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Supramolecular Polymers: Recent Advances Based on the Types of Underlying

Interactions

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ABSTRACT

Supramolecular polymers are in broad brushstrokes self-assembled structures built up from small building blocks *via* the use of noncovalent interactions. In favorable cases, supramolecular polymers embody the best features of covalent polymers while displaying unique reversibility, responsiveness, adaptiveness, and stability. This has made them of interest across a wide variety of fields, running the gamut from molecular devices, to sensors, drug delivery, cell recognition, and environmentally friendly materials development. This review is concerned with the determinants that underlie supramolecular polymer construction, specifically the driving forces that have been exploited to create them. To date, nearly the full Parthenon of known noncovalent interactions (*e.g.*, hydrogen-bonding, electrostatic interactions, charge transfer effects, and metal coordination, among others) have been exploited to create supramolecular polymers. Typically, one or more of these effects is exploited to link appropriately designed monomers. The choice of noncovalent interaction can have a significant influence on the structure and function of the resulting supramolecular polymer. Understanding the connection between the forces used to assemble supramolecular polymers and the properties of the constructs that ensue can, in our view, provide the foundation for further advances in this fast-moving field. Given the above, the organization of this review will be by interaction types. Most of the work to be reviewed will encompass literature published from 2016 to the present. This time period nevertheless includes a large number of contributions, the numericity of which reflects the fast-moving nature of the field. An overview of future challenges and opportunities for

supramolecular polymers, including their formation, characterization, and applications, is also provided.

KEYWORDS: Supramolecular polymers, Hydrogen bonds, Metal-coordination bonds, Host-guest interactions, Aromatic donor-acceptor interactions

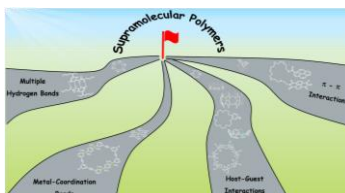


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Acknowledgements

References

Abbreviations: AIE, aggregation-induced emission; BTA, 1,3,5-benzenetricarboxamide; Bip, 2,6-bis(*N*-alkyl-benzimidazolyl)pyridine; BM, Brooker's merocyanine; BrBP, 4-(4-bromophenyl)-pyridin-1-ium; CHCl₃, chloroform; CH₃CN, acetonitrile; CD, circular dichroism; CDs, cyclodextrins; CB[n], cucurbit[n]urils; CPT, camptothecin; C₆H₁₃OH, 1-hexanol; DCM, dichloromethane; DMSO, dimethyl sulfoxide; DP, degree of polymerization; DAE, diarylethene; DMAD, N,N-dimethyl adamantanyl ammonium; DB24C8, dibenzo-24-crown-8; EET, excitation energy transfer; FLP, frustrated Lewis pairs; GSH, glutathione; *K*_a, binding constant; MCH, methylcyclohexane; M:L, metal:ligand; MRL, mechano-responsive luminescent; NDI, naphthalenediimide; NOTA, 1,4,7-triazacyclononane-N,N',N''-triacetic acid; OLEDs, organic light-emitting diodes; PET, positron emission tomography; POMs, polyoxometalates; PEG, polyethylene glycol; RTP, room-temperature phosphorescence; RGD, cyclo(-Arg-Gly-Asp-D-Phe-Lys) trifluoroacetate salt; SNPs, supramolecular polymeric nanoparticles; SOC, spin orbit coupling; SPNPs, supramolecular polymeric nanoparticles; -SS-, disulfide bond; Tol, toluene; TPE, tetraphenylethylene; UPy, 2-ureido-4-pyrimidone

1. Introduction

Polymers play essential and ubiquitous roles in our lives. Their use in food, textiles, housing, and transportation is readily apparent even to those with no chemical training. The historical view of polymeric properties was that they resulted from the colloidal aggregation of molecules or small particles until Hermann Staudinger (1881-1965) proposed the concept of macromolecules in 1920.[1] Since then, the terms polymers and macromolecules have become synonymous with each other. Many pioneers, including Carothers, Ziegler, Natta and Szwarc *et al.*, made seminal contributions to different generations of novel macromolecules.[2-6] With the diversification of structures and properties, more sophisticated functions and practical applications of polymers are continually being developed.[7, 8] However, the ubiquity of polymeric materials is not without environmental consequences, including those associated with their manufacture and degradation, as well as the buildup of persistent plastic wastes. One possible means of mitigating this latter impact involves relying more heavily on the nexus between supramolecular chemistry and polymer science, *viz.* the development and application of supramolecular polymers.[9-12] The concept of supramolecular polymers is relatively new and, in many respects, was only codified in the 1990s. However, the foundation of this field rests on several earlier contributions that help highlight its intellectual connections to polymer science. In 1937, Scheibe and co-workers described phenomena associated with the dissolution of pseudoisocyanine chloride, including the appearance of new absorption bands and enhancement of the solution viscosity upon increasing concentration, which viewed in hindsight are features readily attributable to supramolecular polymerization.[13] In 1988,

Aida and co-workers reported a water-dispersible supramolecular assembly composed of amphiphilic porphyrins with polyether side chains.[14] The formation of the resulting one-dimensional architectures was noted as being driven by a combination of hydrophobicity and π - π donor-acceptor interactions; however, the assembly was discussed within the context of amphiphiles rather than as being articulated as an example of supramolecular polymerization *per se*. In the same year, Ducharme and Wuest developed a strategy to amplify the strength of hydrogen-bonds *via* connecting 2-pyridones by appropriate spacers. A polymeric array could then be formed by controlling the pattern of hydrogen-bond donors and acceptors.[15] In 1990, Whitesides and co-workers arranged the hydrogen bond interactions between melamine and barbituric acid to form triply hydrogen-bonded molecular “tapes”. [16] However, the resulting structures, although driven by noncovalent interactions, were studied as crystalline solids and hence their generalized materials properties were largely ignored. In 1990, Lehn and co-workers reported a supramolecular liquid crystalline polymer, which displayed polymer-like properties, including fiber formation and gelation.[17] These conceptual advances, coupled with seminal contributions from other pioneers in the field (i.e., the groundbreaking work of Meijer and collaborators involving the design, synthesis, and applications of functional supramolecular systems; *vide infra*), [18-24] helped launch supramolecular polymers as a new research discipline lying at the crossroads between polymer science and supramolecular chemistry.[25-30]

As aggregates endowed with typical polymer characteristics, supramolecular polymers are built up from small building blocks *via* the use of noncovalent bonds, including hydrogen-bonding,[18, 31, 32] metal-ligand coordination,[33, 34] electrostatic and van der

Waals forces,[35, 36] π - π donor-acceptor interactions,[37-39] *etc.*[40] As a consequence of the dynamic nature of noncovalent bonds, supramolecular polymers typically exhibit not only the fundamental features of conventional polymers, but also some less-common characteristics, such as easy processing, self-healing, and stimulus responsiveness.[41-47] One point that we see as worthy of particular emphasis is the general effect of different solvents on noncovalent bonds, which can influence greatly the formation of supramolecular polymers. For example, apolar solvents are often employed for the construction of hydrogen-bonded supramolecular polymers since water or polar solvents (e.g., DMSO) serving as hydrogen-bond donors and acceptors can disturb the hydrogen bonding between monomers.[40] Likewise, the coordination between transition metal centers and organic ligands in metallosupramolecular polymers must be strong enough to overcome the influence of solvents as potentially competing ligands.[48] As for the supramolecular polymers based on π - π stacking interactions, the binding strength between two π -conjugated moieties can be enhanced by solvophobic forces in polar or nonpolar solvents.[19, 49] With regard to supramolecular polymers constructed *via* crown ethers or pillararenes, the corresponding host-guest interactions are typically enhanced in organic solvents, such as chloroform, acetone and acetonitrile. However, cyclodextrin- and cucurbituril-based host-guest recognition is generally stronger in aqueous solution on account of their hydrophilic structures. Particularly, both organic solvents and water are used as suitable media for the fabrication of calixarene-based supramolecular polymers. These attributes, and the ability to tune interactions through the choice of medium, have made supramolecular polymers attractive in the context of applications, including molecular

machines,[50-53] sensors,[54-57] drug delivery,[58, 59] cell recognition,[60-64] and biomedicine.[22, 65, 66]

Notwithstanding the seminal suggestion by Lehn and co-workers regarding the concept of supramolecular polymers in 1990, it remained a challenge to design monomeric units that would provide reversible interactions of sufficient strength to support supramolecular polymerization. In 1997, Meijer and co-workers reported 2-ureido-4-pyrimidone (UPy) as a new class of quadruple hydrogen-bonded self-complementary monomers,[18] and showed that they could be used to construct supramolecular polymers with high viscosity and outstanding rheological properties.[67-74] The emergence of UPy-based polymers marked the beginning of the rapid development of supramolecular polymeric materials. Since then, research on supramolecular polymers blossomed, with key advances coming not only from Meijer,[21-23, 74-77] but also Leibler,[41, 78] Zimmerman,[79, 80] Craig,[81-83] Bouteiller,[84-86] Binder,[87, 88] Zhang,[89-91] Gibson,[92-94] Long,[95, 96] and others.[97] Several of the authors of this review have also contributed to the development of the field.[47, 98-103]

To date, supramolecular polymers have received widespread attention across a variety of disciplines, including those beyond the traditional frontiers of supramolecular and materials chemistry. Not surprisingly, it is a topic that has been the focus of several reviews.[9, 10, 19, 103-106] Many of these reviews bring a unique perspective to the topic.[107-109] For instance, in 2015, Zhang and co-workers reviewed different driving forces that could be exploited to prepare supramolecular polymers with various topologies and applications.[110] Moreover, in 2020 Aida and Meijer *et al.* summarized their views on

supramolecular polymerization and how the concepts could be extended.[111] Also in 2020, the Stupp group reviewed seminal contributions to the area, including hierarchical structures and applications of supramolecular polymeric materials.[112] That same year, Würthner and coworkers reviewed methods of controlling supramolecular polymerization by controlling the kinetics and thermodynamics of noncovalent interactions.[113] In 2020, Sessler and Huang *et al.* highlighted functional supramolecular polymers formed from covalent polymers connected by macrocycle-based host-guest interactions.[114] In 2021, the Zhang group summarized recent studies of supramolecular polymers with controllable structures and intriguing functions.[29] Meanwhile, several contributions have noted the wide choices of monomers (*e.g.*, biomolecules, nanoparticles, nanotubes, and nanosheets)[115-118], media (*e.g.*, solvents, liquid crystals, bulk environments, on electrodes, and at interfaces),[71, 119-122] and mechanisms (*e.g.*, chain-growth supramolecular polymerization,[123] sequence-specific supramolecular copolymerization,[124] and seeded supramolecular polymerization[125, 126]) that are available for supramolecular polymerization. Perhaps as a result, supramolecular polymers have been studied for a range of practical applications. On a more fundamental level, research efforts are moving beyond simply fabricating new constructs to studying systematically their structure-function properties, controlling their structures, and exploring their potential functions, etc. Nevertheless, the types of noncovalent interactions that underpin the construction of supramolecular polymers are increasingly being appreciated as being indispensable to a detailed understanding of supramolecular polymeric materials.

In this review, we emphasize the types of noncovalent interactions that have been and are being used to generate supramolecule polymers. This treatment is designed to extend and complement the coverage of other recent review articles. Through this lens, we provide coverage of supramolecular polymers (from 2016 to the present) built up from small building blocks based on the types of underlying interactions, including multiple hydrogen bonds, metal-coordination bonds, host-guest interactions, aromatic donor-acceptor interactions, among others. An overview of future challenges and opportunities associated with supramolecular polymers, including their formation, characterization, and application, is also provided.

2. Supramolecular Polymers Based on Multiple Hydrogen Bonds

2.1. Multiple Hydrogen Bonds: An Historical Perspective

Nature relies in part on hydrogen bonds to regulate the interactions between biological molecules and to impart advanced functionality.[127] For decades, scientists have been inspired to take advantage of hydrogen bonds, *e.g.*, their strength and directionality, to create artificial systems with new properties.[128] In this context, it is now essentially axiomatic that under most conditions a single hydrogen bond is too weak to stabilize specific aggregates. Starting in the 1980s, chemists began using multiple hydrogen bonds to construct inclusion compounds and to control the intermolecular complexation.[129-131] In 1988, Wuest *et al.* designed motifs with extensive arrays of hydrogen-bond donors and acceptors with a view to amplifying their inherent binding affinities.[15] Viewed through the lens of history, we now appreciate that the synergistic use of multiple hydrogen bonds can significantly increase the strength and directionality of the interactions they

stabilize.[132, 133] This phenomenon became the initial key to effective supramolecular polymerization. In 1990, Lehn *et al.* described the first example of a linear supramolecular polymer that was formed by triple hydrogen-bonded complementary units.[17] Later on, numerous architectures emerged after the quadruple hydrogen-bonded unit UPy was reported by Meijer[74, 134-139] and coworkers; this subunit was a game changer due to its high binding constant (K_a) and synthetic accessibility. To date, multiple hydrogen-bonding motifs have been used to create a plethora of exciting structures that run the gamut from simple linear supramolecular polymers to complex polymeric materials.[61, 140, 141] Per the objectives of this review, we now summarize contributions to supramolecular polymer chemistry with a focus on binding motif.

2.2. Recent Advances in Hydrogen-Bonded Supramolecular Polymers

In 2017, Tang and co-workers reported two dramatically different supramolecular aggregates formed from pure stereoisomeric monomers; these two precursors were synthesized concurrently *via* a one-pot McMurry coupling reaction and then separated by simple column chromatography.[98] These researchers demonstrated that the differing molecular configurations influenced the supramolecular polymerization, leading to distinct fluorescence colors and morphologies in the self-assembled states produced from the monomeric stereoisomers. Of note was the finding that the (*Z*)-derived isomer could be used as an Hg^{2+} fluorescent sensor, while its (*E*)-based congener formed 2D and 3D photopatterns. This work provided a useful illustration of how ostensibly similar stereogenic structures could be exploited for supramolecular polymer engineering.

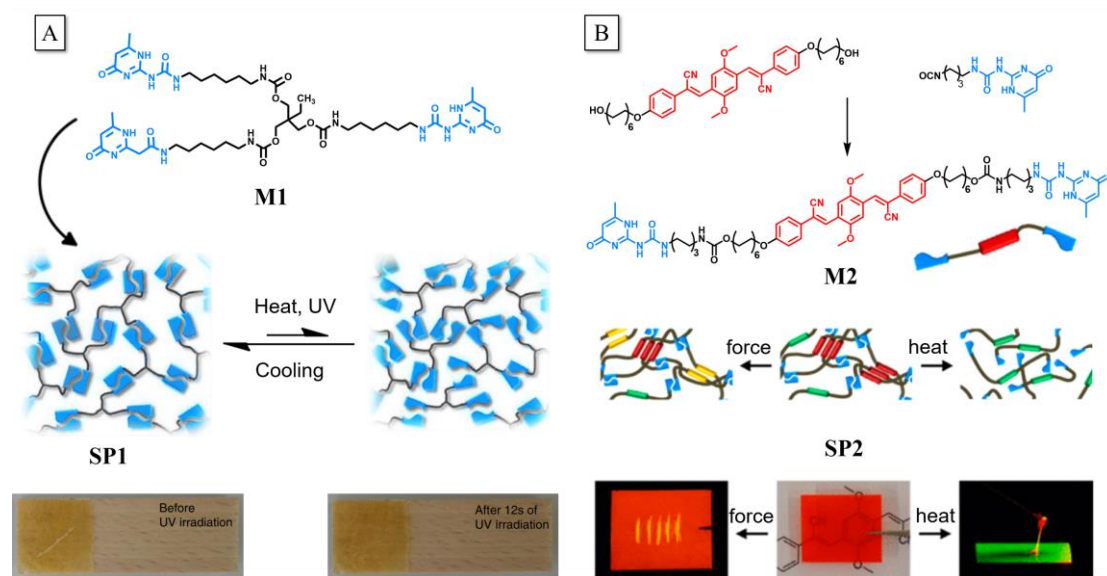


Figure 1. (A) Chemical structure of **M1**, and the schematic representation of reversible dissociation of **SP1**; Images showing a damaged coating (left) on wood and after healing (right) under conditions of ultraviolet light irradiation. [142], Copyright 2016. Adapted with permission from Springer Nature. (B) Chemical structure of **M2**, and schematic images of **SP2** showing different molecular packings and images showing the as-formed material (center) and its the mechano- (left) and thermo- (right) responsive luminescent behavior of **SP2** films. [143], Copyright 2017. Adapted with permission from the American Chemical Society.

In 2016, the Weder group used UPy motifs to create several stimuli-responsive supramolecular polymers. In particular, they synthesized monomer **M1** containing a 1,1,1-tris(hydroxymethyl)propane core and three UPy groups that supported formation of the supramolecular network **SP1** (Figure 1A).[142] It was shown that this material could be easily processed into supramolecular glasses possessing high stiffness and useful adhesive features. Furthermore, the **SP1**-based glasses were endowed with optical healing capability, a feature ascribed to the ability of the UPy units to absorb ultraviolet light and convert it

into heat. Later on, the same group reported thermo- and mechano-responsive luminescent (MRL) materials prepared from **M2** (Figure 1B).[143] Supramolecular polymers (**SP2**) formed from **M2** were found to form self-standing films, which exhibited different fluorescence colors under mechanical and thermal stimuli. The thermoresponsive and MRL properties of these supramolecular materials were attributed to changes in the molecular packing of the individual chromophore within the self-assembled materials.

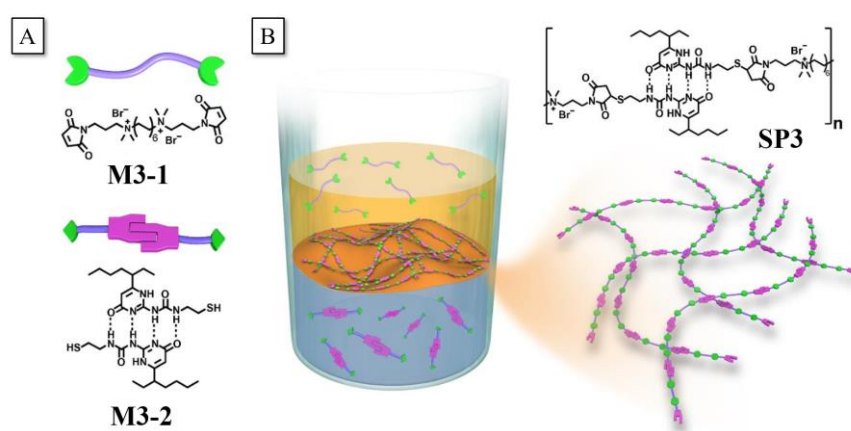


Figure 2. (A) Chemical structures of **M3-1** and **M3-2**. (B) Schematic illustration of the interfacial polymerization of **M3-1** and **M3-2**. [144], Copyright 2017. Adapted with permission from John Wiley & Sons Inc.

In addition to constructing supramolecular polymers, chemists have made efforts to develop new strategies for controllable supramolecular polymerization. In this context, Zhang and Xu *et al.* reported a method to promote supramolecular interfacial polymerization by subjecting **M3-1** and **M3-2** to a thiol-maleimide click reaction (Figure 2).[144] When an aqueous solution of **M3-1** was mixed with a chloroform solution of **M3-2**, a free standing brown film consisting of **SP3** was observed at the water-chloroform interface. As inferred from ¹H NMR spectral and ESI-MS studies, the **SP3** film was

composed of the product of the thiol-maleimide reaction and benefited from stabilizing quadruple hydrogen bonding interactions. The degree of polymerization (DP) of **SP3**, measured by ^1H NMR spectroscopy, was calculated to be 52 in $\text{DMSO-}d_6$. The specific molecular weight of **SP3** could be tuned by changing the temperature and reaction time of the interfacial polymerization reaction.

Supramolecular polymers tend to disassemble upon heating, which limits their applications under harsh conditions. In 2017, Aida *et al.* reported a thermally bistable supramolecular polymerization process wherein a noncovalent polymer of generalized structure **SP4** was formed on heating and cooling.[145] In this study, a metalloporphyrin carrying eight side-chain amide groups (**M4**) was allowed to self-assemble in a dodecane/ CHCl_3 mixture to afford a one-dimensional polymer (**SP4**). Particularly, $\text{C}_6\text{H}_{13}\text{OH}$ was employed as a hydrogen-bond “scavenger”. Upon cooling below $50\text{ }^\circ\text{C}$, molecules of $\text{C}_6\text{H}_{13}\text{OH}$ cluster together and thus do not hydrogen-bond effectively with the amide groups of **M4**. This results in the formation of **SP4** with **M4** constituting the exclusive building block. As the temperature was increased from 50 to $110\text{ }^\circ\text{C}$, **SP4** was found to undergo depolymerization before reassembling. It was proposed that at $\sim 60\text{ }^\circ\text{C}$, the motifs in the **M4** building block that are involved in polymer-supporting hydrogen bonds at lower temperatures interact effectively with $\text{C}_6\text{H}_{13}\text{OH}$, leading to self-dissociation. However, at yet higher temperatures, thermal motion leads to the detachment of the $\text{C}_6\text{H}_{13}\text{OH}$ molecules from **M4**. This results in liberation of the free form of **M4**, which then undergoes repolymerization (Figure 3).[145] Based on detailed spectroscopic and theoretical analyses, the authors concluded that the supramolecular polymerization of **M4** could be fit to an

isodesmic model at low temperatures, *i.e.* the hydrogen-bond scavengers were released synchronously during the cooling process, leading to the polymerization of **M4**. In contrast, the heating-induced supramolecular polymerization occurred sequentially as the release of scavengers takes place in a step-wise manner. Such a detailed understanding of mechanisms underlying this specific thermally bisignate supramolecular polymerization is expected to enable the control over thermally responsive supramolecular polymerization reactions and application of the resulting materials in new areas.[146]

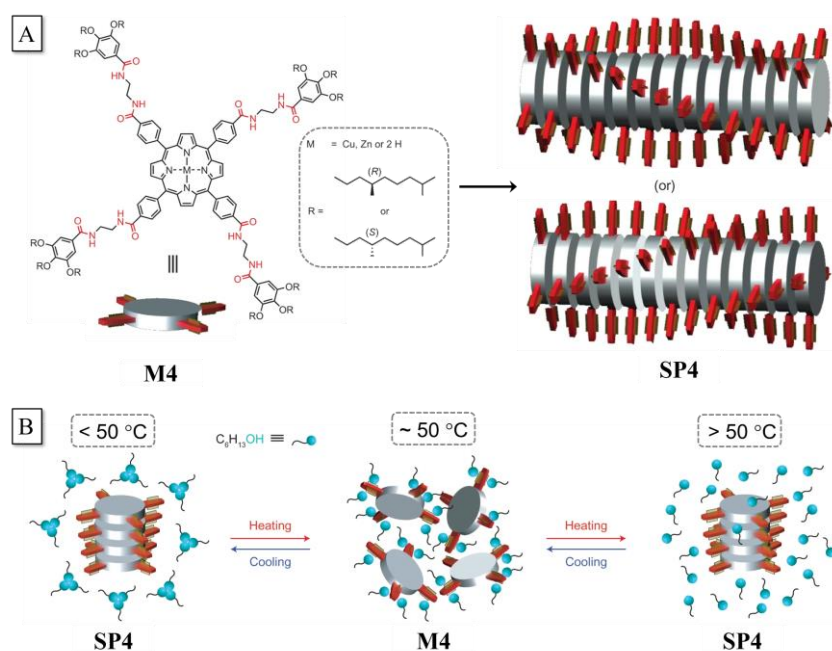


Figure 3. (A) Chemical structure of **M4** and schematic representation of supramolecular polymers **SP4**. (B) Schematic representation of their proposed polymerization chemistry.

[145], Copyright 2017. Adapted with permission from Springer Nature.

With the goal of fabricating programmed one-dimensional topologies, Yagai and co-workers prepared the naphthalene- and anthracene-based monomers **M5-1** and **M5-2**. They then showed that both these monomers would undergo self-association to afford chimeric nanofibers **SP5-1** and **SP5-2** with unique secondary structures (Figure 4).[147] Both

monomers bear barbiturate units designed to stabilize hydrogen-bonded supermacrocyclic ensembles (rosettes), which were expected to polymerize further as the result of π - π donor-acceptor interactions. In practice, it was found that **M5-1** stabilized the formation of the helically folded supramolecular polymer **SP5-1** while self-assembly of **M5-2** gave rise to linear fibers upon cooling (1.0 K min^{-1}) methylcyclohexane solutions from 373 to 293 K. Temperature-controlled supramolecular copolymerization of **M5-1** and **M5-2** at a molar ratio of 1:1.5 was found to produce chimeric fibers ($\text{DP} = 1.6 \times 10^3$) with a well-defined (helical-linear-helical)-type structure (Figure 4B). It was also found that **SP5-2** nucleates before **SP5-1**, presumably reflecting its propensity to undergo aggregation. Interactions between the **M5-1**-rich rosettes and the **M5-2**-rich fibers were then proposed to produce helical segments (Figure 4C). The formation of the chimeric structures was found to be sensitive to the cooling rate and concentrations of the monomers. Finally, it was found that the topology of the supramolecular copolymers could be varied by subjecting **M5-1** to photodimerization.

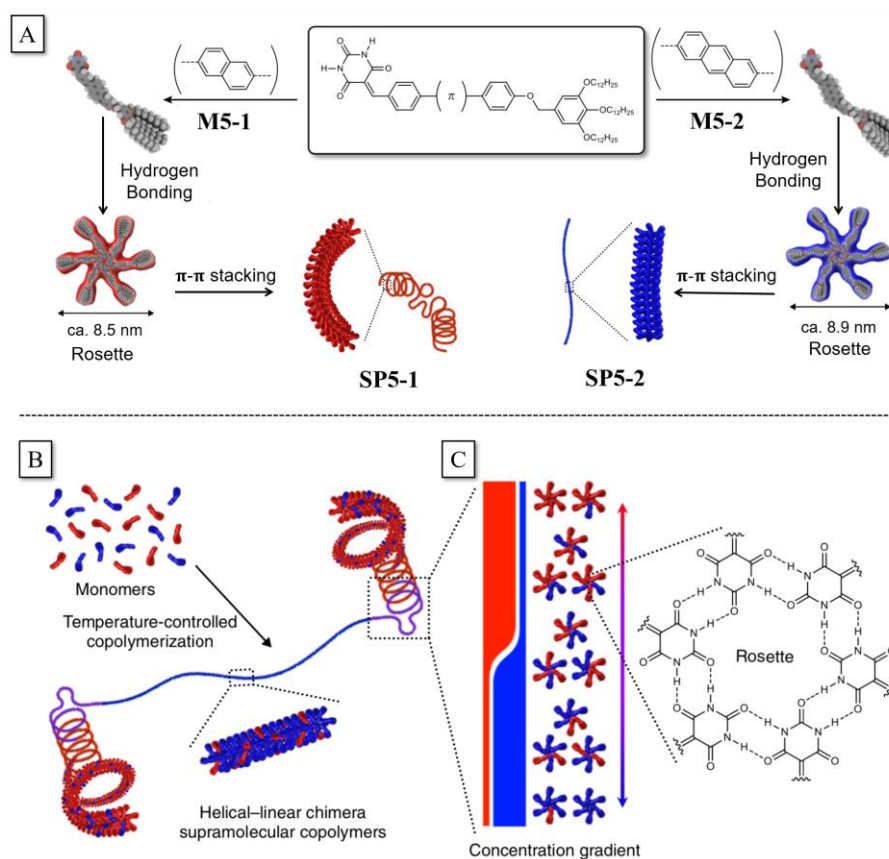


Figure 4. (A) Molecular structures, schematic rosettes and supramolecular polymers, **SP5-1** and **SP5-2**, derived from **M5-1** and **M5-2**. (B) Schematic representation of the supramolecular copolymers of **SP5-1** and **SP5-2** showing their proposed helical-linear-helical structure. (C) Formation of rosettes from red and blue monomers **M5-1** and **M5-2** used in different molar ratios. [147], Copyright 2019. Adapted with permission from Springer Nature.

In 2020, Yagai *et al.* reported a different set of controllable supramolecular copolymers, **SP6-1** and **SP6-2**, comprising six-membered hydrogen-bonded supramolecular rosettes built up from **M6-1** and **M6-2** (Figure 5).[148] By cooling methylcyclohexane solutions of **M6-1** and **M6-2** in a 1:1 molar ratio, amorphous aggregates were produced. Per the authors' design, **M6-1** and **M6-2** are electron-rich and deficient,

respectively; this allows them to interact *via* electrostatic interactions. Under conditions of equilibrium, this results in optimized electrostatic stacking between the monomers and allows for the formation of a multi-component supramolecular system, **SP6-3**, over the course of several days that benefit, presumably, from a maximal enthalpic gain (Figure 5C). Access to the latter form could be accelerated by incorporating a sterically hindered monomer to suppress the formation of rosette intermediates. This study provides an example of how molecular recognition can be tuned to help preorganize a system to favor a specific supramolecular polymerization product, in loose analogy to what is achieved in natural systems.

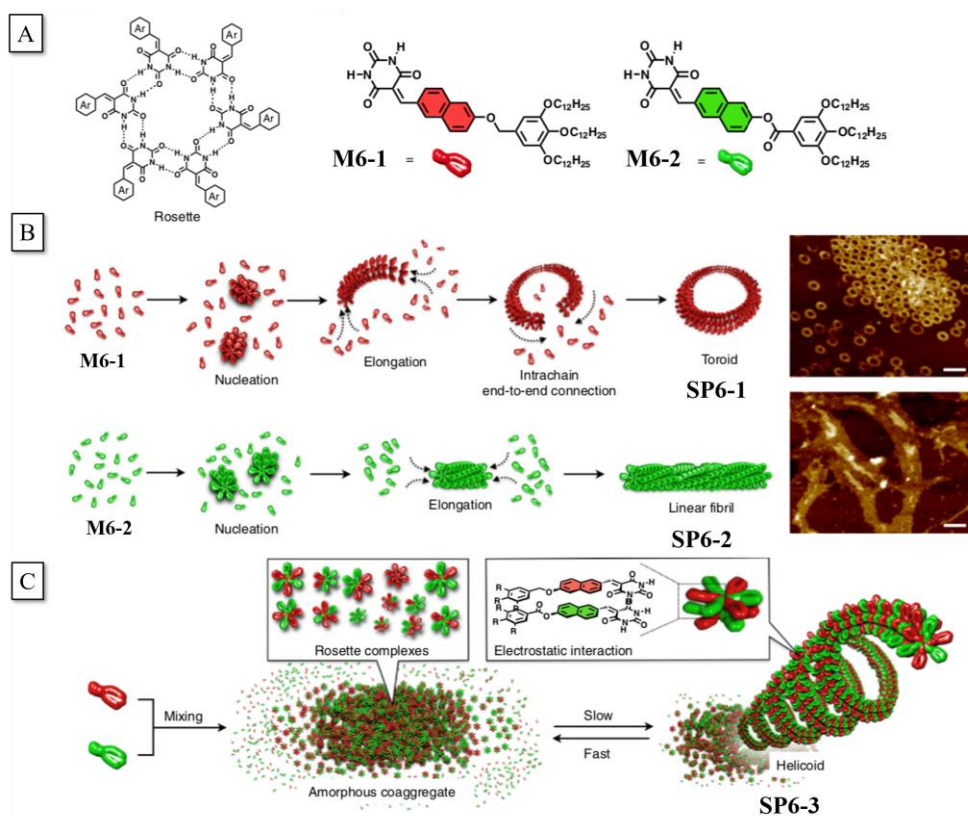


Figure 5. (A) Chemical structures of **M6-1** and **M6-2**. (B) Schematic diagrams showing the formation of **SP6-1** and **SP6-2**. (C) Schematic diagram showing the formation of **SP6-**

3. All scale bars: 50 nm. [148], Copyright 2020. Adapted with permission from Springer Nature.

Controlling the backbone conformation of supramolecular polymers by means of external stimuli remains a recognized challenge. Meijer, Sugiyasu, Takeuchi, Würthner and George *et al.* succeeded in obtaining different polymeric structures by changing the complexity of one monomer involved in the polymer-forming self-assembly process.[24, 125, 149-151] In 2017, Yagai and co-workers made an important contribution to this area by demonstrating the folding and unfolding of supramolecular polymers upon photoirradiation. These researchers appreciated that the barbiturate naphthalene derivative **M6-1** could form toroidal nanofibers containing hydrogen-bonded rosettes (Figure 5). The nature of the resulting supramolecular backbone proved dependent on the spontaneous curvature resulting from π - π stacking between individual rosettes. The authors exploited this curvature, and the associated translational and rotational displacements, to fabricate the helically folded 1D supramolecular polymer **SP7-1**. This system, derived from monomer **M7-1**, comprises an azobenzene motif that leads to increased stacking between the rosettes (Figure 6A).[152] It also provides for photoresponsiveness. Partial photoisomerization of the constituent azobenzene subunit from *trans* to *cis*, was found to cause the helically folded fibers of **M7-1** to be transformed into highly extended fibers characterized by misfolded structures.

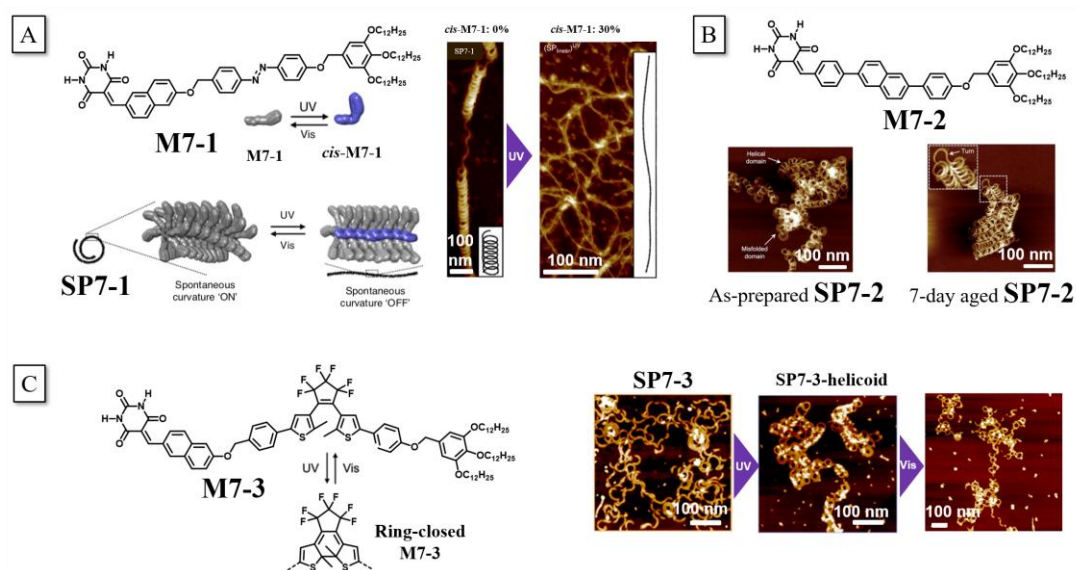


Figure 6. Chemical structures of (A) **M7-1**. [152], Copyright 2017. Adapted with permission from Springer Nature. (B) **M7-2**. [153], Copyright 2018. Adapted with permission from the American Association for the Advancement of Science. (C) **M7-3**. [154], Copyright 2021. Adapted with permission from the American Chemical Society. All scale bars: 100 nm.

To improve the degree of internal order within the supramolecular polymer backbone, Yagai and co-workers synthesized monomer **M7-2** possessing a more rigid molecular scaffold (Figure 6B).[153] Upon polymerization, this system was found to undergo slow self-folding from randomly coiled structures to produce helically folded fibers (**SP7-2**). Reversible folding/unfolding of the supramolecular polymers could be achieved by means of photoirradiation. Subsequently, this same group synthesized a diarylethene (DAE)-containing barbiturate derivative **M7-3**, whose molecular rigidity could be tuned by ring-closing/opening photoreactions (Figure 6C).[154] By cooling a hot methylcyclohexane solution of **M7-3**, randomly coiled supramolecular polymer fibers (**SP7-3**) with a uniform curvature could be obtained. Irradiating a solution of **SP7-3** with UV light to induce ring

closure of the DAE subunit, served to transform the **SP7-3** backbone into a helicoidal conformation (**SP7-3-helicoid**). DAE ring-closure increases the π - π interactions within the fibers leading to compression of the supramolecular backbone. This, in turn, increases the intrinsic curvature of the supramolecular fiber associated with helical folding. Conversely, exposure of solutions of the **SP7-3-helicoid** to visible light leads to ring-opening of the ring-closed DAE and the eventual formation of supramolecular polymer fibers with randomly coiled conformations similar to those seen in **SP7-3**, although only after 1 week of aging. The associated hysteretic process was attributed to interloop van der Waals interactions within **SP7-3-helicoid** that collectively constitute a kinetic barrier to rearrangement. This line of investigation is unique, yet may be viewed as mirroring some of the structural rearrangements of biopolymers, *e.g.*, proteins with 3D tertiary structures.

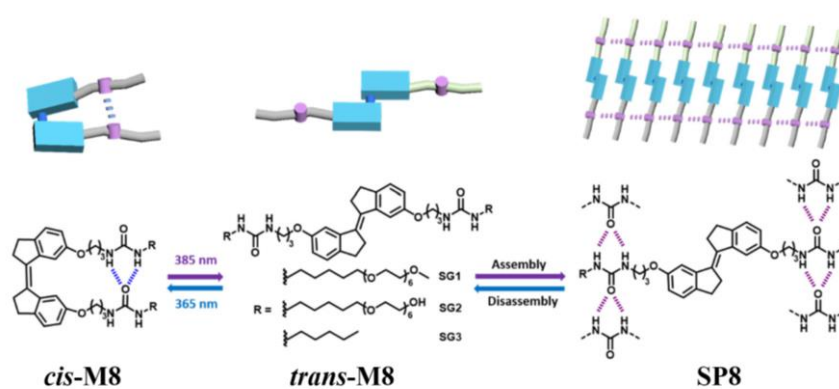


Figure 7. Schematic illustrations of the reversible photoisomerization and self-assembly of **M8**. [155], Copyright 2021. Adapted with permission from the American Chemical Society.

Feringa and co-workers were able to control the macroscopic properties of supramolecular polymers containing urea groups and photoisomerizable stiff-stilbene subunits.[155] They found that **cis-M8**, a monomer with these constituents, could form

intramolecular hydrogen bonds, which precluded effective supramolecular polymerization (Figure 7). Exposing the *cis*-**M8** solution to light (385 nm) for 3 min to induce stilbene photo-isomerization produced the corresponding *trans* system (*trans*-**M8**), which formed a supramolecular polymer, **SP8**, stabilized *via* intermolecular hydrogen bonds. Self-assembly of *trans*-**M8** was found to proceed per a cooperative polymerization mechanism. Using this supramolecular system, the authors were able to demonstrate both *in situ* gelation and gel-sol phase transitions with control over the underlying phenomenon.

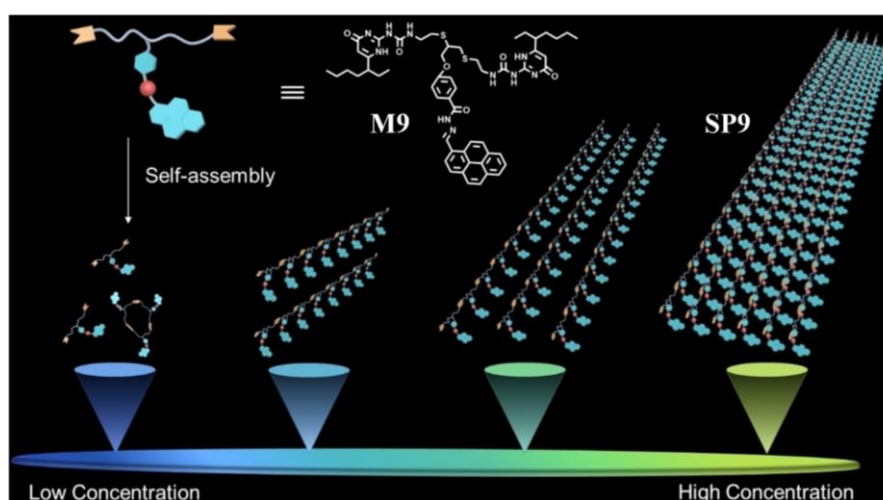


Figure 8. Chemical structures of **M9**, schematic representation of supramolecular polymers **SP9**, and the fluorescence colors associated with the different polymeric forms.

[102], Copyright 2022. Adapted with permission from John Wiley & Sons Inc.

A key aspect of supramolecular polymers is the degree of polymerization. Determining this parameter is typically required for complete structural characterization. Recently, the Ji group suggested an attractive strategy wherein the molecular weight is differentiated visually by monitoring the fluorescence color variations in hydrogen-bonded supramolecular polymers (**SP9**) subject to aggregation-induced emission (AIE).[102] The monomer (**M9**) was synthesized by linking two UPy groups to a pyrene benzohydrazone-

based AIE fluorophore. This monomer was designed to form **SP9** through quadruple hydrogen bonding interactions between the constituent UPy subunits. The average DP for **SP9** was found to increase from 1.00 to 293 as the **M9** concentration was increased from 0.1 to 100 mM. During this increase in DP, the fluorescence color of **SP9** was found to vary from dark blue to yellow-green due to aggregation of the fluorophores. This variation allowed a relationship between the DP and the nature of the **SP9** fluorescence color to be established; as a consequence, the visual distinction of molecular weight in this demonstration system could be readily established.

3. Supramolecular Polymers Based on Metal-Coordination Bonds

3.1. Metal-Coordination Bonds: An Historical Perspective

In the 19th century, the principles of metal-ligand bonding in transition metal complexes were unraveled by Alfred Werner, who was awarded the Nobel Prize in 1913 in recognition of his contribution to the field of coordination chemistry.[156] In the 1950s, John C. Bailar, Jr. and co-workers pioneered polymerization through coordination, *e.g.*, they reported copper phthalocyanine polymers with molecular weights reaching 4000 Da.[157] Subsequently, efforts were devoted to developing alternative synthetic approaches, work that resulted in coordination polymers and a broader vista for metal-based synthetic materials.[158, 159] Starting the 1980s, metal-coordination bonds have been increasingly exploited by supramolecular chemists who have utilized metal ions as templates to synthesize *inter alia* interlocked molecular structures.[160] Sauvage and his coworkers sowed the seeds for this field.[161, 162] In 2000, the Stang group highlighted the main characteristics of metal-mediated supramolecular assembly[163] and in 2005 Würthner and

coworkers specifically offered the definition of metallosupramolecular polymers.[164] In addition, inorganic chemists have pioneered the study of coordination networks, *i.e.* metal-organic frameworks. However, such systems are typically not considered as being coordination polymers *per se* since they exist mainly in the solid state. According to the prevailing view, a metallosupramolecular polymer should retain its backbone, as well as enable reversible polymerization and depolymerization in solution. Per this definition, there exists a range of metallosupramolecular polymers wherein metal-coordination bonds of main-group metals, transition metals and lanthanides are exploited in a rational manner to organize ligand structures and allow the construction of materials endowed with both canonical polymeric properties, as well as optical, electronic and magnetic features characteristic of metal complexes.[48, 165-171]

3.2. Recent Advances in Metal-Containing Supramolecular Polymers



Figure 9. Synthesis of poly[*n*]catenane *via* self-assembly of **M10-1** and **M10-2** into a metallosupramolecular polymer, followed by ring-closure of **M10-1** and demetallation. [172], Copyright 2017. Adapted with permission from the American Association for the Advancement of Science.

In order to create poly[*n*]catenanes, the Rowan group designed a metallosupramolecular polymer based on the coordination of Zn²⁺ and 2,6-bis(*N*-alkylbenzimidazolyl)pyridine (Bip) in a 1:2 stoichiometry (Figure 9).[172] Upon the addition of Zn²⁺ to a mixture of compound **M10-1** and **M10-2** in acetonitrile, self-assembly *via* the binding between Bip and Zn²⁺ ($K_a > 10^6 \text{ M}^{-1}$) occurs to form a metallosupramolecular polymer of general structure **SP10** with a DP = 55.4. Within this polymer, the **M10-1** component could be subject to intramolecular ring-closure. Demetallation then gave the poly[*n*]catenane shown in Figure 9 in crude form. Solid-liquid extraction, which exploited the differences in solubilities of the by-products and the target poly[*n*]catenanes, allowed for further purification. According to NMR spectral analyses and gel permeation chromatographic studies, the poly[*n*]catenane fraction was found to contain cyclic poly[4-7]catenanes, branched poly[7-26]catenanes and linear poly[13-130]catenanes. This work underscored in dramatic fashion the utility of metallosupramolecular polymers as steppingstones to the synthesis of sophisticated smart materials.

In separate work, Li, Tu and Hla *et al.* achieved visualization of a single polymer chain within metallopolymers constructed *via* the coordination of Ru(II) or Fe(II) to a terpyridine ligand.[173] These researchers synthesized hexameric and trimeric precursors bearing azide groups. Reaction with an alkyne-modified pentaethylene glycol crosslinker resulted in the formation of hexameric and trimeric polymers, respectively. The polymers were metalated with Ru(II) and Fe(II), thus introducing distinct strong and weak coordination sites, respectively. On the basis of scanning tunneling spectroscopic studies, it was concluded that the hexameric polymer would stabilize both a cyclic hexagonal structure, as well as linear

chain species. In contrast, the trimeric polymer only gave rise to cyclic trigonal species. The different energy gaps of Ru(II) and Fe(II) allowed the identification of their exact positions within the structures and permitted the conformation of the metallosupramolecular polymers to be determined.

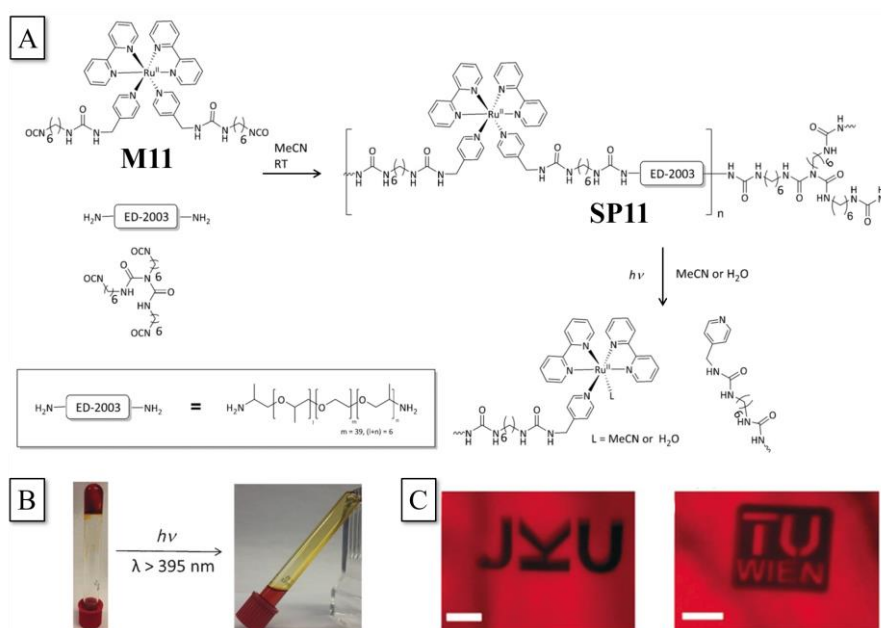


Figure 10. (A) Synthesis and photocleavage of a ruthenium-containing supramolecular polymer. (B) Photo-induced gel-sol transition of the **SP11** gel. (C) Photopattern obtained by scoring the hydrogel of **SP11** using near-infrared light. [174], Copyright 2017. Adapted with permission from John Wiley & Sons Inc.

In 2017, Teasdale and co-workers utilized the photocleavable monomer, **M11**, to synthesize metallosupramolecular polymers of generalized structure **SP11** that were expected to act as photoresponsive gels (Figure 10).[174] When the gel produced by **SP11** was subject to visible light (> 395 nm, 10 min) photoirradiation, a gel-sol transition occurred, a finding ascribed to the photocleavage of the ruthenium-pyridine bonds. Of particular interest was that the liquid obtained by subjecting the organogel to

photoirradiation could be swollen in water to form a hydrogel, which proved photoresponsive only in the regions subjected to photoirradiation. A three-dimensional photopattern could also be obtained by engraving the hydrogel using near-infrared light.

In 2017, supramolecular polymeric materials based on the coordination of lanthanide metal cations with terpyridine ligands were reported by Liu and co-workers.[175] Later on, the He group described a smart polymeric gel stabilized by means of iminodiacetate (IDA)-derived Eu(III) complexation.[176] Europium-based *d-f* transitions made the hydrogel luminescent, while the dynamic nature of the Eu(III)-IDA coordination provided for self-healing. External stimuli, including heating, pH, sonication, metal ion competition, and pressure, were all found to be effective factors in tuning the Eu(III) ion luminescence within the supramolecular gel.

In spite of the proliferation of systems based on metal-ligand coordination and dynamic covalent bonds, it remains a challenge to access multiple states without the requirement of external energetic inputs. In 2018, Sessler and co-workers reported a system based on bispyridine-substituted calix[4]pyrrole (**M12**) that allowed access to six different discrete states *via* the combined use of metal-based self-assembly and molecular recognition. [177] The pyridine-functionalized system **M12** provides latent metal complexation sites in two of its meso positions. Addition of AgBF₄ was found to promote metal coordination-based supramolecular polymerization to give **SP12**, in which the binding constant between **M12** and Ag⁺ was determined to be $9 \times 10^3 \text{ M}^{-1}$ in tetrahydrofuran. As inferred from a Job's plot, a 1:1 molar ratio of Ag⁺ cations and **M12** was present in **SP12** (Figure 23B), in accord with the expected binding stoichiometry set by the pyridine functionality in **M12**. Single crystals

of **SP12** could be grown by evaporating a mixed chloroform/acetonitrile solution of **SP12**. X-ray diffraction analysis then revealed a metal-linked spiral structure. SEM measurements further verified that **SP12** formed helical polymeric assemblies characterized by widespread twisted wire-like shapes with bundles of ~ 80 polymeric chains. This research demonstrated an intriguing approach to creating information-rich functional supramolecular materials. Of no less significance, the authors demonstrated that by adding a proton source or various anionic guests, it was possible to use **M12** to stabilize several capsule-type and monomeric forms, thus allowing access to six different states in total. Only one of these states, **SP12**, was polymeric.

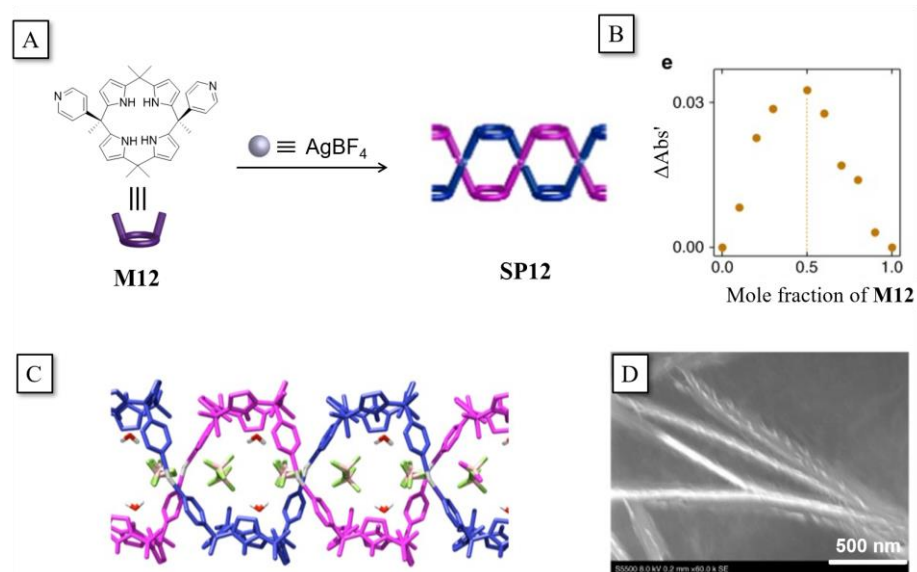


Figure 11. (A) Schematic illustration of **SP12**, a self-assembled polymer formed from **M12** and AgBF₄. (B) Job-plot of **M12** and AgBF₄. (C) Single crystal structure of **SP12** (D) SEM image of the helix. The scale bar is set at 500 nm. [177], Copyright 2018.

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Stang and collaborators have reported a large variety of self-assembled structures, including supramolecular polymers that rely on metal-ligand coordination (*e.g.*,

platinum(II)-pyridine interactions) and other noncovalent interactions.[178-181] These contributions have served *inter alia* as the inspiration for a number of scientists seeking to design so-called smart metal-based supramolecular polymers. In 2020, Yam and co-workers reported a two-dimensional metallosupramolecular polymer, **SP13**, that displayed acid-base responsiveness.[182] This polymer was stabilized *via* Pt···Pt and $\pi\cdots\pi$ donor-acceptor interactions of appropriately chosen monomeric trinuclear platinum(II) polypyridine complexes, **M13** (Figure 12). UV-Vis absorption and emission spectroscopic studies revealed features ascribed to metal-metal-to-ligand charge transfer transitions within **M13** dimers. Although **SP13** does not rely on direct metal-ligand interactions to stabilize the polymeric backbone, it still constitutes a new class of metal-containing supramolecular polymers. Protonation of the dimethylamino groups present in **M13** led to dissociation of these putative dimers (**protonated SP13**). The enhanced electrostatic repulsion between the protonated dimethylamino groups in **protonated SP13** presumably serves to overcome the stabilizing Pt···Pt and $\pi\cdots\pi$ donor-acceptor interactions present in **SP13**, leading to a perturbation in the **SP13** topology. For instance, whereas both **M13** and **protonated M13** exist in the form of sheet-like nanostructures, **SP13** is highly crystalline and possesses a hexagonal lattice structure (Figure 12B). The structural attributes of **SP13**, particularly its ability to stabilize pores, allowed it to be used to fabricate water transport membranes.

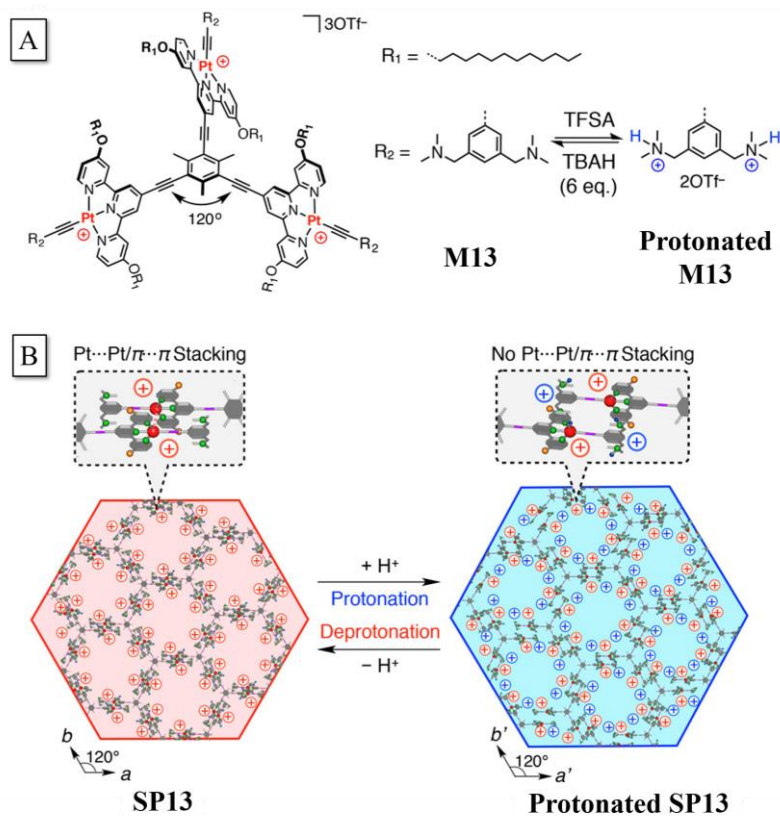


Figure 12. (A) Chemical structures of **M13** and **protonated M13**. (B) Schematic representation of **SP13** and proposed structural changes induced upon protonation and deprotonation. [182], Copyright 2020. Adapted with permission from the American Chemical Society.

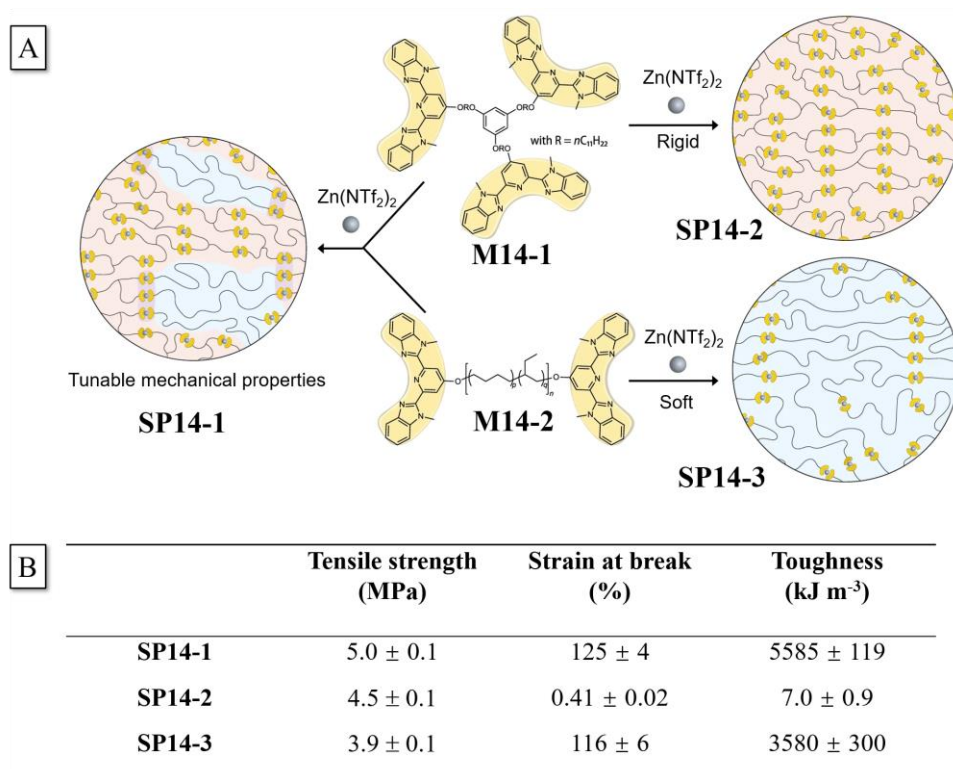


Figure 13. Chemical structures of **M14-1**, **M14-2**, and schematic showing the proposed formation of metallosupramolecular polymers **SP14-2** and **SP14-3**, as well as copolymer **SP14-1**. [183], Copyright 2022. Adapted with permission from Springer Nature.

A general drawback of supramolecular polymers is that they lack the toughness of traditional polymers. In an effort to overcome this shortcoming, Schrettl *et al.* utilized a low-molecular-weight trifunctional monomer (**M14-1**), the telechelic macromonomer (**M14-2**), and stoichiometric amounts of $\text{Zn}(\text{NTf}_2)_2$ to build up metallosupramolecular copolymers (**SP14-1**). [183] Compared with the corresponding rigid polymer and soft material (**SP14-2** and **SP14-3**, respectively) that were assembled separately from **M14-1** + $\text{Zn}(\text{NTf}_2)_2$ and **M14-2** + $\text{Zn}(\text{NTf}_2)_2$ (Figure 13A), the metallosupramolecular polymer **SP14-1** produced *via* co-assembly of the two monomers displayed greater strength, toughness, failure strain and tunable mechanical properties (cf. Figure 13B). It was also free

of the macrophase separation between hard and soft domains that often plague co-assembled materials. It was further found that compositionally graded objects displaying spatially controlled mechanical behavior could be created by welding two **SP14-1** blocks containing different ratios of **M14-1** and **M14-2**.

A redox-responsive metallosupramolecular polymer (**SP15**) based on porphyrin- and viologen-containing tectons was reported by the Bucher group in 2016 (Figure 14).[184] The constituent monomer (**M15**) contains three functional units, *viz.* a zinc porphyrin and an imidazole ligand as self-complementary acceptors and donors, respectively, as well as a bis-viologen linker used as a redox-responsive molecular hinge. The authors established that the self-assembling properties of this trifunctional molecular tecton can be reversibly switched on and off upon controlling the redox state of the central bis(bipyridinium) hinge. In the ground state, electrostatic repulsion between the positively charged viologens was exploited to prevent intramolecular association between the acceptor and donor at the ends of the hinge. This “open” conformation, was found to promote the formation of supramolecular polymers **SP15** stabilized through intermolecular Zn-imidazole coordination bonds, an interaction for which the binding constant was determined to be 360 M^{-1} in CH_3CN . The electrochemical or chemical reduction of the bipyridinium subunits from their cationic to cation radical forms was then found to induce a full dissociation of the polymers in favor of an intramolecularly locked monomer (**Folded M15**) stabilized by π -dimerization of two bipyridinium cation radicals and by intramolecular coordination of the imidazole ligand. Similar strategies making use of the dimerization ability of this bis-viologen-hinge were developed to achieve redox control over the formation of coordination

polymers. For instance, symmetrical systems, where both ends of the hinge were functionalized with terpyridine or bipyridine-like ligands, were reported as supporting metallopolymers in combination with a source of Zn^{2+} , Fe^{2+} or Pd^{2+} cations.[185-189] Photo/redox stimulation of certain of the resulting 1D coordination polymers in solution was found to trigger large scale reorganization along with a macroscopic sol/gel-type phase transition.[186, 190] Also, photo- or electrically responsive metallosupramolecular polymers were fabricated and used to build multiswitchable molecular logic gates.[191]

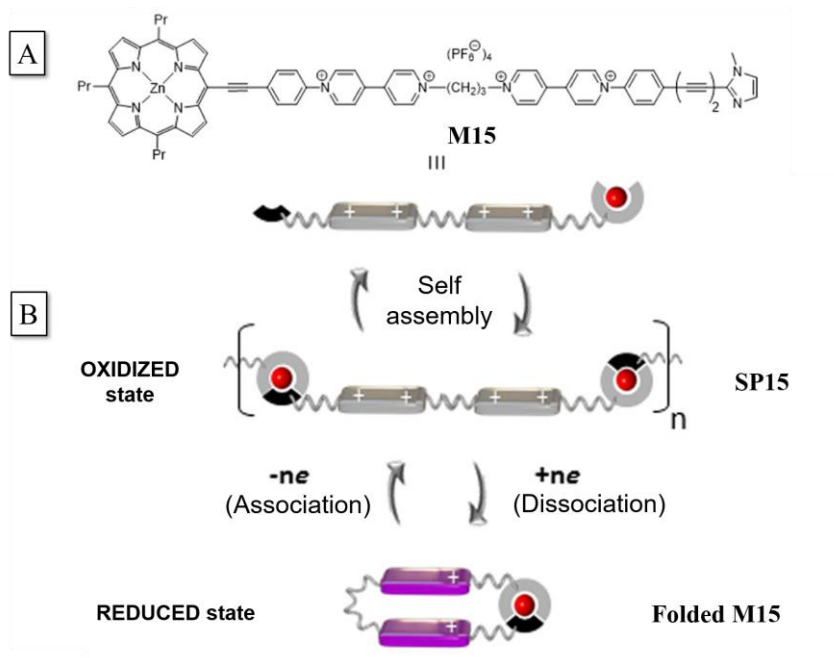


Figure 14. Chemical structure of **M15**, and schematic representation of the formation of metallosupramolecular polymers **SP15**. [184], Copyright 2016. Adapted with permission from the American Chemical Society.

A conceptually simpler simple approach was reported recently that relies on the use two identical metal coordinating units on both sides of a redox-responsive 4,4'-bipyridinium unit (Figure 15).[192] In this case, either discrete 2:2 metal: ligand (M:L) macrocycles (**SP16-1**) or coordination polymers (**SP16-2**) are formed in solution *via* the reaction of a

bis-imidazole-tethered viologen (**M16**) with *cis*-[Pd(en)(NO₃)₂], *trans*-[Pd(CH₃CN)₂(Cl)₂], or [Pd(CH₃CN)₄(BF₄)₂]. Electrochemical reduction of the viologen unit results either in a reversible “inflation/deflation” of the discrete 2:2 (M:L) macrocyclic assemblies (**SP16-3**) or dissociation in the case of the coordination polymers containing Pd(II) centers. It was proposed that the driving force for disassembly process is the formation of discrete box-shaped 2:2 (M:L) assemblies stabilized by π -dimerization of two viologen cation radicals.

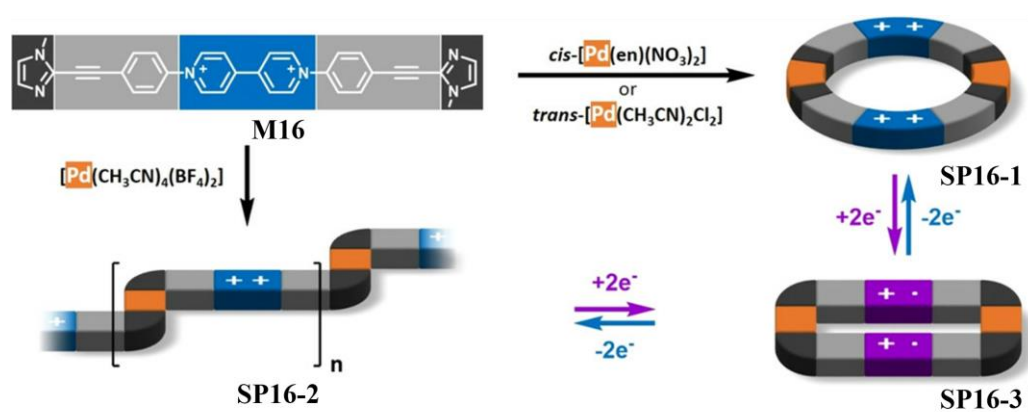


Figure 15. Chemical structure of **M16**, and schematic representation of the supramolecular polymers **SP16-1**, **SP16-2**, and **SP16-3**. [192], Copyright 2021. Adapted with permission from the American Chemical Society.

Usually, controlling the current capacity of electrical circuits relies on top-down approaches. In 2021, Nitchke, Friend, and Nuzzo *et al.* reported a bottoms-up approach. Specifically, they reported a copper-based double-helical supramolecular polymer (**SP17**) that permitted resistive switching (Figure 16).[193] This system was produced *via* the coordination interaction between **M17-1**, **M17-2**, and CuNTf₂ in MeCN, Upon the exposure to electric fields, about 25% of the Cu(I) in **SP17** was oxidized to Cu(II) without producing appreciable damage to the metallopolymer chain. This mixed-valence form

displayed a 10-fold increase in electrical conductivity relative to the starting material, a finding attributed to the presence of partly filled d_z^2 orbitals aligned along the mixed-valence copper array. It was found that this partial oxidation led to the formation of a double-helical structure to accommodate the Cu(II) centers. The need to rearrange this structure was thought to provide a kinetic barrier to re-reduction, which presumably helps account for the observation that the oxidation-induced increase in conductivity was found to persist for several years. The research highlights a new approach to controlling current flow at the nanoscale.

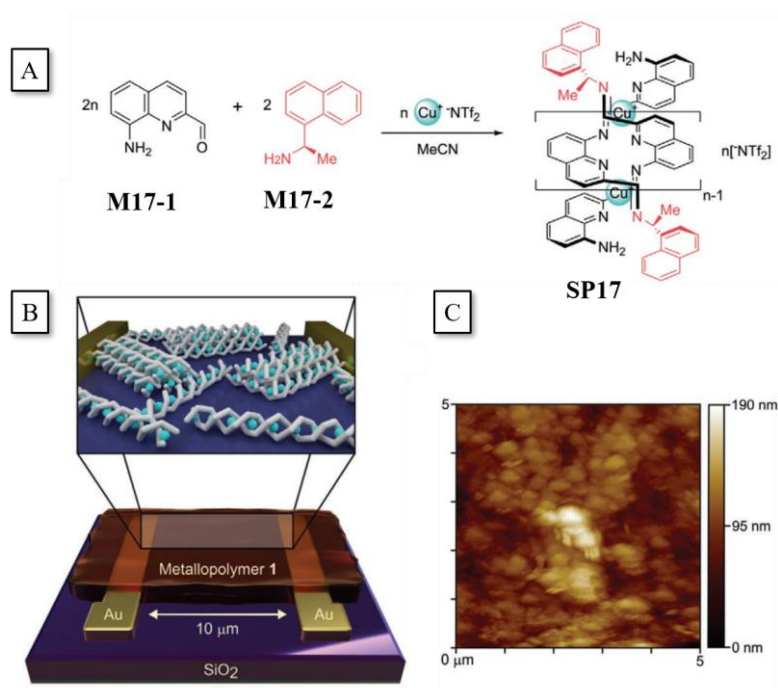


Figure 16. (A) Scheme illustration of **SP17** formed from **M17-1**, **M17-2**, and CuNTf₂ (Tf = O₂SCF₃). (B) Architecture of the two-electrode device used to explore the electrical properties of **SP17**. The thickness of **SP17** is 50 nm. (C) AFM height image of a thin film. [193], Copyright 2021. Adapted with permission from John Wiley & Sons Inc.

4. Supramolecular Polymers Based on Host-Guest Interactions

Classic host-guest complexes are typically stabilized by a range of non-covalent interactions, including hydro- and solvophobic effects, hydrogen bonding, electrostatic interactions and van der Waals forces, while specificity is often guided by size complementarity. Host-guest binding has been identified in numerous biological systems, and forms the basis for a variety of molecular machines, supramolecular polymers, and self-assembled amphiphiles among other synthetic constructs.[105, 194-196] To date, most supramolecular polymers based on host-guest interactions have relied on the molecular recognition features of specific macrocyclic receptors, of which pillar[n]arenes, crown ethers, cyclodextrins, calixarenes and cucurbit[n]urils are the most widely studied.[197] Guests for these hosts have included a large variety of molecules complementary to the host cavities and whose binding supports relatively strong noncovalent interactions. Recent progress in this generalized area is discussed in this section.

4.1. Cyclodextrin-Based Supramolecular Polymers

4.1.1. Cyclodextrin-Based Host-Guest Interactions: An Historical Perspective

Cyclodextrins (CDs) are basket-like macromolecules that comprise glucopyranose units linked by glycosidic groups (Figure 17A). They possess a hydrophobic cavity and a hydrophilic rim and are capable of capturing organic guest molecules from aqueous environments. These time-honored hosts have been studied in applications ranging from drug delivery to catalysis and metal purification.[198] Three cyclodextrins, α , β , and γ , which vary in their size (Figure 17A) have been widely studied and, as might be expected, size dependent effects are seen in their recognition chemistry.[199-202] In 1990, Harada *et al.* studied various inclusion complexes involving CDs and traditional polymers.[203] This

work uncovered a correlation between the sizes of the CD and the thickness of the polymeric guests. This pioneering work can be viewed as being the intellectual precursor to the subsequent development of supramolecular polymers based on CDs and appropriately chosen low-molecular-weight monomers.[204] Many of the resulting systems display good biocompatibility and water solubility, which has made them of interest in the context of potential medical applications, as well as possible eco-friendly materials.[205-208]

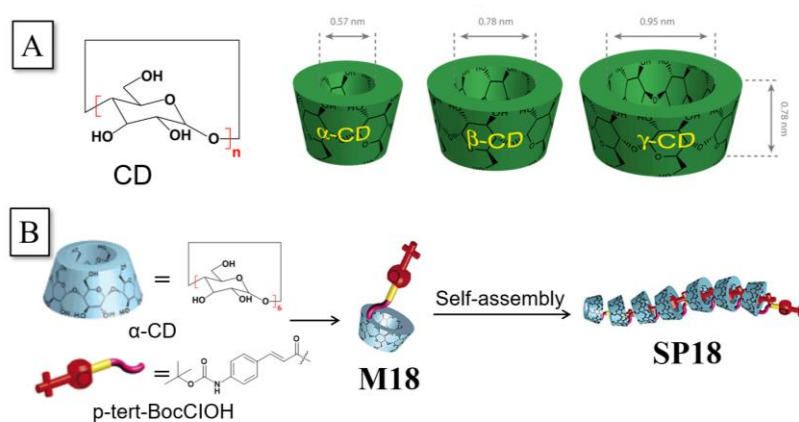


Figure 17. (A) Scheme illustration of α -CD ($n = 6$), β -CD ($n = 7$), and γ -CD ($n = 8$).

[200], Copyright 2014. Adapted with permission from the American Chemical Society.

(B) Chemical structure of **M18** and schematic representation of the supramolecular polymer **SP18** produced through its self-assembly. [209], Copyright 2005. Adapted with permission from the American Chemical Society.

4.1.2. Recent Advances in Cyclodextrin-Based Supramolecular Polymers

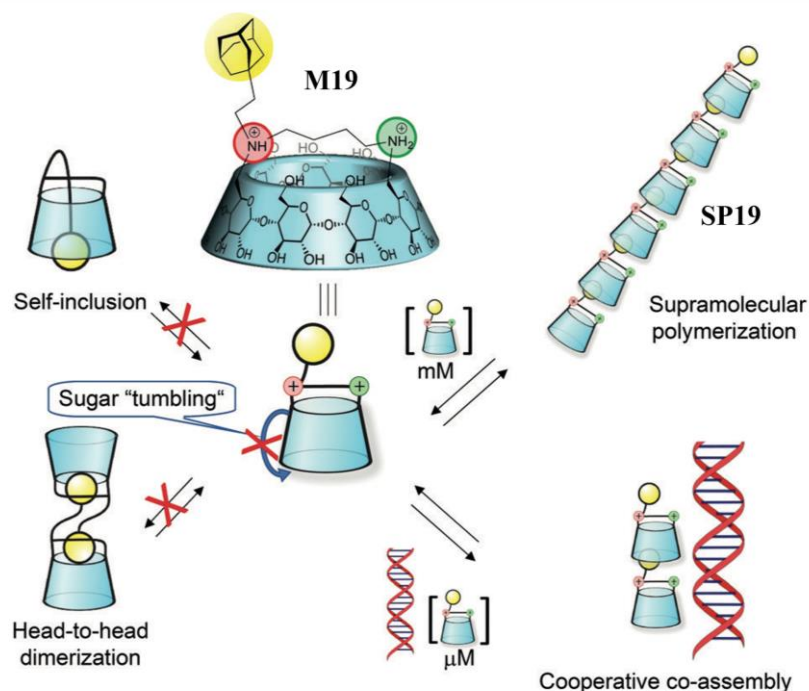


Figure 18. Schematic illustration of the cooperative assembly and supramolecular polymerization of **M19** and avoided self-inclusion and dimerization. [210], Copyright 2020. Adapted with permission from John Wiley & Sons Inc.

To avoid self-inclusion and head-to-head dimerization of the monomers, which would compete with the formation of higher order structures, in 2005 Harada *et al.* attached a guest-like subunit to the lower (wider) rim of α -CD; this resulted in a supramolecular polymer (**SP18**) with degree of polymerization >15 (Figure 17B).[209] In 2018, Sollogoub and co-workers addressed these same issues (*i.e.*, avoiding self-inclusion and dimerization) by bridging two sites on the upper (narrower) β -CD rim with a bis-ammonium linker bearing an adamantane moiety to give monomer **M19** (Figure 18).[210] This bridging strategy prevented self-inclusion of the adamantane subunit within the cyclodextrin cavity. Moreover, the two ammonium groups on the rim of the CD increased the solubility of **M19** in water. On the basis of NMR spectroscopic analyses and concentration-dependent

diffusion coefficient studies, the authors concluded that at millimolar concentrations **M19** ($K_a = 1.1 \times 10^4 \text{ M}^{-1}$ in D_2O) was capable of forming supramolecular polymers of generalized structure **SP19**. The resulting ensembles were found to interact cooperatively with DNA and siRNA, while not inhibiting the transfection of siRNA.

Chen and Huang *et al.* developed the CD-based supramolecular polymer **SP20** and explored some of its potential in biomedical applications.[211] They designed and synthesized monomer **M20**, wherein β -CD was expected to function as a host within an aqueous-compatible supramolecular polymer. The anticancer drug camptothecin (CPT) was linked to the β -CD core as a guest subunit *via* a disulfide linker. The use of CPT was designed to support the formation of a supramolecular polymer, **SP20**, that was expected to function as a cancer theranostic. Specifically, it was anticipated the disulfide linker would be cleaved in the presence of glutathione (GSH) allowing for the release of CPT in environments, such as tumors, where GSH is overexpressed (Figure 19). Characterization studies, including analyses of diffusion coefficients, molecular weights and viscosity, provided support for the proposed formation of the supramolecular polymer **SP20** from **M20** ($K_a = 1.68 \times 10^4 \text{ M}^{-1}$ in D_2O). To construct a self-assembly with suitable surface properties and of a size appropriate for biomedical applications, a CPT-PEG-RGD polymer was allowed to copolymerize with **M20**. It was expected that the polyethylene glycol chains would improve the stability of the resulting supramolecular polymeric nanostructures in aqueous media. Likewise, the cRGDfK (an $\alpha_v\beta_3$ integrin targeting peptide) ligands were designed to impart targeting capability to the nanostructures. The authors put forward evidence that mixing the CPT-PEG-RGD polymer with **M20** resulted in the formation of

supramolecular polymeric nanoparticles (SNPs) with a diameter of 118 nm. These SNPs were then tested *in vitro* and *in vivo*. They were found to be internalized into HeLa cells and localized within the lysosomes. Evidence of cell apoptosis and necrosis was seen after CPT release, presumably as the result of GSH-induced cleavage of the disulfide linkers. Another monomer, CPT-PEG-NOTA, was also copolymerized with **SP20**. The resulting SNPs were found capable of coordinating ^{64}Cu , a radiotracer that allows for positron emission tomography (PET) imaging.

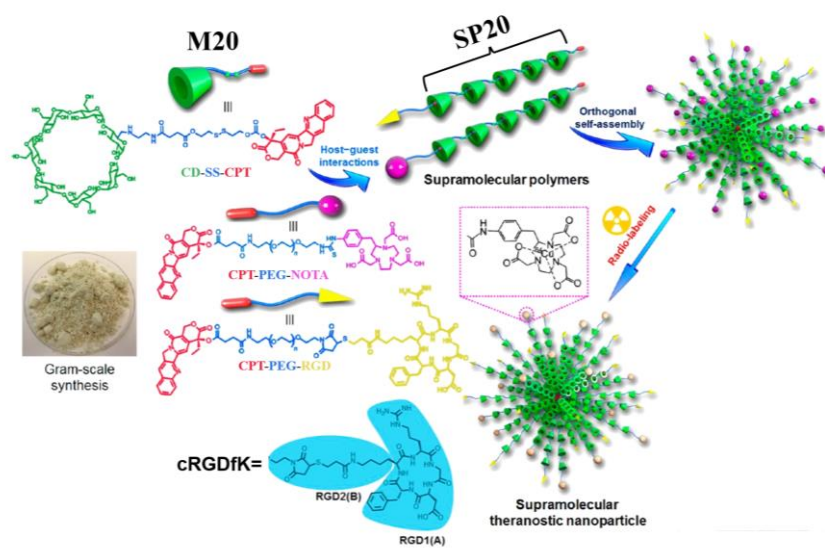


Figure 19. Schematic illustration showing the self-assembly of **M20** leading to the supramolecular polymer **SP20**, as well as copolymers formed from **M20** and other functionalized building blocks. [211], Copyright 2018. Adapted with permission from the American Chemical Society.

In 2020, Liu and co-workers reported a supramolecular polymer (**SP21**) based on the host-guest interaction between β -cyclodextrin and anthraquinone ($K_a = 382 \text{ M}^{-1}$). [212] Under UV photoirradiation, the anthraquinone moieties of **M21** in this supramolecular polymer were photo-reduced to the corresponding hydroquinone. This resulted in the

appearance of a yellow color and a strong fluorescence for aqueous solutions of the polymer **SP21**. This photo-reduction could be reversed by bubbling air into a solution of the polymer, which led to oxidation back to the original hydroquinone-containing species. Taking advantage of interconversion between the oxidized and reduced forms the authors were able to use their smart supramolecular polymers for data encryption and decryption.

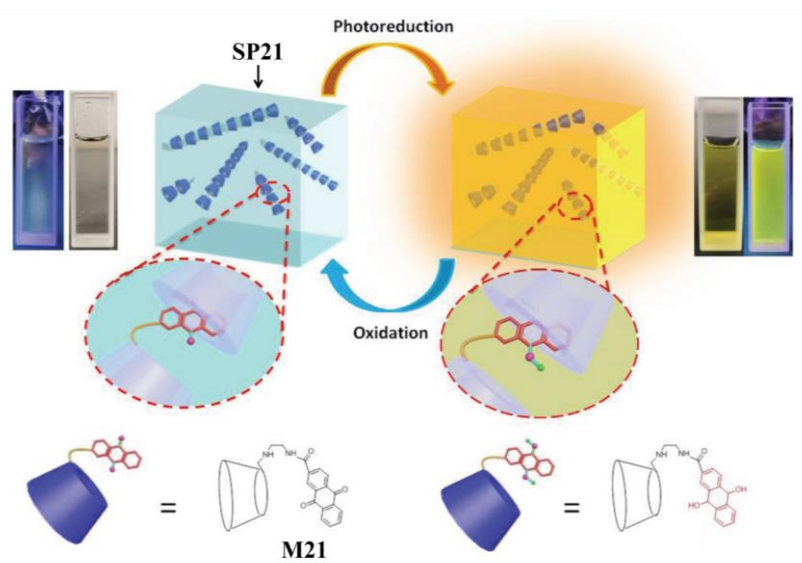


Figure 20. Chemical structure of **M21**, and schematic representation of the supramolecular polymer **SP21**. [212], Copyright 2020. Adapted with permission from John Wiley & Sons Inc.

Another class of stimulus-responsive β -CD-based supramolecular polymeric materials responsive to H_2O_2 and Cu^{2+} was reported by the Hao group (Figure 21).[213] These materials were constructed from monomers (**M22**) bearing β -CD and ferrocene linked by different diamines. Based on 1D and 2D NMR spectroscopic analyses, the tethered ferrocene units could enter the CD cavities giving rise to long linear supramolecular polymers (**SP22**), which further packed to generate microfibers or supramolecular vesicles. A gel was also prepared from the same set of monomers by dissolving them in the mixtures

of N-methyl pyrrolidone and acetone. The polymer-inducing supramolecular interactions could be destroyed by oxidizing the ferrocene subunits or by coordination of Cu^{2+} to the diamine tethers.

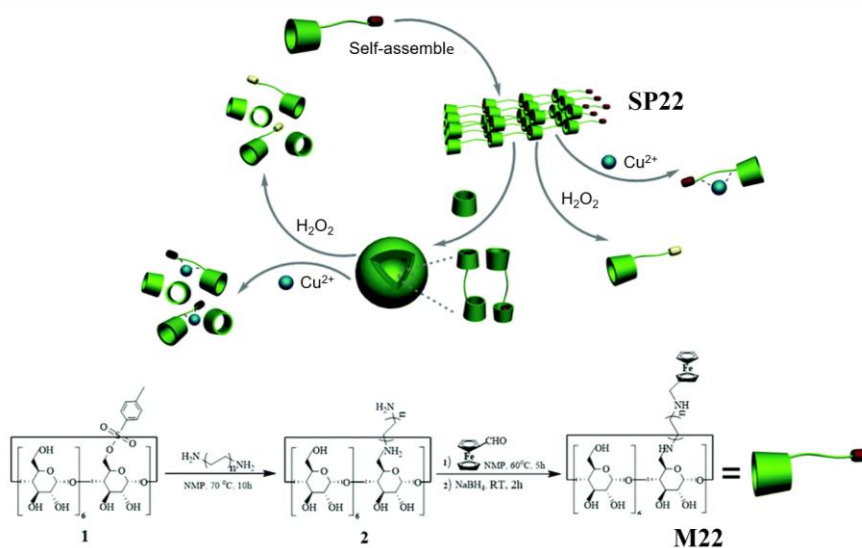


Figure 21. Chemical structure of **M22**, and schematic representation of the corresponding supramolecular polymers **SP22**. [213], Copyright 2017. Adapted with permission from the Royal Society of Chemistry.

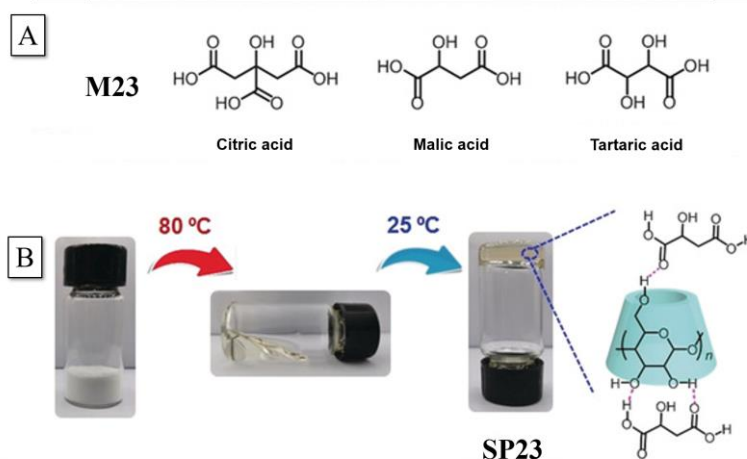


Figure 22. (A) Chemical structure of **M23**. (B) Preparation of deep eutectic supramolecular polymers (**SP23**). [214], Copyright 2020. Adapted with permission from John Wiley & Sons Inc.

Unlike numerous studies on supramolecular polymers in solution or in gel state, Dong and co-workers employed a so-called “deep eutectic solvents” strategy to develop solvent-free supramolecular polymers.[214] For this study, several naturally occurring acids **M23** (Figure 22A), *viz.* citric acid, malic acid and tartaric acid, were chosen as the solvents since their –COOH groups were expected to interact with the –OH groups of a CD *via* hydrogen-bonds. Mixing these acids with various CDs resulted in deep eutectic supramolecular polymers (**SP23**) characterized by high viscosity. Flexible fibers and films were prepared from **SP23**, which was taken as an augury of good processability (Figure 22B). Polymers **SP23** showed very strong adhesion not only to glasses and iron plates, but also to biological tissues. Good adhesion was also observed in dichloromethane and at different temperatures.

Polyoxometalates (POMs) are large, charge diffuse anions that have seen applicability in a number of fields. Wu and co-workers synthesized a hybrid cluster monomer comprising a Mn-centered POM bearing two anthracene groups at opposite sides (cf. Figure 23 for a schematic representation).[215] In the presence of γ -CD, host-guest interactions between the CD cavity and the two anthracene moieties were found to stabilize a set of supramolecular polymers (**SP24-1**). Subsequent photoirradiation led to [4+4] cyclodimerization of the anthracene units held within the CD cavities. The net result was a transformation of the original supramolecular polymers (**SP24-1**) to the corresponding covalent polymers (**SP24-2**). TEM imaging revealed long linear shish kebab structures and provided evidence for a high degree of polymerization (DP >175). Although specific applications of this set of hybrid supramolecular materials have yet to be reported, we believe that this work will pave the way to the construction of useful polymetallic polymers.

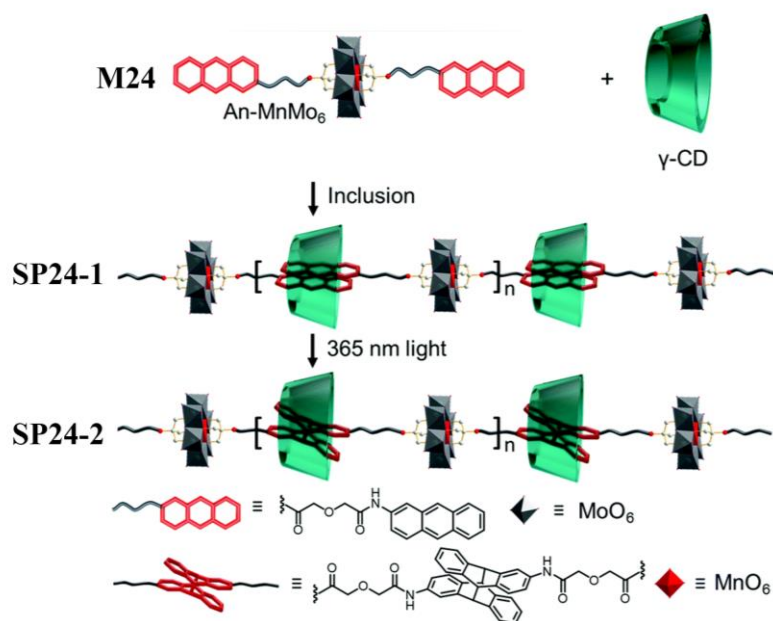


Figure 23. Chemical structure of **M24**, and schematic representation of the supramolecular polymer **SP24-1** and **SP24-2**. [215], Copyright 2019. Adapted with permission from the Royal Society of Chemistry.

4.2. Calixarene-Based Supramolecular Polymers

4.2.1. Calixarene-Based Host-Guest Interactions: An Historical Perspective

Calixarenes are cyclic oligomers synthesized by condensation reactions of phenols and aldehydes. They contain a hydrophobic cavity for host-guest complexation and active sites on the rim for useful chemical modifications (Figure 24A).[216] A number is often inserted between “*calix*” and “*arene*” to represent the number of subunits in the macrocycles. Calix[n]arenes have a time-honored history dating back to pioneering work by Baeyer[217] and then later Zinke and Ziegler.[218] In the 1970s, Gutsche *et al.* carried out seminal studies demonstrating the utility of calixarenes; he also gave them their current name based on the resemblance between calix[4]arene in its cone conformation and a type of Greek vase called a calix crater.[219, 220] In 1997, Rebek *et al.* reported the first calixarene-based

supramolecular polymer, which they termed “polycaps”. These systems were obtained by covalently connecting two calix[4]arenes at their lower rims and linking them noncovalently at their upper rims (Figure 24B).[221] It was found that two cup-shaped calixarene units could come together to form a capsule capable of encapsulating a small guest molecule. In the ensuing years, several other polymers containing calixarenes were reported.[222] However, most did not rely on host-guest recognition involving the calixarene cavity *per se*. Nevertheless, in 2003, Parisi and co-workers disclosed a different class of polycaps whose formation relied on the strong inclusion of bis-alkyldiammonium ions into the cavities of calix[5]arenes.[223] Subsequently, many AB-type heteroditopic (Figure 24C) or AA/BB-type homoditopic (Figure 24D) building blocks bearing calixarenes were developed and used to fabricate supramolecular polymeric systems.[224-226]

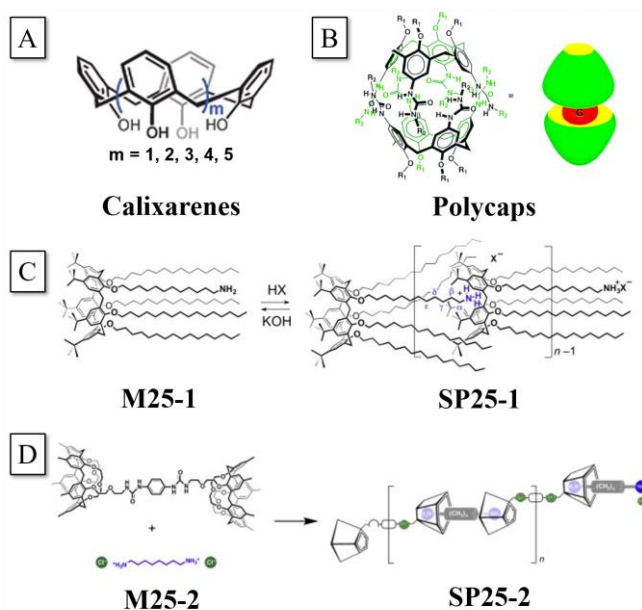


Figure 24. (A) Structural illustration of calixarenes shown in their idealized cone conformations. [224], Copyright 2012. Adapted with permission from the Royal Society of Chemistry. (B) Structural illustration of calixarenes “Polycaps”. [221], Copyright 1997. Adapted with permission from the National Academy of Sciences (USA). (C) Chemical

structure of **M25-1** and schematic representation of the supramolecular polymer **SP25-1** (DP = 25). [225], Copyright 2011. Adapted with permission from Elsevier Science Ltd.

(D) Chemical structure of **M25-2** and schematic representation of the supramolecular polymer **SP25-2**. [226], Copyright 2011. Adapted with permission from Elsevier Science Ltd.

4.2.2. Recent Advances in Calixarene-Based Supramolecular Polymers

In 2017, Sun and co-workers prepared a supramolecular polymer (**SP26**) based on a bisulfonato calix[4]arene **M26-3** and a protonated monomer **M26-2**, which contains a modified dimethylamino fluorophore (**M26-1**) (Figure 25).[227] As inferred from the chemical shifts seen in the ^1H NMR spectrum, only a small portion of the guest molecule actually enters the host cavity. UV and fluorescent spectral studies revealed rational changes consistent with polymerization. The morphologies of the resulting supramolecular assemblies were investigated by atomic force microscopy and transmission electron microscopy. These imaging studies revealed long linear structures and provided support for the formation of calixarene-based supramolecular polymers with well-defined shapes and sizes.

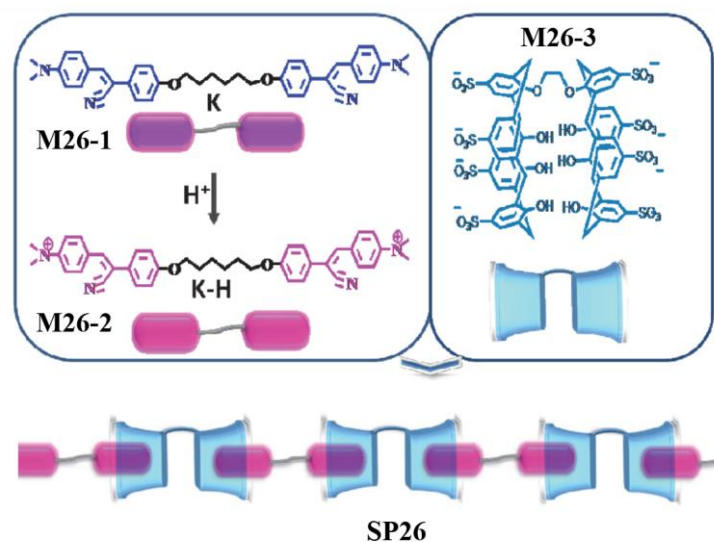


Figure 25. Chemical structure of **M26-1**, **M26-2** and schematic representation of the supramolecular polymer **SP26**. [227], Copyright 2017. Adapted with permission from John Wiley & Sons Inc.

To the best of our knowledge, there are no more recent reports of calixarene-based supramolecular polymers. In a sharp contrast, amphiphilic calixarenes have been used to construct various supramolecular particles for light-harvesting, bioimaging, and targeted phototheranostics, among other applications.[228-230] The paucity of calixarene-based supramolecular polymers could reflect some combination of the following factors:

1) The common calix[*n*]arenes (*n* = 4 and 5) can only chelate metal ions or form 1:1 complexes with small organic molecules owing to their limited cavity sizes; thus, to promote effective self-assembly ditopic hosts need to be synthesized, which adds to the synthetic burden associated with constructing supramolecular polymers.

2) Most *n:n* supramolecular polymers of calixarenes are entropy-disfavored relative to the corresponding 1:1 complexes.[231] Considerable time and efforts are thus required to

design dedicated monomers that favor formation of stable calixarene-based supramolecular polymers.

3) Other molecular motifs are increasingly available that stabilize noncovalent interactions suitable for use in supramolecular polymerization studies.

4.3. Crown Ether-Based Supramolecular Polymers

4.3.1. Crown Ether-Based Host-Guest Interactions: An Historical Perspective

In 1967, Pedersen discovered a “crown” type polyoxygen macrocycle, *viz.* dibenzo-18-crown-6.[232] He demonstrated that this system and its analogues were capable of stabilizing complexes with a number of cations, including alkali and alkaline earth cations and ammonium ions. Nearly contemporaneously, Lehn reported the bicyclic cryptands, and demonstrated their utility as *inter alia* macropolycyclic receptors and molecular catalysts.[233] In 1974, Cram revealed how molecular complexes between a variety of oxygen rich hosts and various cations and codified the concept of preorganization.[234] For developing and using molecules with structure-specific interactions of high selectivity, Donald J. Cram, Jean-Marie Lehn and Charles J. Pedersen were awarded the Nobel Prize in Chemistry 1987. Early on Stoddart, who would later share the 2016 Nobel Prize in Chemistry for his work on molecular machines, reported the molecular inclusion of paraquat by a bisparaphenylene-34-crown-10, work that paved the way for fabricating supramolecular polymers from π -electron rich crown ethers and π -electron deficient guests.[235] In the late 1990s, Gibson and co-workers reported the formation of linear supramolecular polymers from ditopic monomers bearing ammonium ions and crown ethers, respectively.[94, 236] Since then, various functional supramolecular polymers have

been reported that exploit the reversibility and selectivity of crown ether-based host-guest interactions. Below we summarize more recent contributions in this area.

4.3.2. Recent Advances in Crown Ether-Based Supramolecular Polymers

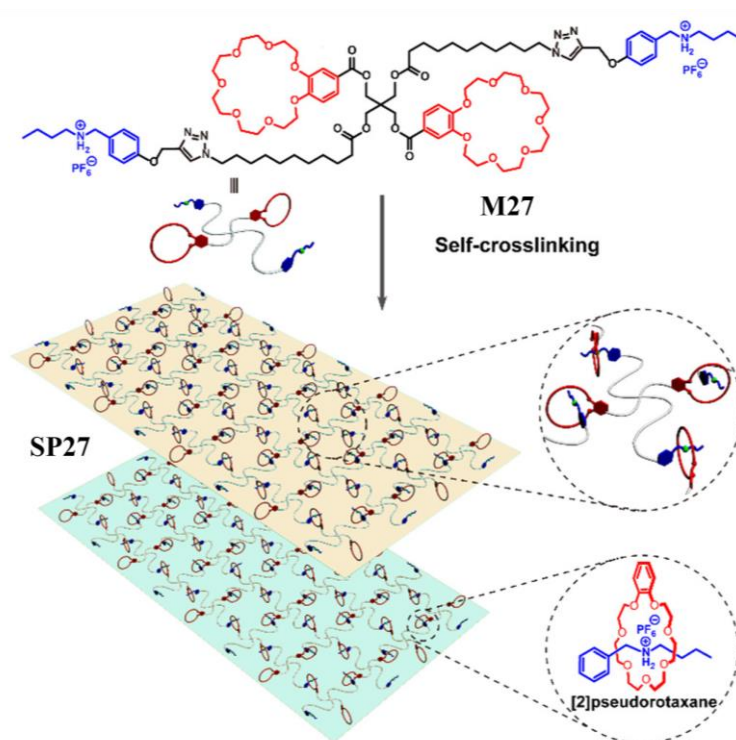


Figure 26. Chemical structure of **M27**, and schematic representation of the supramolecular polymer **SP27**. [237], Copyright 2020. Adapted with permission from the American Chemical Society.

In 2020 Yan and co-workers designed and synthesized a four-arm monomer **M27** containing two dialkylammonium guest units and two benzo-21-crown-7 host components and used it to create self-cross-linking supramolecular polymers of general structure **SP27** stabilized by [2]pseudorotaxane linkages (Figure 26).[237] At high concentrations (≥ 21.0 wt%), **SP27** in acetonitrile was found to form gels that underwent *pH*- and thermo-triggered reversible gel-sol transitions. The dynamic mechanical properties of these and other gels are often described in terms of the storage modulus, G' , and loss modulus, G'' , which reflect

the elasticity and viscosity of the materials, respectively. The gel point is typically defined as the point where $G' = G''$. In the case of gel **SP27**, G' was found to exceed G'' at room temperature. On the other hand, temperature dependent studies revealed a critical temperature T_c (~58 °C), at which G' and G'' were equal. When $T > T_c$, the G'' values were higher than G' , indicating the destruction of the gel form, presumably as the result of breaking up the [2]pseudorotaxane linkages that serve to stabilize the gel form. In contrast, G' values greater than G'' are seen when $T < T_c$, reflecting reformation of the supramolecular network. These findings provide support for the proposed thermoplastic features of **SP27**. Furthermore, rapid glass-liquid conversion of **SP27** was seen at elevated temperatures ascribed to the fast exchange nature of the dynamic host-guest interactions between the benzo-21-crown-7 and ammonium subunits. This, in turn, endowed **SP27** with good processability and malleability and allowed the construction of several architectures with different macroscopic shapes.

In 2016, the Gibson group reported hyperbranched supramolecular polymers **SP28** formed from monomers **M28** consisting of a bis(*m*-phenylene)-32-crown-10 (bis-cryptand) and linked bis-paraquat moieties bearing tris(*p*-*t*-butylphenyl)methane blocking groups (Figure 27A). In contrast with previously reported hyperbranched polymers, the blocking groups in this system were found to prevent dethreading of the guests from the pseudorotaxane units.[238] In 2018, the same group designed and synthesized an array of bis-cryptand monomers based on covalently linked cryptand host units known to bind paraquat derivatives well.[239] Five polymers were successfully obtained by mixing different monomers. It was found that short and rigid linkers between the two subunits

making up the bis-cryptand receptor provided monomers that did not favor supramolecular polymerization, presumably due to an inability to overcome the repulsive electrostatic interactions between the two paraquat guests. On the other hand, the bis-cryptand monomer, **M29-2**, possessing long and flexible linkers was found to complex with the specific bisparaquat **M29-1** ($K_a = 4.36 \times 10^5 \text{ M}^{-1}$ in DCM, Figure 27B). This gave the supramolecular polymer **SP29** with a DP of 126 at 37 mM. In this case, a double logarithmic plot of the specific viscosity vs concentration revealed a critical polymerization concentration of 37 mM. Above 37 mM, a slope of 3.55 was seen, which was taken as evidence for the formation of supramolecular polymeric ensembles with high molecular weights. Polymers such as **SP29** were found to form brittle films; however, their corresponding fibers were all strong and flexible. It was also found that the thermal properties of the polymers were influenced by the paraquat counter anions.

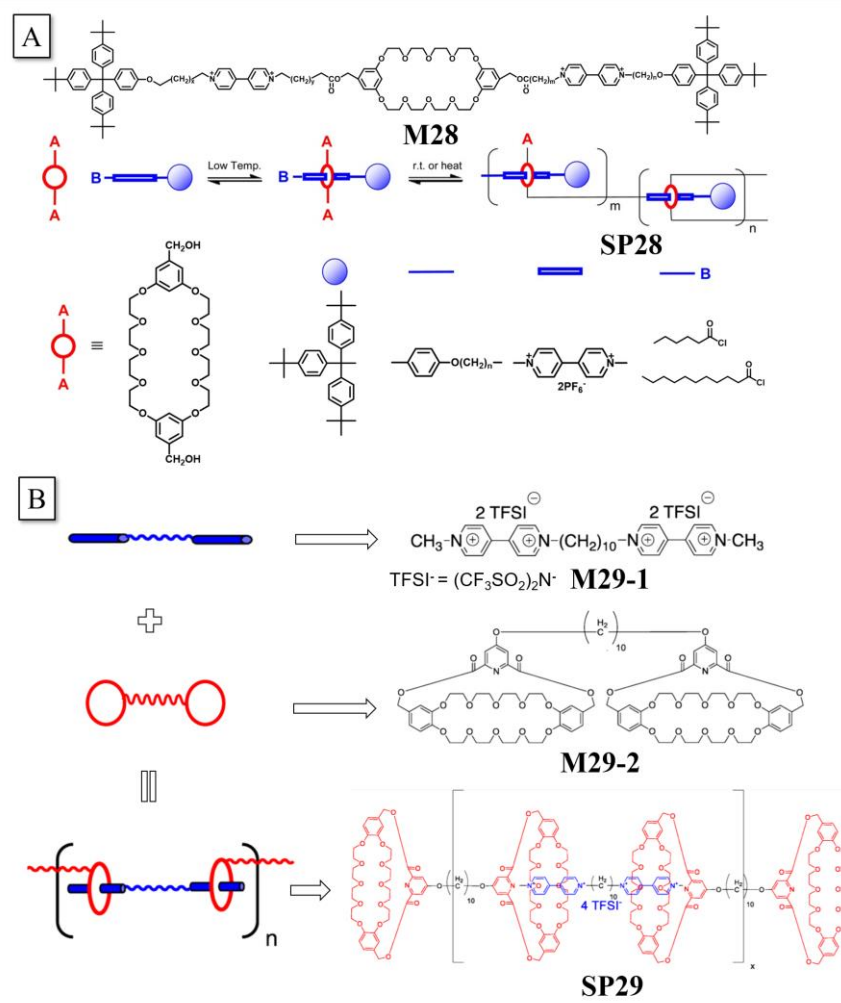


Figure 27. (A) Chemical structures and schematic illustrations of **M28**, and **SP28**. [238],

Copyright 2016. Adapted with permission from John Wiley & Sons Inc. (B) Chemical

structures and schematic illustrations of **M29-1**, **M29-2**, and **SP29**. [239], Copyright 2018.

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The 1,3,5-benzenetricarboxamide (BTA) unit has proved to be a versatile motif for constructing ordered superstructures.[240] Over the past decades, many sophisticated supramolecular polymers have been produced by derivatizing BTA with other functional groups, including benzocrown ethers, porphyrins, amino acids, as well as a number of other substituents.[241-243] For instance, the Dong and Han groups synthesized a monomer **M30**

carrying BTA as the core and three benzo-21-crown-7 units as the arms (Figure 28A). [244] The resulting species were found to self-assemble into one-dimensional supramolecular aggregates (**SP30-1**) in chloroform, presumably as the result of stabilizing hydrogen-bonding and π - π interactions. Guest molecules bearing two ammonium salt groups could then be used to crosslink the supramolecular aggregates (**SP30-2**) to produce the corresponding supramolecular polymers.

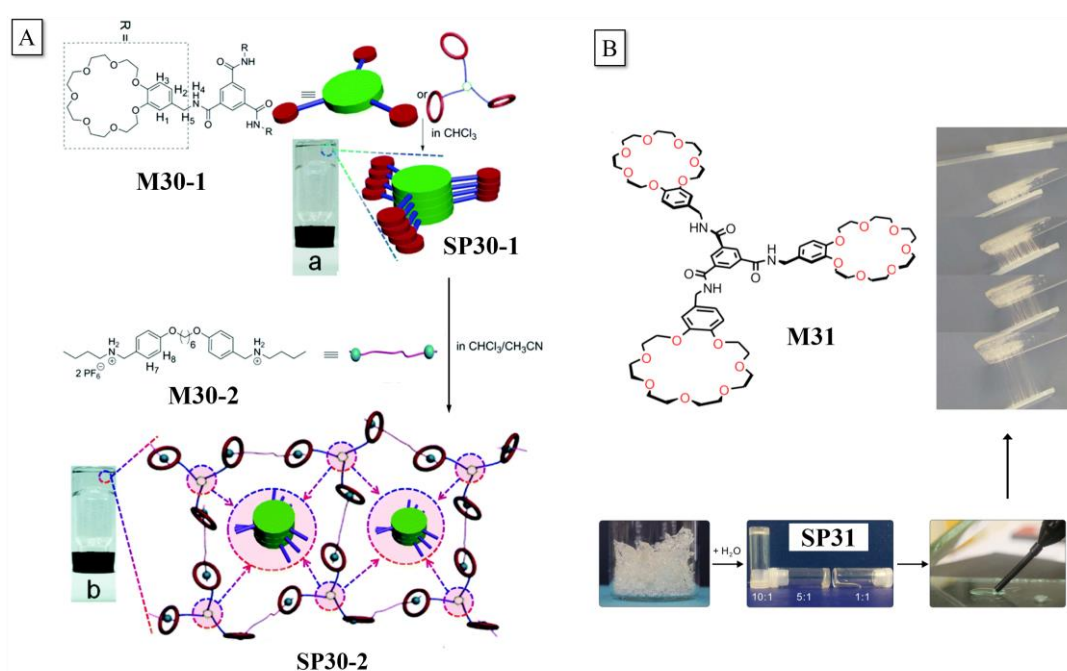


Figure 28. (A) Chemical structures and schematic illustrations of **M30**, and **SP30-1**, **SP30-2**. [244], Copyright 2018. Adapted with permission from the Royal Society of Chemistry. (B) Chemical structure of **M31** and formation of **SP31** seen when dry **M31** is allowed to absorb water. [245], Copyright 2017. Adapted with permission from the American Association for the Advancement of Science.

Another BTA-based supramolecular polymer formed by interactions of a benzo-21-crown-7 derivative and water molecules was studied by Schalley and co-workers (Figure

28B).[245] The pure triply benzo-21-crown-7-substituted BTA host (**M31**) appeared to be a fragile solid when dry. However, a very viscous material (**SP31**) was obtained after **M31** was allowed to absorb water from the air. The viscosity could be tuned by controlling the water content in the samples. At appropriate water ratios relative to **M31**, **SP31** could be easily processed into long and flexible fibers. Reflectance infrared spectroscopic studies led to the conclusion that the water molecules interact with the crown ether subunits of **M31** *via* hydrogen-bonds. Data from broadband dielectric spectroscopy and density functional theory simulations provided support for this conclusion and led to the inference that 4 to 5 water molecules act as crosslinkers by binding in concert to two crown ethers on separate BTA subunits. These supramolecular polymeric materials (**SP31**) were used to glue together substrates with hydrophilic surfaces (*e.g.*, glass and paper). The adhesives proved reusable. Raising the temperature served to release water molecules from **SP31** and undo the gluing effect.

In 2019, the Stang group reported a supramolecular polymeric adhesive (**SP32**) that also relied on hydrogen bonding between water molecules and crown ethers as the main stabilizing interaction (Figure 29A).[246] They found that the use of Pt-pyridine coordination, a key feature of their system, affected the conformation of the monomer, which reduced competitive intermolecular interactions and allowed the water molecules to approach the crown ethers.

In 2020, the Yan group demonstrated that the catalyst-free condensation of acetoacetate groups present in [2]rotaxane monomers (**M33-1** and **M33-2**) with two selected multiamine monomers (**M33-3** and **M33-4**) could be exploited to fabricate mechanically

interlocked supramolecular network polymers (**SP33-1** and **SP33-2**) (Figure 29B).[247] In the case of **M33-1**, the two acetoacetate groups were placed on the wheel and axle, respectively, while the two acetoacetate groups were present only on the axle in **M33-2**. Both **SP33-2** and **SP33-1** demonstrated good mechanical properties with sliding of the wheel being seen under an external force. The associated energy dissipation process was ascribed to the force-induced dissociation of the crown-ether-based host-guest interactions. When **SP33-1** was treated with an excess of a monofunctional amine, it exhibited enhanced swellability that was ascribed to the destruction of the stabilizing host-guest interactions allowing for freer movement of the wheel within the network. Supramolecular polymer **SP33-1** proved reprocessable with the underlying chemical recyclability thought to stem from the exchange of the dynamic covalent (imine) bonds created by initial condensation between the monomers.

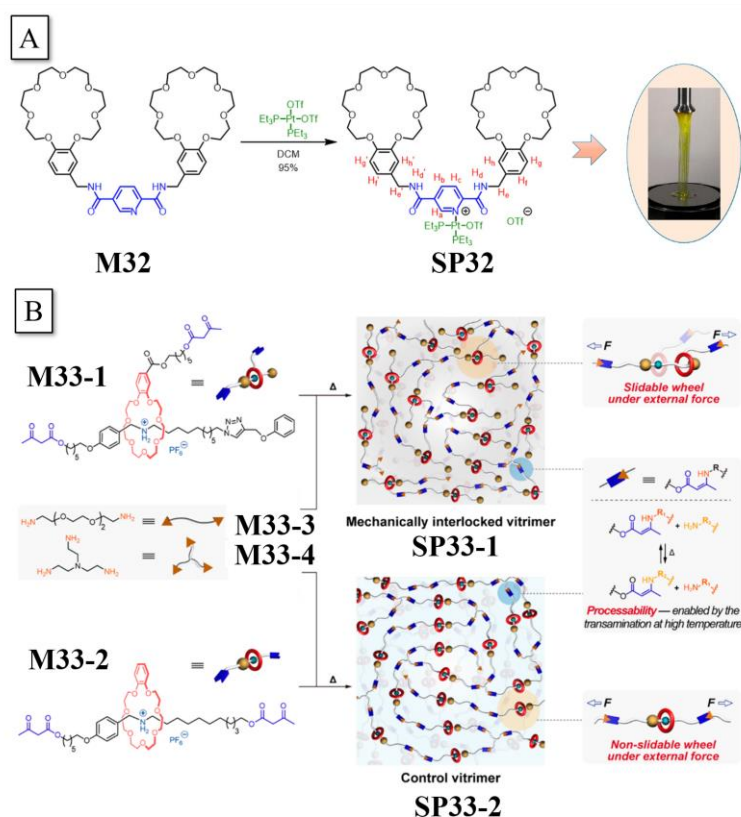


Figure 29. (A) Chemical structures and schematic illustrations of **M32**, and **SP32**. [246], Copyright 2019. Adapted with permission from the American Chemical Society. (B) Chemical structures of monomers **M33-1** – **M33-4** and schematic illustrations of the supramolecular polymers **SP33-1** and **SP33-2** produced through dynamic covalent imine bond formation. [247], Copyright 2021. Adapted with permission from the American Chemical Society.

4.4. Cucurbituril-Based Supramolecular Polymers

4.4.1. Cucurbituril-Based Host-Guest Interactions: An Historical Perspective

Cucurbit[n]urils (CB[n], n = 5-8, 10, 14) are “pumpkin-like” macrocycles containing a differing number of glycoluril units bridged by methylene groups (Figure 30).[248, 249] Their structural rigidity and the large number of heteroatoms they contain has made CB[n]s receptors *par excellence* for appropriately chosen guests. Hydrophobic interactions and charge-dipole attraction between positively charged guests and the oxygen atoms in CB[n] are thought to be key to the underlying host-guest interactions. Of particular note is the fact that CB[8] is capable of forming ternary complexes by incorporating a homo- or hetero-guest pair within its relatively large cavity. This is a key feature that has been widely employed to build supramolecular polymeric materials.[250-252] Recently, a number of researchers, including Isaacs, Day, and Tao *et al.* have reported other CB[n]-related cyclic macrocycles, such as CB[10], CB[14], *nor-seco*-CB[10], and *nor-seco*-CB[6], the extending the frontiers of CB chemistry.[253-256] Of these newer systems, only CB[10] has to our knowledge been exploited to create a supramolecular polymer (*vide infra*).

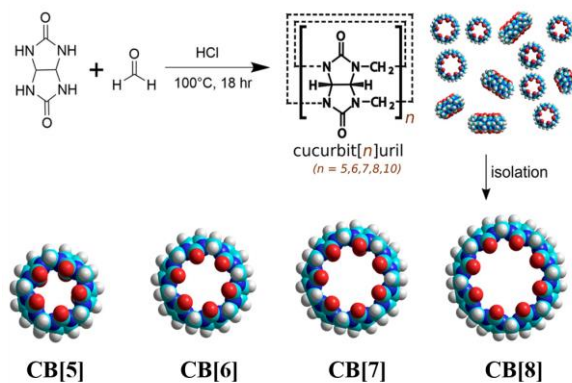


Figure 30. Space-filling models of CB[5]–CB[8]. [249], Copyright 2015. Adapted with permission from the American Chemical Society.

4.4.2. Recent Advances in Cucurbituril-Based Supramolecular Polymers

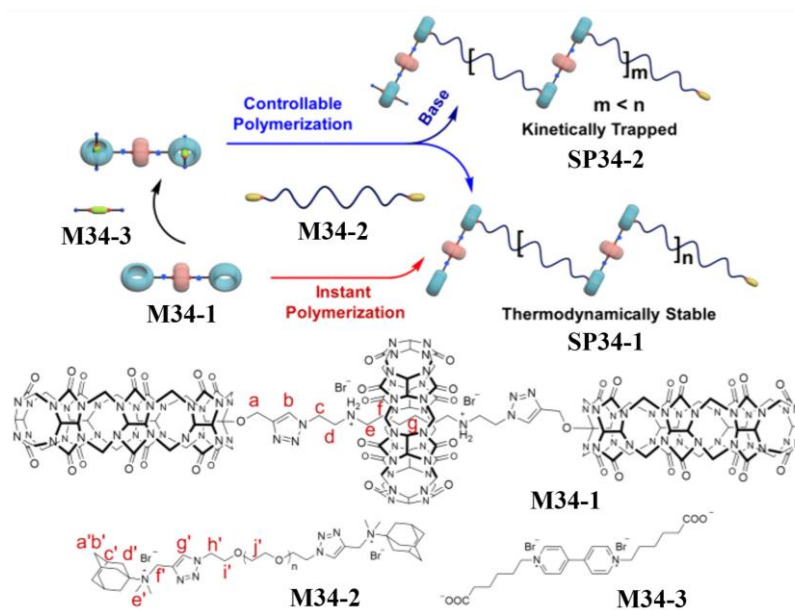


Figure 31. Schematic representation of supramolecular polymer formation controlled by kinetic trapping triggered by changing the effective pH . [90], Copyright 2017. Adapted with permission from John Wiley & Sons Inc.

In 2017, supramolecular polymers based on CB[n]s ($n = 5-7$) with relatively small cavities were still rare. At that time, Zhang and co-workers successfully demonstrate their use in controlling supramolecular polymerization.[90] Specifically, they synthesized

bifunctional building blocks **M34-1** and **M34-2**, bearing CB[6], CB[7], and N,N-dimethyl adamantanyl ammonium (DMAD), respectively (Figure 31). When monomers **M34-1** and **M34-2** were mixed in a molar ratio of 1:1, the chemical shifts of the proton peaks in the ^1H NMR spectrum and the diffusion coefficients determined by diffusion-ordered NMR spectroscopy underwent changes consistent with the formation of a supramolecular polymer (**SP34-1**). The binding constant between **M34-1** and **M34-2** was determined to be $1.4 \times 10^{14} \text{ M}^{-1}$ in D_2O . To control the supramolecular polymerization process, the authors designed a competitive guest **M34-3** endowed with pH-responsiveness. When monomer **M34-2** (1mM) was added into a solution of **M34-1/M34-3** (0.5 mM) in D_2O (pD 9.7) at 298K, slow polymerization, characterized by a rate constant of $9.7 \times 10^{-6} \text{ s}^{-1}$ was determined. It was inferred that the slow dissociation of **M34-3** from the CB[7] cavity controlled the **M34-1/M34-2** polymerization kinetics. By changing the effective pD in NaOD- D_2O , supramolecular polymers of general structure **SP34-2** with different molecular weights could be obtained. Presumably, this reflects the fact that the extent of dissociation of **M34-3** from the CB[7] cavity is affected by protonation, thus allowing the polymerization process to be trapped at different stages.

Later on, the same group successfully employed CB[8] as a supramolecular catalyst for covalent polymerization.[257] The key to this advance was an appreciation that CB[8] could encapsulate two Brooker's merocyanine (BM) groups into its cavity and that once bound they could be subject to photodimerization. Also critical was the observation that the photodimerized product was bound less effectively than the two original BM substrates. Thus, after photoirradiation, the dimer would be replaced from the cavity by new

merocyanines, setting up the next dimerization cycle. When a bifunctional monomer carrying two BM end groups was used, the effect of photodimerization and release was the formation of a covalent polymer. This study from the Zhang group thus served to illustrate the potential of appropriately chosen CB[n] hosts in controlling polymerization.

In 2019, the Scherman group reported the formation of nanoscale assemblies from supramolecular polymers comprising CB[8] and the naphthalene-containing salts **M35-1** and **M35-2** (Figure 32A).[258] These researchers showed that a mixture of CB[8] and **M35-1** in a 1:1 molar ratio formed platelet-like aggregates containing polymer chains. In contrast, the host-guest interaction of CB[8] and **M35-2** yielded nanofibers. Based on liquid AFM and cryo-TEM measurements, the authors suggested that the fibers were formed through a two-step self-assembly process that included first linear supramolecular polymer formation of the host-guest complexation of CB[8] and **M35-2** followed by laterally assembly of the polymers **SP35** as the result of O··HC hydrogen-bonding interactions between the carbonyl groups and the methylene groups in CB[8] (Figure 32B). The differing self-assembly behavior seen for **M35-1** and **M35-2** was ascribed to differences in the hydrophobic-hydrophilic ratio of the host-guest complexes. In operational terms it was found that **M35-2/CB[8]** with two imidazolium groups produced higher-order self-assemblies. On the other hand, both the platelet-like aggregates and nanofibers proved to be crystalline materials with viscoelastic properties. This makes these nanostructures of interest in the context of potential applications such as, *e.g.*, drag reducers and viscosity modifiers. This work was seminal in its time because it showed how aggregate morphologies can be controlled by

modulating the hydrophobic-hydrophilic ratio of the constituent building blocks. It also advanced our understanding of CB[8]-based self-assembly.

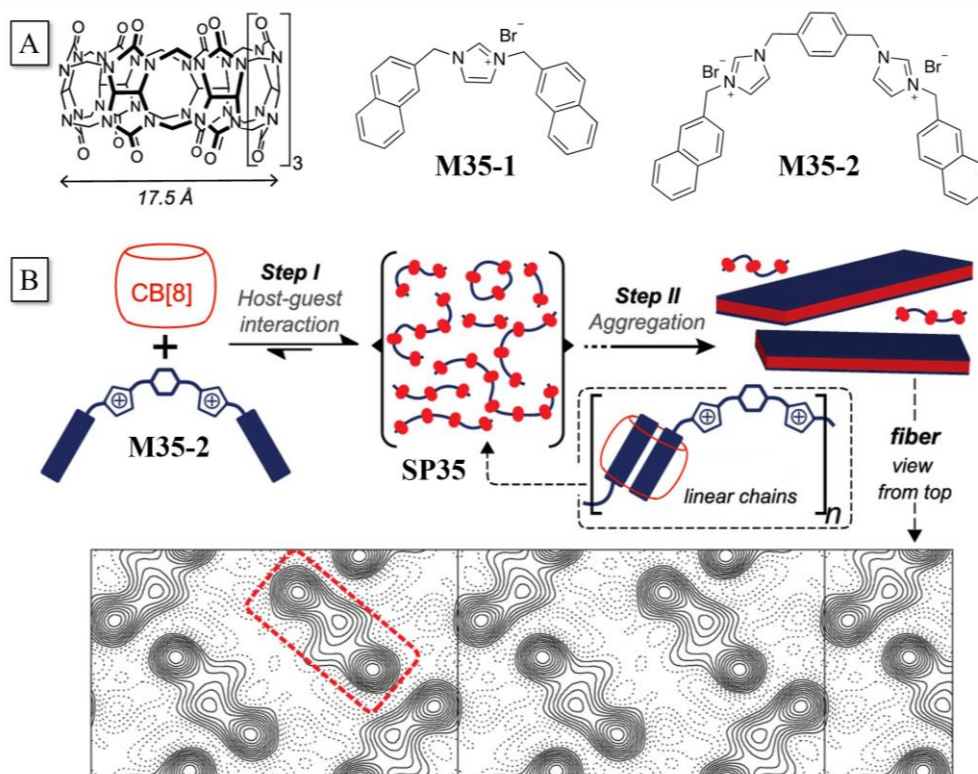


Figure 32. (A) Chemical structures of CB[8], **M35-1**, and **M35-2**. (B) Schematic representation of the step-wise self-assembly of **M35-2**. The bottom image is a cryo-TEM map of CB[8] + **M35-2** fibers at a resolution of 5 Å. [258], Copyright 2019. Adapted with permission from John Wiley & Sons Inc.

In separate work, Cao and co-workers constructed cuboid and spheroid supramolecular organic frameworks from CB[8] and tetraphenylethylene (TPE) precursors.[259] The use of different linkers (rigid or flexible) between the pyridinium moieties and the TPE cores led to the formation of distinct framework structures that displayed intriguing photophysical properties and stimuli-responsive behavior. These features were ascribed to the aggregation-

induced emission of the constituent TPE subunits, as well as the supramolecular association/disassociation of the supramolecular networks.

CB[n] hosts have been used to enhance the room-temperature phosphorescence (RTP) of supramolecular polymeric materials. For instance, the Liu group prepared a hyaluronic acid polymer bearing 4-(4-bromophenyl)-pyridin-1-ium (BrBP) subunits.[63] This polymer was found to undergo further cross-linking as the result of 2:1 complexation of the BrBP subunits by CB[8], as well as hydrogen bonding between the main chains of the polymers. The resulted networks exhibited a strong phosphorescence with a lifetime of 4.33 ms and a quantum yield of ca. 7.6%. These desirable RTP features were attributed to restricted motion and a corresponding reduction in the triplet state annihilation.

Recently, the same group reported another supramolecular luminescent polymer **SP36** that was stabilized as the result of interactions between CB[8] and an anthracene-conjugated bromophenylpyridinium salt. The binding constant between these entities was determined to be $3.13 \times 10^{12} \text{ M}^{-1}$ in water and $6.98 \times 10^{12} \text{ M}^{-1}$ in phosphate buffer (Figure 33).[260] **SP36** with a DP of 15 was found to emit a red fluorescence that was proposed to result from a host-stabilized charge-transfer state involving the electron-rich anthryl group and the electron-deficient pyridinium group. When the anthracene group of **M36** was oxidized to the corresponding anthraquinone by means of UV photo-irradiation, **SP36** was transformed to a ternary inclusion complex in which two bromophenylpyridinium units are localized in one CB[8] cavity. The resulting ternary assembly gave a photoluminescent emission at 529 nm, which was assigned to a long-lived phosphorescence. According to supporting theoretical calculations, a relatively small S_1 - T_1 energy gap and large spin orbit coupling

(SOC) coefficient results in an improved intersystem crossing rate and an efficient RTP for the ternary complex.

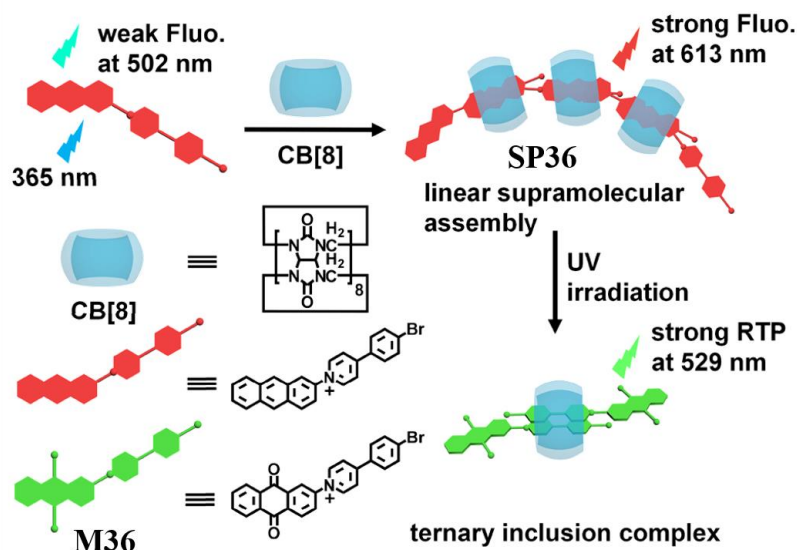


Figure 33. Schematic illustration of the supramolecular structures of **SP36**, the ternary complex formed following UV photo-irradiation, and the associated photoluminescence modulation. [260], Copyright 2021. Adapted with permission from the American Chemical Society.

In 2006 Isaacs *et al.* reported the host-guest properties of *nor-seco*-CB[10], which remains a relatively new member of the CB[n] family.[261] They showed, in particular, that a single *nor-seco*-CB[10] can accommodate two guest molecules. In 2019, Xu and Ni *et al.* designed a cationic monomer (**M37**) bearing naphthalene groups at the ends and a phenyl group in the middle (Figure 34).[262] It was demonstrated that *nor-seco*-CB[10] and CB[7] when used as a mixture would undergo a self-sorting process in the presence of **M37**. In particular CB[7] was found to bind the phenyl linker, whereas the *nor-seco*-CB[10] was found to bind the naphthalene moieties of two separate **M37** monomer thus stabilizing the

formation of a supramolecular polymer. As inferred from a diffusion-ordered NMR spectroscopic analysis, the molecular weight of **SP37** was estimated to be 5.6×10^4 Da, which is consistent with a DP = 16. At present, studies of supramolecular polymers based on CB[10] and other less-explored members of the CB[n] superfamily remain rare. We believe their further use could advance the supramolecular polymer field.

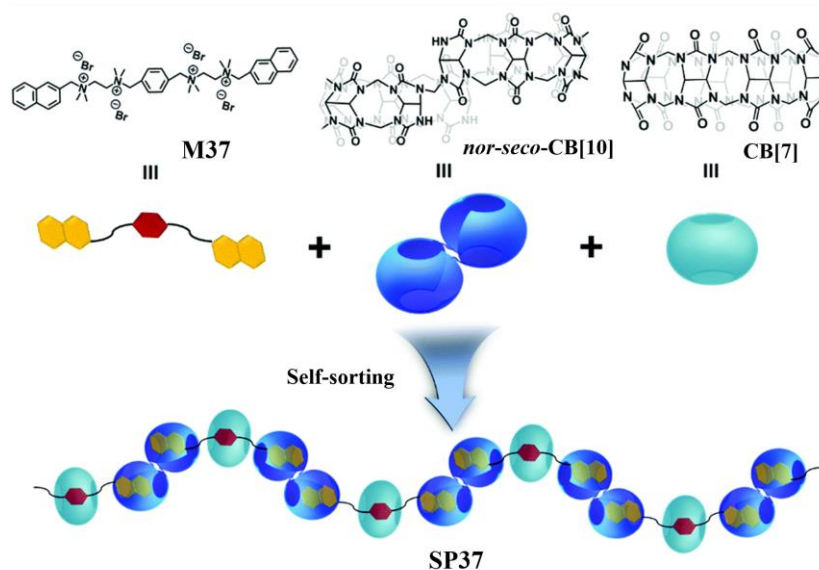


Figure 34. Schematic illustration of **SP37** formed from **M37**, nor-seco-CB[10], and CB[7] by means of self-sorting. [262], Copyright 2019. Adapted with permission from the Royal Society of Chemistry.

In order to promote the development of cucurbit[10]uril-based supramolecular biomaterials, Xiao and co-workers prepared an AIE fluorescent **SP38** comprised of the AIE molecule **M38** and CB[10] and assembled *via* host-guest interactions (Figure 35).[263] In **SP38**, monomer **M38**, with four rotating “arms”, was employed as a guest, while the relatively large CB[10] cavity was used to accommodate the arms of two separate **M38** subunits through host-guest interactions, thus providing crosslinking. In the supramolecular

polymer **SP38**, the molar ratio of **M38**: CB[10] is 1:2. The formation of **SP38** was evidenced by thermodynamic analysis, DLS measurements, and DOSY studies. Additionally, high content analysis system imaging of HUVEC (normal) and HeLa (cancer) cells incubated with **M38** before and after treatment with CB[10] was carried out (Figure 35B). In the absence of CB[10] only a weak fluorescence signal ascribed to **M38** was seen in the cytoplasm. However upon adding CB[10], particularly upon reaching a molar ratio of 1:2, an enhanced fluorescence was observed. The **SP38** produced in situ as the result of this addition displayed an extraordinary blue fluorescence while displaying low bio-toxicity and excellent cytocompatibility. Due to the unique binding properties of CB[10] we believe that supramolecular systems analogous to **SP38** will soon see application in numerous fields, including those associated with drug delivery and sensing.

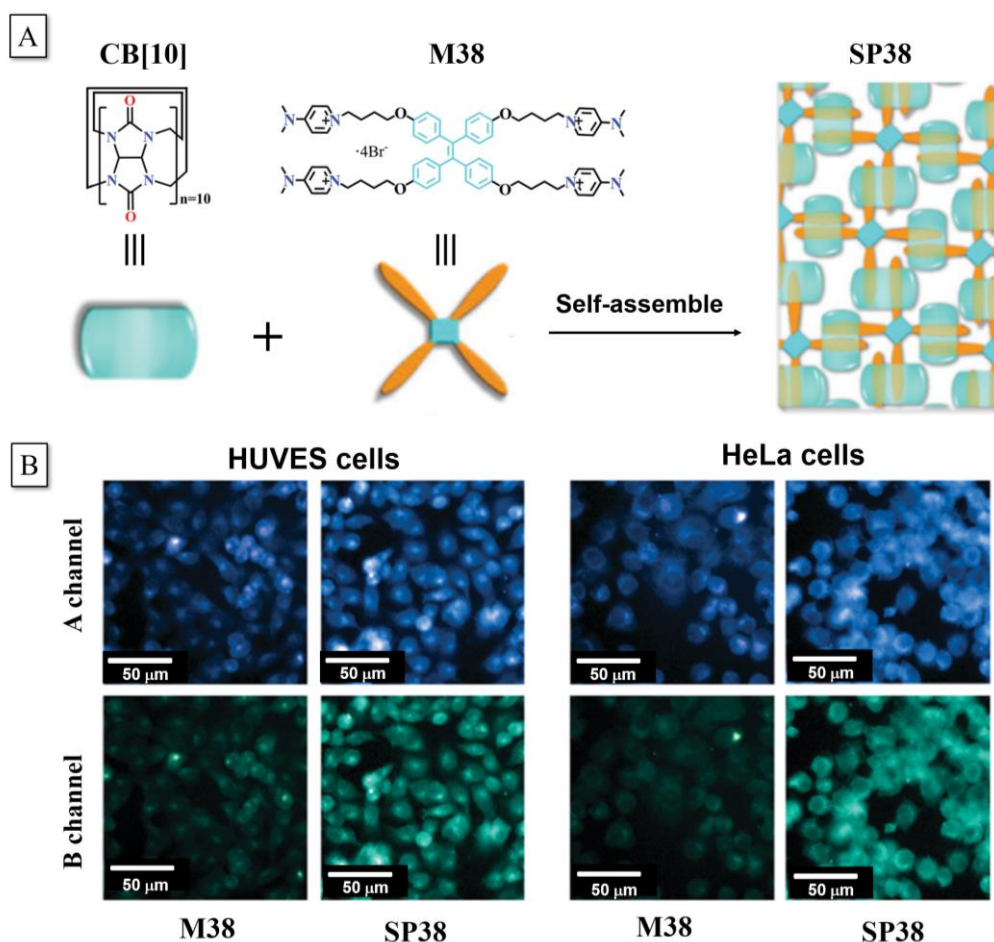


Figure 35. (A) Schematic illustration of **SP38** formed from **M38** and CB[10]. (B) High content analysis system images showing the addition of **M38** and then CB[10] (to form **SP38**) into HUVEC cells (normal) and HeLa cells (cancer). Conditions: A channel: $\lambda_{ex} = 355\text{--}385\text{ nm}$, $\lambda_{em} = 430\text{--}500\text{ nm}$; B channel: $\lambda_{ex} = 355\text{--}385\text{ nm}$, $\lambda_{em} = 470\text{--}515\text{ nm}$. Scale bars: $50\ \mu\text{m}$. [263], Copyright 2022. Adapted with permission from the Royal Society of Chemistry.

4.5. Pillararene-Based Supramolecular Polymers

4.5.1. Pillararene-Based Host-Guest Interactions: An Historical Perspective

In 2008, Ogoshi *et al.* synthesized a pillar-shaped macrocyclic host which they named “pillar[5]arene” and reported their host-guest interactions with pyridinium and viologen

derivatives.[264] The five hydroquinone units of pillar[5]arene are bridged by methylene groups at their 2 and 5 positions and can be easily functionalized *via* pre- or post-modification. Later, Meier and Cao *et al.* optimized the synthesis of pillar[5]arenes and achieved the isolation of pillar[6]arenes as minor products.[265] The distinct cavity sizes of these two classes of pillar[n]arenes (i.e., $n = 5$ and 6) led to investigations into their respective chemical features. One such study was carried out by the Huang group, which in 2010 reported the first pillar[6]arene crystal structure.[266] Subsequently, the same group reported the first pillararene-based supramolecular polymer (**SP39**) derived from a pillar[5]arene derivative monomer (**M39**) bearing an octyl group designed to act as a guest for the pillar[5]arene host (Figure 36A).[267] The authors proposed that the driving force for supramolecular polymer formation involved a combination of host-guest C-H \cdots π interactions and favorable entropic effects associated with desolvation of the pillar[5]arene cavity. Since then, pillar[n]arenes ($n = 5, 6$) have been used to create a variety of supramolecular assemblies.[197, 268-271]

Although larger pillar[n]arene homologues ($n \geq 7$) have been known since 2012,[272] studies of their host-guest interactions remain limited. Presumably, this reflects the fact that they have to date only been prepared in low yield as the result of cumbersome synthetic procedures. For insights into early development of pillar[n]arene chemistry, the reader is referred to a 2016 review by the Ogoshi group.[273]

4.5.2. Recent Advances in Pillararene-Based Supramolecular Polymers

Zhang and co-workers prepared a multiresponsive supramolecular polymer (**SP40**) based on a naphthalimide-functionalized monomer that contained pillar[5]arene (Figure

36B).[274] Host-guest interactions between the pillar[5]arene (**M40-1**) and a pyridinium guest (**M40-2**) combined with donor-acceptor interactions involving the constituent naphthalimides and pillar[5]arenes, allowed these small monomers to self-assemble and form gels in DMSO/water solution (9/1, v/v). Under UV photo-irradiation, a bright yellow emission ascribed to the naphthalimide chromophores in the gel was observed. Addition of a small amount of iodine was found to quench completely the fluorescence, presumably as the result of the iodine out-competing the pyridinium moieties for the pillar[5]arene receptor sites. The redox features of iodine were then exploited. Specifically, the nonfluorescent gel produced upon exposure to iodine was shown to undergo a “turn-on” increase in the presence of CN^- , Hg^{2+} and L-Cys with high sensitivity. This detection capability was further verified in living cells.

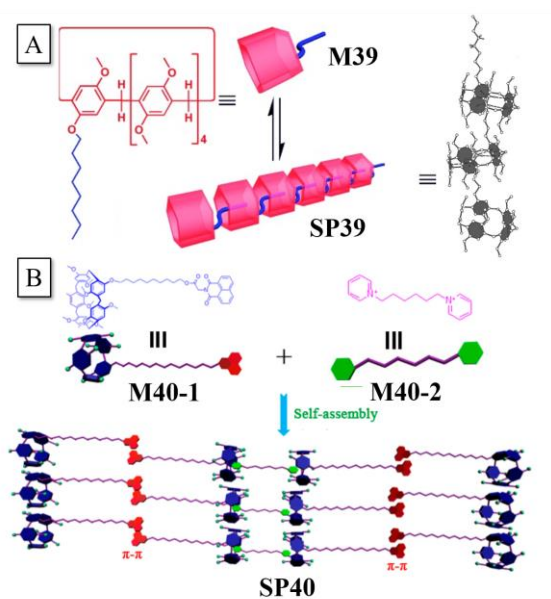


Figure 36. (A) Chemical structures and schematic illustrations of **M39**, and **SP39**. [267], Copyright 2011. Adapted with permission from John Wiley & Sons Inc. (B) Chemical structures and schematic illustrations of **M40-1**, **M40-2**, and **SP40**. [274], Copyright 2017. Adapted with permission from the American Chemical Society.

Another pillar[n]arene-based supramolecular polymeric material that proved useful in the detection of heavy metal ions was reported by Yang and co-workers.[275] They synthesized a [2]biphenyl-extended pillar[6]arene. Subsequently, this macrocyclic arene was modified by two thymine binding sites (**M41-1**; Figure 37). Separately, a tetraphenylethylene (TPE) chromophore **M41-2** bearing two quaternary ammonium groups was synthesized. On the basis of NMR spectroscopic analyses, it was concluded that quaternary ammonium groups, such as those present in **M41-2**, could be included within **M41-1** to form a 2:1 complex. As a result, a linear AABB-type supramolecular polymer **SP41** was obtained upon mixing **M41-2** with **M41-1**. This polymer contains numerous thymine arms and was found capable of binding Hg^{2+} as the result of thymine- Hg^{2+} -thymine interactions. The binding of the Hg^{2+} ions to **SP41** was thought restrict intramolecular rotations of the TPE chromophore, resulting in a strong Hg^{2+} induced turn-on fluorescence. Treatment with Na_2S allowed removal of the Hg^{2+} ions and recycling of the supramolecular polymer. The same group also reported several other fluorescent supramolecular polymers based on host-guest recognition. For example, they combined pillar[5]arene/imidazole pairings with diselenium dynamic covalent bonding to create a supramolecular polymer that proved responsive to certain reductants, such as D,L-dithiothreitol, as well as competitive guests, such as adiponitrile.[276]

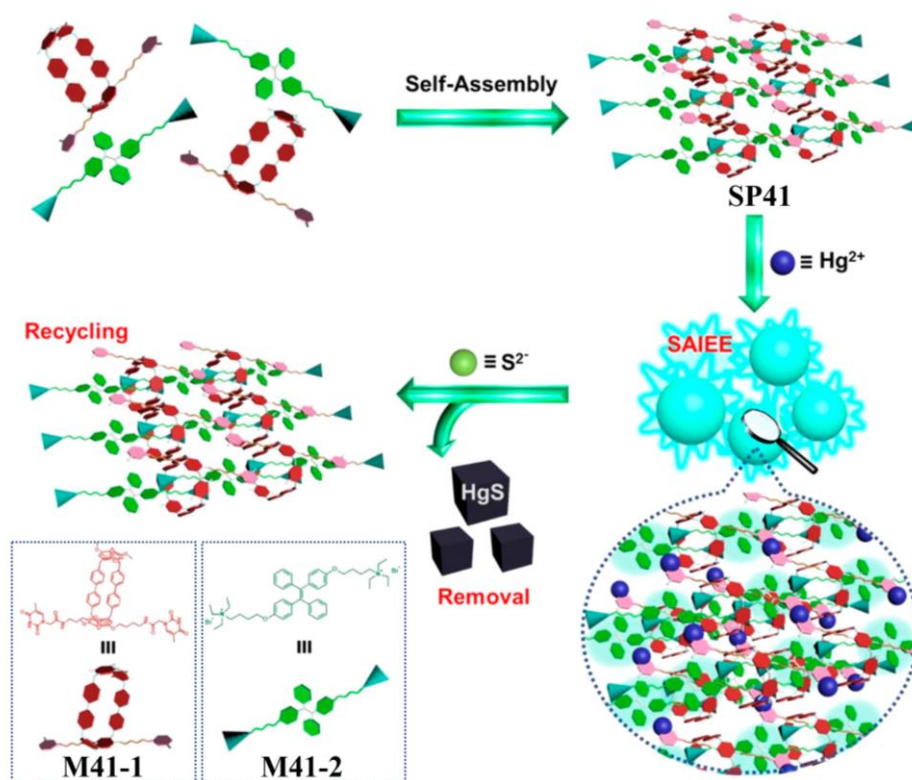


Figure 37. Chemical structures of **M41-1** and **M41-2**, and schematic illustration of the formation of **SP41**, a system that proved useful for Hg^{2+} sensing and removal. [275], Copyright 2019. Adapted with permission from the American Chemical Society.

In 2017, Huang *et al.* reported the preparation of layers of potential utility in emissive organic light-emitting diodes (OLEDs) based on pillar[n]arene-based supramolecular polymers.[277] These layers were prepared *via* the copolymerization of a pillar[5]arene derivative **M42-1** with the neutral guests **M42-2** and **M42-3** (Figure 38). According to NMR spectroscopic studies and viscosity measurements, doping the blue-emitting species **M42-1** and **M42-2** with different ratios of the green-emitting monomer **M42-3** leads to the formation of linear supramolecular polymers, such as **SP42-1** and **SP42-2**, that are characterized by different fluorescent emission colors. These supramolecular polymers could be used to enhance the brightness of OLEDs. This work underscores the application

potential of pillar[n]arene-based materials in optoelectronics and is thus likely to stimulate further research efforts.

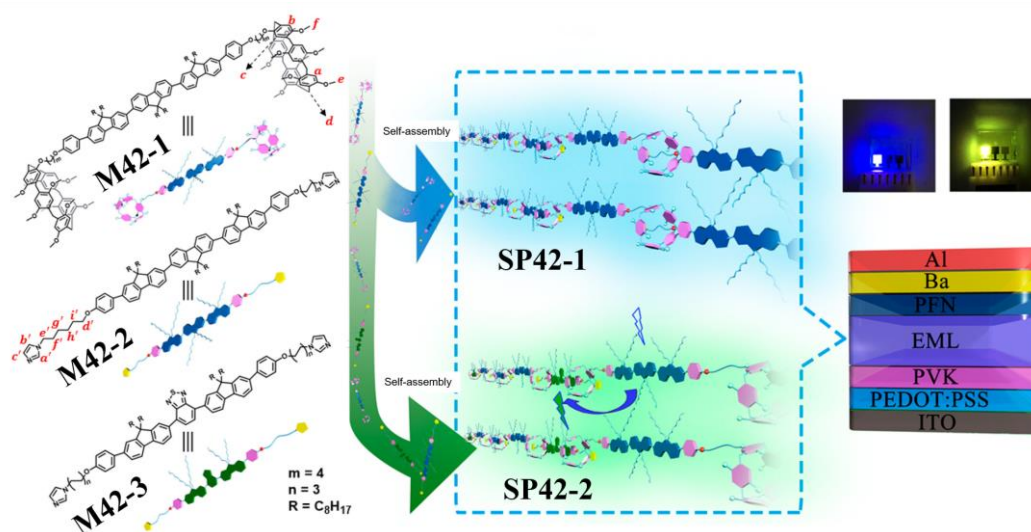


Figure 38. Chemical structures of **M42-1**, **M42-2** and **M42-3**. Also shown is a schematic illustration showing the construction of **SP42-1** and **SP42-2** with different emitting colors and their use in OLEDs. [277], Copyright 2017. Adapted with permission from the American Chemical Society.

Efficient excitation energy transfer (EET) in pillar[5]arene-based supramolecular polymers was also utilized by the Yang group to fabricate an artificial light-harvesting system.[278] Here, fluorescent supramolecular polymers, **SP43**, were used as precursors to construct water-dispersible supramolecular polymeric nanoparticles (SPNPs) (Figure 39). The supramolecular polymer, **SP43**, in turn was prepared *via* the self-assembly of three key monomers, **M43-1**, **M43-2**, and **M43-3**. The binding constant between pillar[5]arene and the guests was determined to be $1.2 \times 10^4 \text{ M}^{-1}$ in CHCl_3 . Within **SP43** and the resulting SPNP, host-guest interactions served to shorten the distance between the chromophores thus facilitating EET. The presence of the bulky pillar[5]arene units also precluded self-

quenching of the excitation energy within the SPNPs. As a result, the fluorescence quantum yield of the **M43-2** fluorophores in SPNPs proved ~4.2-fold higher than in seen prior to self-assembly. A maximal energy transfer efficiency of 85% was seen at a **M43-2/M43-3** molar ratio of 97:3. The antenna effect, a parameter used to quantify the light-harvesting ability of a system, was found to reach a maximum of 22 at a 99.5:0.5 molar ratio of **M43-2/M43-3**. This work is likely to inspire the design of yet-more efficient artificial light-harvesting systems *via* macrocycle-based self-assembly.

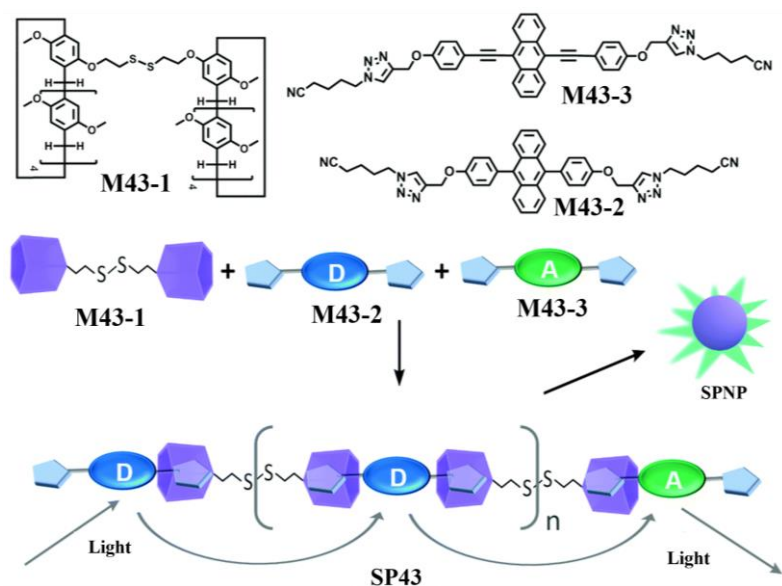


Figure 39. Chemical structures of **M43-1**, **M43-2** and **M43-3**. Also shown is a schematic illustration showing their self-assembly to give **SP43** and **SPNP** and their potential utility in light-harvesting. [278], Copyright 2018. Adapted with permission from the Royal Society of Chemistry.

Nonporous adaptive crystals of pillar[n]arenes have attracted increasing attention due to their use in small molecule separations.[279] Recently, Huang and Zhou *et al.* reported a solid-state supramolecular polymer **SP44-1** prepared by mixing ethylated pillar[5]arene (**M44-1**) with 1,2,4,5-tetracyanobenzene (**M44-2**) in CH_2Cl_2 (Figure 40).[99] In the solid

state, two CH_2Cl_2 molecules occupy the cavity of pillar[5]arene, which presumably forces **M44-2** to interact with the exo-wall of **M44-1** *via* charge-transfer and C-H $\cdots\pi$ interactions. Polymer **SP44-2** was then obtained by heating crystals of **SP44-1** at 80 °C to remove the bound CH_2Cl_2 . Exposure of **SP44-1** to alkyl aldehyde vapors was found to produce different packing modes, leading to formation of species such as those shown generically as **SP44-2** and the observation of vapochromic behavior. This work demonstrates what may be a new and generalizable strategy for the design of responsive supramolecular polymers and the creation of sensors that might prove more effective than classic solution-based systems.

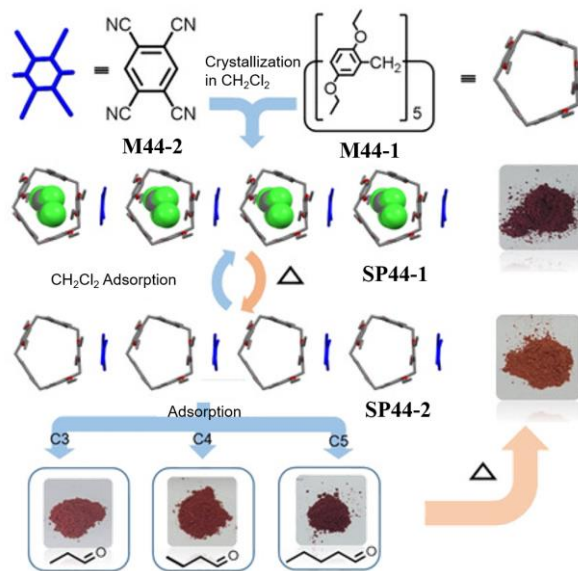


Figure 40. Chemical structures of **M44-1**, **M44-2**, *n*-propanal, *n*-butanal and *n*-pentanal, as well as schematic illustration of the formation of the solid state materials **SP44-1** and **SP44-2** obtained before and after subjected to vapor capture. [99], Copyright 2021.

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4.6. Other Macrocyclic-Based Supramolecular Polymers

Although the above-mentioned macrocycles have played a significant role in advancing our understanding of supramolecular polymers, there remain opportunities to

exploit new host molecules in the context of materials-related supramolecular self-assembly. Of particular interest in this regard are underexplored host-guest interactions, such as those involving anion recognition, radical-radical interactions, and metallacycle-based neutral substrate binding. Recent efforts to exploit some of these less-common motifs are detailed below.

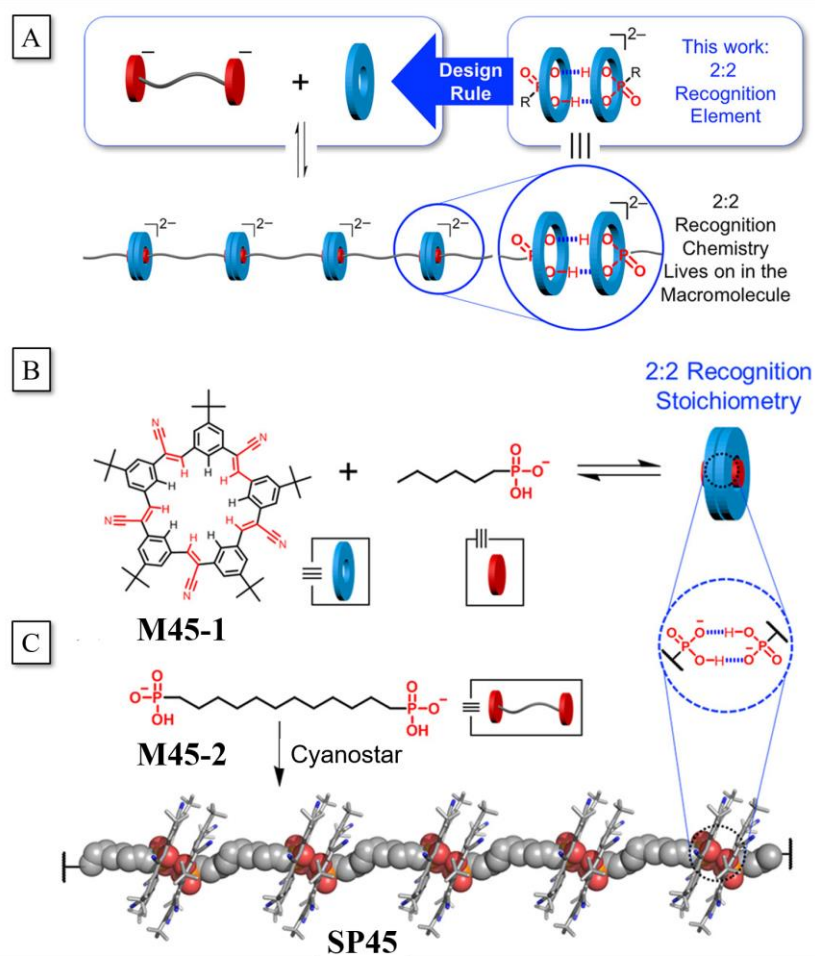


Figure 41. (A) Design rule of the anion-directed supramolecular polymer. (B) Chemical structures of the cyanostar host and its phosphonate guest for 2:2 complexation. (C) **M45-2** with two phosphonates undergoes dimerization within **M45-1** dimers to form **SP45**.

[280], Copyright 2019. Adapted with permission from the American Chemical Society.

Although prior to the coverage period of this review, in 2015, Sessler, Anslyn and coworkers showed it was possible to create a self-assembled polymer as the result of anion recognition. They exploited a combination of highly acidic dicarboxylates and expanded porphyrins capable of forming 1:2 complexes with anions to produce a set of linear polymers, whose disassembly could be induced in a solvent dependent manner. This allowed the creation of a new class of solvent specific sensors.[281]

In 2019, the Flood group reported a new class of anion-driven supramolecular polymers based on anion-anion dimerization of phosphonate hydroxyanions within the cavity of π -stacked cyanostar dimers (Figure 41A).[280] The 2:2 stoichiometry of the cyanostar host **M45-1** and the hydroxyanion guest allowed for the formation of linear supramolecular polymers (Figure 28B). Several diphosphonate monomers with different alkyl linkers were studied. It was found that longer alkyl linkers were more flexible, which led to greater monosomic polymerizability with an average degree of polymerization of nine emerging at 10 mM. The formation of **SP45** (DP = 9) from dodecylene diphosphonates (**M45-2**) and the cyanostar host **M45-1** was established by means of a single crystal X-ray diffraction analysis (Figure 28C). Viscosity measurements led the authors to suggest that the supramolecular polymerization in chloroform was concentration dependent with a critical polymerization concentration of 5 mM. The anion-driven polymerization process could be reversed *via* the addition of acid or competing anions, such as picric acid or hexyl monophosphate.

In subsequent work, Flood and co-workers showed that an appropriate choice of monomers allowed for the construction of supramolecular homo- and copolymers with well-

defined structures (Figure 42).[282] In this latter study, a cyanostar, **M46-1**, bearing triethylene glycol chains for enhanced solubility was used. When **M46-1** and phenylene diphosphate (**M46-2**) were mixed in a 2:1 stoichiometric ratio, **SP46-1** formed, presumably as the result of strong anion-anion dimerization within the π -stacked cyanostar dimers. However, when a 1:1 ratio of the two monomers (**M46-1** and **M46-2**) was used, alternating copolymers (**SP46-2**) containing both cyanostar-stabilized phosphate dimers (A) and cation-stabilized phosphate dimers (B) were obtained. Polymer **SP46-1** was tested for its adhesive properties and found to support a 10-lb weight with a pull-off strength of about 4.2 MPa. In contrast, **SP46** displayed an adhesion strength that was only 20% of **SP46-1**, leading to the conclusion that linkage A is stronger than that of B. This work served to demonstrate one practical consequence of being able to modulate the nature of supramolecular polymers *via* a simple change in monomer stoichiometry.

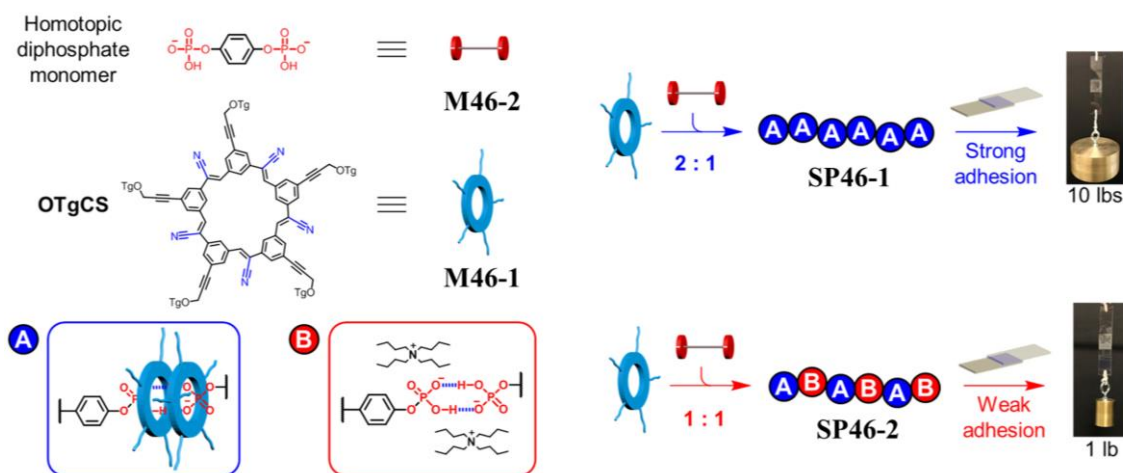


Figure 42. Chemical structures of the cyanostar **M46-1**, phenylene diphosphate **M46-2**, and schematic illustration of their use in preparing supramolecular homo- and copolymers with different adhesion strengths. [282], Copyright 2020. Adapted with permission from the American Chemical Society.

Recently, Stoddart and co-workers synthesized monomer **M47** containing a cyclobis(paraquat-*p*-phenylene) ring and moieties designed to function as molecular pump at the end of a long linker (Figure 43).[52] When the bipyridinium groups in **M47** were reduced by Zn dust, radicals were produced that stabilize radical-pair interactions; this, in turn, allowed for the construction of a supramolecular daisy chain polymer **SP47** with a DP of 11. Reoxidation with Ag_2SO_4 led to preferential interactions with the *p*-phenylene units within the long chain linker resulting in the formation of a different mechanically interlocked daisy chain polymer. A key aspect of this work was the demonstration of redox control over self-assembly and the use of radical-radical interactions to stabilize one particular state.

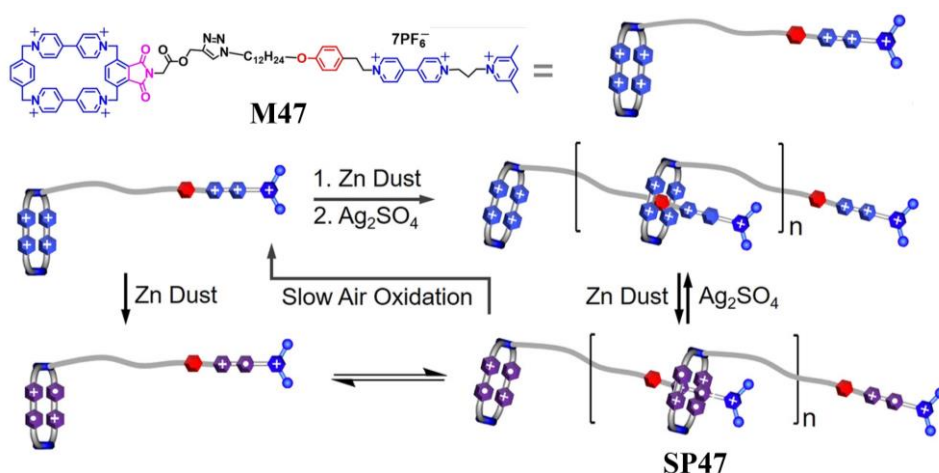


Figure 43. Chemical structures of **M47** and schematic illustration of the supramolecular polymeric forms it permits under redox control. [52], Copyright 2020. Adapted with permission from the American Chemical Society.

Other macrocycle hosts, such as chalcogen- and metal-containing macrocycles, have been used to create supramolecular polymers.[283] In 1990s, Fujita and coworkers and Stang *et al.* independently reported the preparation of platinum(II)- and palladium(II)-based

macrocycles and demonstrated their utility in the context of host-guest recognition.[284, 285] Later, the Stang group made efforts to develop supramolecular polymers by modifying the exterior vertices of selected metallacycles to support non-covalent crosslinking interactions.[286, 287] However, difficulties were encountered that were ascribed to the dynamic nature of the metallacycle cores. In 2019, Stang and Huang *et al.* synthesized a platinum(II) metallacycle **M48** bearing two pyrene groups.[288] In the solid state, it was found that one of the pyrene moieties on **M48** could enter into the cavity of another AA-BB unit to form a host-guest complex (Figure 44). Moreover, C-H... π and C-H...O interactions between the pyrene group and metallacycle, as well as π - π donor-acceptor interactions between the benzene rings on different **M48** molecules, were observed that were thought to stabilize supramolecular polymerization (**SP48**). Following a similar molecular design strategy, the same group reported other supramolecular polymers based on host-guest interactions of platinum(II) metallacycles.[289] This body of work extends the lexicon of receptors that may be considered in the design of new supramolecular macromolecular materials.

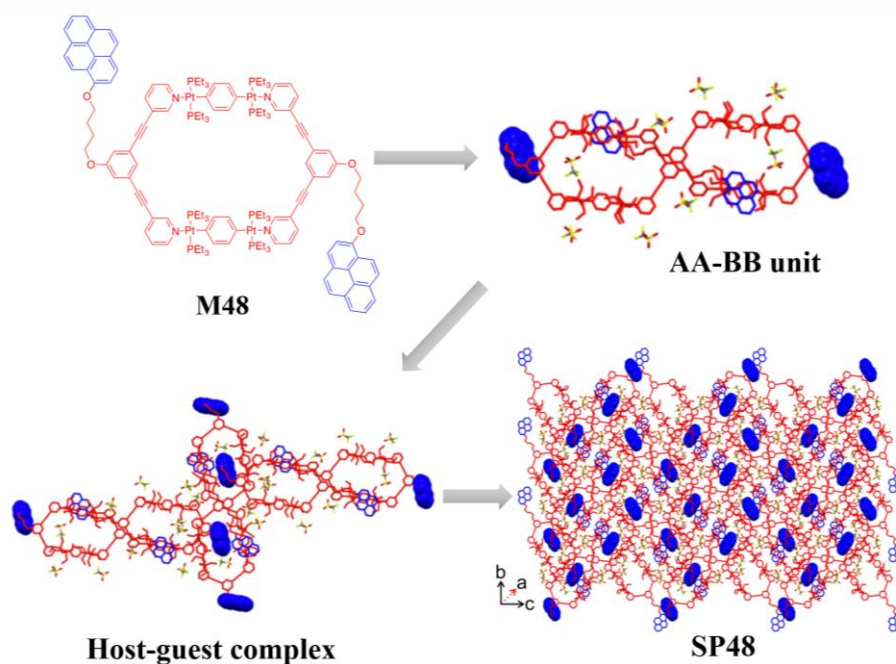


Figure 44. Chemical structure of **M48**, corresponding AA-BB unit, host-guest complex, and the supramolecular polymer observed in the solid state. [288], Copyright 2019.

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5. Supramolecular Polymers Based on Aromatic Donor-Acceptor Interactions

5.1. Aromatic π - π /Donor-Acceptor Interactions: An Historical Perspective

Strong attractive interactions between aromatic structures have been known for many years and are widely recognized as playing a crucial role in biological systems. In 1960, Patrick and Prosser discovered a complex formed between benzene and hexafluorobenzene and attributed the underlying association to electron donor-acceptor or charge-transfer interactions.[290] In 1971, a crystal structure of the 1:1 complex of mesitylene and hexafluorobenzene was reported by Dahl, who emphasized the synergy between π - π bonding interactions and other weak intermolecular forces in stabilizing the observed stacked arrangement.[291] In the 1990s, Williams *et al.* suggested that the underlying complexation was driven by interactions between the positive and negative electric

quadrupole moments of benzene and hexafluorobenzene.[292] In this same time frame (albeit slightly earlier), Sanders *et al.*, using porphyrins as specific examples, described π - π interactions as being the result of π - σ attractions that outweigh π - π repulsions.[293] Although the determinants of π - π interactions are still not completely understood, their importance in self-assembly has been demonstrated in numerous instances. For example, the Stoddart group prepared rotaxanes and catenanes by exploiting the interactions between π -electron-rich and π -electron-deficient components.[294] In the early 2000s, reports of supramolecular polymers driven by π - π interactions, including electron donor-acceptor interactions began to appear.[295-297] The Iverson and the Li groups mimicked biological duplexes by donor-acceptor interaction-driven oligomers.[298, 299] In addition, Colquhoun and Hayes gave the first report of the generation of self-healing supramolecular polymers using a chain-folding polydiimide as the π -electron acceptor and a pyrene end-capped siloxane as the π -electron donor.[300] Also in the 1990s, Adam, *et al.* reported that a highly ordered arrangement of stacked disk-like organic molecules displayed a high photoinduced charge mobility.[295] These early examples have paved the development of polymeric materials wherein π - π interactions play a stabilizing role with many groups, including the authors,[301] contributing to the development of the field. While the packing of π -conjugated molecules is often a key feature of the resulting supramolecular constructs, it is important to appreciate that the term π - π stacking constitutes a geometric descriptor, rather than an energetic driving force *per se*.

5.2. Recent Advances in Supramolecular Polymers Involving Aromatic Stacking

To modulate the sequence structures of supramolecular polymers, Haino and co-workers designed a cleft-like tetraporphyrin **M49-1** that was expected to interact with **M49-2** *via* donor-acceptor interactions (Figure 45).[302] On its own, **M49-1** was found to self-associate to form a supramolecular polymer of general structure **SP49-1** ($K_a = 2.8 \times 10^5 \text{ M}^{-1}$ in 1,2-dichloroethane) in chloroform solution. However, formation of **SP49-1** was not observed in the presence of the electron-deficient monomer **M49-2**. Rather a copolymer **SP49-2** derived from **M49-1** and **M49-2** (interacting with a $K_a = 1.0 \times 10^5 \text{ M}^{-1}$ in 1,2-dichloroethane) was obtained. The degree of polymerization (DP) of the supramolecular polymer was evaluated by monitoring the diffusion coefficient of its monomer and found to be concentration dependent as expected for a two-component self-assembled system. At a concentration of 30 mmol L^{-1} in both **M49-1** and **M49-2**, a high degree of supramolecular polymerization, on the order of 10^3 , could be achieved. Differences in the diffusion coefficients and viscosities were seen as the ratio of **M49-1** to **M49-2** varied, leading the authors to suggest that different supramolecular structures were being formed. Moreover, **SP49-2** was found to form highly ordered nanostructures; presumably this is a consequence of its constituent long alkyl chains, which were able to interact laterally.

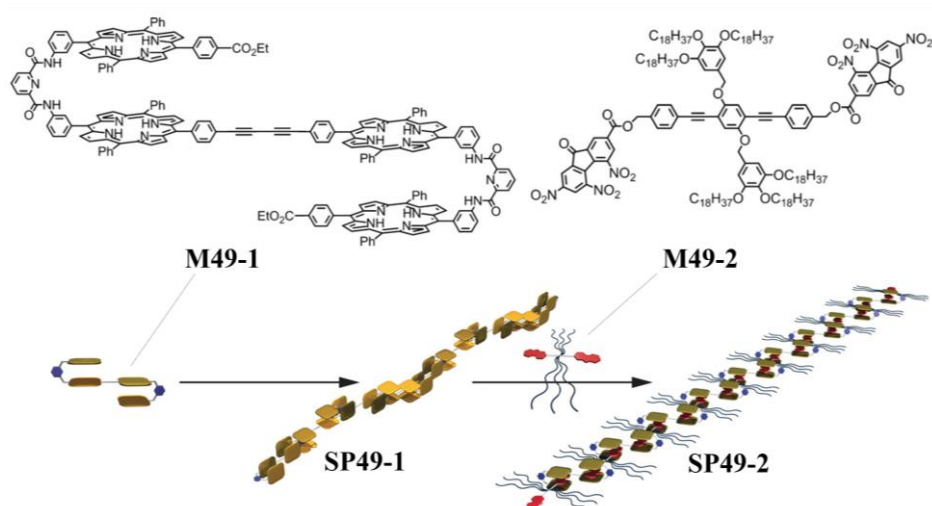


Figure 45. Chemical structures of **M49-1** and **M49-2**, and schematic illustration showing their proposed supramolecular polymerization. [302], Copyright 2018. Adapted with permission from John Wiley & Sons Inc.

A number of supramolecular polymers based on DAD- or ADA-type molecular tweezers and appropriately chosen di- or polytopic guests are known. However, often the systems in question suffer from low degrees of polymerization reflecting weak underlying binding interactions. The Wang group overcame this limitation by creating a DADA-type system embodied in monomers **M50-1** and **M50-2** wherein hydrogen-bonding and multivalency combine to enhance the binding affinity and stabilize supramolecular high molecular weight polymers of general structure **SP50** with a DP = 395. In contrast, when **M50-1** was combined with the control monomer **M50-3** that is unable to support effective hydrogen-bonding interactions little self-assembly was seen (Figure 46). Competitive agents, including hexafluoro-2-propanol and trifluoroacetic acid, could be used to induce the depolymerization of **SP50**. On this basis it was proposed that **SP50** constitutes a *bona fide* stimuli-responsive supramolecular polymeric system.

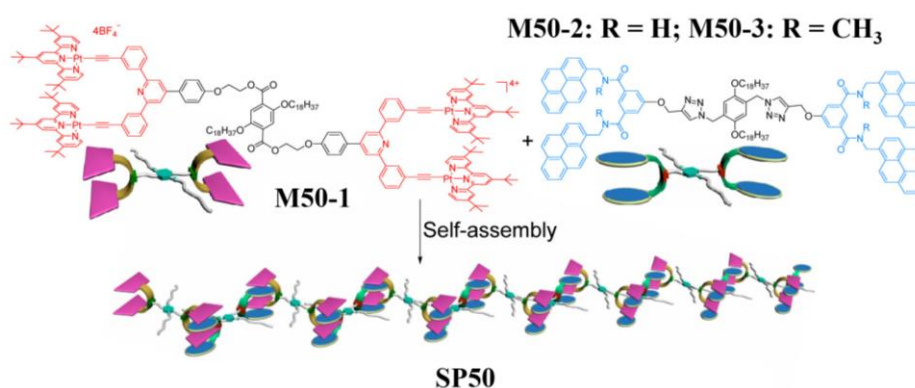


Figure 46. Chemical structures of **M50-1**, **M50-2** and **M50-3**, and schematic illustration showing the proposed formation of **SP50**. [303], Copyright 2016. Adapted with permission from the American Chemical Society.

In 2020, the George group used an amphiphilic, donor-acceptor monomer (**M51-1**) to prepare monodisperse charge-transfer supramolecular polymers (**SP51**) (Figure 47).[304] Monomer **M51-1** was synthesized by covalently linking a pyrene donor to a naphthalenediimide (NDI) acceptor using hexaethylene glycol as a flexible linker. Presumably as the result of the strong intramolecular charge-transfer interactions between the pyrene and NDI subunits, **M51-1** in an acetonitrile-water (1:1 v/v) mixture at a concentration of 50 μM was found to adopt a foldameric conformation and further self-assemble into supramolecular polymers of general structure **SP51** characterized by stacked bilayers. However, as formed, the self-assembled material (**SP51**) proved polydisperse (*i.e.*, broad length distribution). As part of their study, the authors reduced the NDI chromophores to its radical anion (**M51-2**) and dianionic (**M51-3**) forms by treating with sodium dithionite. Neither species was found to support strong charge-transfer interactions. As a consequence, **M51-2** and **M51-3** remain unfolded and exist as spherical nanoparticles. Both **M51-2** and **M51-3** could be oxidized back in a controlled manner to give the folded **M51-1** form. The net is a kinetically controlled supramolecular polymerization giving rise to relatively monodisperse **SP51** structures possessing a higher degree of polymerization than seen when **M51-1** was allowed to undergo direct self-assembly.

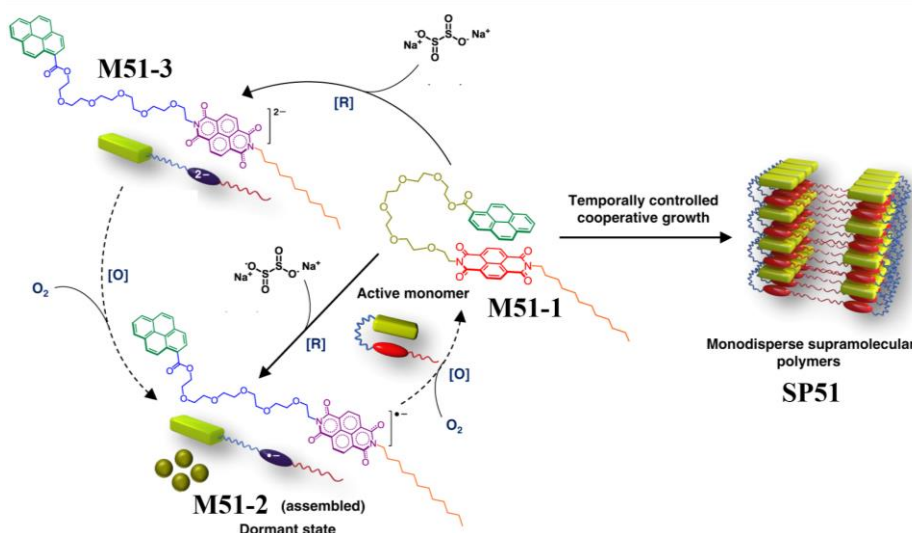


Figure 47. Chemical structures of **M51-1**, **M51-2**, and **M51-3**, and schematic illustration of the formation of a polymeric form (**SP51**) *via* the controlled reoxidation of the monomeric radical anion (**M51-2**) and dianionic (**M51-3**) species. [304], Copyright 2020. Adapted with permission from Springer Nature.

George and Meijer *et al.* prepared a supramolecular polymer **SP52** from monomer **M52** that is stabilized *via* presumed π - π interactions involving the coronene bisimide cores (Figure 48).[305] Monomer **M52** contains alkoxy chains ((*R*)-dihydrocitronellol ethers) at the 3 and 5-positions of the aryl substituents. This results in a pocket or a cavity in the self-assembled construct that is able to incorporate solvent molecules. Analysis of the circular dichroism (CD) spectrum of **M52** recorded in methylcyclohexane (MCH) at 288 K provided support for the suggestion that the chirality of the alkoxy chains could be transferred to the supramolecular polymers to give structures with (*P*)-type helicity. The authors found that when the temperature of the MCH solution was decreased below 283 K, the supramolecular helicity was reversed. It was proposed that solvent molecules intercalate into the **M52** pocket leading to rigidification at low temperatures that, in turn, modulated the

conformation of the alkoxy chains thus triggering stereomutation of **SP52**. By recording CD cooling curves of **SP52** in different solvents, it proved possible to correlate the helicity transition temperatures with the corresponding solvent crystallization temperatures. This work provided a new approach to control supramolecular assemblies by exploiting the interactions between appropriately designed monomers and solvents.

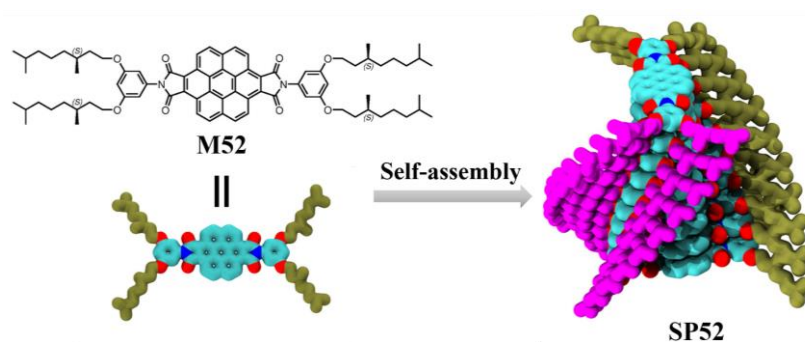


Figure 48. Chemical structure of **M52** and schematic illustration of its proposed self-assembly to generate **SP52**. [305], Copyright 2017. Adapted with permission from the American Chemical Society.

In 2019, Würthner and co-workers used a seeded living polymerization approach to prepare supramolecular copolymers with well-defined structural backbones (Figure 49).[306] They first prepared three perylene bisimides bearing methoxy, chlorine and methylthio groups in the so-called 1,7 bay-positions (**M53-1**, **M53-2**, and **M53-3**). In a 2:1 (v/v) solvent mixture of MCH and toluene (Tol) these PBIs were found to undergo thermodynamically favored supramolecular polymerization, resulting in the formation of ordered J-aggregates. These J-aggregates were found to exist as helical fibers, with the helical pitch of the **M53-2**-derived fibers (10 nm) being much wider than those of **M53-1** or **M53-3** fibers (both 5 nm). It was also found that when **M53-1**, **M53-2**, and **M53-3** were

subject to rapid cooling in MCH/Tol (2:1, v/v) (15 °C/min, 90 to 20 °C), metastable H-aggregates were formed. When short seeds of the linear J-aggregates (produced by ultrasonication) were added to a MCH/Tol (2:1, v/v) solution of the kinetically trapped H-aggregates, transformation to the corresponding thermodynamically stable supramolecular polymeric J-aggregate form occurred. Exploiting this strategy, the authors prepared A-B-A type and B-A-B type supramolecular block copolymers (**SP53-1** and **SP53-2**) by means of a two-component seeded polymerization, wherein the same two monomers were used to produce kinetically trapped species and as transformation-promoting seeds.

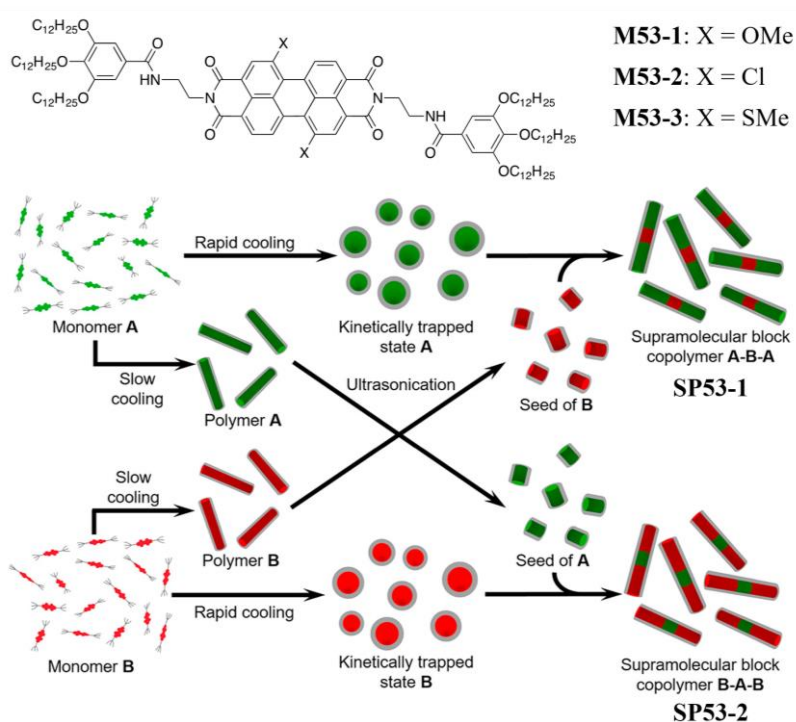


Figure 49. Chemical structures of the PBI monomers **M53-1**, **M53-2**, and **M53-3** and schematic illustration of the two-component seeded polymerization strategy used to produce A-B-A and B-A-B type supramolecular copolymers. [306], Copyright 2019.

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Chirality can be used to monitor dynamic assembly processes associated with supramolecular polymerization. An example of this utility is provided by the work of Meijer and Yamaguchi *et al.* These researchers exploited B-N frustrated Lewis pairs (FLP) of π -electron donors and acceptors to construct several supramolecular copolymers.[307] They found that when a partially *O*-bridged triphenylborane (**M54-1**) containing a boron (B) core as the acceptor was treated with various chiral and achiral triphenylamine donors (*e.g.*, **M54-2**, **M54-3** and **M54-4**) containing nitrogen (N) cores (Figure 50A) supramolecular polymers were obtained (Figure 50B). The red-shifted emissions of **SP54-1** derived from **M54-1** + **M54-2** and **SP54-2** from **M54-1** + **M54-3** was taken as evidence for the formation of noncovalent B-N bonds between the π -conjugated donor and acceptor. Both **SP54-1** and **SP54-2** displayed remarkably long-lived excited state lifetimes and circularly polarized exciplex emissions. In addition, **M54-1** could transfer its chirality to achiral **M54-4** by means of supramolecular copolymerization (Figure 50C). This demonstration of FLP-based supramolecular copolymer formation will likely lead to further studies of self-assembled materials with chiral features and potentially useful optoelectronic properties.

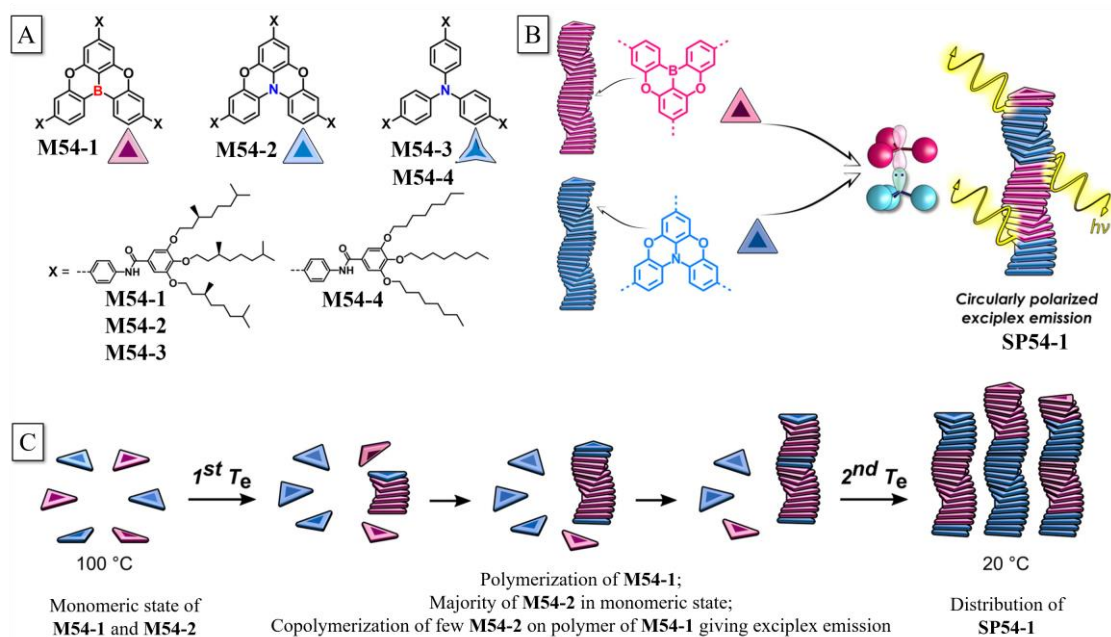


Figure 50. (A) Chemical structures of monomers with boron- and nitrogen-cores. (B) Supramolecular copolymerization of **M54-1** and **M54-2** to yield **SP54-1**, a system displaying a circularly polarized exciplex emission. (C) Schematic illustration of the copolymerization of **M54-1** and **M54-2** *via* slow cooling. [307], Copyright 2020. Adapted with permission from the American Chemical Society.

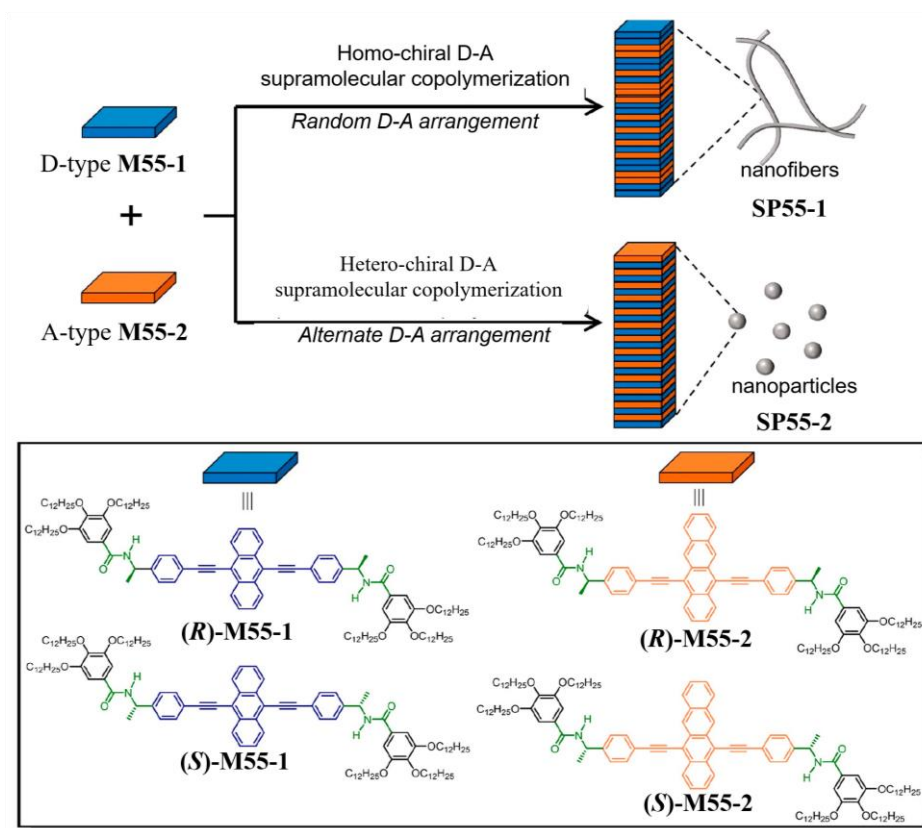


Figure 51. Chemical structures of the monomers **M55-1** and **M55-2**, as well as a schematic illustration of their proposed self-assembly to give **SP55-1** and **SP55-2**. [308], Copyright 2022. Adapted with permission from the American Chemical Society.

In 2020, Wang and co-workers reported a supramolecular donor-acceptor copolymer the formation of which could be controlled by modulating the organization of the chiral comonomers at the molecular level.[308] In this work, two structurally similar comonomers, **M55-1** and **M55-2**, were designed, that contain π -aromatic diethynylacene core and alkyl chain peripheries linked by enantiopure N-[(1R or 1S)-phenylethyl]benzamides. As the result of either homochiral or heterochiral supramolecular copolymerization, it proved possible to access, respectively, either a nanofiber, **SP55-1**, with a random arrangement of the constituents, or a nanoparticle **SP55-2** with an alternate monomer arrangement. The relatively reduced steric hindrance between the stereogenic methyl groups

in the heterochiral supramolecular ensemble led to an increase in the donor-acceptor complexation strength of the monomers, resulting in the formation of the alternate copolymer **SP55-2**. It was also found that, upon photoexcitation, **M55-1** could serve as an energy donor, while **M55-2** acted as an acceptor. The specifics of the resulting photo-induced energy transfer, as well as the circular polarized luminescence, could be controlled *via* the choice of **SP55-1** vs **SP55-2** at the supramolecular level. This makes structures such as **SP55-1** vs **SP55-2** of possible interest in the context of chiral sensing, recognition, and optoelectronics development.

6. Supramolecular Polymers Based on Multiple Interactions

In addition to supramolecular polymers constructed through primarily one non-covalent interaction, systems wherein more than one recognition mode is used to stabilize the system have begun to receive increasing attention. Recent developments along these lines are summarized in this section.

In 2020, the Stang group reported a set of supramolecular polymers with attractive properties that are stabilized by a combination of metal-ligand and other weak interactions.[309] For instance, they showed that it was possible to create a supramolecular polymer based on a combination of platinum(II)-pyridine coordination, zinc-terpyridine complexation, and crown ether-based host-guest interactions (Figure 52).[180] These three binding modalities proved orthogonal to one another, allowing for stepwise self-assembly of a macromolecular system. In this study, a rhomboidal metallacycle **M56-3** was first prepared *via* coordination of the platinum(II) centers on the crown ether monomer **M56-2** with the dipyrindyl moieties on monomer **M56-1**. The terminal terpyridine groups on

metallacycle **M56-3** were then treated with Zn(II) to afford linear supramolecular polymers of generalized structure **SP56-1**. The binding constant between **M56-3** and Zn(II) was determined to be $3.8 \times 10^4 \text{ M}^{-1}$ in dichloromethane/acetonitrile. Finally, a supramolecular network **SP56-2** was obtained by cross-linking these polymers by taking advantage of host-guest interactions between an added bis-ammonium salt and the benzo-21-crown-7 units present in the **M56-2** subunits of **SP56-1**. At high concentrations, **SP56-2** in appropriate solvents was found to gel, a state that necessarily endowed the system with stimuli-responsiveness and an ability to self-heal.

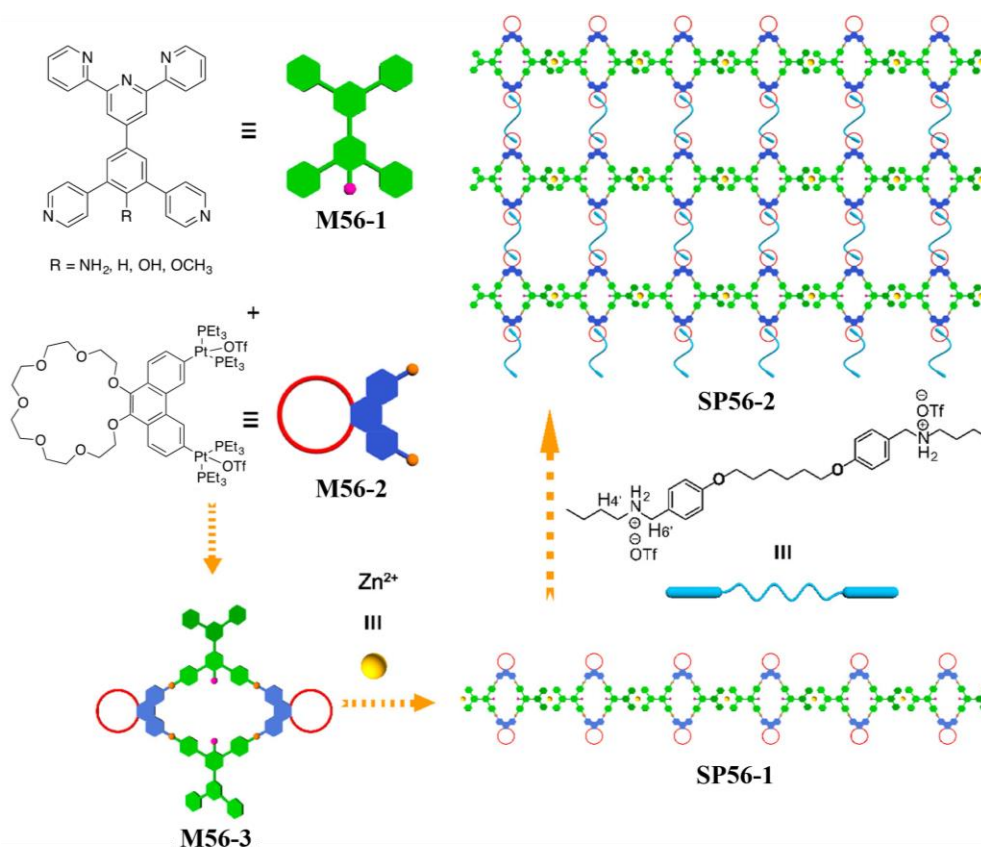


Figure 52. Chemical structures of **M56-1**, **M56-2**, **M56-3**, and schematic illustration of the supramolecular polymers (**SP56-1** and **SP56-2**) formed by treating **M56-3** with first zinc(II) cations and then a flexible bis-ammonium salt. [180], Copyright 2019. Adapted with permission from the American Chemical Society.

In another 2020 contribution, Bai and co-workers reported two functionalized tetraphenylethene-derived monomers, **M57-1** and **M57-3**, which bear four crown ether and four pillar[5]arene capping subunits, respectively (Figure 53).[310] A dialkylammonium salt tethered to a nitrile was also synthesized; it was designed to bridge **M57-1** and **M57-3** as the result of orthogonal binding of the nitrile and ammonium groups to the pillarene and crown ether moieties, respectively. In accord with the authors' design expectations, mixing these precursors led to the formation of the cross-linked supramolecular polymer **SP57**. The binding constants between **M57-1** and **M57-2** and between **M57-2** and **M57-3** in chloroform-*d*/acetone-*d*₆ (2/1, v/v) were calculated to be $9.1 \times 10^3 \text{ M}^{-1}$ and 675 M^{-1} , respectively. It was found that **SP57** could be depolymerized by adding K^+ as a competitive guest, but also that it would gelate at high monomer concentrations. Moreover, the tetraphenylethene cores endowed the system with aggregation-induced emission features. In the monomeric states, the tetraphenylethene-based building blocks **M57-1** and **M57-3** were non-fluorescent due to presumed nonradiative decay of the respective excited states. However, the corresponding cross-linked supramolecular networks exhibited enhanced fluorescence, a result ascribed to a reduction in molecular motions. This work thus provided an illustration of how supramolecular polymerization (or lack thereof) could be monitored *via* changes in aggregation-induced emission.

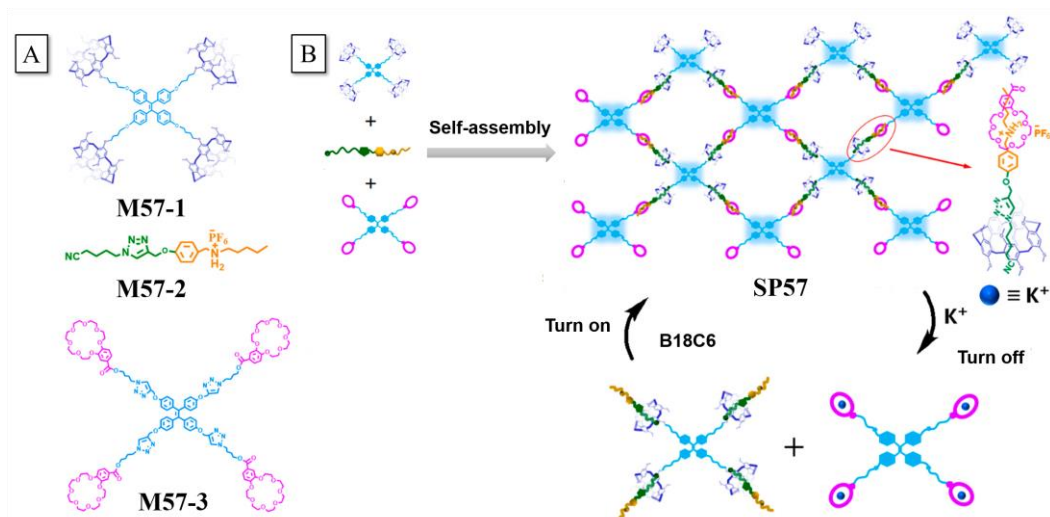


Figure 53. (A) Chemical structures of **M57-1**, **M57-2**, **M57-3**, and (B) schematic illustration of how they can undergo self-association to give **SP57**, supramolecular polymer displaying stimuli responsiveness and aggregation-induced emissive features.

[310], Copyright 2020. Adapted with permission from the American Chemical Society.

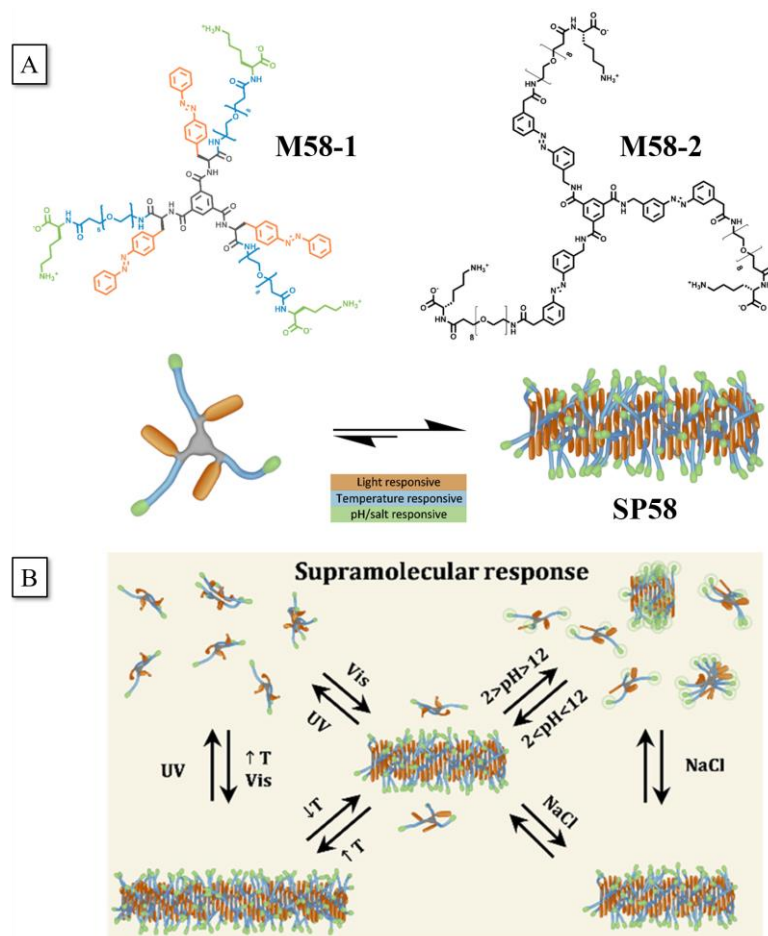


Figure 54. (A) Chemical structures of **M58-1**, **M58-2** and schematic illustration of how they undergo supramolecular polymerization to yield **SP58**. (B) Schematic illustration of the stimuli responsiveness seen in the case of **SP58**. [311], Copyright 2020. Adapted with permission from the American Chemical Society.

Albertazzi and Pujals *et al.* designed monomer **M58-1**, a star-like system that contains a benzene-1,3,5-tricarboxamide (BTA) core, three amphiphilic wedges, and three azobenzene moieties as substituents (Figure 54).[311] This monomer was found to self-assemble to give supramolecular polymers of general structure **SP58** that the authors propose is stabilized by hydrogen-bonding between the BTA subunits, as well as hydrophobic interactions involving the amphiphilic wedges. Microscopic morphological

studies of **SP58** revealed long fibers with a diameter of about 6 nm. The authors also studied an ostensibly analogous monomer **M58-2** bearing azobenzene units on the main backbone of the wedges; this derivative failed to self-assemble, underscoring the seemingly unique nature of **M58-1** in terms of supporting supramolecular polymerization. In the case of **M58-1**, (*E*)-/(*Z*)-isomerization of the three azobenzene units imparted light responsiveness to the corresponding fibers **SP58**. By irradiating the samples alternatively with 365 nm and 455 nm light, and thus changing the proportion of the azobenzene subunits in the (*E*) configuration, self-assembly of **M58-1** could be fine-tuned. This supramolecular system also exhibited responsiveness to temperature, ionic strength and pH, and in a reversible manner.

In 2021, Huang *et al.* reported a chemoresponsive supramolecular polymer (**SP59**) driven by host-guest complexation and metal coordination-based interactions between a bis(*p*-phenylene)-34-crown-10 macrocycle (**M59-1**) and a viologen-centered bis-benzonitrile guest (**M59-2**) (Figure 55).[312] Upon initial contact, the two monomers were found to form a [2]pseudorotaxane with a binding constant of $6.1 \times 10^2 \text{ M}^{-1}$ in acetone-*d*₆ in which the nitrile groups remained accessible. **SP59** was then generated *via* metal-ligand coordination of Ag(I) cations to the exposed nitrile groups. Specifically, it was found that the Ag atoms formed N⋯Ag⋯N bonds characterized by an angle of 135.43° and distances of 2.203 and 2.268 Å, respectively, as inferred from a single crystal structure of **SP59**. Interactions with the three O atoms on **M59-1** were also inferred. When **M59-1** and the Ag⁺ cations were added in excess to an acetone solution of **SP59**, the supramolecular polymer was found to depolymerize to give a [3]pseudorotaxane with one Ag⁺ coordinated to one

nitrile group, one acetone molecule and three O atoms. The [3]pseudorotaxane could be converted back to the initial state *via* the subsequent addition of **M59-2**. The resulting depolymerization/repolymerization processes could be operated for a large number of cycles without apparent system fatigue. This feature could prove useful in fabricating degradable or self-healing functional materials.

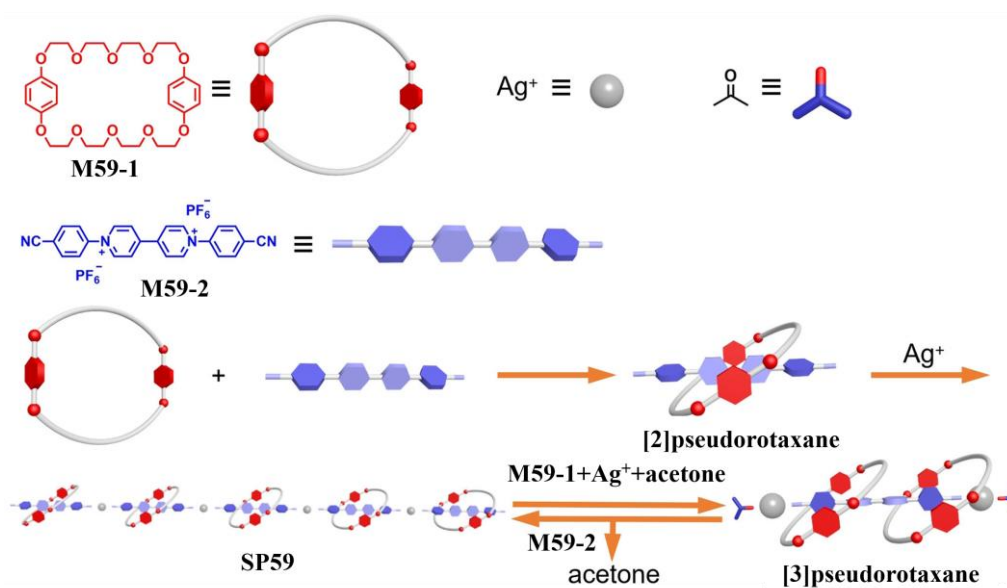


Figure 55. Chemical structures of **M59-1**, **M59-2** and schematic illustrations showing the proposed formation of a [2]pseudorotaxane, the supramolecular polymer **SP59** and a [3]pseudorotaxane. [312], Copyright 2021. Adapted with permission from John Wiley & Sons Inc.

In 2022, Yan *et al.* prepared a covalent polymer containing dibenzo-24-crown-8 (DB24C8) moieties (**M60-1**). They then showed that the presence of a hexagonal metallacycle formed from the bis-platinum and bis(pyridinium) precursors (**M60-2** and **M60-3**, respectively), a mechanically interlocked supramolecular network (**SP60**) would be stabilized as the result of threading of **M60-1** through the metallacycle (Figure 56).[313]

Owing to the multivalent interactions, rigid metallacycle skeleton, and motions involving the threaded structures, **SP60** exhibited attractive mechanical properties in terms of stiffness (Young's modulus = 47.3 MPa), toughness (49.3 MJ/m³), and strength (breaking stress = 12.1 MPa). This system also displayed dynamic responsiveness. Specifically, the addition of K⁺ cations, which would compete for the crown ether moieties, led to release of the metallacycle from **SP60** and a breakdown of the network. The addition of Br⁻ was also found to decompose **SP60** presumably as the result of destroying the labile Pt-N bond in the metallacycle.

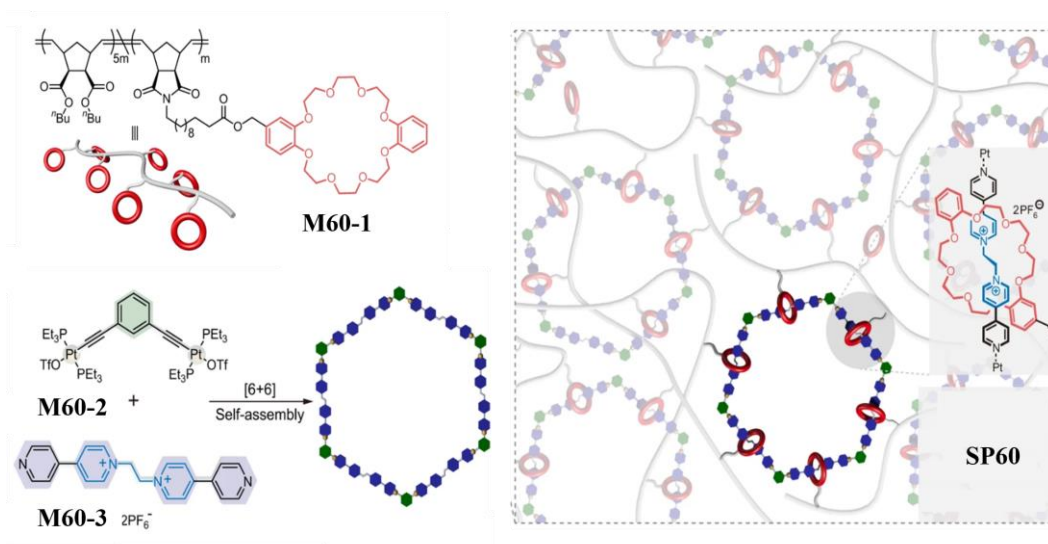


Figure 56. Chemical structures of **M60-1**, **M60-2**, and **M60-3**, as well as schematic illustrations of the formation of a molecular necklace cross-linked supramolecular copolymer **SP60**. [313], Copyright 2022. Adapted with permission from Springer Nature.

In 2021, Aida and Itoh *et al.* reported an alternating heterochiral supramolecular copolymer (**SP61**) prepared from two enantiomeric thiophene-fused cyclooctatetraene precursors, namely (+)-**M61-1** and (-)-**M61-1** (Figure 57A).[314] When the monomers were mixed in a methylcyclohexane/dichloroethane solution in an equal molar ratio, a larger

hydrodynamic diameter was recorded that was taken as evidence of supramolecular polymerization. Under these same conditions no change in the diameter as a function of time was seen for either enantiomer of the monomer ((+)-**M61-1** and (-)-**M61-1**). A crystal structure of the polymeric assembly of **M61-2**, an analogue of **M61-1** bearing shorter side chains, allowed this finding to be rationalized in structural terms. This structure revealed alternating hydrogen-bonded and polar π -stacked domains stabilized separately by two out of four side-chain amide groups and a one out of the 4 thiophene amide units present in (+)-**M61-2** and (-)-**M61-2**. A computational investigation using density-functional theory led to the conclusion that two thiophene amide moieties facing one another would effectively cancel their in-plane dipole moments, resulting in the observed alternating heterochiral preference. In contrast, the computational studies led to the inference that the alternative homochiral stacking arrangement would suffer from steric repulsion between the thiophene plane and the alkylamide units, which would hamper effective supramolecular polymerization of the enantiomerically pure monomers.

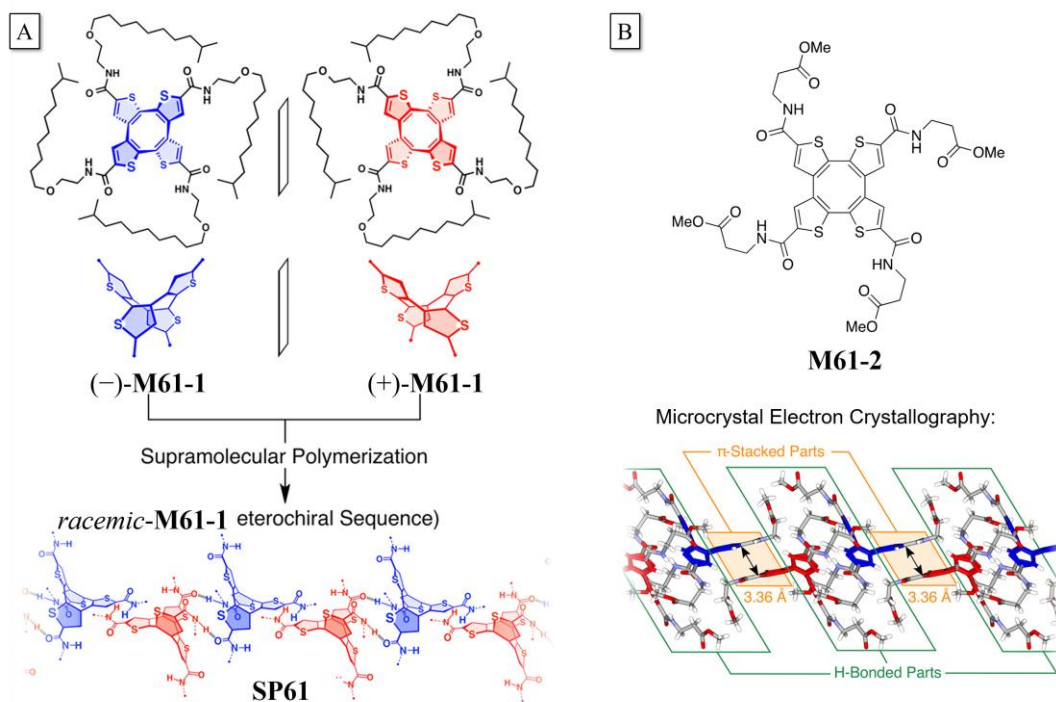


Figure 57. (A) Chemical structures of (-)-**M61-1**, (+)-**M61-1** and their supramolecular copolymerization to produce a heterochiral sequence. (B) Chemical structure of **M61-2** and crystal structure of its polymeric assembly. [314], Copyright 2021. Adapted with permission from the American Chemical Society.

In 2017, the Wang group reported one-dimensional structures that could be used in optical waveguiding.[315] These systems relied on the platinum acetylide monomer **M62-1** (Figure 58). In methylcyclohexane, **M62-1** displays a 2x greater fluorescence intensity than seen in chloroform, a finding that was taken as evidence that this monomer could undergo π -aggregation even in moderately polar media, such as chloroform. It was also noted that **M62-1** gives rise to a bisignate Cotton effect. This was ascribed to its propensity to self-assemble in a helical manner to form the supramolecular polymer **SP62** with a DP = 242. When the amide bonds present in **M62-1** were replaced by ester bonds (giving **M62-2**), no Cotton effect was observed. The high-molecular-weight of the ensembles formed as

the result of **M62-1** self-assembly allowed the authors to fabricate macroscopic fibers by electrospinning technique. These macrofibres were used for optical waveguiding applications and were found to exhibit outstanding optical waveguiding capability with low light propagation loss.

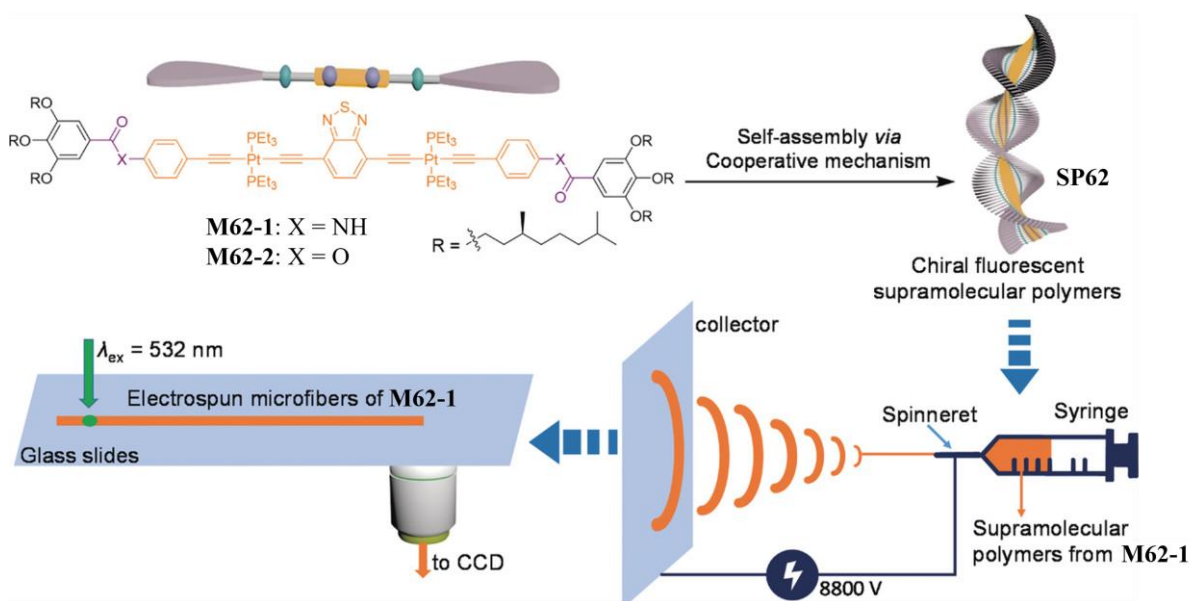


Figure 58. Schematic illustration of the supramolecular polymerization of **M62-1** and its proposed use in optical waveguide applications. [315], Copyright 2017. Adapted with permission from John Wiley & Sons Inc.

7. Conclusion and Outlook

In this review, we have summarized representative recent advances in the area of supramolecular polymers (from 2016 to the present). The organization is based on the types of noncovalent interactions supporting the formation of the self-assembled material in question. The progress in this field reflects an increasing appreciation that such systems are attractive in terms of *inter alia* facile material fabrication, superior processing and recycling, self-healing and stimuli-responsiveness. They also show promise in a variety of potential

applications including light harvesting, light waveguide generation, sensing, adsorption and separations, OLED device construction, and biomedicine development, to name a few. This progress notwithstanding, it is clear from considerations of natural oligomeric and self-assembled systems that the field of supramolecular polymers is still in its infancy, particularly with regard to the degree of complexity and functionality that can be incorporated into rationally designed materials. Challenges and opportunities in this area thus abound. Three directions that we see as worthy of particular emphasis are detailed below:

- 1) Development of new methods for supramolecular polymer synthesis. This encompasses both the creation of new monomers with a diversity of topologies and functions and their conversion into pre-designed supramolecular polymers. Complementing these efforts, attention should be devoted to developing or exploiting new non-covalent interactions that provide for both a high driving force for supramolecular polymerization and control over structure and function. These are points that, not surprisingly, have been emphasized in other reviews.[110] Nevertheless, they remain crucial if the field is to advance. We anticipate that additional supramolecular recognition motifs could be exploited to fabricate novel monomers, thus allowing in principle the creation of supramolecular polymers with novel properties. For example, halogen bonding as well as multiple interactions, including ion pair binding, could be incorporated into monomers. In addition, we believe that more effort should be devoted to optimizing the effects of the interactions that underlie current systems and their use in controlling the polymerization dynamics. As a recent example of this approach, Scherman *et al.* strengthened the polar- π

interactions of perfluorobenzene and benzene by encapsulating them within CB[8].[316, 317] By tuning dissociation kinetics of these host-enhanced polar- π interactions, they were able to generate a glass-like supramolecular polymer networks exhibiting ultra-high compressibility and fast self-recovery. This work highlights a new direction in the design and construction of smart polymeric materials.

2) Characterization of supramolecular polymers: More precise determination of various self-assembled structures and pathways for their formation is expected to lead to a deeper understanding of the structure-function relationships that make supramolecular polymer so appealing in terms of both aesthetics and targeted applications. To date, UV-Vis absorption and ^1H NMR spectroscopies, diffusion-ordered NMR spectroscopy, electron microscopy, specific viscosity determination, dynamic light scattering, and differential scanning calorimetry have been widely used to verify the formation of supramolecular polymers.[318] However, new methods, such as small-angle neutron scattering, microcrystal electron crystallography and high level calculations, could be informative if brought to bear on the problems of supramolecular polymer characterization. The use of time-resolved optical methods, including fluorescence- and phosphorescence tools, are also appealing. Indeed, efforts to use the effects of aggregation-induced emission to characterize various dynamic processes associated with supramolecular polymers and their preparation.[319-321] However, extensions to other spectroscopies, including polarized luminescence and optically driven paramagnetic resonance methods, can easily be envisioned.

3) Applications of supramolecular polymers: Practical applications of supramolecular polymers are facing challenges for several reasons: i) The relatively weak nature of noncovalent bonds compared to covalent bonds leads to weaker inherent mechanical properties of supramolecular polymers. ii) The formation of supramolecular polymers with certain mechanical strength usually requires high concentrations of the building blocks in the medium; otherwise, their performances will be adversely affected. iii) The dynamic nature of noncovalent bonds makes the resulting supramolecular polymers sensitive towards environment stimuli, including those that can induce supramolecular depolymerization. However, this same lability, in turn, generally endows supramolecular polymers with dynamic reversibility and environmental responsiveness and has made them of interest as possible self-healing materials that may be readily recycled or used as sustainable/degradable green materials. Nevertheless, further developments along these lines are necessary if effective translation into the marketplace is to be realized. In a related vein, the design of so-called smart supramolecular polymers that produce one-dimensional fibers could lead to market opportunities in the areas of optical and electronic materials. In this context, we note that work to date serves to highlight the potential of supramolecular polymer engineering to create advanced photonic devices.[322-324] Also of potential commercial interest and practical importance would be the development of supramolecular biomimetic materials and biomaterials. Here, the inherent responsiveness of supramolecular polymers, as well as an ability to tune their materials features, such as hardness, stretchiness, and toxicity, are appealing. We predict that in due course these attributes will lead to advances in diagnosis and treatment.

Notes

The authors declare no competing financial interest.

8. Acknowledgements

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