrin/Azobenzene Host-Guest Recognition Motifs

The network properties of supramolecular hydrogels and biomaterials can be manipulated by a number of strategies

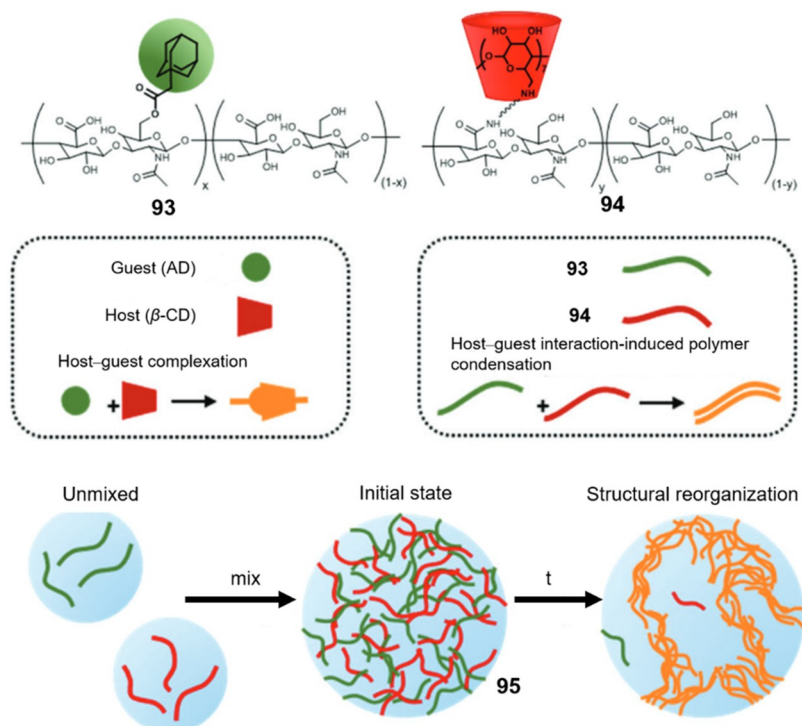


Figure 27. Polymer structure and self-assembly. (a) Chemical structures of the component polymers 93 and 94. (b) Schematic illustration of host-guest hydrogelation and temporal evolution leading to hierarchical organization at the molecular, polymeric and micro scales. Reproduced with permission from ref 282. Copyright 2016 The Royal Society of Chemistry.

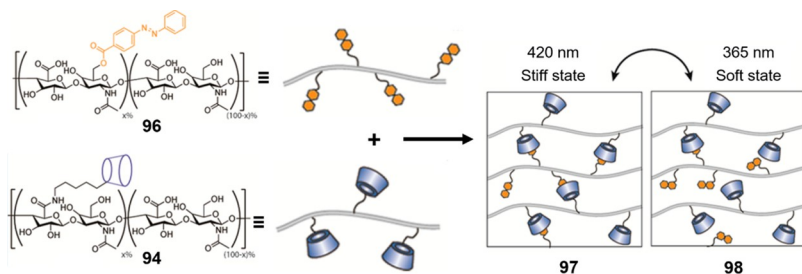


Figure 28. Chemical structures of polymers 94 and 96 and schematic illustration of light-controlled supramolecular hydrogelation and its corresponding soft state. Reproduced with permission from ref 287. Copyright 2018 American Chemical Society.

that exploit the dynamic nature of the underlying non-covalent interactions.<sup>283</sup> Among the stimuli used to modulate the properties of hydrogels, light has a particular appeal because of its inherent cleanliness and ease of energetic tuning; the general rapidity of the response it engenders; and the high degree of spatiotemporal control it permits.<sup>284–286</sup> Rosales and co-workers illustrated some of these advantages by using light to effect reversible control over the network properties of hydrogels based on β-CD/Azo host-guest interactions.<sup>287</sup> Here, the β-CD-containing hyaluronic acid 94 and the Azo-containing hyaluronic acid 96 were mixed to form the supramolecular hydrogel 97 as shown in Figure 28. This supramolecular assembly occurs under physiological conditions, even in the presence of cells. Upon irradiation with light at 365 nm and 400–500 nm, the β-CD/Azo binding interactions disassociate and reforms, respectively; presumably, these changes reflect isomerization of the Azo moiety between its trans and cis states. This, in turn, results in a change in the network connectivity.

Specifically, toggling between a stiff state 97 and a soft state (denoted as 98) could be achieved. This hydrogel proved useful after the introduction of late because of their wide applications in many in effecting the light-induced controlled release of a fluorescent entity.<sup>446,240,289</sup>

labeled protein under conditions compatible with cell studies. Zhao and co-workers reported a light-switchable self-healing hydrogel obtained by cross-linking AAM with a β-CD/Azo host-guest macro-cross-linker as shown in Figure 29, AAM-modified Azo 99 in conjunction with the poly(β-CD) 83 produced the host-guest macro-cross-linker 100. After polymerization of 100 and AAM in water containing APS at 60 °C for 6 h, the cross-linked hydrogel 101 was obtained. Due to the light-responsive nature of the β-CD/Azo host-guest interactions, the rheological property of hydrogel 101 could be tuned by means of a light stimulus. As the result, this hydrogel demonstrated self-healing features that could be switched off upon irradiation with UV light, and switched back on by means of visible light irradiation.

### 3.5 β-Cyclodextrin/Ferrocene Host-Guest Recognition Motifs

Stimuli-responsive hydrogels have attracted considerable attention after the introduction of late because of their wide applications in many in effecting the light-induced controlled release of a fluorescent entity.<sup>446,240,289</sup>

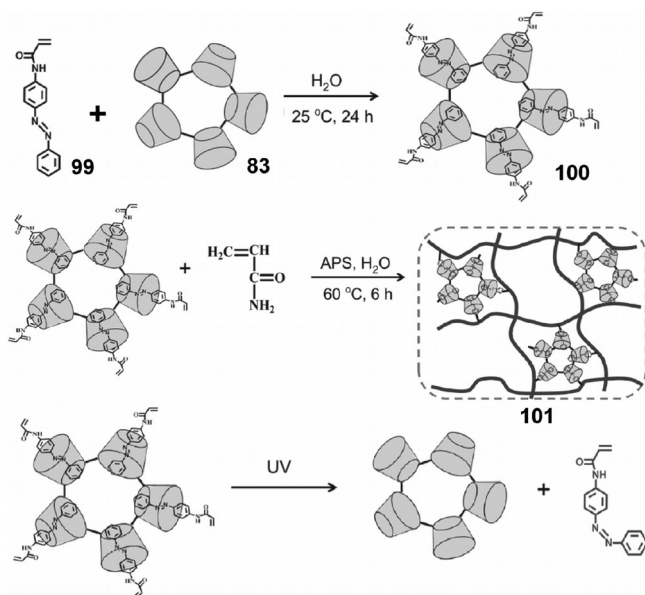


Figure 29. Chemical structures of AAM-modified Azo 99 and host 83. Also shown in schematic form is the light-switchable self-healing expected for hydrogel 101 and the light-responsiveness of the host-guest macro-cross-linker 100. Reproduced with permission from ref 288. Copyright 2017 John Wiley and Sons.

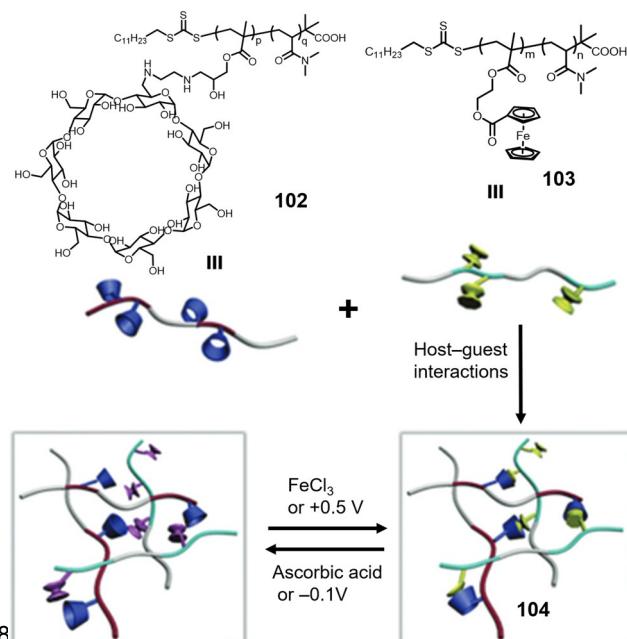


Figure 30. Chemical structures of  $\beta$ -CD-containing copolymer 102, Fc-containing copolymer 103, and the supramolecular hydrogel 104 formed by mixing these components. Also shown in schematic form is the electrochemical redox responsiveness expected for hydrogel 104. Reproduced with permission from ref 289. Copyright 2015 The Royal Society of Chemistry.

feature of many of these systems and makes them of interest in the context of several biomedical fields. Electrochemical-based redox changes represent a mild stimulus that can often be applied without changing the chemical composition of the systems. Yuan and co-workers reported an electrochemical redox-responsive supramolecular self-healing hydrogel based on the  $\beta$ -CD/Fc host-guest recognition motif. Specifically, as shown in Figure 30, the random copolymers, poly(DMAAM-*r*-glycidol MA- $\beta$ -CD) 102 and poly(DMAAM-*r*-HEMA-Fc) 103, were prepared. In these two polymers, DMAAM was used to improve the solubility, whereas  $\beta$ -CD and Fc units were used to modify the glycidol MA and HEMA polymers, respectively. After mixing these components, a cross-linked supramolecular hydrogel 104 was formed that is presumably stabilized by host-guest interactions between the  $\beta$ -CD and Fc subunits. The latter moieties respond to changes in the redox potential. As a consequence, applying alternatively either a positive or negative potential to hydrogel 104 was found to engender reversible sol transitions. Chemical oxidants and reductants could also be used. In addition, cytotoxicity experiments provide support for the notion that hydrogel 104 would display good biocompatibility.

Electrically responsive self-healing polymers are attractive stimulus-modulated materials. Their appeal stems in part from the fact that electrical fields may be easily and quickly applied over large surface areas.<sup>291</sup> Liu and co-workers reported that a multifunctional Fc-modified poly(glycidyl MA) 105 and a difunctional  $\beta$ -CD derivative 106 formed a self-healing polymeric network 107 that was expected to be redox active (Figure 31).<sup>292</sup> In fact, SPN 107 displayed electrically driven self-healing behavior that could be promoted by increasing the electrical conductivity by wetting the sample. SPN 107 was deemed attractive in the context of commercial painting since it was found to undergo highly efficient self-healing when subjected to deep cuts or widespread scraping.

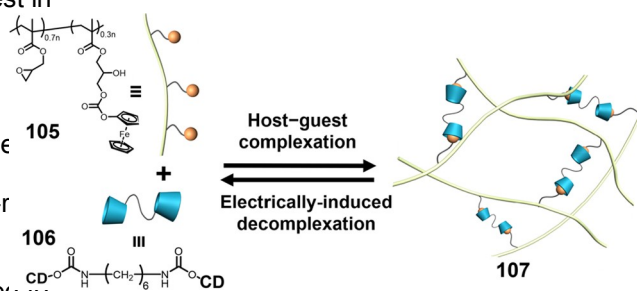


Figure 31. Schematic views of the Fc-containing polymer 105, the difunctional  $\beta$ -CD 106, and the electrically driven reversibly cross-linked polymeric network, 107 produced via their paired self-assembly.

The incorporation of metallosupramolecular structures into polymer matrices has allowed access to hybrid materials endowed not only with the tunable viscoelastic properties characteristic of organic polymers, but also ones with unique features that originate from the metal centers.<sup>114,293–303</sup> Chan and co-workers reported a series of metallo-SPNs constructed from  $\beta$ -CD-containing copolymers and triangular metallocycles functionalized with Ad and Fc guest moieties, as shown in Figure 32. The Ad- or Fc-modified triangular terpyridine of generalized structure 108 was found to coordinate Fe(II) and Zn(II) ions to form triangular metallocycles (shown schematically as 109). Host-guest interactions between 108 and PNIPAM- or poly(acrylamide) (PAAM)-based  $\beta$ -CD-containing copolymers 110 gave rise to a series of supramolecular polymeric gels, 111, which proved responsive to various external stimuli. Adhesion tests led to the suggestion that the  $\beta$ -CD/Fc or  $\beta$ -CD/Ad complexes could be viewed as stimuli-responsive points of molecular attachment that could be used to adhere cross-linked gel blocks containing  $\beta$ -CD subunits.



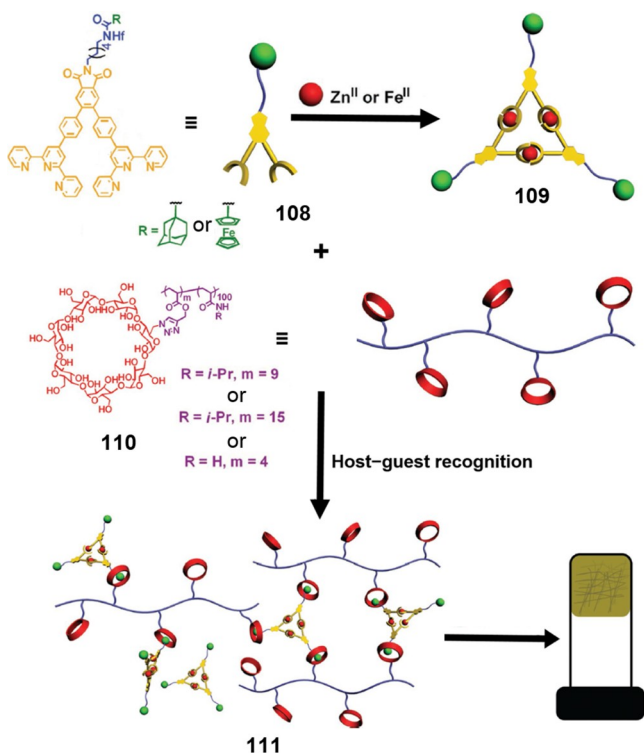


Figure 32. Chemical structures of 108, 109, and 110. Also shown in schematic form is the SPN gel 111 constructed through hierarchical self-assembly driven by metal–ligand complexation and  $\beta$ -CD/Ad CD/Fc host–guest interactions. Reproduced with permission from 304. Copyright 2018 John Wiley and Sons.

### 3.6. $\beta$ -CD/Cholesterol Host–Guest Recognition Motifs

Access to biocompatible self-healing hydrogels containing biodegradable polymers viewed as being a key to many practical applications. Poly(L-glutamic acid) (PLGA) is noteworthy for its absence of appreciable toxicity and biodegradability, high hydrophilicity and low antigenicity and immunogenicity.<sup>305</sup> These properties make it an excellent biomedical polymer from which to construct self-healing hydrogels. Yin co-workers reported a degradable and biocompatible self-healing polypeptide hydrogel stabilized by means of  $\beta$ -CD/cholesterol host–guest interactions. As shown in Figure 33,  $\beta$ -CD could be linked to PLGA to form the  $\beta$ -CD grafted polymer 112. Cholesterol was also linked to triblock PLGA-b-PEG-b-PLGA to form the cholesterol-grafted polymer 113. Mixing these two polymers led to formation of the cross-linked hydrogel 114, with the underlying self-assembly presumably being driven by  $\beta$ -CD/cholesterol host–guest interactions. The concentration of the polymers, the PLGA molecular weight in 113 and the molar ratio between  $\beta$ -CD/cholesterol affected some properties of the hydrogel, including viscoelastic characteristics, mechanical performance and degradation rate. Macroscopic damage-based tests and rheological measurements confirmed the ability of this hydrogel to self-heal, while cytotoxicity experiments provided support for it having good cytocompatibility. Excellent flexibility and a propensity to take up colorants quickly was also seen.

### 3.7. $\beta$ -Cyclodextrin/Cholic Acid Host–Guest Recognition Motifs

Stimuli-responsive SPNs based on naturally occurring biocompatible compounds could find use in a variety of potential

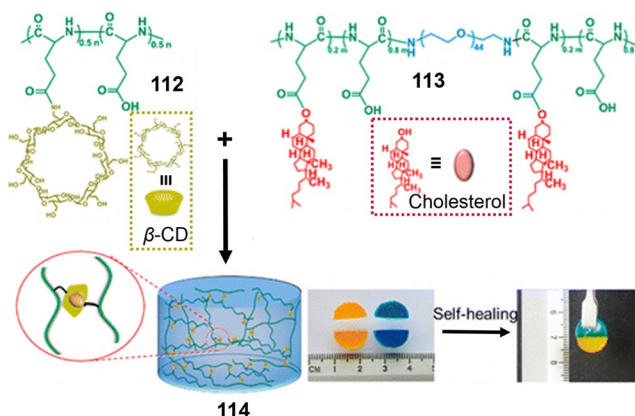


Figure 33. Preparation and self-healing features of the supramolecular cross-linked hydrogel 14 obtained by mixing the  $\beta$ -CD-grafted polymer 112 and the cholesterol-grafted polymer 113. Reproduced with permission from 306. Copyright 2015 American Chemical Society.

biomedical applications.<sup>240,307</sup> However, to be effective these systems must respond to stimuli that are sufficiently mild so as to produce no off-target or otherwise undesirable side effects. Carbon dioxide ( $\text{CO}_2$ ) is a key endogenous metabolite with good biocompatibility. It is thus attractive as stimulus for use in conjunction with SPNs. Zhu and co-workers reported a  $\text{CO}_2$  switchable self-healing cross-linked hydrogel based on host–guest interactions between cholic acid and  $\beta$ -CD. In this study, copolymer 115, a  $\beta$ -CD-containing PDMAAM copolymer, and a cholic acid dimer 116, tethered with a PEG spacer, were used to prepare the self-healing cross-linked hydrogel 117 (cf. Figure 34). Hydrogel 117 exhibited  $\text{CO}_2$  responsiveness in the presence of a competitive guest, (1H-benzimidazolyl)propan-1-amine (Bzl-A). Reversible gel–sol transitions could be induced by treating alternatively with  $\text{CO}_2$  and  $\text{N}_2$ . This triggering was ascribed to protonation and deprotonation of the Bzl-A substrates.

### 3.8. $\beta$ -Cyclodextrin/Dansyl Group Host–Guest Recognition Motifs

Supramolecular macroscopic assemblies are of interest as functional materials.<sup>310,311</sup> An example of such an assembly was reported by Harada and co-workers in this study. PAAM-based gels carrying dansyl group and  $\beta$ -CD residues, dansyl-gel 119 and  $\beta$ -CD-gel 120, respectively, were used to prepare the pH-responsive self-assembled network 121 (Figure 35). In aqueous solution, gel 119 interacted only with the  $\beta$ -CD-gel 120 but not with the corresponding  $\alpha$ -CD- or  $\gamma$ -CD-gels. This selectivity was ascribed to the cavity of  $\beta$ -CD being appropriately sized for the dansyl moiety. Gels 119 and 120 were found to self-assemble at pH  $\geq 4.0$ , but then disassemble at pH  $\leq 3.0$ . This change was ascribed to the dansyl residues being protonated at lower pH and a commensurate reduction in the pair-wise interactions that would otherwise stabilize the network material (121).

### 3.9. $\beta$ -Cyclodextrin/Phenolphthalein Host–Guest Recognition Motifs

The ability to visualize changes in the structure of polymeric materials under different conditions can provide important insights into both the underlying chemistry and the bulk properties. Harada and co-workers reported a stimuli-responsive colored polymeric material based on  $\beta$ -CD/phenolphthalein host–guest recognition. As shown in Figure 36, phenolph-

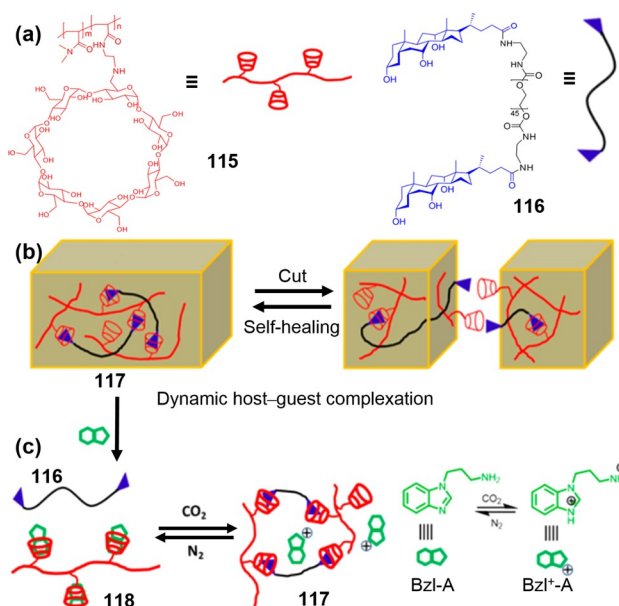


Figure 34. (a) Chemical structures of the  $\beta$ -CD-containing polymer 115 and the cholic acid dimer 116. (b) Schematic illustration of the cross-linked hydrogel 117 based on 115 and 116 and its self-healing behavior. (c) Reversible association-dissociation of hydrogel 117 in the presence of the competitive guest Bzl-A. This latter substrate forms a complex with 115 to form complex 118. Treating with  $\text{CO}_2$  was then found to effect substrate release, presumably as the result of protonation. Reproduced with permission from ref 309. Copyright 2017 American Chemical Society.

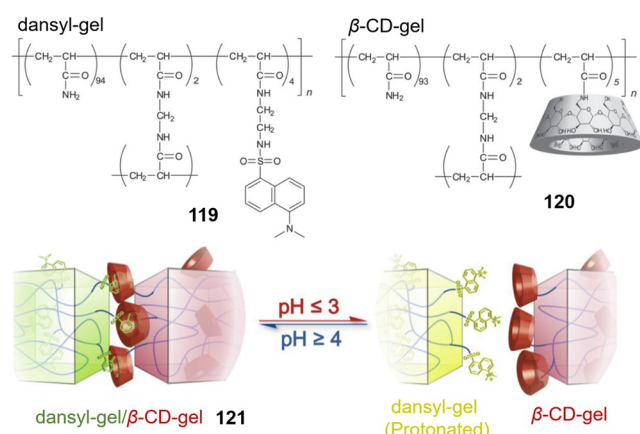


Figure 35. Chemical structures of dansyl-gel 119 and  $\beta$ -CD gel 120. Also shown are cartoon views of the pH-responsive assembly and disassembly of the supramolecular cross-linked gel. Reproduced with permission from ref 310. Copyright 2013 John Wiley and Sons.

thalein and  $\beta$ -CD were linked as side chains to an AAM backbone; this structure gave polymer 122 that was used, in turn, to prepare hydrogel 123. Due to the pH dependence of the absorbance features of phenolphthalein, this hydrogel was expected to be purple under basic aqueous conditions. However, it proved colorless, a finding ascribed to complexation of the phenolphthalein moiety by the  $\beta$ -CD subunits. Heating, exposure to an electric current, treating with a competing substrate (AdCANa) in a  $\text{KPO}_4/\text{NaOH}$  buffer solution (pH 8) led to formation of a colored material. Gel 123 was also found to possess an ability to self-heal under dry conditions.

### 3.10. $\beta$ -Cyclodextrin/Reduced Methyl Viologen Host–Guest Recognition Motifs

Stimuli-responsive hydrogels have been extensively studied from both the fundamental and applied perspectives.<sup>242,289,314–319</sup> Hydrogels constructed from identical constituents but which respond to the same stimulus in a different way are of particular interest within the context of this general paradigm since they may expand the lexicon of potential applications. By exploiting host–guest interactions between  $\beta$ -CD and MV, Mesia and co-workers were able to prepare hydrogels with single or double network gel structures.<sup>320</sup> As shown in Figure 37, the single-network gel 126 was obtained by subjecting N,N'-methylenebis-(acrylamide) (MBAAM), AAM,  $\beta$ -CD monomer 124, and  $\text{MV}^{2+}$  monomer 125 to radical polymerization. The first  $\beta$ -CD-containing gel network 127-1 was prepared via the polymerization of AAM, MBAAM, and 124. Network 127-1 was immersed into an aqueous solution of AAM, MBAAM and 125 for 3 days. The double network gel 128 was then obtained by in situ polymerization of these mixed monomers in a solution of 127-1. Gel 128 consisted of two polymer networks, namely the  $\beta$ -CD-containing polymer network 127-1 and the  $\text{MV}^{2+}$ -containing polymer network 127-2. Characterized by different structures, gels 126 and 128 were found to exhibit opposing responses when the MV subunits were subject to reduction. Both gels 126 and 128 could be stretched to approximately 3 times their original lengths. After reduction of the constituent  $\text{MV}^{2+}$  groups within gel 126 to corresponding MV forms, the tensile strength of 126 was found to increase, presumably because the newly produced MV groups thread into the  $\beta$ -CD cavities to form reversible supramolecular cross-linked structures; this threading creates non-covalent bonds that can be broken to relax tensile stress across the network. In contrast, the tensile strength of 128 decreased after reduction of the MV groups. Presumably, this weakening reflects the fact that after  $\text{MV}^{2+}$  reduction, polymer networks 127-1 and 127-2 form a cross-linked hydrogel network that cannot delocalize the tensile stress. Spectroscopic measurements and rheological studies both provided support for these suggestions.

### 3.11. $\beta$ -Cyclodextrin/Polypropylene Glycol Host–Guest Recognition Motifs

SPNs constructed from biomacromolecules are expected to have attractive biomedical features.<sup>287,321</sup> Alginate, a plant-derived polysaccharide, has been studied as a scaffold in a number of biomedical contexts, including drug delivery and tissue engineering.<sup>322–324</sup> Oldinski and co-workers reported a self-healing and thermally responsive dual-cross-linked alginate hydrogel based on  $\beta$ -CD/PPG host–guest interactions.<sup>325</sup> Toward this end, the  $\beta$ -CD-containing alginate 129 was prepared (cf. Figure 38). A difunctional block copolymer, PEG-b-PPG-b-PEG (Pluronic F108), was then added as a guest to create the dual-cross-linked and moderately stiff hydrogel 130. Hydrogel 130 displayed self-healing and thermo-responsive features. In addition, the shear storage modulus of hydrogel 130 was found to be 30 kPa at body temperature, which is a biologically relevant value. Hydrogel 130 proved to be minimally cytotoxic and could be used to encapsulate and release bovine serum albumin.

### 3.12. $\beta$ -Cyclodextrin/N-Isopropylacrylamide Host–Guest Recognition Motifs

Electrically conductive self-healing polymeric hydrogels, with excellent flexibility, porosity, desirable mechanical property, and good conductivity, have shown promise in a number of

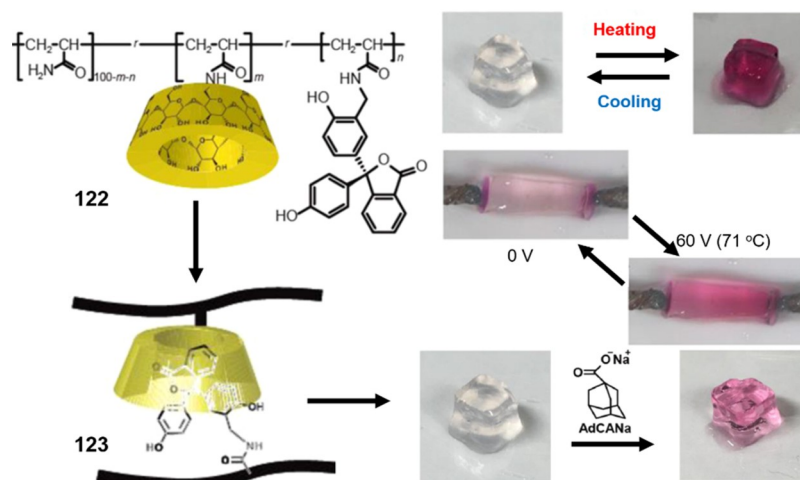


Figure 36. Schematic illustration of polymer 122 and the hydrogel supports. Also shown are some of its stimuli-responsive color features. Reproduced with permission from ref 313. Copyright 2017 American Chemical Society.

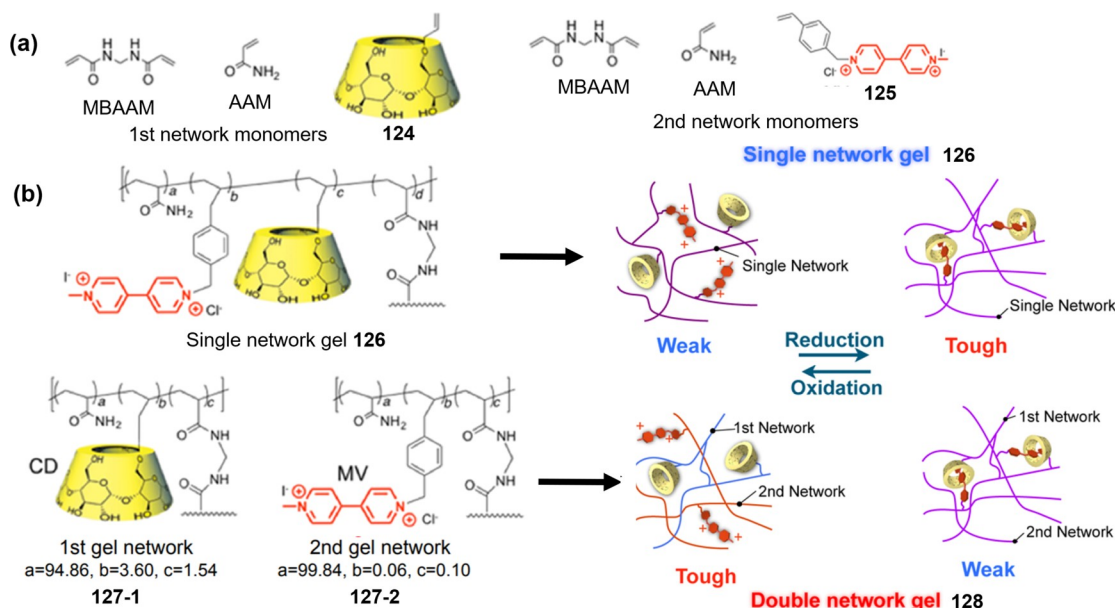


Figure 37. (a) Chemical structures of the monomers: MBAAM, AAM,  $\beta$ -CD monomer 124, and MV 125. (b) Schematic representation of single-network gel 126, the  $\beta$ -CD-containing polymer network 127-1, and the double network gel 128. Also shown in schematic form is the disparate response displayed by 126 and 128 toward the same redox reaction. Reproduced with permission from ref 320. Copyright 2018 American Chemical Society.

application areas, including as self-healable electronic devices, drug delivery systems, and wound dressings.<sup>23,326–330</sup> Guo and co-workers reported a self-healing conductive hydrogel based on  $\beta$ -CD, NIPAM, multi-walled carbon nanotubes (CNTs), and nanostructured polypyrrole. As shown in Figure 39, acryloyl-modified  $\beta$ -CD 131 and NIPAM were used to prepare hydrogel 132 after copolymerization. In addition, hydrogel 133 was obtained via the copolymerization of NIPAM, and CNT. Hydrogel 134 was obtained via the in situ polymerization of 133 and pyrrole.

In hydrogel 134,  $\beta$ -CD/NIPAM host–guest interactions provide for cross-linking. CNTs act as a separate physical cross-linker and, in conjunction with polypyrrole, provide for conductivity. Hydrogels 132, 133, and 134 exhibited rapid, stable thermo-responsive features, mechanical properties, and an ability to self-heal. Compared with hydrogel 132, the

hybrid hydrogels 133 and 134 exhibited lower swelling ratios and enhanced compressive stress and storage moduli. In addition, relative to hydrogels 132 and 133, hydrogel 134, containing both CNT and polypyrrole components, showed excellent NIR light sensitivity and good conductivity. As a result, the superior features of 134, including good mechanical properties, excellent self-healing ability and desirable electrical conductivity, it has been studied in the context of large-scale human motion monitoring devices and self-healable electronic circuits.

### 3.13. $\gamma$ -Cyclodextrin/Polyethylene Glycol Host–Guest Recognition Motifs

Polymeric hydrogel microspheres (microgels) are a special type of responsive colloidal material.<sup>331</sup> Microgels display rapid swelling/deswelling transitions and can be tuned to respond to other stimuli. This has made them of interest in a number of



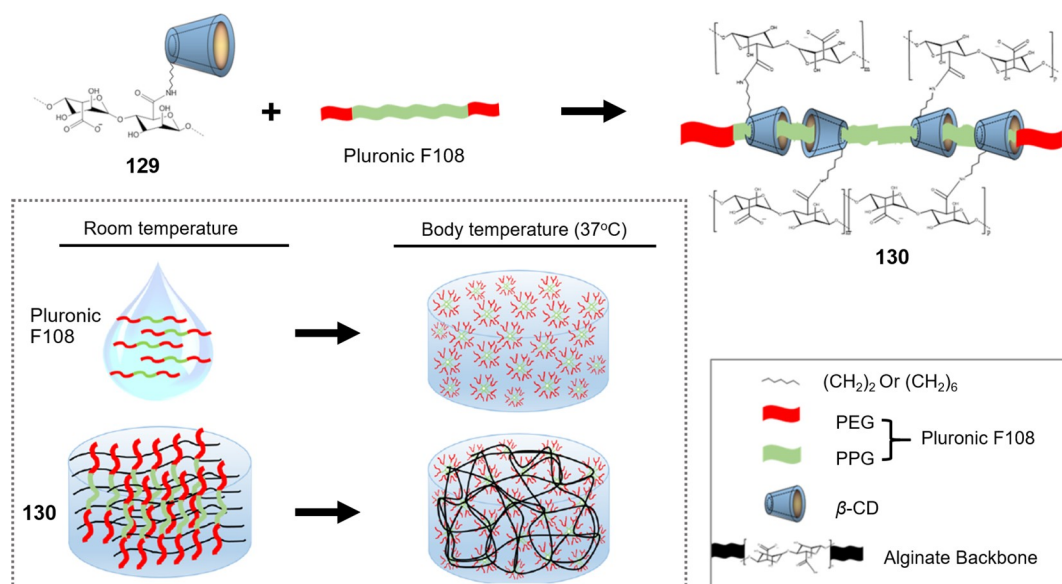


Figure 38. Schematic representation of the alginate-graft- $\beta$ -CD 129, Pluronic F108, and the hydrogel network 130 prepared from these two components. Also shown in schematic form is the effect of Pluronic F108 on the thermo-responsive features of the hydrogel network 130. Reproduced with permission from ref 325. Copyright 2015 American Chemical Society.

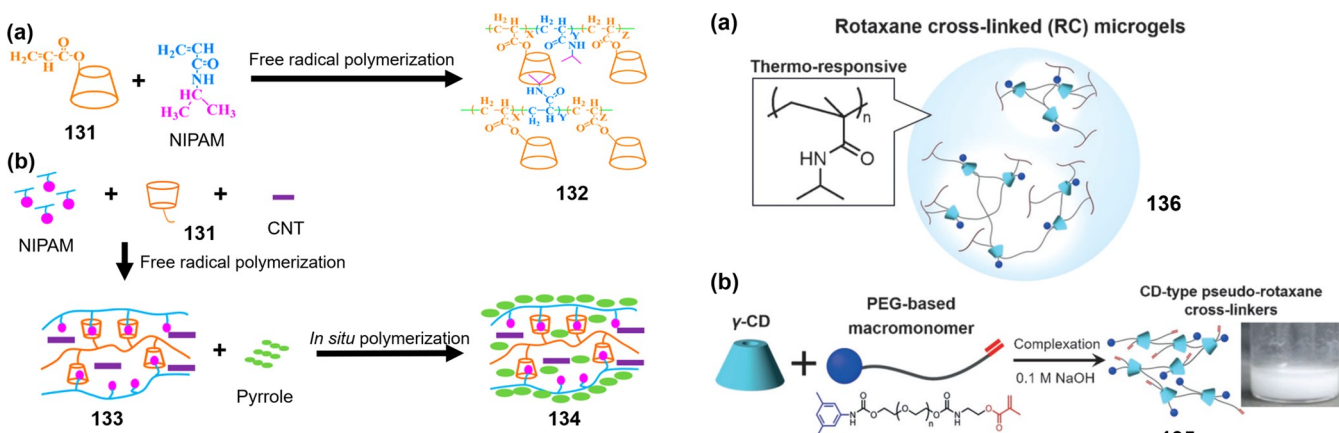


Figure 39. (a) Schematic illustration of the synthesis of self-healing hydrogel 132 from 131 and NIPAM via free radical polymerization. (b) Scheme showing the preparation of hydrogel 133 from NIPAM and 131, followed by the synthesis of conductive self-healing hydrogel 134 by in situ polymerization with pyrrole and CNT. (c) Schematic of Rotaxane cross-linked (RC) microgels 136, showing their thermo-responsive nature and the formation of CD-type pseudo-rotaxane cross-linkers 135 from  $\gamma$ -CD and PEG-based macromonomer 63. Reproduced with permission from ref 230. Copyright 2018 American Chemical Society.

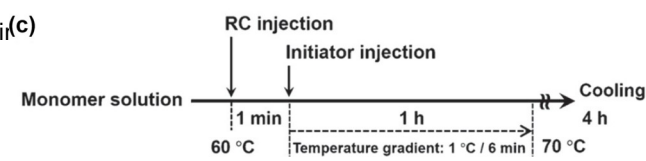


Figure 40. Schematic illustrations of (a) RC microgel 136, (b)  $\gamma$ -CD, the PEG-containing bulky macromonomer 63, and the CD-type pseudo-rotaxane cross-linker 135, and (c) modified precipitation polymerization procedure used to obtain the RC microgel 136. Reproduced with permission from ref 230. Copyright 2017 John Wiley and Sons.

areas.<sup>332,333</sup> Takata and co-workers reported  $\gamma$ -CD/PEG-based rotaxane-cross-linked microgels which exhibited decoupled thermo- and pH-responsive behaviors. As shown in Figure 40,  $\gamma$ -CD can be threaded by one or two molecules of the PEG-bearing bulky macromonomer 63 to form the pseudorotaxane cross-linker 135. Modified precipitation polymerization (Figure 40c) of a mixture of N-isopropylmethacrylamide (NIPAM) monomer and 135 in which the total concentration was fixed at 150 mM then gave the rotaxane cross-linked microgel 136. The aggregation or disaggregation of  $\gamma$ -CD subunits in 136 is driven by hydrogen bonding; this in turn is affected by the pH of the solution. Therefore, as a result of the differences in the underlying supramolecular interactions, microgel 136 was found to display pH-responsive swelling/deswelling behavior. However, these pH effects were found to have little direct effect on the PNIPAM part of 136. On the other hand, the latter portion of the construct was found to be sensitive to changes in

the temperature. As a consequence, microgel 136 displays decoupled thermal and pH responsive behavior.

#### 3.14. $\gamma$ -Cyclodextrin/Adamantane or Fluoroalkane Host-Guest Recognition Motifs

Many of the SPNs cross-linked by CD-based host-guest interactions rely on recognition chemistry that is effective in aqueous media,<sup>334,335</sup> but inappropriate for use in hydrophobic environments (including the interior confines of many hydrophobic polymers). In an effort to address this latter deficiency, Takashima and co-workers reported several self-healing alkyl

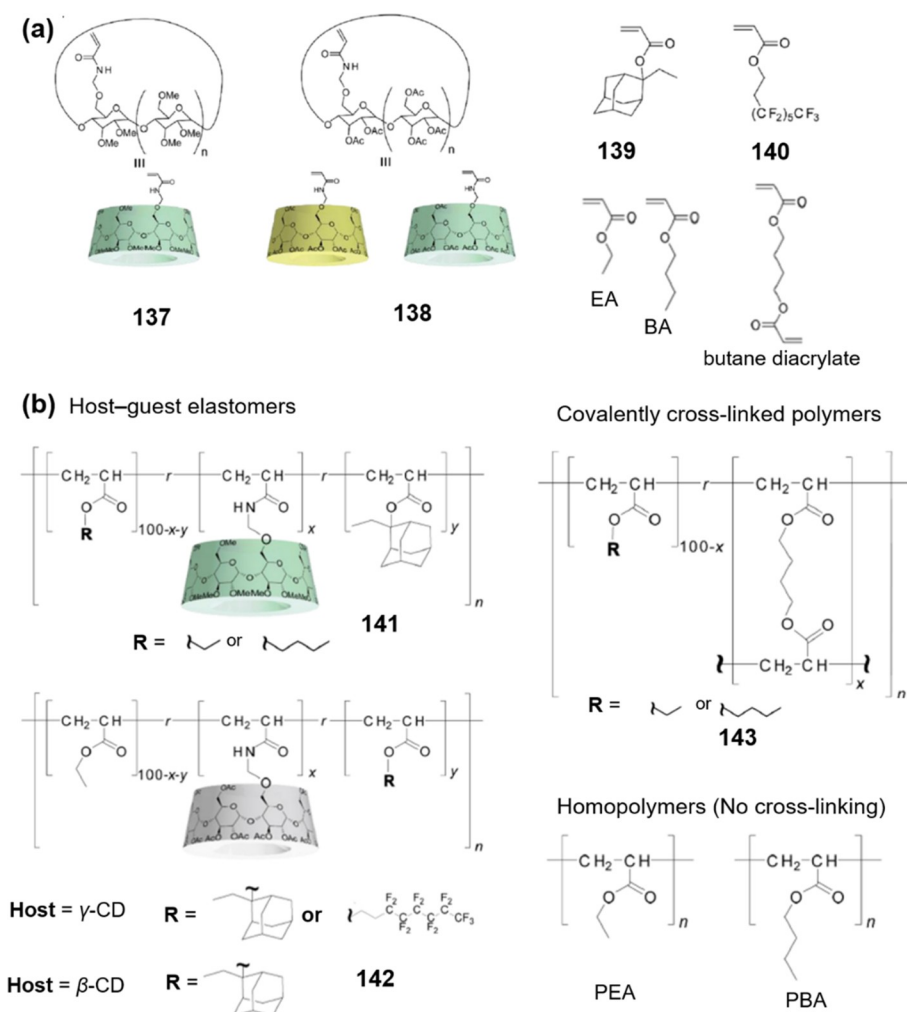


Figure 41. (a) Chemical structures of the host monomers permethylated  $\gamma$ -CD 137, peracetylated  $\gamma$ -CD 138, guest monomers 2-ethyladamantyl acrylate 139 and fluoro-octyl acrylate 140, main-chain monomers EA and BA, and chemical cross-linking reagent diacrylate (BDA). (b) Chemical structures of copolymers bearing host/guest abilities. The host-guest elastomers 141 and 142 are based on permethylated  $\gamma$ -CD 137 and peracetylated CD 138, respectively. Also shown is the structure of the covalently cross-linked polymer 143 and the non-cross-linked homopolymers PEA and PBA. Reproduced with permission from ref 336. Copyright 2019 American Chemical Society.

acrylate-based supramolecular elastomers cross-linked by permethylated or peracetylated CD-based host-guest interactions.<sup>336</sup> These researchers took advantage of permethylated  $\gamma$ -CD 137 and peracetylated  $\gamma$ -CD and peracetylated  $\beta$ -CD 138, which proved soluble in a variety of hydrophobic liquid acrylate monomers. The monomers 2-ethyladamantyl acrylate 139 and fluoro-octyl acrylate 140 (see Figure 41) were then prepared as guests for 137 and 138. The host-guest elastomer 141 was constructed via the polymerization of the main chain monomers with host-guest inclusion complexes based on 137 and 139. Likewise, the host-guest elastomer 142 was prepared by polymerizing the main chain monomers with host-guest inclusion complexes based on 139 or 140 in conjunction with 138. The covalent cross-linked polymers 143 and the non-cross-linked polymers PEA and poly(n-butyl acrylate) (PBA) were also prepared as controls. From tensile tests, elastomers 141 and 142 that benefit from host-guest cross-linking showed higher toughness and flexibility than the conventional covalently cross-linked elastomer 143 and the non-cross-linked polymers PEA and PBA. The fracture energies of 141 and 142 were found to be 12 times greater than those of 143. These findings were rationalized in terms of the applied stress being dispersed into the supramolecular elastomers by a reversible host-guest interactions during the deformation process. Elastomers 141 and 142 also displayed self-healing behavior ascribed to the reversible cross-linking provided by the host-guest interactions.

### 3.15. $\gamma$ -Cyclodextrin/Tetraaniline and Polyethylene Glycol Host-Guest Recognition Motifs

Polyaniline is an electrically conducting polymer that has attracted considerable attention in recent years due to its ease of synthesis, environmental stability, and the control over structure and function it provides.<sup>337,338</sup> Combining the advantages of polyaniline and hydrogels allows for the preparation of electrically conducting hydrogels.<sup>339,340</sup> Ma and co-workers reported an injectable electroactive hydrogel stabilized via host-guest interactions between  $\gamma$ -CD, aniline, and PEG.<sup>215</sup> As shown in Figure 42, combining the tetraaniline-grafted PEG-containing hydrophilic copolymer 144 with the  $\gamma$ -CD dimer 145 gives rise to hydrogel 146, a system cross-linked by host-guest interactions involving the various constituent subunits. Hydrogel 146 proved to be a material that was not only readily injectable and degradable, but also one with good electroactivity. In addition, sol-gel transitions involving 146 could be induced

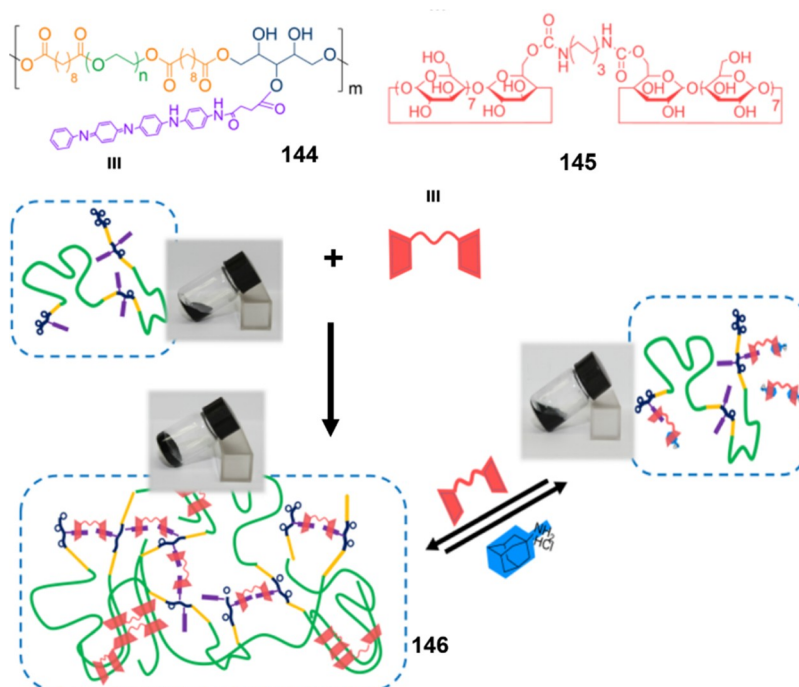


Figure 42. Chemical structures of the tetraaniline-containing copolymer 144 and the  $\gamma$ -CD dimer 145. Also shown in schematic form is the preparation of an injectable electroactive hydrogel, 146, stabilized via host-guest interactions involving the  $\gamma$ -CD units and the PEG and tetraaniline subunits, as well as the reversible sol-gel transitions induced via the sequential addition of 1-adamantanamine hydrochloride and 145. Reproduced with permission from ref 215. Copyright 2014 American Chemical Society.

by adding in sequence 1-adamantanamine hydrochloride and the host dimer 145. undesirable stimuli-responsive properties, including changes due to variations in pH, temperature, solvent polarity, and redox environment.

### 3.16. Comparisons between Supramolecular Polymeric Networks Constructed by Cyclodextrin-Based Host-Guest Recognition Motifs

As underscored by the summaries provided above, to date a large number of covalent polymers have been subject to cross-linking by means of various CD-based host-guest interactions. This has allowed the preparation of SPNs with diverse structures and properties. A comparative listing of these systems and the motifs upon which they are based is provided in Table 2. This listing is organized according to the underlying covalent polymer.

## 4. SUPRAMOLECULAR POLYMERIC NETWORKS CONSTRUCTED FROM COVALENT POLYMERS THAT EXPLOIT CALIX[N]ARENE-BASED HOST-GUEST INTERACTIONS

Calix[n]arenes, a class of phenol-formaldehyde cyclic oligomers, arose from studies that led to the Bakelite process.<sup>341</sup> Calix[n]arenes can be modified readily on their upper rim, lower rim, or even on the bridging linkages; they have thus been described as being macrocycles with (almost) unlimited possibilities.<sup>342,343</sup> Many host-guest recognition systems based on calix[n]arenes have been investigated, including those based on calix[5]arenes with primary ammonium salts or  $C_{60}$ ,<sup>89,344,345</sup> as well as sulfonatocalix[n]arenes with MV alkylpyridinium salts, trimethylammonium salts, imidazolium salts, or crystal violet.<sup>344,346–357</sup> Due to their facile modification, unique structure, and tunable host-guest recognition properties, calix[n]arenes have been widely used in the field of polymer science, including as catalysts for polymerization, polymer backbones or cores, and as polymer-based grafting units.<sup>89,352–354</sup> Calix[n]arene-based SPNs often show

undesirable stimuli-responsive properties, including changes due to variations in pH, temperature, solvent polarity, and redox environment. This feature has led to their use in a number of applications-related areas, including self-healing, polymer blending, sensing, controlled release, and photo-electricity.<sup>844,355–357</sup> Recent progress involving SPNs produced from covalent polymers and stabilized by calix[n]arenes-based host-guest interactions (Figure 43) is summarized in this section.

### 4.1. Calix[4]arene/Methyl Viologen Host-Guest Recognition Motifs

Polymeric hydrogels are an important class of water-containing soft materials. They have seen use in a variety of biomedical and industrial applications due to their easily varied mechanical properties and generally good biocompatibility.<sup>358–364</sup> Supramolecular hydrogels or non-covalently cross-linked hydrophilic polymer networks based on specific non-covalent and dynamic binding motifs are a subset of polymeric hydrogels that have attracted considerable attention in recent years.<sup>146,240,365</sup> Liu and co-workers reported a supramolecular cross-linked hydrogel with a three-dimensional network structure (149) based on an amphiphilic sulfonatocalix[4]arene, 147, and a poly(vinyl alcohol) 148.<sup>366</sup> As shown in Figure 44, hydrogel 149 can be considered as being produced as the result of (i) initial self-assembly of 147 followed by (ii) host-guest driven secondary assembly of the resulting micelles with 148. Hydrogel 149 proved responsive to a range of external stimuli, including changes in temperature, redox environment, and ionic strength. Depending on the choice of conditions, both reversible and irreversible gelation behavior could be induced.



Table 2. SPNs Based on CD-Based Host–Guest Recognition Motifs Classified by the Underlying Covalent Polymers

molecular recognition	figure number	cross-linking motif	SPN	ref
Polyethylene Glycol (PEG)				
$\alpha$ -CD/Azo	Figure 15	[c2]daisy chain 39 with PEG after polycondensation reaction	41	238
	Figure 16	pseudorotaxane 44 with PEG after polycondensation reaction	45	239
$\alpha$ -CD/PEG	Figure 18	$\alpha$ -CD-containing PA 52 and PEG derivative 53	54	244
	Figure 19	polyrotaxane 55 with poly(AAM-co-4-vinylphenylboronic acid) cross-linked by dynamic covalent bonds	56	254
		polyrotaxane 55 with poly(AAM-co-acrylate) cross-linked by covalent bonds	57	
	Figure 20	vinyllic supramolecular cross-linkers 64 after polymerization with DMAAM	66	257
		vinyllic supramolecular cross-linkers 65 after polymerization with DMAAM	67	
$\beta$ -CD/Ad	Figure 25	tetronic-Ad conjugate 87 with poly( $\beta$ -CD) 83	88	274
$\beta$ -CD/cholesterol	Figure 33	$\beta$ -CD-containing PLGA polymer 112 with cholesterol-bearing triblock PLGA-b-PEG-b-PLGA polymer 113	116	306
$\beta$ -CD/cholic acid	Figure 34	$\beta$ -CD-containing PDMAAM copolymer 115 with cholic acid dimer-containing PEG polymer 116	117	309
$\beta$ -CD/PPG	Figure 38	$\beta$ -CD-containing alginate 129 with PEG-b-PPG-b-PEG copolymer (Pluronic F108)	130	325
$\gamma$ -CD/PEG	Figure 40	$\gamma$ -CD with PEG-containing terminal bulky macromonomer 63 after polymerization with NIPAM	136	230
$\gamma$ -CD/ tetraaniline and PPG	Figure 42	tetraaniline-grafted and PEG-containing hydrophilic copolymer 144 with $\gamma$ -CD dimer 145	146	215
Polyacrylate (PA)				
$\alpha$ -CD/PEG	Figure 18	$\alpha$ -CD-containing PA 52 with PEG derivative 53	54	244
$\beta$ -CD/Ad	Figure 24	poly( $\beta$ -CD) 83 with HEMA-modified Ad unit 84 after polymerization with HEA	86	270
	Figure 26	Ad-modified acryloylated tetra-ethylene glycol 89 with $\beta$ -CD-functionalized 2-isocyanatoethyl acrylate molecule 90 after polymerization with gelatin methacryloyl	92	272
$\beta$ -CD/Fc	Figure 31	Fc-modified poly(glycidyl MA) 105 with a difunctional $\beta$ -CD derivative 106	107	292
$\gamma$ -CD/PEG	Figure 40	$\gamma$ -CD with PEG-containing terminal bulky macromonomer 63 after polymerization with NIPAM	136	230
$\gamma$ -CD/Ad or $\gamma$ -CD/fluoroalkane	Figure 41	permethylated $\gamma$ -CD AAM monomer 137, 2-ethyladamantyl acrylate 139 with EA or BA after polymerization	141	336
		peracetylated $\gamma$ -CD or peracetylated $\beta$ -CD AAM monomers 211, 213, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 250, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 273, 274, 275, 276, 277, 278, 279, 280, 281, 282, 283, 284, 285, 286, 287, 288, 289, 290, 291, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353, 354, 355, 356, 357, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419, 420, 421, 422, 423, 424, 425, 426, 427, 428, 429, 430, 431, 432, 433, 434, 435, 436, 437, 438, 439, 440, 441, 442, 443, 444, 445, 446, 447, 448, 449, 450, 451, 452, 453, 454, 455, 456, 457, 458, 459, 460, 461, 462, 463, 464, 465, 466, 467, 468, 469, 470, 471, 472, 473, 474, 475, 476, 477, 478, 479, 480, 481, 482, 483, 484, 485, 486, 487, 488, 489, 490, 491, 492, 493, 494, 495, 496, 497, 498, 499, 500, 501, 502, 503, 504, 505, 506, 507, 508, 509, 510, 511, 512, 513, 514, 515, 516, 517, 518, 519, 520, 521, 522, 523, 524, 525, 526, 527, 528, 529, 530, 531, 532, 533, 534, 535, 536, 537, 538, 539, 540, 541, 542, 543, 544, 545, 546, 547, 548, 549, 550, 551, 552, 553, 554, 555, 556, 557, 558, 559, 560, 561, 562, 563, 564, 565, 566, 567, 568, 569, 570, 571, 572, 573, 574, 575, 576, 577, 578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588, 589, 590, 591, 592, 593, 594, 595, 596, 597, 598, 599, 600, 601, 602, 603, 604, 605, 606, 607, 608, 609, 610, 611, 612, 613, 614, 615, 616, 617, 618, 619, 620, 621, 622, 623, 624, 625, 626, 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650, 651, 652, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 692, 693, 694, 695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708, 709, 710, 711, 712, 713, 714, 715, 716, 717, 718, 719, 720, 721, 722, 723, 724, 725, 726, 727, 728, 729, 730, 731, 732, 733, 734, 735, 736, 737, 738, 739, 740, 741, 742, 743, 744, 745, 746, 747, 748, 749, 750, 751, 752, 753, 754, 755, 756, 757, 758, 759, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 783, 784, 785, 786, 787, 788, 789, 790, 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 825, 826, 827, 828, 829, 830, 831, 832, 833, 834, 835, 836, 837, 838, 839, 840, 841, 842, 843, 844, 845, 846, 847, 848, 849, 850, 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879, 880, 881, 882, 883, 884, 885, 886, 887, 888, 889, 890, 891, 892, 893, 894, 895, 896, 897, 898, 899, 900, 901, 902, 903, 904, 905, 906, 907, 908, 909, 910, 911, 912, 913, 914, 915, 916, 917, 918, 919, 920, 921, 922, 923, 924, 925, 926, 927, 928, 929, 930, 931, 932, 933, 934, 935, 936, 937, 938, 939, 940, 941, 942, 943, 944, 945, 946, 947, 948, 949, 950, 951, 952, 953, 954, 955, 956, 957, 958, 959, 960, 961, 962, 963, 964, 965, 966, 967, 968, 969, 970, 971, 972, 973, 974, 975, 976, 977, 978, 979, 980, 981, 982, 983, 984, 985, 986, 987, 988, 989, 990, 991, 992, 993, 994, 995, 996, 997, 998, 999, 1000	211	338
		peracetylated $\gamma$ -CD or peracetylated $\beta$ -CD AAM monomers 211, 213, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 250, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 273, 274, 275, 276, 277, 278, 279, 280, 281, 282, 283, 284, 285, 286, 287, 288, 289, 290, 291, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353, 354, 355, 356, 357, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419, 420, 421, 422, 423, 424, 425, 426, 427, 428, 429, 430, 431, 432, 433, 434, 435, 436, 437, 438, 439, 440, 441, 442, 443, 444, 445, 446, 447, 448, 449, 450, 451, 452, 453, 454, 455, 456, 457, 458, 459, 460, 461, 462, 463, 464, 465, 466, 467, 468, 469, 470, 471, 472, 473, 474, 475, 476, 477, 478, 479, 480, 481, 482, 483, 484, 485, 486, 487, 488, 489, 490, 491, 492, 493, 494, 495, 496, 497, 498, 499, 500, 501, 502, 503, 504, 505, 506, 507, 508, 509, 510, 511, 512, 513, 514, 515, 516, 517, 518, 519, 520, 521, 522, 523, 524, 525, 526, 527, 528, 529, 530, 531, 532, 533, 534, 535, 536, 537, 538, 539, 540, 541, 542, 543, 544, 545, 546, 547, 548, 549, 550, 551, 552, 553, 554, 555, 556, 557, 558, 559, 560, 561, 562, 563, 564, 565, 566, 567, 568, 569, 570, 571, 572, 573, 574, 575, 576, 577, 578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588, 589, 590, 591, 592, 593, 594, 595, 596, 597, 598, 599, 600, 601, 602, 603, 604, 605, 606, 607, 608, 609, 610, 611, 612, 613, 614, 615, 616, 617, 618, 619, 620, 621, 622, 623, 624, 625, 626, 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650, 651, 652, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 692, 693, 694, 695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708, 709, 710, 711, 712, 713, 714, 715, 716, 717, 718, 719, 720, 721, 722, 723, 724, 725, 726, 727, 728, 729, 730, 731, 732, 733, 734, 735, 736, 737, 738, 739, 740, 741, 742, 743, 744, 745, 746, 747, 748, 749, 750, 751, 752, 753, 754, 755, 756, 757, 758, 759, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 783, 784, 785, 786, 787, 788, 789, 790, 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 825, 826, 827, 828, 829, 830, 831, 832, 833, 834, 835, 836, 837, 838, 839, 840, 841, 842, 843, 844, 845, 846, 847, 848, 849, 850, 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879, 880, 881, 882, 883, 884, 885, 886, 887, 888, 889, 890, 891, 892, 893, 894, 895, 896, 897, 898, 899, 900, 901, 902, 903, 904, 905, 906, 907, 908, 909, 910, 911, 912, 913, 914, 915, 916, 917, 918, 919, 920, 921, 922, 923, 924, 925, 926, 927, 928, 929, 930, 931, 932, 933, 934, 935, 936, 937, 938, 939, 940, 941, 942, 943, 944, 945, 946, 947, 948, 949, 950, 951, 952, 953, 954, 955, 956, 957, 958, 959, 960, 961, 962, 963, 964, 965, 966, 967, 968, 969, 970, 971, 972, 973, 974, 975, 976, 977, 978, 979, 980, 981, 982, 983, 984, 985, 986, 987, 988, 989, 990, 991, 992, 993, 994, 995, 996, 997, 998, 999, 1000	142	
Poly(acrylamide) (PAAM)				
$\alpha$ -CD/PEG	Figure 19	polyrotaxane 55 with poly(AAM-co-4-vinylphenylboronic acid) cross-linked by dynamic covalent bonds	56	254
		polyrotaxane 55 with poly(AAM-co-acrylate) cross-linked by covalent bonds	57	
	Figure 20	vinyllic supramolecular cross-linkers 64 after polymerization with DMAAM	66	257
		vinyllic supramolecular cross-linkers 65 after polymerization with DMAAM	67	
$\beta$ -CD/Ad	Figure 21	$\beta$ -CD-modified AAM monomer 68 with Ad-modified AAM monomers 69 after polymerization with AAM	71	258
	Figure 22	$\beta$ -CD-containing PAAM 72 with Ad-containing PAAM 73	76	262
$\beta$ -CD/Azo	Figure 29	AAM-modified Azo 99 with poly( $\beta$ -CD) 83 after polymerization with AAM	101	288
$\beta$ -CD/Fc	Figure 30	poly(DMAAM-r-glycidolMA- $\beta$ -CD) 102 with poly(DMAAM-r-HEMA-Fc) 103	104	290
$\beta$ -CD/Fc or $\beta$ -CD/Ad	Figure 32	Ad- or Fc-based triangular metallocycles 109 with PNIPAM- or PAAM-based $\beta$ -CD-containing copolymers 110	110	304
$\beta$ -CD/cholic acid	Figure 34	$\beta$ -CD-grafted PDMAAM copolymer 115 with cholic acid dimer 116	117	309
$\beta$ -CD/dansyl group	Figure 35	PAAM-based dansyl-gel 119 with $\beta$ -CD gel 120	121	312
$\beta$ -CD/phenolphthalein	Figure 36	$\beta$ -CD- and phenolphthalein-modified polymer 122	123	313
$\beta$ -CD/MV	Figure 37	MBAAM, AAM, CD monomer 124 with MV monomer 125 after polymerization	126	320
		$\beta$ -CD-containing PAAM polymer network 127-1 with PAAM-containing PAAM polymer network 127-2	128	
$\beta$ -CD/NIPAM	Figure 39	acryloyl-modified $\beta$ -CD 131 after polymerization with NIPAM	132	214
		acryloyl-modified $\beta$ -CD 131 after polymerization with NIPAM and CNT	133	
		SPN 133 after polymerization with pyrrole	134	
Poly( $\beta$ -cyclodextrin) (Poly( $\beta$ -CD))				
$\beta$ -CD/Ad	Figure 24	poly( $\beta$ -CD) 83 with HEMA-modified Ad unit 84 after polymerization with HEA	86	270
	Figure 25	poly( $\beta$ -CD) 83 with tetronic-Ad conjugate 87	88	274
$\beta$ -CD/Azo	Figure 29	poly( $\beta$ -CD) 83 with AAM-modified Azo 99 after polymerization with AAM	101	288
Polysaccharide				
$\beta$ -CD/Ad	Figure 27	$\beta$ -CD-grafted hyaluronic acid 93 with Ad-grafted hyaluronic acid 94	95	282
$\beta$ -CD/Azo	Figure 28	$\beta$ -CD-containing hyaluronic acid 94 with Azo-containing hyaluronic acid 96	97	287
$\beta$ -CD/PPG	Figure 38	$\beta$ -CD-containing alginate 129 with PEG-b-PPG-b-PEG copolymer (Pluronic F108)	130	325

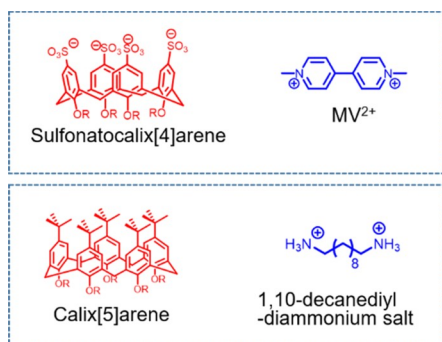


Figure 43. Chemical structures of sulfonatocalix[4]arene and calix[5]arene and two representative guests, MV<sup>2+</sup> and 1,10-decanediyl-diammonium salt.

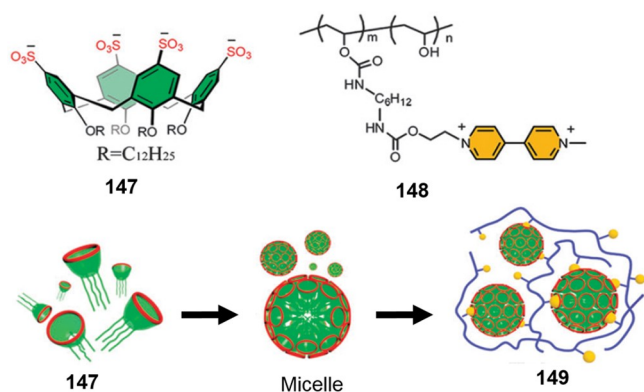


Figure 44. Chemical structures of amphiphilic sulfonatocalix[4]arene 147 and MV<sup>2+</sup>-containing poly(vinylalcohol) polymer 148. Also shown in schematic form is the supramolecular cross-linked hydrogel 149 prepared through 148 with secondary assembled micelles from 147. Reproduced with permission from ref 369. Copyright 2015 The Royal Society of Chemistry.

#### 4.2. Calix[5]arene/1,10-Decanediyl-diammonium Salt Host-Guest Recognition Motifs

Conjugated polymer materials generated through application of supramolecular strategies have been explored in the context of optoelectronic devices. This activity reflects in part the fact that non-covalent interactions can be used to control the assembly of individual polymer chains, which in turn allows the optoelectronic properties of conductive polymer-based devices to be readily tuned.<sup>367</sup> Pappalardo and co-workers reported an SPN constructed from a conjugated polymer that exploited calix[5]arene-based host-guest interactions.<sup>367</sup> In this work, a calix[5]arene-modified PPE polymer 150 and a 1,10-decanediyl-diammonium guest, 151, were prepared and combined to obtain the SPN 152 (Figure 45). AFM analysis revealed a homogeneous and continuous network of nearly uniform thickness that could be used to cover a surface when the molar ratio of 150 and 151 was 2:1. It was also found that by changing the host/guest ratio, the fluorescent properties of the system could be modulated. Finally, disassembly/assembly of 152 could be induced via the successive addition of base and acid.

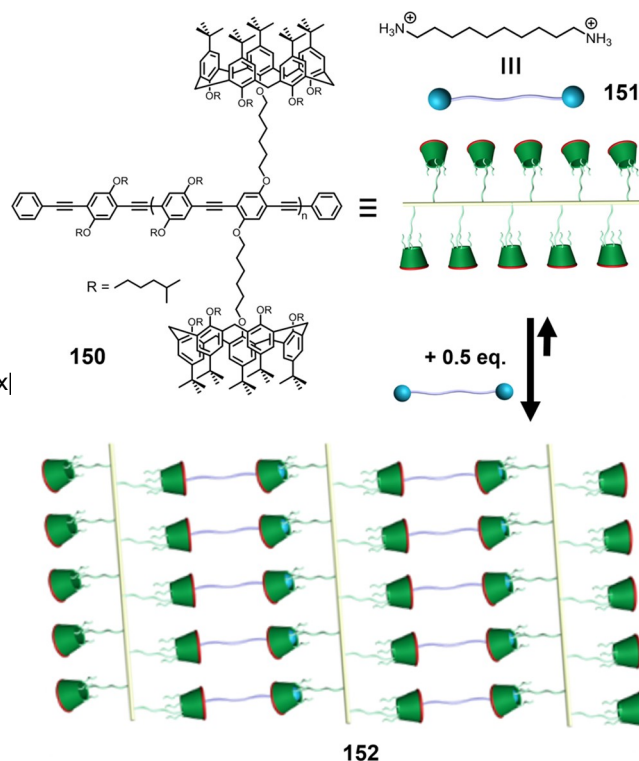


Figure 45. Schematic view of the calix[5]arene-containing PPE system 150, the 1,10-decanediyl-diammonium guest 151, and the SPN 152 produced via their host-guest-driven self-assembly.

#### SUPRAMOLECULAR POLYMERIC NETWORKS CONSTRUCTED THROUGH THE COMBINATION OF COVALENT POLYMERS AND CUCURBIT[N]URIL-BASED HOST-GUEST INTERACTIONS

Cucurbit[n]urils (CB[n]s) are a family of barrel-shaped macrocyclic compounds containing n-glycoluril units. They possess hydrophilic exterior and hydrophobic cavities and can form inclusion complexes with various guests particularly in aqueous media.<sup>368,369</sup> Compared with other supramolecular host systems such as CDs and calix[n]arenes, CB[n]s typically display enhanced guest binding affinities. This is especially true for appropriately selected cationic species where binding is driven by a combination of ion-dipole interactions, hydrogen bonding, and hydrophobic effects.<sup>370–373</sup>

The number of repeating glycoluril units defines the portal size and cavity volume of CB[n]. Reflecting the differences in size, it has been discovered empirically that CB[5] is best suited for the encapsulation of gases.<sup>374</sup> CB[6] can bind alkylamines or alkylammonium salts,<sup>375</sup> CB[7] can accommodate small organic compounds, such as 2-methylsilyl groups, Ad, or Fc derivatives,<sup>376–378</sup> whereas CB[8] can complex two guest molecules to form 1:2 homodimer complexes or 1:1:1 heteroternary complexes in the case of aromatic guests.<sup>379–384</sup>

The host-guest properties of CB[n]s have made them attractive in the area of polymer science, including catalyzing the formation of polymers<sup>393,394</sup> and constructing cross-linked supramolecular polymeric materials, particularly in aqueous media.<sup>58,388,395–398</sup> In this section, we summarize recent progress involving SPNs prepared via the combination of

CB[n]-based host-guest interactions (Figure 46) and covalent polymers.

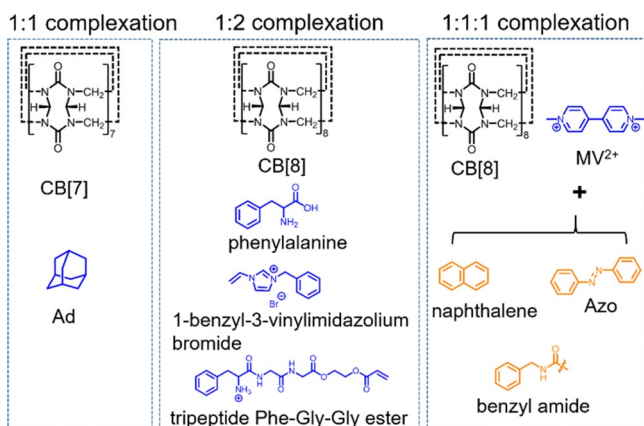


Figure 46. Chemical structures of CB[7] and CB[8] and complementary guests that have been used to prepare SPNs.

### 5.1. Cucurbit[7]uril/Adamantane Host-Guest Recognition Motifs

The kinetics of hydrogel formation touch on many application areas including inter alia the development of injectable and printable hydrogels.<sup>399,400</sup> In fact, an ability to control the gelation kinetics of hydrogels without affecting the structure and properties of the resulting materials represents a recognized challenge. Appreciating this, an and co-workers reported an approach to controlling the gelation kinetics of a cross-linked supramolecular hydrogel based on CB[7]/Ad host-guest recognition that relied on the use of competing guests.<sup>481</sup> As shown in Figure 47, two DMAAM-based polymers with CB[7]

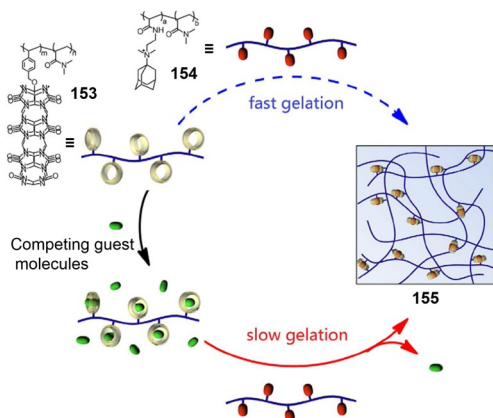


Figure 47. Chemical structures of the CB[7]-functionalized polymer 153 and the Ad-bearing polymer 154. Also shown in schematic form is how competing guests may be used to control the gelation kinetics of the cross-linked hydrogel 155 generated from 153 and 154. Reproduced with permission from ref 401 under a Creative Commons Attribution 4.0 International License, copyright 2016 Springer Nature.

and Ad pendants, namely 153 and 154, were used to create a supramolecular cross-linked hydrogel 155. The interaction between the CB[7] and Ad subunits on the polymer backbone could be reduced by pre-occupying the CB[7] cavity with competing guest molecules. By varying the guest molecules, within the set defined by  $MV^{2+}$ , 1,6-diaminohexane dihydrochloride, and (ferrocenylmethyl)trimethylammonium iodide,

the rate of gelation could be varied from seconds to hours. On the other hand, once formed the strong interactions between the CB[7] and Ad moieties endowed hydrogel 155 with high elasticity, good stability, and shape persistence. The regulation of gelation kinetics of the hydrogel could thus be used for injection and printing operations.

### 5.2. Cucurbit[8]uril/Phenylalanine Host-Guest Recognition Motifs

Liu, Scherman and co-workers reported a responsive double network hydrogel based on DNA hybridization and CB[8]/phenylalanine host-guest recognition motifs. As shown in Figure 48, phenylalanine-functionalized carboxymethyl cellulose 156

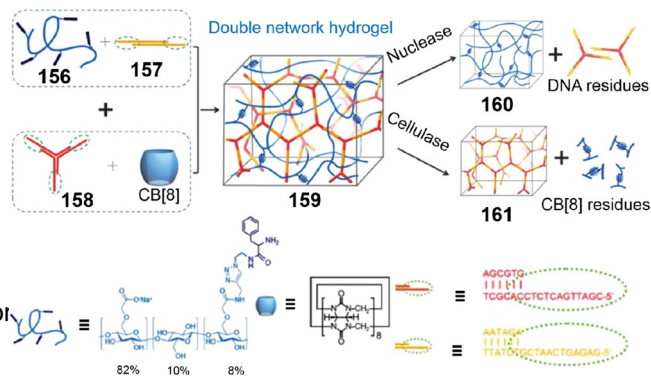


Figure 48. Chemical structures of 156, 157, and 158. Also shown in schematic form is their use in preparing the double network hydrogel 159 and the single network hydrogels 160 and 161, both of which are produced through controlled enzymatic degradation. Reproduced with permission from ref 402. Copyright 2015 John Wiley and Sons.

and CB[8] interact with each other with a 1:2 host-guest stoichiometry to form a cross-linked hydrogel network 160 (termed CB[8]). Alternatively, the DNA linker 157 and the DNA Y-scaffold 158 interact as the result of their complementary DNA sequences; this forms a second cross-linked hydrogel network 161, a so-called "DNA network". Upon mixing these four individual components a double network, hydrogel 159, is formed. In 159, the CB[8] and DNA networks 160 and 161 were found to interpenetrate, which was thought to contribute to the outstanding properties, such as thermal stability, mechanical strength, stretching ability and ductility, as well as excellent shear-thinning and thixotropic properties. It was expected that hydrogel 159 would possess a good biodegradability profile because each constituent network could be selectively digested by specific enzymes (e.g., cellulases and nucleases). In fact, because different enzymes are involved, selective degradation of one network could be achieved while retaining the structure and mechanical properties of the other.

### 5.3. Cucurbit[8]uril/1-Benzyl-3-vinylimidazolium Bromide Host-Guest Recognition Motifs

Synthetic constructs that imitate biological systems in their ability to self-repair and adapt to environmental stimuli, are particularly appealing in terms of creating hierarchical structures and new materials with good durability and functional utility.<sup>403</sup> Inspired by the structure and function of titin, Scherman and co-workers constructed an aqueous dual network that takes advantage of dynamic CB[8]/1-benzyl-3-vinylimidazolium bromide host-guest interactions and their force-induced dissociation.<sup>404</sup> As shown in Figure 49, the imidazolium guest can complex with CB[8] in a 2:1 manner,  $K_{12} = 4.21 \times 10^4 M^{-1}$ ,  $K_{22}$



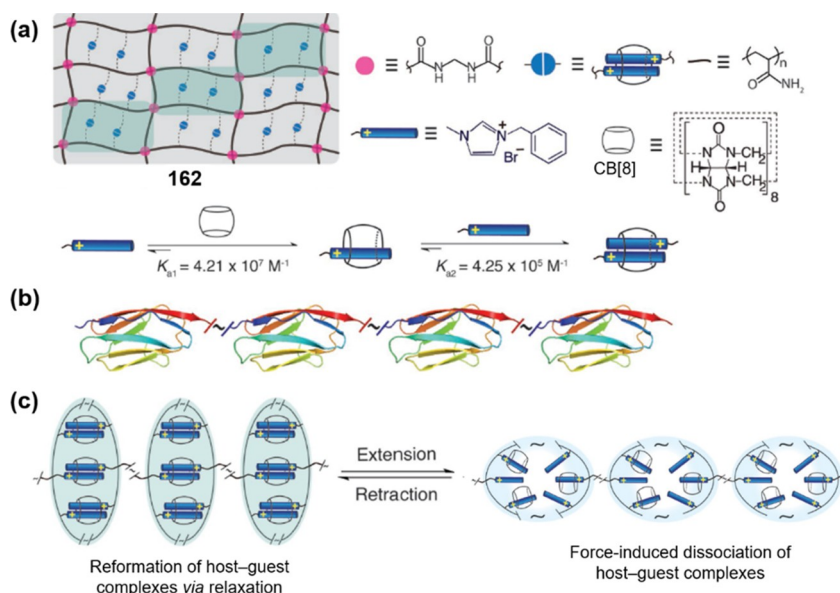


Figure 49. (a) Schematic illustration of a modular dual network 162 that relies on the judicious use of host–guest interactions (blue circles) and chemical cross-links (pink circles) and the host–guest complexation between CB[8] and the imidazolium guest. (b) Modular section of titin showing its basic structure. (c) Schematic illustration of the fundamental mechanism for energy dissipation within 162. Reproduced with permission from ref 404. Copyright 2017 John Wiley and Sons.

$= 4.25 \times 10^5 \text{ M}^{-1}$ ). In addition, it can also act as a non-covalent supramolecular cross-linker that may be polymerized in the presence of the chemical cross-linker MBAAM and a hydrophobic monomer AAM; this polymerization was found to give an aqueous dual network 162. In 162, dynamic “loops” formed based on the CB[8] host–guest complexes (Figure 49c). “loops” that were along the polymer chains exist between two covalent cross-linkers. Covalent chemical cross-linking was used to maintain the shape of the dual network and impart elasticity. Concurrently, CB[8]-based dynamic host–guest interactions were used to improve the mechanical features, including imparting fracture and fatigue resistance, self-recovery, and energy dissipation.

Supramolecular interactions play a critical role in many natural adhesion phenomena. Synthetic supramolecular adhesives could provide interfacial materials with intriguing properties, including an ability to dissipate energy or self-heal. Scherman and co-workers reported a supramolecular hydrogel network 163 that can function as a dynamic adhesive for a variety of nonporous and porous materials.<sup>408</sup> As shown in Figure 50, hydrogel 163 relies on a 1-benzyl-3-vinylimidazolium bromide-containing AAM polymer that is cross-linked by adding CB[8]. The result is a system that can form a tough and healable adhesive interlayer between a range of substrates.

#### 5.4. Cucurbit[8]uril/Methyl Viologen and Naphthalene Host–Guest Recognition Motifs

Inspired by spider silk, which possesses high strength, elasticity, and recognized “supercontract” features (a term reflecting the considerable shrinkage that occurs when exposed to water), Scherman and co-workers reported a supercontractile fiber 166. This fiber contracts by up to 50% of its original length at high humidity, in analogy to what is seen in the case of spider silk. As shown in Figure 51, polymer 164 could be functionalized with  $\text{MV}^{2+}$  and then grafted onto silica nanoparticles. The naphthalene- and methacrylic anhydride-functionalized hydrogel polymer 165 was also prepared in which methacrylic anhydride can bring further cross-linking into the

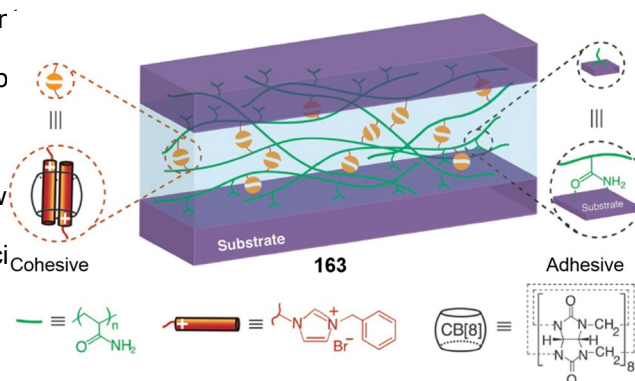


Figure 50. Schematic illustration of the SPN 163 and its use as an adhesive to attach two substrates. Reproduced with permission from ref 408. Copyright 2018 John Wiley and Sons.

system. CB[8]-based cross-linking of the two polymers and further UV cross-linking in aqueous media was then used to generate the supercontractile fiber 166 which possessed double network. This latter system possessed the viscoelastic properties required for directly drawing fibers with high aspect ratio from the hydrogel.

Colloidal reinforcement has been used to increase the strength, stiffness, and even the toughness of materials.<sup>410–414</sup>

The combination of supramolecular interactions with solid colloidal nanocrystals and nanocomposites has been pursued as a strategy to reinforce hydrogel materials.<sup>415–416</sup> Scherman and co-workers reported a supramolecular hydrogel that is bridged by colloidal nanofibrillated cellulose (NFC) domains.<sup>417</sup> As shown in Figure 52, the naphthalene-functionalized hydroxyethyl cellulose 167 and the  $\text{MV}^{2+}$ -functionalized PS-based copolymer 168 were used to prepare the supramolecular hydrogel network 169. This network could be attached to the NFC colloidal hydrogel to form a reinforced hybrid hydrogel 170; this was done by adsorbing 167 onto the surface of the NFC hydrogel. The hybrid hydrogel 170 exhibited significantly enhanced

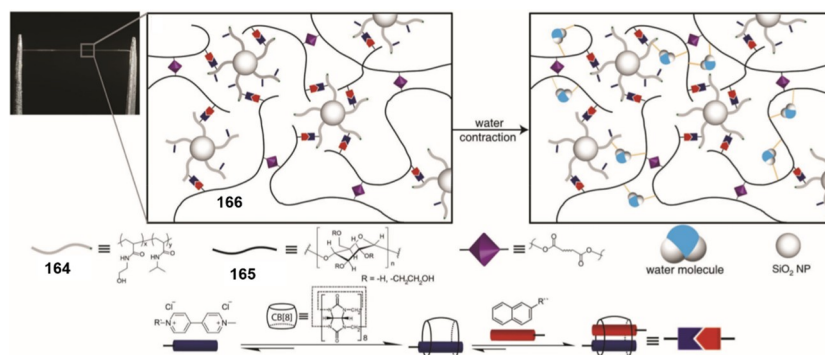


Figure 51. Chemical structures of 164 and 165 and schematic illustration of the supercontractile fiber 166 undergoing supercontraction at high humidity. Also shown is a photograph of the supercontractile fiber. Reproduced with permission from ref 409 under a Creative Commons Attribution License (CC BY), copyright 2018 John Wiley and Sons.

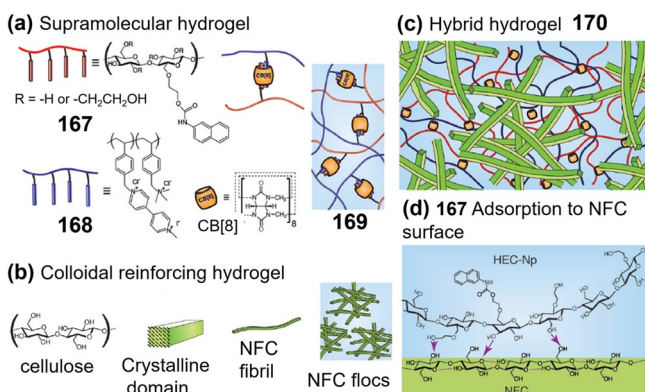


Figure 52. (a) Chemical structures of the naphthyl-functionalized hydroxyethyl cellulose 167 and cationic polymer 168. Also shown in schematic form is the supramolecular hydrogel 169 stabilized by host-guest interactions between CB[8] and 168. (b) Colloidal reinforcing nanofibrillated cellulose. (c) Interpenetrating hybrid hydrogel 170 comprised of the supramolecular hydrogel 169 and the colloidal-level NFC hydrogel. (d) Adsorption of 167 onto an NFC surface. Reproduced with permission from ref 417. Copyright 2015 John Wiley and Sons.

rheological yield strain and storage modulus values, as well as improved maximum elasticity values; presumably this phenomenon reflects a favorable combination of CB[8]-based host-guest dissociation/association dynamics and the stabilizing interactions between the supramolecular hydrogel 169 and the NFC nanofibers present in the hybrid system 170.

Scherman and co-workers reported a supramolecular hydrogel network based on CB[8]/MV<sup>2+</sup> and naphthalene host-guest recognition motifs.<sup>418</sup> As shown in Figure 53, CB[8] host moieties were mechanically locked onto a highly branched hydrophilic N-hydroxyethylacrylamide (HEAAM) polymer backbone through selective binary complexation with viologen derivatives. This locking serves to stabilize the highly branched CB[8]-threaded polyrotaxane-containing system. A linear HEAAM polymer 172 containing MV<sup>2+</sup> groups on the side chains was also prepared, and the naphthyl-functionalized hydroxyethyl cellulose 173. When 173 and CB[8] were added to 171 and 172, respectively, two kinds of supramolecular hydrogels, namely 174 and 175, were obtained. Relative to 171, the mechanically interlocked and highly branched network 174 displayed an improved viscoelastic modulus, greater thermal stability, and enhanced self-healing.

### 5.5. Cucurbit[8]uril/Tripeptide Phe-Gly-Gly Ester Derivative Host-Guest Recognition Motifs

Hydrogels have been used extensively for wound dressings.<sup>419,420</sup> Supramolecular hydrogels constructed via dynamic non-covalent interactions are capable of dissolution upon the application of a stimulus, such as they are attractive as wound dressings since they are expected to promote healing with reduced risk of damaging the newly formed tissues. Zhang and co-workers reported a supramolecular hydrogel designed to provide an easily removable wound dressing. The material in question was based on a polymeric network cross-linked by host-guest interactions between CB[8] and the Phe-Gly-Gly tripeptide ester, 176.<sup>421</sup> As shown in Figure 54, the supramonomer 177, formed as the result of host-guest interactions between 176 and CB[8], was first prepared. Radical copolymerization with AAM as a cross-linker then produced the desired supramolecular hydrogel 178. Hydrogel 178 proved transparent, nontoxic, and self-repairable. It also exhibited desirable mechanical properties that could be readily tuned. In particular, hydrogel 178 could be loaded and used to deliver therapeutic agents to wounds. When exposed to the mild chemical irritant memantine hydrogel 178 dissolved within 2 min. This conversion was ascribed to the fact that CB[8] interacts more strongly with memantine ( $K_a = 4.3 \times 10^{11} \text{ M}^{-1}$ ) than with 176 ( $K_a = 2.0 \times 10^{11} \text{ M}^{-1}$ ); as a result, supramonomer 177 is destroyed by the competitive guest memantine. These features are expected to translate into reduced patient pain and shortened wound-healing times.

### 5.6. Cucurbit[8]uril/Methyl Viologen and Benzyl Amide or Azobenzene Host-Guest Recognition Motifs

Interfacial adhesion promoted by means of host-guest interactions constitutes an attractive means of creating functional interfaces for wound dressings and tissue adhesives.<sup>422–424</sup>

Appreciating this, Scherman and co-workers used CB[8]-threaded highly branched polyrotaxanes to form dynamically bonded soft material that could adhere two wet surfaces through CB[8]/MV<sup>2+</sup> and benzyl amide/Azo host-guest interactions ( $K_a = 2.0 \times 10^6 / 4.0 \times 10^5 \text{ M}^{-1}$ ).<sup>425</sup> As shown in Figure 55, the MV<sup>2+</sup> groups in the CB[8]-threaded highly branched polyrotaxanes 171 act as a first set of guests. Azo- and benzyl amide-containing AAM polymers 179 and 180 then act as a second set of guests. When 179 or 180 were molded into thin strips, aqueous solutions containing 171 could be used to the interfaces of these samples, allowing macroscopic adhesion to be achieved. The adhesion was ascribed to the formation of SPNs 181 and 182 stabilized by host-guest interactions involving the CB[8]/MV<sup>2+</sup> and the benzyl amide or



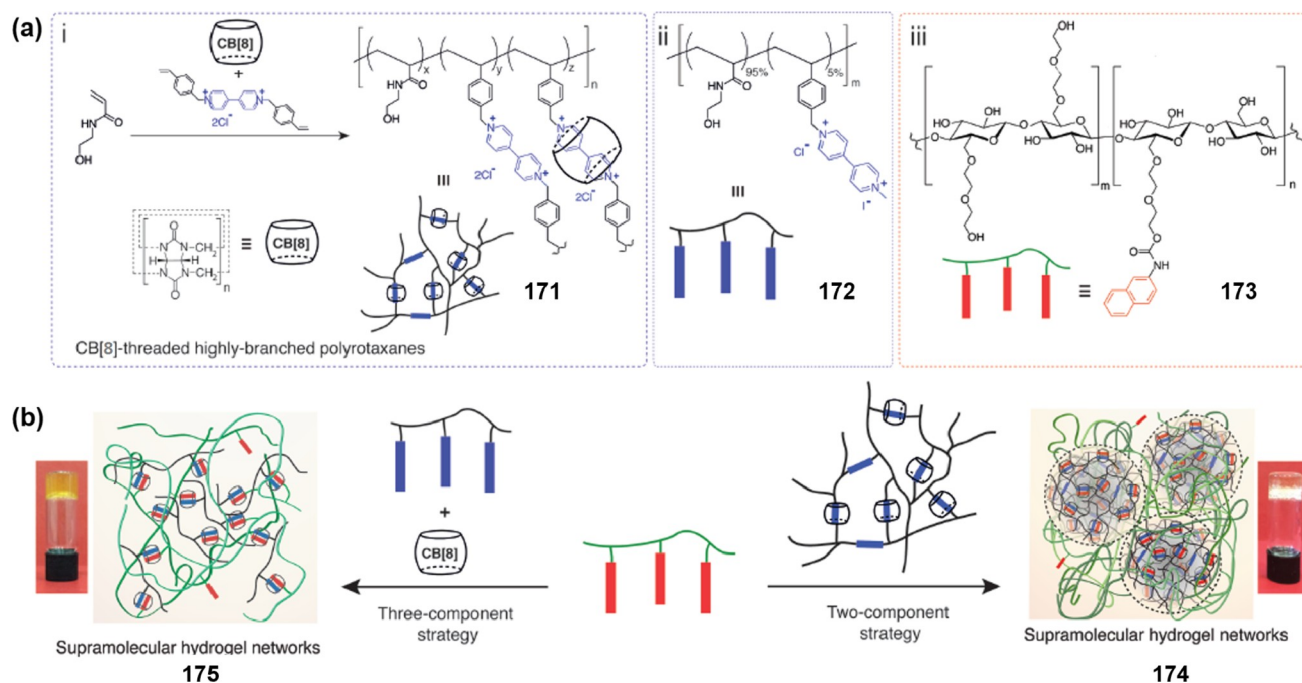


Figure 53. (a) Synthesis of the highly branched CB[8]-threaded polyrotaxane 171 (i) and chemical structures of (ii) linear polymer 172 and (iii) naphthyl-functionalized hydroxyethyl cellulose 173. (b) Schematic illustration of the hydrogel networks 174 and 175 created via a two-component strategy that involves combining 171 with 173, as well as a three-component strategy that relies on the combined use of CB[8], 172, and 173. Reproduced with permission from ref 418. Copyright 2017 John Wiley and Sons.

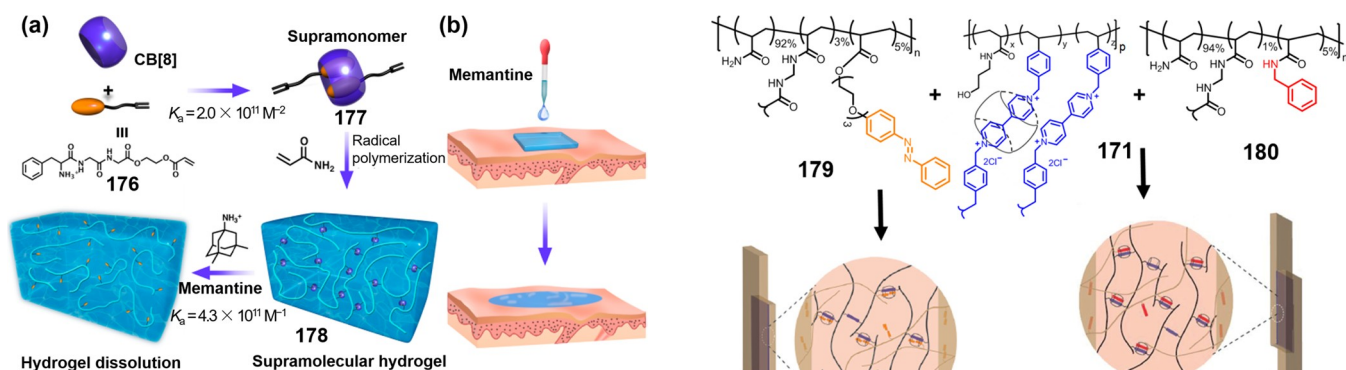


Figure 54. Schematic depiction (a) supramolecular hydrogel 178 fabricated from supramonomers 177 based on CB[8] and 176; shown is its dissolution chemistry triggered by irrigation with memantine (b) Application of 178 as a potential wound dressing material. Reproduced with permission from ref 420. Copyright 2017 American Chemical Society.

Azo subunits, respectively. The dynamic nature of the host-guest complexes present in 181 and 182 was found to support adhesive contact that, in turn, allowed for recovery and reversible adhesion. Under non-extreme aqueous conditions, the adhesive could be set and would undergo self-healing without the need for additional curing materials. Moreover, SPN 181, a system based on adhesion between 171 and 179, proved responsive to photo-irradiation. This feature was ascribed to photo-isomerization of the constituent azo groups under conditions of photo-irradiation.

### 5.7. Comparisons between Supramolecular Polymeric Networks Constructed by Cucurbit[n]uril-Based Host-Guest Recognition Motifs

To date, most CB[n]-based host-guest recognition motifs used to support SPNs have relied on PAAM and polysaccharide

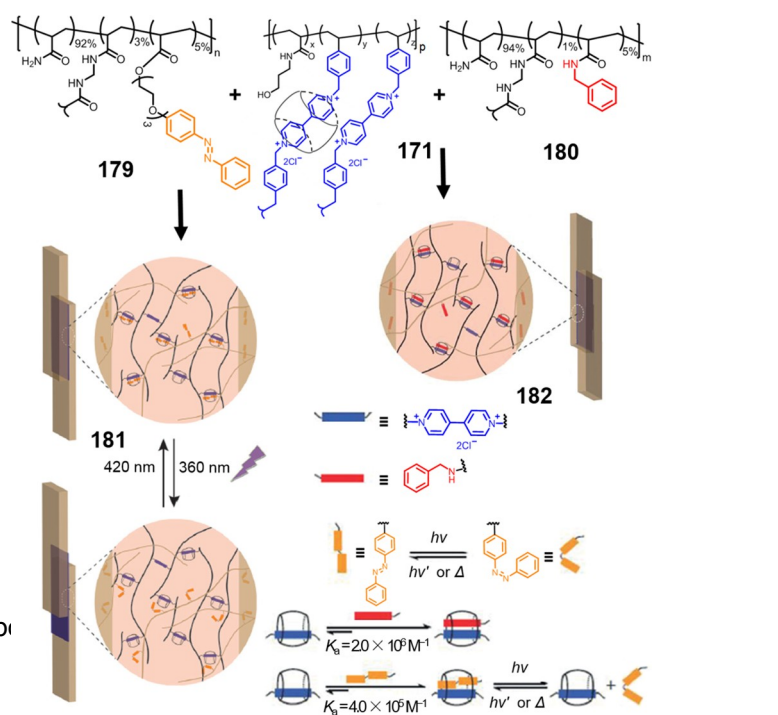


Figure 55. Chemical structures of CB[8]-threaded highly branched polyrotaxanes 171, hydrogel 179, and hydrogel 180. Also shown are schematic depictions of SPNs 181 and 182, and the dynamic interfacial gluing of these two hydrogels using 171 as the adhesive. Reproduced with permission from ref 425. Copyright 2018 John Wiley and Sons.

backbones. Nevertheless, a range of systems predicated on CB[n]-based host-guest recognition have been produced. These include ones based on 1:1 CB[7]/Ad complexes and 1:2 interactions between CB[8]/1-benzyl-3-vinylimidazolium



Table 3. SPNs Based on CB[n]-based Host–Guest Recognition Motifs Classified by the Underlying Covalent Polymer

molecular recognition	figure number	cross-linking motif	SPN	ref
Poly(acrylamide) (PAAM)				
CB[7]/Ad	Figure 47	CB[7]-containing PDMAAM 153 with Ad-containing PDMAAM 154	155	401
CB[8]/1-benzyl-3-vinylimidazolium bromide	Figure 49	MBAAM, AAM, CB[8] and 1-benzyl-3-vinylimidazolium bromide after polymerization	162	404
	Figure 50	AAM, 1-benzyl-3-vinylimidazolium with CB[8] after polymerization	163	408
CB[8]/MV <sup>2+</sup> and naphthalene	Figure 51	MV <sup>2+</sup> -containing PAAM 164 grafted silica nanoparticles with naphthalene- and methacrylic anhydride-functionalized hydroxyethyl cellulose polymer 165 with CB[8]	166	409
	Figure 53	highly branched CB[8]/MV <sup>2+</sup> polyrotaxane 171 with naphthyl-functionalized hydroxyethyl cellulose 173	171	418
		MV <sup>2+</sup> -containing PHEAAM 172 with naphthyl-functionalized hydroxyethyl cellulose 173 with CB[8]	172	418
CB[8]/tripeptide Phe-Gly-Gly ester derivative	Figure 54	CB[8]/tripeptide Phe-Gly-Gly ester derivative-based supramolecular monomer 177 after polymerization with AAM	177	421
CB[8]/MV <sup>2+</sup> and Azo	Figure 55	highly branched CB[8]/MV <sup>2+</sup> polyrotaxane 171 with Azo-containing PAAM 179	181	425
CB[8]/MV <sup>2+</sup> and benzyl amide		highly branched CB[8]/MV <sup>2+</sup> polyrotaxane 171 with benzyl amide-containing PAAM polymer 180	182	
Polysaccharide				
CB[8]/phenylalanine	Figure 48	phenylalanine-functionalized carboxymethyl cellulose 156 and CB[8] with DNA linked to DNA Y-scaffold 158	156	402
CB[8]/MV <sup>2+</sup> and naphthalene	Figure 51	MV <sup>2+</sup> -containing PAAM 164 grafted silica nanoparticles with naphthalene-functionalized hydroxyethyl cellulose polymer 165 with CB[8]	166	409
	Figure 52	naphthalene-functionalized hydroxyethyl cellulose 167 with MV <sup>2+</sup> -functionalized PS-based copolymer 168 with CB[8]	169	417
		SPN 169 with colloidal-level NFC hydrogel	170	
	Figure 53	highly branched CB[8]/MV <sup>2+</sup> polyrotaxane 171 with naphthyl-functionalized hydroxyethyl cellulose 173	171	418
		MV <sup>2+</sup> -containing PHEAAM 172 with naphthyl-functionalized hydroxyethyl cellulose 173 with CB[8]	172	418

bromide, phenylalanine, or Phe-Gly-Gly ester, as well as CB[6],<sup>488</sup> and Ad ammonium salts. Pillar[9]arenes can form MV<sup>2+</sup> in conjunction with naphthalene or benzyl amide and Azobenzene inclusion complexes with 2,7-diazapyrenium salt<sup>490</sup> and in a 1:1:1 manner. Table 3 provides a summary of the systems MV<sup>2+</sup>. Pillar[10]arenes can bind MV<sup>2+</sup>.<sup>492,493</sup> These host–guest systems respond to various external stimuli, including pH changes,<sup>489</sup> redox,<sup>494</sup> temperature and so on. This endows the resulting supramolecular architectures with environmental responsiveness and makes them of interest in the context of a wide number of potential applications. Many of these host–guest recognition features have been exploited to construct supramolecular polymeric materials with applications in a variety of areas such as detection, analyte adsorption, and light-harvesting.<sup>495,496,497,498,499,500,501,502,503,504,505,506,507,508,509,510,511,512,513,514,515,516,517,518,519,520,521,522,523,524,525,526,527,528,529,530,531,532,533,534,535,536,537,538,539,540,541,542,543,544,545,546,547,548,549,550,551,552,553,554,555,556,557,558,559,560,561,562,563,564,565,566,567,568,569,570,571,572,573,574,575,576,577,578,579,580,581,582,583,584,585,586,587,588,589,590,591,592,593,594,595,596,597,598,599,600,601,602,603,604,605,606,607,608,609,610,611,612,613,614,615,616,617,618,619,620,621,622,623,624,625,626,627,628,629,630,631,632,633,634,635,636,637,638,639,640,641,642,643,644,645,646,647,648,649,650,651,652,653,654,655,656,657,658,659,660,661,662,663,664,665,666,667,668,669,670,671,672,673,674,675,676,677,678,679,680,681,682,683,684,685,686,687,688,689,690,691,692,693,694,695,696,697,698,699,700,701,702,703,704,705,706,707,708,709,710,711,712,713,714,715,716,717,718,719,720,721,722,723,724,725,726,727,728,729,730,731,732,733,734,735,736,737,738,739,740,741,742,743,744,745,746,747,748,749,750,751,752,753,754,755,756,757,758,759,760,761,762,763,764,765,766,767,768,769,770,771,772,773,774,775,776,777,778,779,780,781,782,783,784,785,786,787,788,789,790,791,792,793,794,795,796,797,798,799,800,801,802,803,804,805,806,807,808,809,810,811,812,813,814,815,816,817,818,819,820,821,822,823,824,825,826,827,828,829,830,831,832,833,834,835,836,837,838,839,840,841,842,843,844,845,846,847,848,849,850,851,852,853,854,855,856,857,858,859,860,861,862,863,864,865,866,867,868,869,870,871,872,873,874,875,876,877,878,879,880,881,882,883,884,885,886,887,888,889,890,891,892,893,894,895,896,897,898,899,900,901,902,903,904,905,906,907,908,909,910,911,912,913,914,915,916,917,918,919,920,921,922,923,924,925,926,927,928,929,930,931,932,933,934,935,936,937,938,939,940,941,942,943,944,945,946,947,948,949,950,951,952,953,954,955,956,957,958,959,960,961,962,963,964,965,966,967,968,969,970,971,972,973,974,975,976,977,978,979,980,981,982,983,984,985,986,987,988,989,990,991,992,993,994,995,996,997,998,999,1000</sup>

## 6. SUPRAMOLECULAR POLYMERIC NETWORKS CONSTRUCTED VIA THE COMBINATION OF COVALENT POLYMERS AND PILLAR[N]ARENE-BASED HOST–GUEST INTERACTIONS

Pillar[n]arenes are a relatively new class of macrocyclic hosts that since their introduction in 2008 have already taken their place as stalwarts of supramolecular chemistry. The repeat units in pillar[n]arenes are connected via methylene bridges in the para positions of the constituent phenyl moieties; this results in the formation of uniquely rigid, pillar-like structures.<sup>426,427,428</sup> The syntheses, conformational mobility, functionalization, host–guest chemistry, self-assembly features, and a variety of applications have been actively explored over the past 10 years.<sup>429–449</sup> Much of this effort has been reviewed elsewhere.<sup>93,427,428,450–454</sup> However, a brief synopsis of some of the key host–guest recognition features of pillar[n]arenes is appropriate here. Typically, pillar[5]arenes will form stable complexes with alkylamines,<sup>455–457</sup> organic ammonium salts,<sup>458–460</sup> nitriles,<sup>461–463</sup> alkanes,<sup>464,465</sup> pyridinium salts,<sup>466,467</sup> imidazole/imidazolium salts,<sup>443,468–470</sup> haloalkanes,<sup>471,472</sup> MV<sup>2+</sup>,<sup>434,473,474</sup> salicylaldehyde,<sup>475</sup> 10-methyl-acridinium,<sup>476</sup> alkylsulfonate salts,<sup>477</sup> and azastilbene derivatives.<sup>99,478</sup> Pillar[6]arenes can accommodate Azo,<sup>284,285,479</sup> MV<sup>2+</sup>,<sup>480</sup> ferrocenium salts (Fc<sup>+</sup>),<sup>481,482</sup> azastilbene derivatives,<sup>483,484</sup> pyridinium salts,<sup>438,485</sup> and nitrile-containing guests.<sup>486</sup> Pillar[7]arenes are able to complex MV<sup>2+</sup>,<sup>487</sup>

### 6.1. Pillar[6]arene/Ferrocenium Salt Host–Guest Recognition Motifs

Functional supramolecular materials based on redox-responsive host–guest interactions are attractive due to their potential utility in a number of applications-related areas. The Fc/Fc<sup>+</sup> couple is among the most widely used motifs used to construct redox-responsive supramolecular materials. Fc and its derivatives have considerable appeal due to the well-developed synthetic methods allowing their access, the fact they bind well to suitable hosts, and permit redox control over many host–guest interactions.<sup>505,506</sup> Wang and co-workers reported a dual-responsive SPN (185) based on redox-controllable pillar[6]arene/Fc recognition motifs that proved responsive to redox changes and chemical stimuli.<sup>507</sup> As shown in Figure 57, the polymeric backbone in question was constructed using a pillar[6]arene-grafted PMA 183 and a Fc-functionalized PS copolymer 184 in a mixture of CH<sub>3</sub>COCH<sub>3</sub> (5:1, v/v). After oxidation, SPN 185 was obtained. SPN 185 exhibited increased viscosity relative to the non-cross-linked mixtures.

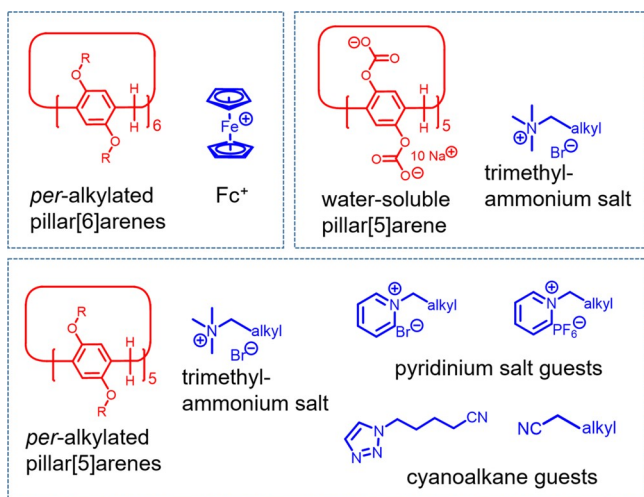


Figure 56. Chemical structures of per-alkylated pillar[6]arene, per-alkylated pillar[5]arene, and a water-soluble pillar[5]arene, as well as representative guests that have been used to fabricate SPNs.

was also found to stabilize a gel-like state. SPN 185, the supramolecular network cross-linking could be controlled by a variety of external stimuli, including exposure to chemical reductants and by means of competing host–guest interactions. The resulting changes could be monitored readily by monitoring the viscoelastic properties of 185.

### 6.2. Pillar[5]arene/Pyridinium Salt Host–Guest Recognition Motifs

Multi-responsive polymeric gels that can reversibly switch between free-flowing liquid and free-standing states are of both inherent interest and practical importance. Host–guest interactions can endow supramolecular systems with stimuli-responsive properties that allow the conversion between these limiting states to be effected as a function of environmental changes. In this context, Liao and co-workers reported a multi-responsive supramolecular cross-linked gel based on pillar[5]arene/pyridinium salt host–guest recognition.<sup>512</sup> As shown in Figure 58, addition of the bis(pyridinium) dicationic guest 186 to the PMMA-based copolymer 187 bearing pillar[5]arenes as pendent groups generated a supramolecular cross-linked polymeric gel 188 in  $CHCl_3$ . This gel

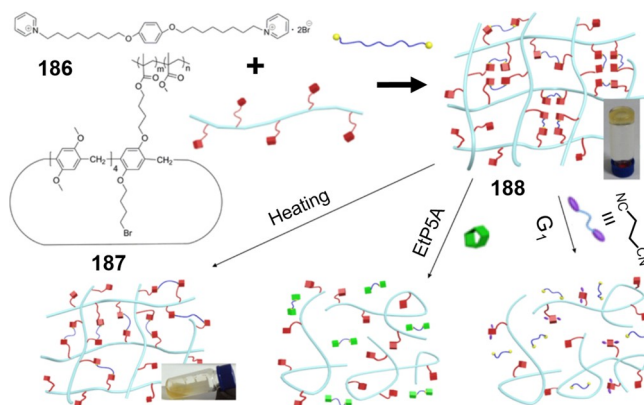


Figure 58. Schematic representation of the multi-responsive supramolecular gel 188 constructed from the bis(pyridinium) dicationic guest 186 and copolymer 187. Reproduced with permission from ref 512. Copyright 2016 American Chemical Society.

could be transformed to the corresponding sol form by adding a competitive host–ethyl-substituted pillar[5]arene (EtP5A), or a competitive guest, butanedinitrile. It was proposed that the ordered stacking structure of pillararenes plays an important role in this supposition. Reversible gel–sol transitions were seen as a function of temperature.

Arunachalam and co-workers reported an anion-responsive SPN based on the pillar[5]arene/pyridinium salt host–guest recognition motif.<sup>513</sup> In this case, the pillar[5]arene pendent polymer 189 was first synthesized from a pillar[5]arene-based oxanorbornene unit by means of a ring-opening metathesis polymerization using Grubbs' first generation catalyst (Figure 59). Mixing 189 with the ditopic bis(pyridinium) guest 190 in a mixture of  $CHCl_3/CH_3COCH_3$  (1:1, v/v) then gave rise to the SPN 191, presumably as the result of self-assembly driven by pillar[5]arene/pyridinium salt host–guest interactions. SPN 191 could be readily disassembled via the addition of tetrabutylammonium chloride.

### 6.3. Pillar[5]arene/Cyanoalkane Host–Guest Recognition Motifs

Adronov and co-workers reported a supramolecular polymeric organogel based on non-covalent pillar[5]arene/cyanoalkane interactions.<sup>514</sup> Here, a strain-promoted azide–alkyne cyclo-

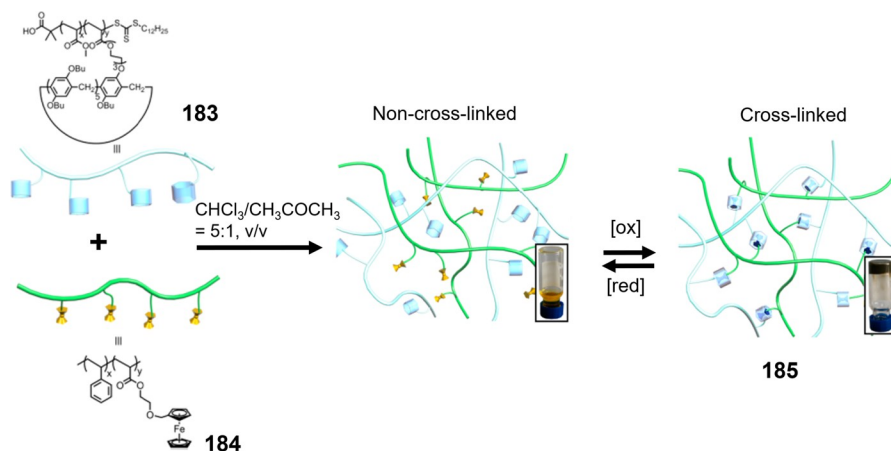


Figure 57. Representation of the redox-controllable supramolecular network 185 based on the functionalized polymers 183 and 184. Reproduced with permission from ref 50. Copyright 2015 American Chemical Society.

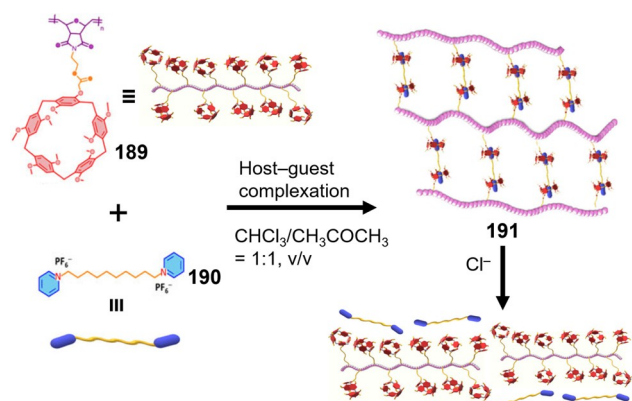


Figure 59. Schematic views showing the chemical structures of the pillar[5]arene-bearing polymer 189 and its ditopic bispyridinium guest 190. Also shown in cartoon representation is the SPN 191 obtained as the result of host-guest driven self-assembly and its response to a stimulus. Reproduced with permission from ref 513. Copyright 2019 John Wiley and Sons.

addition (SPAAC) was used to prepare a conjugated poly(dibenzocyclooctyne) polymer 192 decorated with pillar[5]arene subunits. Upon mixing 192 with polymer 193 decorated with cyanoalkane guests, the supramolecular cross-linked polymeric organogel 194 was formed (Figure 60). Organogel 194 is presumably stabilized through formation of pillar[5]arene/cyanoalkane inclusion complexes. On the other hand, it could be disassociated by treating with trifluoroacetic acid (TFA). This latter stimulus responsiveness was attributed to acid-catalyzed hydrolysis of the imine linkages with 194. Dehydration with 3 Å molecular sieves followed by treatment with triethylamine (TEA), served to restore the original system. The gel also proved capable of undergoing self-healing if severed and reattached.

TPE, as noted earlier in this Review, is a fluorogen with AIE properties. It and various derivatives have been extensively applied in the areas of bioimaging and molecular sensing. TPEs have also been used as fluorogenic components in the fabrication of supramolecular polymeric materials. Huang and co-workers reported a fluorescent SPN with

aggregation induced enhanced emission (AIEE) features based on the host-guest interactions between pillar[5]arene and triazole-containing cyanoalkane. In this work, a conjugated poly(tetraphenylethene) polymer 195 bearing pillar[5]arene hosts was cross-linked by adding the homoditopic triazole-containing cyanoalkane 196 in  $\text{CHCl}_3$ . This resulted in the formation of the AIEE SPN 197 (Figure 61) compared with

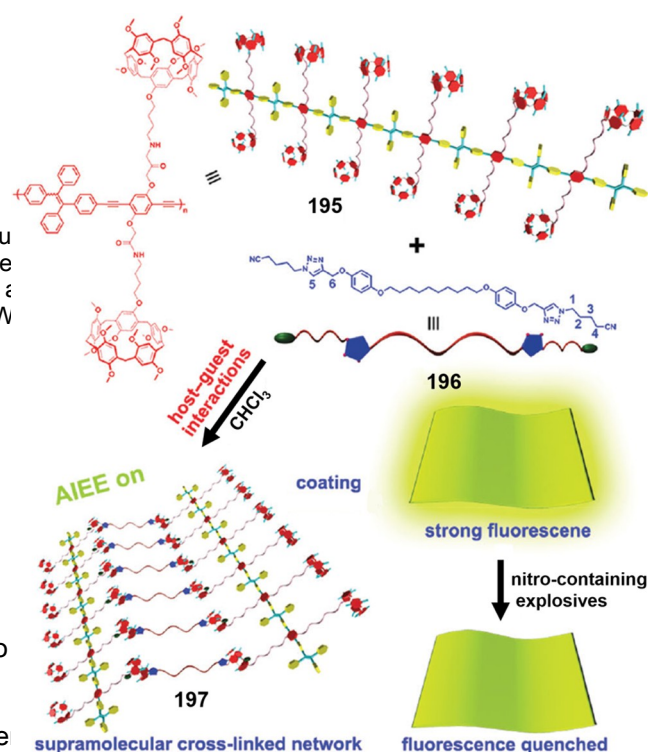


Figure 61. Chemical structures of 195 and 196. Also shown in schematic form is the formation of the AIEE fluorescent SPN 197 and its use in the detection of nitro-containing explosives. Reproduced with permission from ref 520. Copyright 2018 The Royal Society of Chemistry.

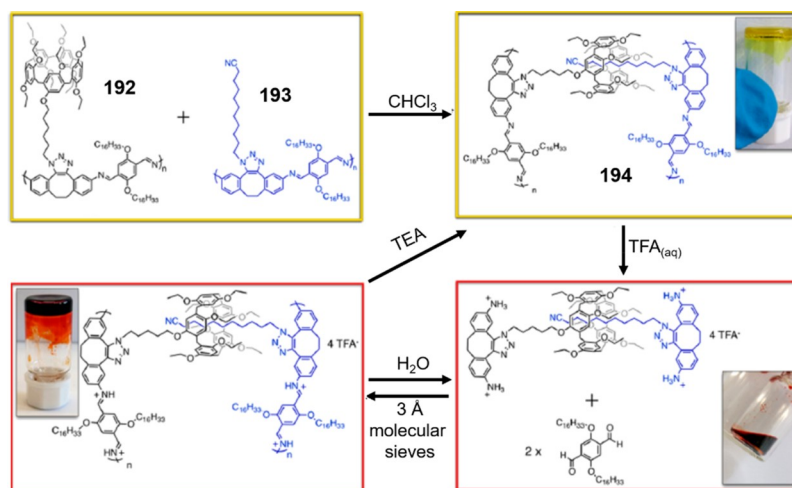


Figure 60. Formation of supramolecular polymeric organogel 194 from pillar[5]arene-containing poly(dibenzocyclooctyne) 192 and cyanoalkane-containing poly(dibenzocyclooctyne) 193 and its response to TFA and the associated recovery process. Reproduced with permission from ref 515. Copyright 2017 American Chemical Society.



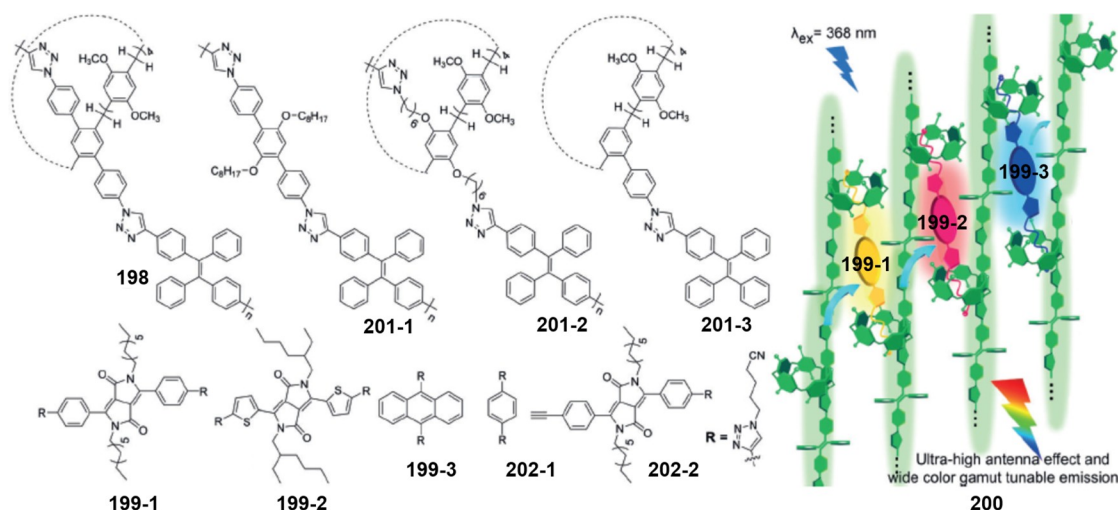


Figure 62. Chemical structures of the conjugated polymeric host 198, the ditopic guests 199-1, 199-2, and 199-3, the control polymers or hosts 201-2, and 201-3, and the control guests 202-1 and 202-2. Also shown in schematic form in the conjugated SPN 200. Reproduced with permission from ref 522 Copyright 2019 John Wiley and Sons.

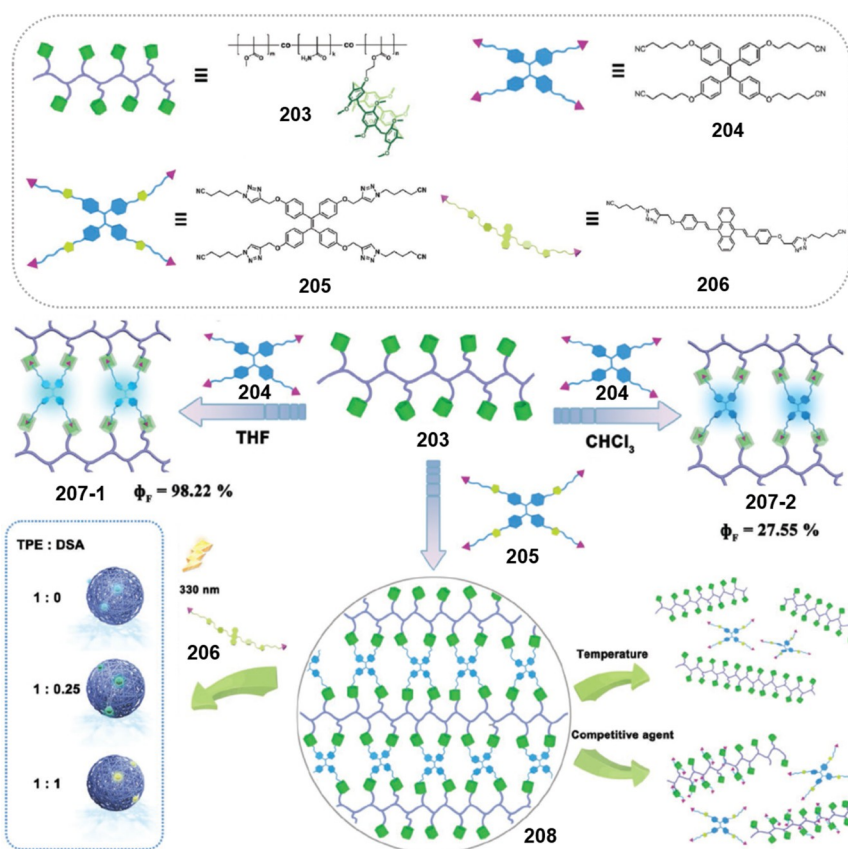


Figure 63. Chemical structures of the pillar[5]arene-grafted copolymer 203, the triazole-based cyanoalkane tetramer 204, the triazole-based triazole-containing cyanoalkane tetramer 205, and the 9,10-distyrylanthracene (DSA)-based triazole-containing cyanoalkane dimer 206. Also shown in schematic form in the conjugated SPN 208 and light-harvesting supramolecular nanoparticles from 206 and 208. Reproduced with permission from ref 524. Copyright 2019 John Wiley and Sons.

free 195, the incorporation of the cross-linker 196 (to give 197) was found to lead to an enhancement in the fluorescence emission intensity. Presumably this enhanced fluorescence reflects restriction in the motion of the TPE subunits as the result of host-guest interactions and activation of the anticipated AIEE effect. SPN 197 was found to respond to external stimuli, including temperature and the addition of

competitive guests, as readily monitored by changes in the fluorescence intensity. SPN 197 was also applied to the detection of nitro-containing explosives.

Artificial light-harvesting systems are considered as being critical to mimicking photosynthesis and creating synthetic constructs capable of capturing efficiently light energy.<sup>521</sup> Supramolecular strategies may have a role to play in creating

artificial light-harvesting systems<sup>446</sup> Cao, Tang and co-workers reported an artificial light-harvesting systems constructed by a supramolecular cross-linked network based on a pillar[5]arene<sup>209</sup> bearing trimethylammonium subunits in conjunction with the water-soluble pillar[5]arene 210 and a related small molecule, 211.<sup>528</sup> As shown in Figure 64, the shrinking behavior

of hydrogel 209 could be controlled via the encapsulation and release of two types of drug models (anionic calcein and cationic rhodamine B). After release, the supramolecular cross-linked hydrogel 212 formed via the host–guest interactions between 210 and the trimethylammonium side chains on 209, exhibited an equilibrium shrinking percentage of approximately 89.2% by weight. Relative to what was achieved using the simple model compound 211 and NaCl control experiments, 210 showed good selective release of anionic calcein, presumably reflecting an enhanced host–guest complexation effect in the case of 210.

A number of pillararene-based supramolecular polymer gels with interesting properties have been reported in recent years.<sup>97,448,512,528,529</sup> An SPN displaying high elasticity and rapid self-healing capability was generated by Chen and co-workers by exploiting an acrylate monomer that allowed for stabilization of a pillar[5]arene/trimethylammonium salt host–guest complex after polymerization.<sup>530</sup> Specifically, as shown in Figure 65, in this contribution the ditopic trimethylammonium salt guest 213 and the acrylate-modified pillar[5]arene 214 were allowed to form the host–guest complex 215 in DMSO. After photo-induced polymerization in the presence of monomer tetra(ethylene glycol) acrylate (TEGA) and the UV initiator I2959, the supramolecular polymer gel 216 was obtained. Mechanical studies revealed that SPN 216 possessed high elasticity and strong fatigue-resistance. In addition, this gel showed good self-healing, presumably because of the underlying host–guest interactions between the pillar[5]arene host subunits and the trimethylammonium guests. Gel 216 also displayed good temperature and pH dual stimuli-responsive features. The temperature-induced response was thought to reflect the inherent temperature-dependence of the host–guest interactions. A pH-induced gel-to-sol transition could be achieved by treating with NaOH, a finding ascribed to the

workers reported a method to achieve the supramolecular-based shrinking of hydrogels by using the PAAM-based copolymer bearing trimethylammonium subunits in conjunction with the water-soluble pillar[5]arene 210 and a related small molecule, 211.<sup>528</sup> As shown in Figure 64, the shrinking behavior

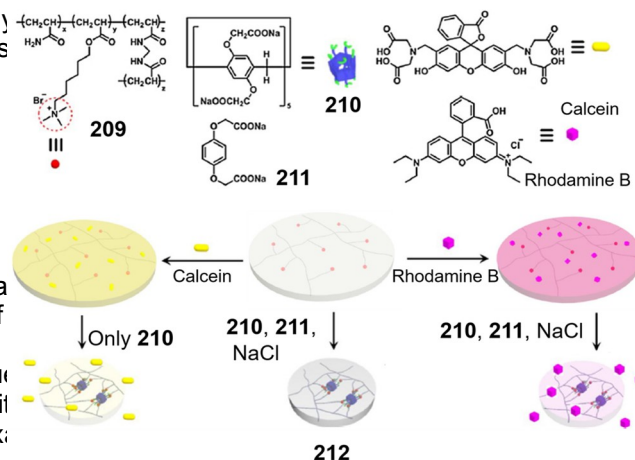


Figure 64. Structures of 209, 210, 211, calcein, and rhodamine B and illustration of the dramatically shrinking seen for samples under conditions of controlled release of calcein and rhodamine from the calcein- and rhodamine B-loaded hydrogels by different triggers. Shown in schematic form is the SPN 212 obtained after release. Reproduced with permission from ref 528. Copyright 2018 Elsevier.

An AIEE SPN 208 based on 203 and the TPE-based triazole-containing cyanoalkane tetram<sup>205</sup> could be produced by mixing in solution. This construct displayed responsiveness, fluorescence quenching, sensitivity to temperature, and changes in form when exposed to the competitive guest adiponitrile.

Supramolecular nanoparticles that act as artificial light-harvesting systems could be prepared by combining 205 and the 9,10-distyrylanthracene (DSA)-based triazole-containing cyanoalkane dimer 206 with the pillar[5]arene host-containing polymer 203 in a mixture of THF and water. By adjusting the molar ratio of 205 and 206, the fluorescent colors of the artificial light-harvesting systems could be tuned (Figure 63).

#### 6.4. Pillar[5]arene/Trimethylammonium Salt Host–Guest Recognition Motifs

Supramolecular hydrogels are well known for their self-healing, shape retention, adhesive, water uptake, and swelling features.<sup>146,525,529</sup> The introduction of host–guest interactions can further endow hydrogels with shrinking capability. This shrinking ability provides a complement to swelling and is potentially useful in the context of hydrogels. Shen and co-

workers reported a method to achieve the supramolecular-based shrinking of hydrogels by using the PAAM-based copolymer bearing trimethylammonium subunits in conjunction with the water-soluble pillar[5]arene 210 and a related small molecule, 211.<sup>528</sup> As shown in Figure 64, the shrinking behavior

of hydrogel 209 could be controlled via the encapsulation and release of two types of drug models (anionic calcein and cationic rhodamine B). After release, the supramolecular cross-linked hydrogel 212 formed via the host–guest interactions between 210 and the trimethylammonium side chains on 209, exhibited an equilibrium shrinking percentage of approximately 89.2% by weight. Relative to what was achieved using the simple model compound 211 and NaCl control experiments, 210 showed good selective release of anionic calcein, presumably reflecting an enhanced host–guest complexation effect in the case of 210.

A number of pillararene-based supramolecular polymer gels with interesting properties have been reported in recent years.<sup>97,448,512,528,529</sup> An SPN displaying high elasticity and rapid self-healing capability was generated by Chen and co-workers by exploiting an acrylate monomer that allowed for stabilization of a pillar[5]arene/trimethylammonium salt host–guest complex after polymerization.<sup>530</sup> Specifically, as shown in Figure 65, in this contribution the ditopic trimethylammonium salt guest 213 and the acrylate-modified pillar[5]arene 214 were allowed to form the host–guest complex 215 in DMSO. After photo-induced polymerization in the presence of monomer tetra(ethylene glycol) acrylate (TEGA) and the UV initiator I2959, the supramolecular polymer gel 216 was obtained. Mechanical studies revealed that SPN 216 possessed high elasticity and strong fatigue-resistance. In addition, this gel showed good self-healing, presumably because of the underlying host–guest interactions between the pillar[5]arene host subunits and the trimethylammonium guests. Gel 216 also displayed good temperature and pH dual stimuli-responsive features. The temperature-induced response was thought to reflect the inherent temperature-dependence of the host–guest interactions. A pH-induced gel-to-sol transition could be achieved by treating with NaOH, a finding ascribed to the

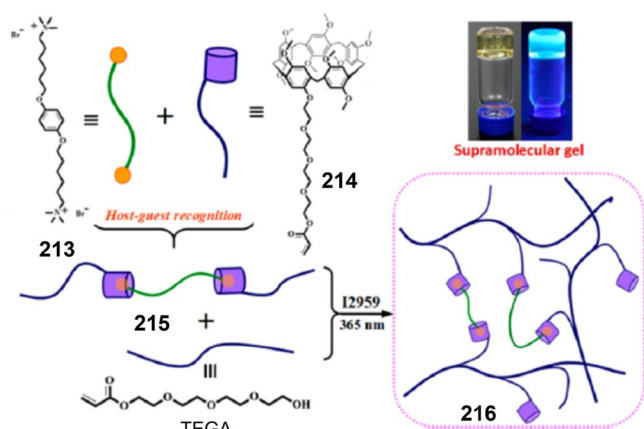


Figure 65. Chemical structures of the ditopic trimethylammonium guest 213, the acrylate-modified pillar[5]arene 214, and the monomer III. Also shown in schematic form is the proposed host-guest complex 215 and the supramolecular polymer gel 216 host-guest interactions between these precursors support. Reproduced with permission from ref 530. Copyright 2019 American Chemical Society.

reaction of the ammonium guest or the destruction of the ester groups on the polymer under alkaline conditions.

#### 6.5. Comparisons between Supramolecular Polymeric Networks Constructed by Pillar[n]arene-Based Host-Guest Recognition Motifs

Most covalent polymers used to construct SPNs on the basis of pillar[n]arene-based host-guest interactions contain PAPS, poly(oxanorbornene imide), poly(dibenzocyclooctyne), poly(tetraphenylethene), and PAAM covalent backbones. Among them, PA and PAAM have been reported as being cross-linked by means of different pillar[n]arene-based host-guest interactions to form SPNs. The key features of these PA and PAAM-based SPN are summarized in Table 4.

### 7. SUPRAMOLECULAR POLYMERIC NETWORKS CONSTRUCTED THROUGH THE COMBINATION OF COVALENT POLYMERS AND OTHER MACROCYCLE-BASED HOST-GUEST INTERACTIONS

In addition to the five general classes of macrocyclic hosts discussed above, other macrocycles such as calix[4]pyrroles (C4Ps),<sup>102,531,532</sup> a “Texas-size” tetracationic imidazolium macrocycle,<sup>533–536</sup> and cyclobis(paraquat-p-phenylene) (CBPQT<sup>4+</sup>),<sup>537–539</sup> are known that display interesting host-guest recognition features (Figure 66). Some examples of SPNs predicated on the use of these macrocyclic receptors are presented in this section.<sup>540–544</sup>

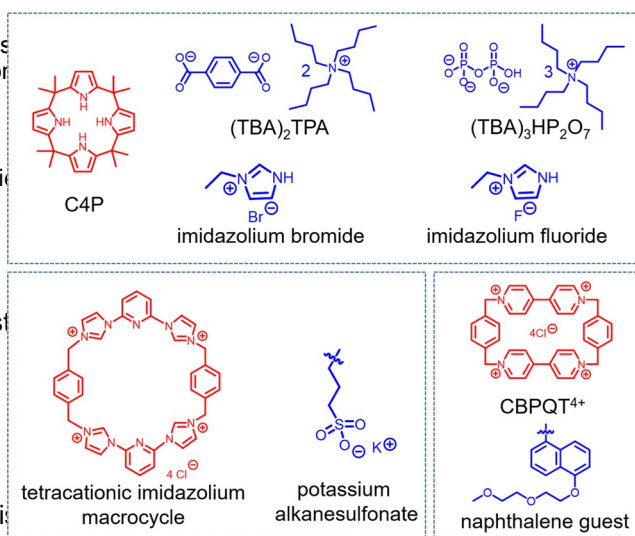


Figure 66. Chemical structures of C4P, a “Texas-size” tetracationic imidazolium macrocycle, and CBPQT<sup>4+</sup> that have been used to fabricate SPNs. Also shown are representative guests.

#### 7.1. Calix[4]pyrrole/Anion Host-Guest Recognition Motifs

Many non-covalent interactions have been used to create SPNs displaying controlled response features. Included within this lexicon are hydrogen bond-based systems as well as those stabilized through charge-transfer interactions and cation

Table 4. SPNs Based on Pillar[n]arene-Based Host-Guest Recognition Motifs Classified by the Underlying Covalent Polymer Backbones

molecular recognition	figure number	cross-linking motif	SPN	ref
Polyacrylate (PA)				
pillar[6]arene/Fc	Figure 57	pillar[6]arene-grafted PMA 183 with the Fc-functionalized PS copolymer 184 after oxidation	185	507
pillar[5]arene/pyridinium salt	Figure 58	bis(pyridinium) guest 186 with the pillar[5]arene-grafted PMMA-based copolymer 187	188	512
pillar[5]arene/cyanoalkane	Figure 63	pillar[5]arene-grafted copolymer 203 with TPE-based cyanoalkane tetramer 204	207	524
		pillar[5]arene-grafted copolymer 203 with TPE-based triazole-containing cyanoalkane tetramer 205	208	528
pillar[5]arene/trimethylammonium salt	Figure 65	host-guest complex 215 with TEGA after polymerization	216	530
Poly(acrylamide) (PAAM)				
pillar[5]arene/cyanoalkane	Figure 63	pillar[5]arene-grafted copolymer 203 with TPE-based cyanoalkane tetramer 204	207	524
		pillar[5]arene-grafted copolymer 203 with TPE-based triazole-containing cyanoalkane tetramer 205	208	528
pillar[5]arene/trimethylammonium salt	Figure 64	trimethylammonium unit grafted PAAM-based copolymer 209 with water-soluble pillar[5]arene 210	211	528



complexation, to name a few.<sup>154,230,241,312,366,418</sup> In spite of this progress, much of which is reviewed in earlier sections of this Review, anion binding-based SPNs remain relatively rare. Sessler and co-workers reported a supramolecular polymer stabilized via C4P/bis-anion cross-linking interactions<sup>540</sup> as shown in Figure 67, polymer 217, a PMMA scaffold bearing

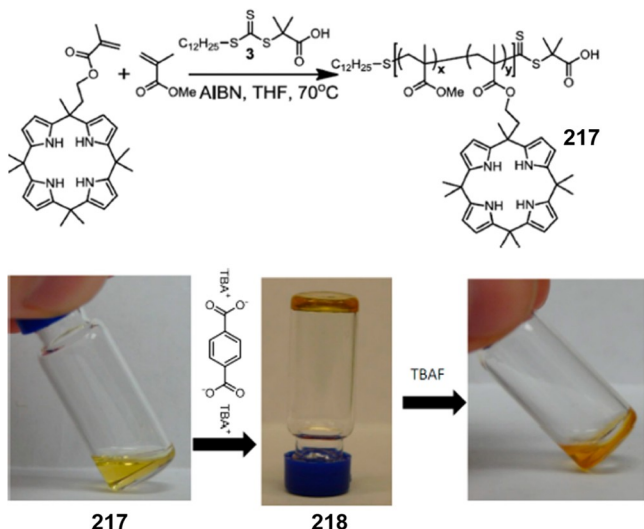


Figure 67. Syntheses of poly(calix[4]pyrrole ethyl methacrylate-co-MMA) 217. Photographs: gel 218 formed after addition of bis(tetrabutylammonium) terephthalate ((TBA)<sub>2</sub>TPA) and the break-up of the gel seen upon addition of excess tetrabutylammonium fluoride (TBAF). Reproduced with permission from ref 540. Copyright 2014 American Chemical Society.

groups, was synthesized from a MA-derived C4P monomer through controlled reversible addition/fragmentation chain-transfer polymerization (RAFT). The polymer obtained in this way was found to undergo cross-linking upon exposure to a dianionic C4P guest, tetrabutylammonium terephthalate (TBA)<sub>2</sub>TPA. This process led to formation of a supramolecular gel-like material 218. The gelation could be reversed by adding TBAF or by applying heat.

In addition, dianions in aqueous media can be extracted and separated by copolymer 217 under conditions of liquid/liquid extraction. When (TBA)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> was used as a polyanion source, extraction followed by gelation was observed. However, in this instance the gelation process took 3 days, and a lower extraction efficiency was noted than in the case of (TBA)<sub>2</sub>TPA. Presumably, this phenomenon reflects a better charge matching in the case of TPA than H<sub>2</sub>P<sub>2</sub>O<sub>7</sub><sup>3-</sup>.

Sessler and co-workers also reported a two-layer gel that permits the on-site detection of the chloride anion by means of a hand-held UV-vis lamp and a smart phone “app” through host-guest recognition between C4P and anion guests.<sup>541</sup> In this case, polymer 219 and its analogues bearing different fluorescent groups, namely polymer 220, 221, and 222, were used to synthesize eight fluorescent polymeric gels 223–230 (Figure 68). Fluorescent gels 223–226, based on C4P/imidazolium-F<sup>-</sup> anion recognition motifs, were used to construct a fluorescent pattern (Code A) as a 3D color code (Info A) that could be read out by a smart phone. Fluorescent gels 227–230 containing C4P/imidazolium-Br<sup>-</sup> anion recognition motifs were used to construct another fluorescent pattern (Code B) that could be read as Info B. In addition, Code B was adhered to the surface of Code A to generate a stacked double layer code system stabilized

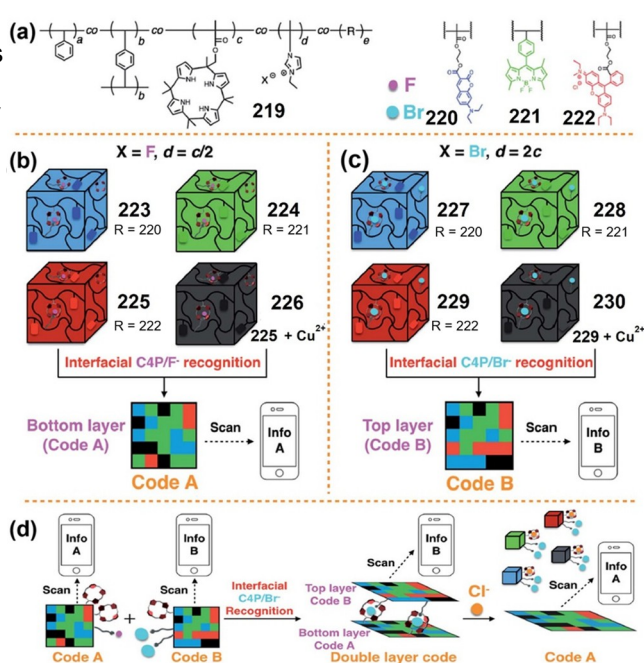


Figure 68. (a) Chemical structures of the polymers 219 and the related fluorescent systems 220, 221, and 222. Cartoon representations of (b) gels 223–226 and the formation of 3D color Code A via interfacial C4P/imidazolium-F<sup>-</sup> interactions, (c) gels 227–230 and the formation of 3D color Code B via interfacial C4P/imidazolium-Br<sup>-</sup> anion interactions and (d) formation of a double-layer code based on interfacial C4P/receptor interactions and site-specific recognition. Reproduced with permission from ref 541. Copyright 2018 The Royal Society of Chemistry.

by interfacial C4P/imidazolium-Br<sup>-</sup> anion interactions. Readout of the top layer (Code B) was not affected by Code A of the bottom layer. On the other hand, once treated with anion source the top layer was found to undergo delamination. A single layer degradation process served to reveal the bottom layer (Code A), whose information could then be read out. The disparate information inherent in Codes A and B (bottom and top layers, respectively) allowed the on-site recognition of the Cl<sup>-</sup> anion. An advantage of this system is that it permitted the detection of an anionic analyte using a barcode reader, thus illustrating what at the time appeared to be a new application for soft materials.

## 7.2. Tetracationic Imidazolium Macrocycle/Anion Host-Guest Recognition Motifs

Barcodes including 1D, 2D, and 3D codes are widely used to provide convenient readouts of encoded information in modern life. A fluorescent supramolecular polymeric material could provide a way to handle and transform the encoded information. Sessler and co-workers reported the preparation of five hydrogels 231–235 cross-linked through tetracationic imidazolium macrocycle/anion interactions that allowed them to achieve readout of encoded information<sup>542</sup> as shown in Figure 69. The gel-specific fluorophores were used as building blocks to construct physically adhered fluorescent color 3D codes that could be read out using a smart phone. The encoded information generated by patterns of these hydrogels could be changed by either physically moving gel elements or by exposing the dye-containing gels to a chemical stimulus. Moreover, one or more of the gel components making up the overall gel-based pattern could be replaced with another gel element via a cut and pasting

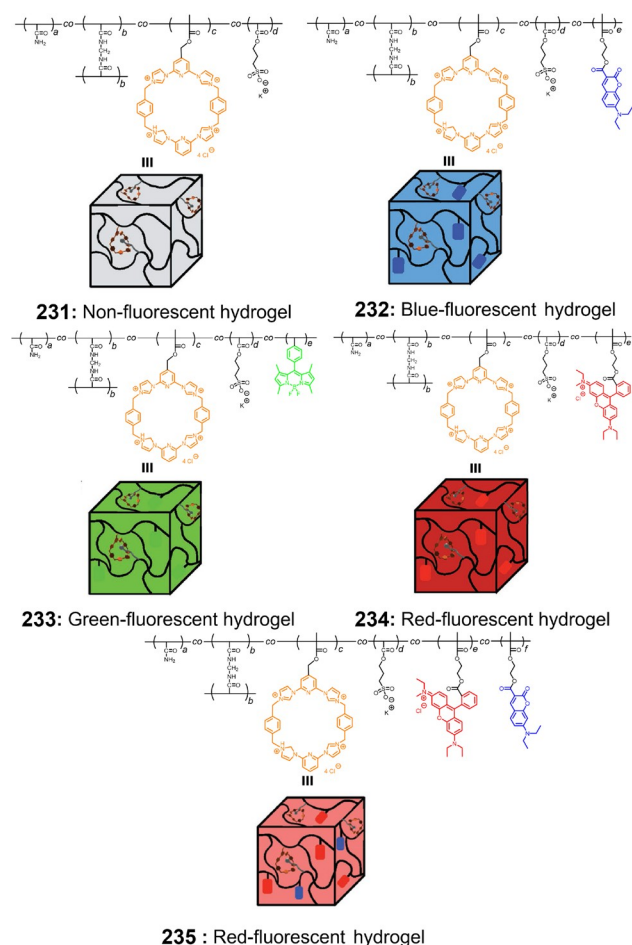


Figure 69. Chemical structures and cartoon representations of the non-fluorescent hydrogel 231, the blue-fluorescent hydrogel 232, the green fluorescent hydrogel 233, the non-responsive red-fluorescent hydrogel 234, and the ammonia-responsive red-fluorescent hydrogel 235. Reproduced with permission from ref 542. Copyright 2018 John Wiley and Sons.

approach thus giving rise to another code. Meanwhile, the ability to undergo transformation in response to a chemical stimulus was demonstrated by exposure to ammonia. This interaction with ammonia caused a red gel element to become blue; again, this interaction created a new pattern that could be read out in terms of its inherent information content.

### 7.3. Cyclobis(paraquat-p-phenylene)/Naphthalene Host-Guest Recognition Motifs

SPNs that are stable in aqueous environments are attractive for use as coatings and adhesives, as well as in the context of biomedical engineering applications.<sup>146,421,425,546</sup> As shown in Figure 70, Hourdet and co-workers reported a SPN that self-assembles in aqueous solution as the result of stabilizing CBPQT<sup>4+</sup>/naphthalene host-guest interactions.<sup>543</sup> Specifically, when copolymer 236, a system bearing naphthalene diether pendant groups, was mixed with the homoditopic bis-CBPQT derivative 237, a supramolecular cross-linked hydrogel 238 was produced. This latter system was found to display Maxwellian behavior in that a correlation between the plateau modulus and the relaxation time with the effective amount of interchain cross-linking interactions was observed.

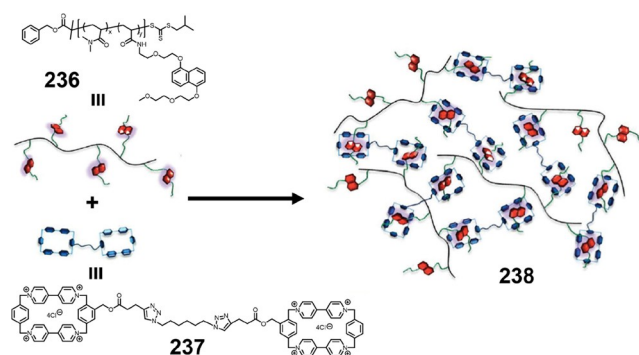


Figure 70. Formation of a supramolecular cross-linked hydrogel 238 stabilized by host-guest interactions between naphthalene-containing polymer 236 and the homoditopic bis-CBPQT cross-linker 237. Reproduced with permission from ref 543. Copyright 2017 The Royal Society of Chemistry.

## 8. COMPARISONS BETWEEN SUPRAMOLECULAR POLYMERIC NETWORKS CONSTRUCTED BY MEANS OF DIFFERENT NON-COVALENT INTERACTIONS

Based on the wide range of SPN systems produced to date, it is clear that a variety of macrocycle-based host-guest interactions may be used to stabilize such non-covalently associated systems. In fact, hydrogen bonding, metal coordination, donor-acceptor  $\pi$ - $\pi$  donor-acceptor, hydrophobic, and electrostatic interactions have all been explored in this context. In this section we consider SPNs from the perspective of the specific interactions employed.

### 8.1. Macrocycle-Based Host-Guest Interactions

(a) Crown ether-based SPNs are typically endowed with excellent dynamic properties, including favorable viscosity, elasticity, and rheology features.<sup>80,88</sup> In many instances, these attributes can be ascribed to the slow-exchange kinetics seen on the proton NMR spectral time scale for classic recognition motifs, such as B21C7/DAAS and DB24C8/DBAS.<sup>178,547</sup> In addition, due to the flexibility of crown ether rings, the use of mechanically interlocked structures generally gives rise to SPNs with outstanding mechanical properties. (b) CDs have been applied extensively in the preparation of SPNs due to their accessibility on large scale, compatibility, and favorable biodegradability characteristics.<sup>548,549</sup> CDs are also attractive because of their ability to bind a range of guest molecules. A number of SPNs that rely on CDs-based host-guest interactions have been found to be stable in water. As a result, such systems have been explored as potential biomedical materials.

(c) Calix[n]arenes<sup>342</sup> are recognition units par excellence. This has made calix[n]arene-based hosts attractive for creating SPNs compatible with organic solvents or aqueous media.

(d) CB[n]s, another classic type of water-soluble macrocycle, have been widely used to prepare SPNs in water. This ability reflects (1) the fact that the underlying association constants for guest recognition are relatively high compared to what is seen for other macrocycles and (2) that CB[8], in particular, can serve as a cross-linker without modification because it can complex two guests to form 1:2 homodimeric complexes, or, in the case of certain guests, 1:1:1 heteroternary complexes.

(e) SPNs stabilized by pillar[n]arene-based host-guest cross-linking interactions are attractive because they can be prepared in both organic solvents and aqueous media. Moreover,



pillar[n]arenes can be easily linked to different covalent polymers. The rigid and symmetrical structure of most pillar[n]arenes and their particular guest recognition features, has led them to be used in certain specialty application areas including substrate adsorption.

(f) SPNs constructed by means of other macrocycle-based host–guest interactions are also of interest since some have displayed unique properties that are not recapitulated in the of other non-covalent polymer systems. For example, SPNs based on C4P/anion and tetracationic imidazolium macrocycle/anion host–guest recognition have shown promise in the area of anion extraction, detection of anionic analytes, and the construction of gel systems that allow for the facile encoding/reading out of stored information. SPNs based on the CBPQT<sup>4+</sup>/monimion interactions, have seen use as supramolecular and naphthalene diether motifs are likewise notable for their special dynamic features.

## 8.2. Other Kinds of Non-covalent Interactions

(a) Hydrogen-bonding interactions have been extensively exploited to construct SPNs. To achieve good stability, typically multiple hydrogen bonding interactions are required. This has allowed for the creation of hydrogen bonding-mediated SPNs that run the gamut from elastomers to thermoplastics and even to duroplastics and networks. Many of these systems display self-healing and are thus attractive as adaptive coatings and as shape-memory retaining materials.

(b) Metal coordination has proved useful for the construction of SPNs. This utility reflects the fact that the thermodynamics and kinetics of the underlying structure-defining interactions can be controlled by varying the metal without necessarily having to modify the polymer backbone. Most SPNs stabilized through metal–receptor interactions exhibit excellent self-healing capability while displaying good shear-thinning behavior. These attractive features are ascribed to the reversibility of metal coordination and the high mobility of the chains containing the metal complexants.

(c) Donor–acceptor  $\pi$ – $\pi$  interactions have been exploited extensively in the fabrication of SPNs. In this case, the system properties may be adjusted by varying the strength and cross-linking density of the motifs giving rise to the  $\pi$ – $\pi$  donor–acceptor interactions. Meanwhile, the unique nature of these interactions can be exploited to produce SPNs with attractive electronic and photophysical features.

(d) Finally, hydrophobic and electrostatic interactions, combinations thereof, have been used to cross-link covalent polymers and to prepare SPNs that are stable in aqueous media among other environments. In favorable instances, hydrogels with tunable features are obtained.

Since supramolecular recognition can be the result of multiple host–guest interactions, it is possible to create SPNs that rely on more than one type of binding motif. This greatly increases the design possibilities in that various types of non-covalent interactions can be combined, at least in principle, in a variety of orthogonal or cooperative ways.

## 9. CONCLUSIONS AND FUTURE PERSPECTIVES

This Review was designed to summarize recent progress in the area of functional SPN chemistry. A variety of SPNs constructed through the judicious combination of covalent polymers and macrocycle-based host–guest interactions were highlighted. SPNs constructed by means of crown ether-based host–guest interactions have, to date, relied primarily on the B21C7/DAAC and DB24C8/DBAS recognition motifs. The resulting systems

have shown promise in a number of areas, including the generation of multi-responsive polymer materials, polymer blending, doubly supramolecular cross-linked polymeric gels, fluorescent sensors, elastomer microspheres, and supramolecular gels. Various CD-based host–guest interactions have been exploited to produce SPNs that are suitable for use in aqueous environments. These SPNs are of potential interest as molecular actuators, stimuli-responsive hydrogels, self-healing materials, shear-thinning injectable hydrogels, SiMP anode layers, and CD-taxane-cross-linked microgels, among other application areas. SPNs have also been constructed by exploiting calix[n]arenes as the key recognition subunit. The resulting systems, including those based on calix[4]arene/MV<sup>2+</sup> and calix[5]arene/diammonium interactions, have seen use as supramolecular hydrogels and as conjugated polymer materials. CD-based SPNs, mainly exploiting CB[8]-derived host–guest recognition events, have likewise been made and studied as injectable and printable hydrogels, double network hydrogels, biomimetic adhesive materials, and as wound dressing. Pillar[6]arene/Fc and pillar[5]arene/guest (where guest = pyridinium salts, cyano-containing species, trimethylammonium salts) interactions have also been used to build SPNs. Many of the resulting constructs have been studied as supramolecular gels, fluorescent polymers, light-harvesting systems, and controlled release materials. Other macrocycle-based host–guest interactions including calix[4]pyrrole/anion, tetracationic imidazolium macrocycle/anion, and CBPQT<sup>4+</sup>/naphthalene recognition motifs, have been explored as a complement to more traditional approaches to constructing SPNs. These latter systems have been explored in a number of areas, including anion sensing and information encoding.

The progress made to date reveals that macrocycle-based host–guest interactions bring reversibility and responsiveness to the resulting SPNs. Specifically, the dynamic and reversible nature of macrocycle-based host–guest interactions gives networks with good processability, recyclability, self-healing, and shape memory. In addition, the stimuli-responsiveness typically seen for macrocycle/guest interactions provides a facile entry into the area of environmental-responsive materials. On the other hand, the fact that most SPNs are based on covalent polymeric backbones, typically provided by use of PAA, PEG, polysaccharides, and PS, means that they often display good chemical stability and mechanical integrity.

For the realization of the applications of SPNs described in this Review, the syntheses of both the constituent macrocycles and the requisite covalent polymers are key. There are three kinds of situations:

- (1) The macrocycles and the related covalent polymers are both commercially available, for example, macrocycles CDs and the polymers PEG, PPG, PEG-b-PPG-b-PEG (Pluronic F108), PNIPAM, and some polysaccharides, or macrocycle CB[8] and cellulose.
  - (2) One of the components of the SPNs based on macrocycles and covalent polymers is commercially available, such as CDs and CB[n], however, the related covalent polymers require synthesis.
  - (3) Neither the macrocycles nor the covalent polymers are commercially available, including, for instance, crown ethers, calix[n]arenes, and pillar[n]arenes and the corresponding covalent polymers.
- Considering these limiting scenarios, it is easy to visualize the first one realizing relatively quickly its potential in terms of



practical applications. However, for the latter two scenarios, it is likely that their full potential will only be realized once the required synthetic processes have become facile and the starting materials are easy to obtain. Nevertheless, due to their excellent features and the diversity of approaches they encompass, we believe that SPNs have a bright future.

Although a reasonable number of functional SPNs based on covalent polymers and macrocycle host–guest interactions are now known, there is considerable room for further fundamental developments and applications-based translation in some areas where further progress could be envisioned including the following:

- (1) Using larger crown ethers, such as BMP32C10 and BPP34C10, to prepare SPNs and applying known systems, with their recognized dynamic features, to create smart, stimulus-responsive materials.
- (2) Translating SPNs based on CDs-based host–guest interactions into a clinical setting as for example drug delivery vehicles. For this potential to be realized, the loading capacity and release features of SPNs will likely need to be enhanced.
- (3) Exploiting a greater range of pillar[n]arene-based host–guest interactions and creating SPNs that might have different materials and guest binding/release features.
- (4) Applying more extensively CB[n]-based SPNs in various biomedical fields. Particular progress can be envisioned as the methods needed to prepare functionalized CB[n] systems improve.
- (5) Exploiting pillar[n]arenes to create SPNs that can be used for applications, such as separations, that benefit from an ability to recognize a variety of guests not typically captured by other receptors and to do so in both organic solvents and aqueous media.
- (6) Generating further classes of SPNs based on what we have been referring to as “other” macrocycle-base host–guest interactions and using these to target ionic guests for information storage systems, colorimetric sensors, novel responsive materials, and the like. Here, advances would benefit from an ability to access additional classes of functionalized macrocycles in addition to the limited set that has been explored to date.
- (7) Expanding the scope of guests beyond those typically considered as supramolecular cross-linkers to include substrates such as C<sub>60</sub> hydrocarbon mixtures, stereoisomers, and a variety of new ionic species. This may allow SPNs to target a range of technological challenges that lie beyond the scope of current research efforts.
- (8) Developing new classes of functionalized covalent polymers. The resulting materials whose nature and forms remain to be envisioned, might allow for the construction of new SPNs with properties and applications that are beyond the current horizon and thus limited in some respects only by our imagination. In this context, improvements in elastic recovery, optoelectronic devices, sustainable materials, targeted drug delivery, and biomaterials are all attractive goals.

As authors of this Review, it is our hope that the current summary of the state of the art in the SPN area will provide the inspiration and knowledge base needed to create these and other new systems that combine the best features of covalent polymeric and macrocycle-based host–guest interactions.

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### Notes

The authors declare no competing financial interest.

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Jonathan L Sessler received a B.S. degree in chemistry in 1977 from the University of California, Berkeley. He obtained his Ph.D. from Stanford University in 1982. After postdoctoral stays in Strasbourg and Kyoto, he accepted a position as an Assistant Professor of Chemistry at The University of Texas at Austin where he is currently the Doherty-Welch Chair. He was also a WCU Professor at Yonsei University and between September 2015 and August 2020 held a summer research professorship and laboratory directorate at Shanghai University. Sessler is currently working on supramolecular chemistry, drug discovery, soft materials, and expanded porphyrin chemistry. He has published over 780 papers (including more than 150 in *J. Am. Chem. Soc.*). His Web of Science h-index is 107.

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## ABBREVIATIONS

AAM acrylamide

Ad	adamantane
AdCNa	1-adamantane carboxylic acid sodium salt
AIE	aggregation-induced emission
AIEE	aggregation-induced enhanced emission
APS	ammonium peroxodisulfate
Azo	azobenzene
BA	n-butyl acrylate
B18C6	benzo-18-crown-6
B21C7	benzo-21-crown-7
BDA	butane diacrylate
BMP32C10	bis(m-phenylene)-32-crown-10
BPP34C10	bis(p-phenylene)-34-crown-10
Bzl-A	3-(1H-benzimidazolyl)propan-1-amine
CB[p]	cucurbit[n]uril
CBPQ1 <sup>+</sup>	cyclobis(paraquat-p-phenylene)
CGC	critical gelation concentration
CNT	carbon nanotube
C4P	calix[4]pyrrole
DAA	dialkylammonium salt
DAN	2,7-diamido-1,8-naphthyridine
DBAS	dibenzylammonium salt
DB24C8	dibenzo-24-crown-8
DMAAM	N,N-dimethylacrylamide
DPBS	Dulbecco's phosphate-buffered saline
DeUG	deazaguanosine
DOX	doxorubicin hydrochloride
DSA	9,10-distyrylanthracene
EA	ethyl acrylate
EHA	2-ethylhexyl acrylate
EP5A	per-ethyl-substituted pillar[5]arene
Fe	ferrocene
Fe <sup>+</sup>	ferrocenium
HEA	2-hydroxyethyl acrylate
HEAAM	N-hydroxyethylacrylamide
HEMA	hydroxyethyl methacrylate
LCST	lower critical solution temperature
MA	methyl acrylate
MBAAM	N,N'-methylenebis(acrylamide)
MMA	methyl methacrylate
Adv. Mater.	reduced methyl viologen
Mv <sup>2+</sup>	methyl viologen
NFC	nanofibrillated cellulose
NIPAM	N-isopropylacrylamide
NIPMAM	N-isopropylmethacrylamide
PA	polyacrylate
PAA	polyacrylic acid
PAAM	poly(acrylamide)
PBMA	poly(butyl methacrylate)
PTAS	pyridinium-modified cyclic tertiary ammonium salt
PEG	polyethylene glycol
PLGA	poly(L-glutamic acid)
PMA	poly(methyl acrylate)
PMMA	poly(methyl methacrylate)
PNIPAM	poly(N-isopropylacrylamide)
PNIPMAM	poly(N-isopropyl methacrylamide)
PPE	poly(p-phenylene-ethynylene)
PPG	polypropylene glycol
PS	polystyrene
RAFT	reversible addition/fragmentation chain-transfer polymerization
RC	rotaxane cross-linker
RCP	rotaxane cross-linked polymer

SPAAC	strain-promoted azide–alkyne cycloaddition
SEI	solid electrolyte interphase
SiMP	silicon microparticle
SPN	supramolecular polymeric network
TBAF	tetrabutylammonium fluoride
(TBA) <sub>2</sub> TPA	tetrabutylammonium terephthalate
TEA	triethylamine
TEGA	tetra(ethylene glycol) acrylate
TEMED	N,N,N',N'-tetramethylethylenediamine
TFA	trifluoroacetic acid
TPE	tetraphenylethylene

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