Supramolecular polymers constructed by orthogonal self-assembly based on host-guest and metal-ligand interactions

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Supramolecular polymers constructed by orthogonal self-assembly based on host–guest and metal-ligand interactions

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Supramolecular polymers constructed by orthogonal self-assembly based on host–guest and metal-ligand interactions are attracting increasing attention currently because of their interesting properties and potential applications. Host–guest interactions impart these polymers with good selectivity and convenient enviro-responsiveness, and metal-ligand interactions endow them with various coordination geometries, strong yet tunable coordination binding abilities, as well as magnetic, redox, photophysical, and electrochromic properties. Therefore, supramolecular polymers constructed by orthogonal host–guest and metal-ligand interactions have wide applications in the field of soft matter, fluorescence sensing, heterocatalysis, electronics, gas storage, *etc*. In this *critical review*, we will address the recent development of supramolecular polymeric systems involving metal-ligand interactions and host–guest molecular recognitions. Specifically, we classify the related supramolecular polymers depending on the types of macrocyclic hosts and highlight their intriguing properties originating from the elegant combination of host–guest complexation and metal centers.

1. Introduction

Polymeric materials have exerted significant impact on our daily life. Scientific researchers are always on their way to obtain elaborate artificial polymers with fascinating structures and functionalities. Compared to the conventional covalently bonded polymers, supramolecular polymers are aggregate arrays of building blocks brought together by a series of reversible noncovalent interactions (hydrogen bonding, host–guest interaction, π–π stacking, metal-coordination, *etc*.) and/or dynamic covalent connections (imine bonds, olefin metathesis, and disulfide bonds, *etc*.).[1–3] Both low molecular weight monomers and macromolecular components can be used as building blocks in the preparation of supramolecular polymers. As supramolecular polymers are the fruits of the perfect connection between supramolecular chemistry and polymer science, they not only possess traditional polymeric properties, but also show some unique functions, such as recyclability, adaption, and self-healing characteristics. Considering their dynamic/reversible nature and unique physical/chemical properties, supramolecualr polymers have found a wide range of applications, ranging from smart devices to bioactive scaffolds, nanotechnology, and functional materials.[4,5]

Compared with self-assembly utilizing only one type of noncovalent interactions, orthogonal self-assembly, in which "orthogonal" is used to describe that different types of noncovalent interactions do not interfere with each other, combining multiple noncovalent interactions has some superior properties.[6,7] First, intricate and tedious organic synthesis and purification processes in conventional systems are avoided to some degree. Second, simultaneous incorporation of multiple noncovalent bonds endows the resulting polymers with a higher degree of complexity and more specific functionalities. Third, the dimensionality of the materials can grow through iteratively increasing well-defined steps, so we can manipulate each unique noncovalent bond separately to address adaptive properties of the supramolecular polymers. Up to now, a variety of supramolecular polymers with different chain topologies, such as linear, star-type, cross-linked, hyperbranched, and dendronized, have been fabricated and prepared under the direction of this methodology.[8,9]

Among various noncovalent interactions used in the construction of supramolecular polymers, host–guest complexation and metal-ligand coordination are two main classes of noncovalent interactions and have been studied widely. Host–guest recognition refers to the formation of supramolecular inclusion complexes between two or more entities connected together in a highly controlled and cooperative manner. Many of the macrocyclic hosts, such as crown ethers, cucurbiturils, cyclodextrins, calixarenes, and pillararenes, have been used to fabricate supramolecular polymers based on their recognition to complementary guests.[10–16] Host–guest interactions endow supramolecular polymers with inherent reversibility and adaptability, therefore broadening responsiveness to external stimuli and producing accordingly more sophisticated functions.[17] Metal-coordination has emerged as another powerful tool to construct supramolecular coordination polymers based on the spontaneous formation of metal-ligand bonds. Metal-ligand interactions are strong, directional, and highly versatile driving forces, allowing various coordination geometries and supramolecular polymers with considerable stability yet reversibility.[18,19] Moreover, metal-ligand coordination may bring unique magnetic, redox, optical, and electrochromic properties, beneficial for potential applications in the fields of heterocatalysis, electronics, gas storage, *etc*. Therefore, engineering orthogonal host–guest and metal-coordination interactions in supramolecular polymers will definitely endow them with unprecedented complexity and diverse functions.

In this *critical review*, we mainly focus on recent progress in supramolecular polymers involving orthogonal metal-coordination and host–guest molecular recognition. Specifically, we classify the resulting supramolecular polymers depending on the types of macrocyclic hosts and highlight their intriguing properties originating from the elegant combination of host–guest complexation and metal centers. Meanwhile, metal-organic *rotaxane* frameworks (MO*R*Fs) involving rotaxanes as linkers and metals as nodes will not be covered much; for these, readers can refer to the wonderful reviews by Loeb[20] and Stoddart[21] *etc*. We aim to illustrate the general concepts and structure–function–application relationships of supramolecular polymers constructed by orthogonal metal-coordination and host–guest chemistry. We hope to shed some light on the future work and inspire continuous endeavors in this emerging and exciting research area.

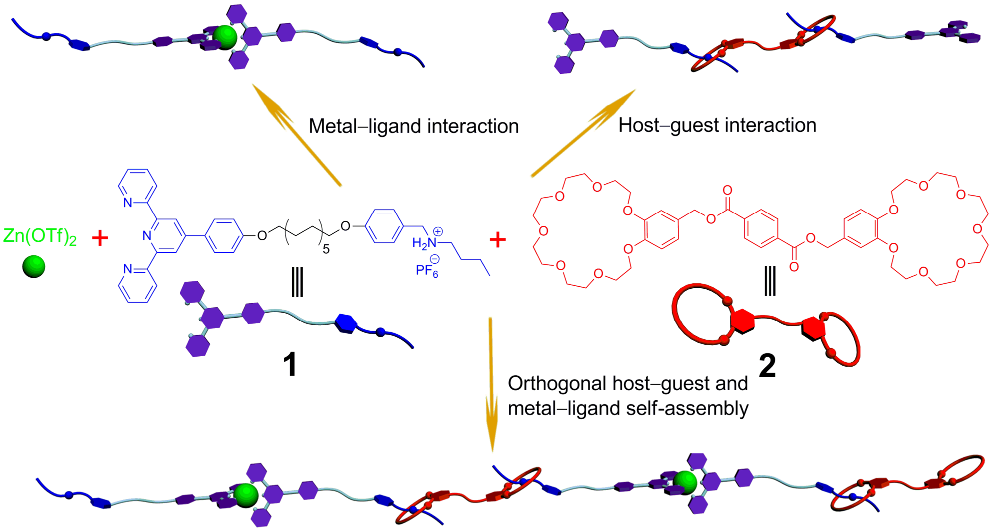

Fig. 1 Cartoon representation of the formation of a linear supramolecular polymer and the corresponding intermediates from monomers **1** and **2**.

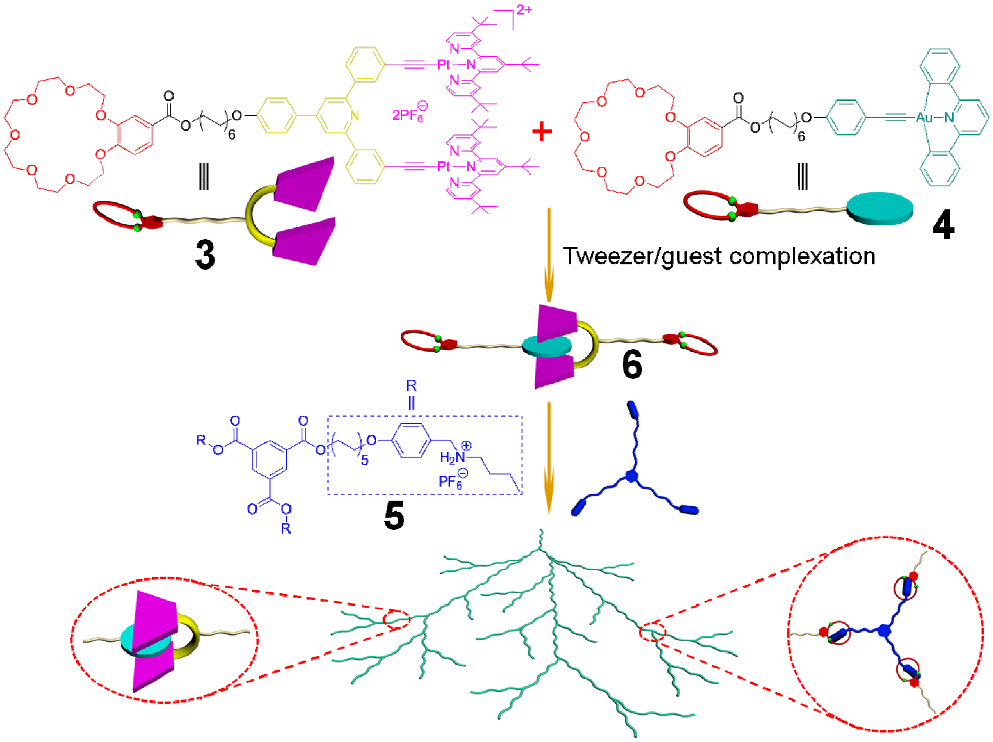

Fig. 2 Cartoon representation of the construction of a supramolecular hyperbranched polymer from monomers **3**, **4**, and **5**.

2. Supramolecular polymers constructed by orthogonal metal-coordination and crown ether-based host–guest motifs

2.1 Benzo-21-crown-7-based molecular recognition

It has been demonstrated by our group that benzo-21-crown-7 (B21C7) is the smallest benzo-crown ether which can form threaded structures with secondary dialkylammonium salts.[22] Many complicated mechanically interlocked structures have been constructed on the basis of this B21C7/secondary dialkylammonium salt recognition motif. The requirements of new functions push scientists to explore novel types of building blocks. Orthogonal self-assembly based on this recognition motif and metal-coordination provides an efficient way to construct highly functional supramolecular polymeric assemblies. For example, Wang and co-workers integrated the terpyridine (tpy)–Zn^{2+} and B21C7/secondary ammonium salt motifs in an orthogonal manner to deliver a linear supramolecular polymer.[23] Heteroditopic monomer **1** bearing a secondary ammonium salt guest moiety and a tpy ligand on two sides of a long flexible aliphatic chain was designed, which would reduce the percentage of cyclic oligomers and favor the linear extension, thereby resulting in a relatively low critical polymerization concentration (CPC) during the supramolecular polymerization. Monomer **1** could complex with B21C7-based AA-type monomer **2** to form a [3]pseudorotaxane structure (Fig. 1). Additionally, UV-vis and ^{1}H NMR titration measurements illustrated the specific complexation between Zn^{2+} and tpy. The orthogonal self-assembling properties of these two noncovalent interactions were also confirmed. Subsequently, concentration-dependent ^{1}H NMR and two-dimensional diffusion-ordered NMR (DOSY) experiments both suggested that monomer concentration exerted a significant impact on the reversible supramolecular polymerization process. Specific viscosities of the linear supramolecular polymer increased exponentially with the increase of the monomer concentration, while those of the dimeric $Zn(tpy)_2^{2+}$ complex and the host–guest paired dimer showed slight increase, indicating that both of the orthogonal interactions are necessary for the formation of supramolecular polymers. Multistimuli responsiveness of the resulting supramolecular polymers were evaluated with heat, pH, or a competitive ligand, 1,4,7,10-tetraazacyclododecane. Following this work, the same group designed another heteroditopic monomer which bore B21C7 and tpy units on two sides and a complementary BB-type homoditopic secondary ammonium salt monomer.[24] Then a main-chain supramolecular polymer was obtained *via* “one-pot” mixing of the two recognition motifs and metal ions. Because the noncovalent interactions used in these systems were the same as we mentioned above, the materials showed almost similar dynamic and responsive properties. These two adaptive supramolecular polymers are appealing choices for further fabriction of intelligent supramolecular materials with tailored properties.

Recently, Wang and co-workers have successfully constructed well-organized supramolecular polymeric arrays based on a novel “tweezering directed self-assembly” strategy.[25] Heteroditopic monomers **3** and **4** were designed and synthesized (Fig. 2).[26] Considering that the two electron-deficient alkynylplatinum(II) terpyridine pincers on the molecular tweezer unit could specifically encapsulate electron-rich alkynylgold(III) diphenylpyridine, the mixing of equivalent amounts of **3** and **4** delivered the dimeric complex **6** (Fig. 2). Subsequent addition of the homotritopic monomer **5** afforded the expected A_2B_3-type supramolecular hyperbranched polymers with potassium cation responsive character. Meanwhile, the supramolecular polymerization process could also be realized by “one-pot” mixing of the three monomers **3**, **4**, and **5**, indicating the highly specific noncovalent recognition behavior of the tweezer–guest recognition motif. This novel recognition motif expands the host–guest toolboxes and represents a versatile strategy for the fabrication of supramolecular polymeric assemblies.

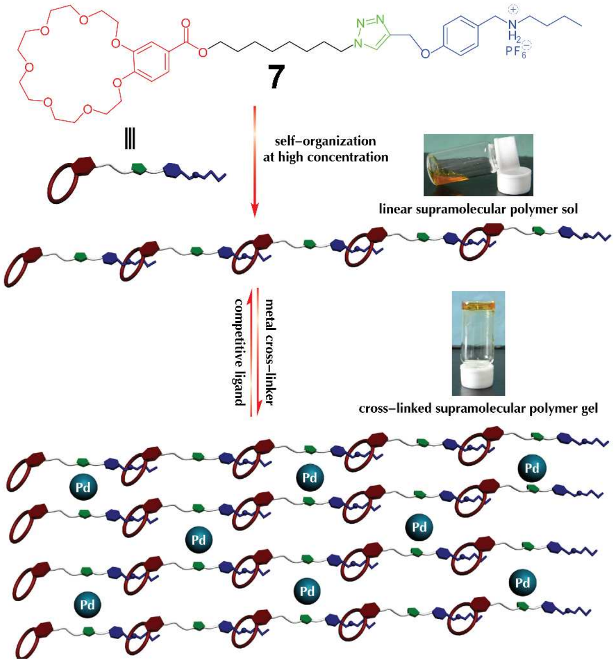

Fig. 3 Cartoon representation of the formation of linear and cross-linked supramolecular polymers *via* orthogonal self-assembly based on monomer **7** (reproduced with permission of John Wiley & Sons, Inc. from ref. 27).

Our group endeavors to utilize orthogonal self-assembly strategy to achieve more complicated and functionalized supramolecular polymers. For this purpose, we designed and synthesized a heteroditopic monomer **7** containing a 1,2,3-triazole group between a B21C7 unit and a complementary secondary ammonium salt moiety. The 1,2,3-triazole group could form a disubstituted palladium(II) complex with $[PdCl_2(PhCN)_2]$.[27] Large polymeric aggregates formed at high concentration by the self-aggregation of monomer **7**. This linear supramolecular polymer was shown to be highly dependent on temperature, monomeric concentration, and association constant, all of which exerted a big impact on the reversible conversion between the cyclic oligomers and linear aggregates. What is more, this linear supramolecular polymer could not only form smooth nanofibers *via* electrospinning technology,[28] but also could be used to prepare interesting film-type microstructures by the breath figure method.[29] When 0.5 equiv of $[PdCl_2(PhCN)_2]$ was added to a concentrated solution of monomer **7**, a cross-linked supramolecular polymer formed which showed a lower measured weight-average diffusion coefficient than its linear counterpart

(Fig. 3). At the critical gel concentration, a metal coordination-mediated supramolecular polymer network gel formed. Because of the introduction of weak and reversible supramolecular interactions, this supramolecular gel exhibited interesting reversible gel–sol transitions in response to quadruple distinct stimuli (pH-, thermo-, cation-, and metallo-induced). It has also been demonstrated that the pore size of the resultant gel could be modulated by the amount of the cross-linker added to the system. More interestingly, this gel showed prominent physical properties, such as self-standing, shape-persistence, and elasticity, which were mainly attributable to the orthogonal metal-coordination and B21C7/secondary ammonium salt noncovalent interactions. It is worth noting that this elastomer is made of only small molecules instead of macromolecular chains used in the traditional elastomers. Therefore, it is a wonderful supramolecular organogel that possesses multiple-responsive, shape-persistent, and elastic properties in a single material.

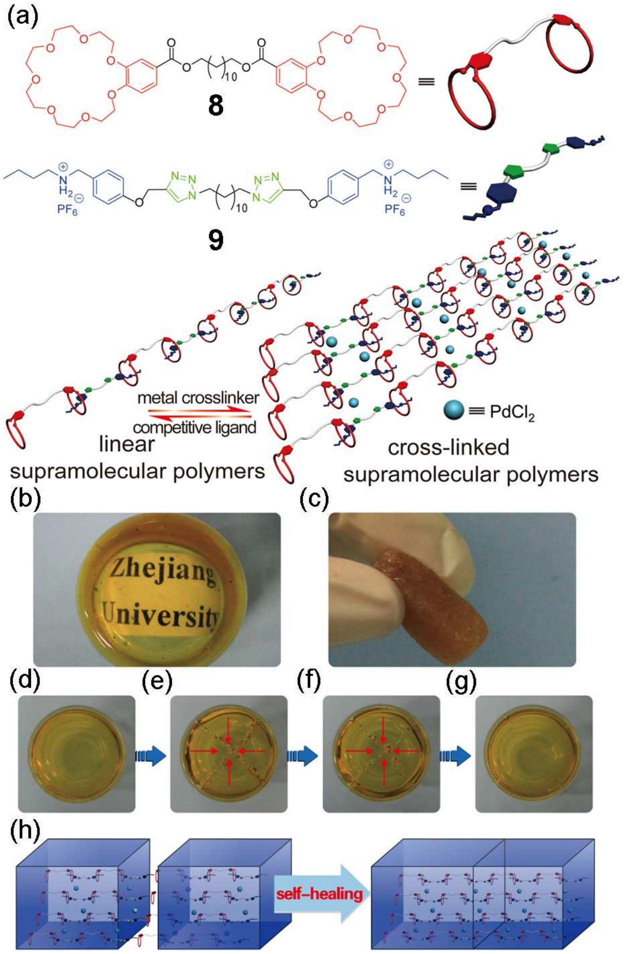

Fig. 4 (a) Cartoon representation of controlling the topology of the supramolecular polymer from the self-assembly of AA-type monomer **8** and BB-type monomer **9**. (b) Transparent and (c) free-standing cross-linked supramolecular polymer gels. Photographs: (d) the supramolecular polymer gel; (e) after damage; (f) after free-standing for 1.5 min; (g) after free-standing for 3 min. (h) Cartoon illustration of the proposed mechanism of self-healing (reproduced with permission of The Royal Society of Chemistry from ref. 31).

The ability of biological systems to spontaneously self-heal and then regenerate their functions has been attracting the attention of scientists. Therefore, imparting materials with self-healing properties is enormously attractive. On account of their dynamically adaptive features, supramolecular polymer gels are ideal candidates for the preparation of advanced soft materials with self-healing properties.[30] Though many different types of self-healing materials have been developed, self-healing systems based on host–guest interactions and metal-coordination have been rarely addressed. Our group has successfully prepared a supramolecular polymer network gel *via* a three-component self-assembly strategy: orthogonal self-assembly of two homoditopic monomers, bis(crown ether) monomer **8** and bis(secondary ammonium salt) monomer **9**, and a metallic cross-linker, $PdCl_2(PhCN)_2$ (Fig. 4).[31] The gel was transparent and exhibited interesting gel–sol transitions in response to external stimuli. Considering the dynamic and reversible nature of host–guest and metal-coordination interactions, this gel displayed good viscoelastic properties and could be processed into free-standing and shape-persistent objects. Furthermore, the gel self-healed *in situ* within a short time, and the healed gel retained its shape well, even after several mechanical movements. All these could be seen by the naked eye and confirmed by rheological experiments. This multi-functional supramolecular polymer gel represents a promising candidate for practical applications.

Metal-ligand bonding has proven to be a strong and directional force and the formation of metal-ligand bonds represents a particularly valuable method to guide the organization of molecular precursors through strategies such as coordination-driven self-assembly. By combining suitable building blocks, a diverse range of discrete supramolecular coordination complexes (SCCs) can be obtained based on the number and orientation of the coordination sites.[32] We prepared a B21C7-functionalized hexagonal metallacycle **12** with high efficiency by means of the *directional bonding* approach.[33] Then this macrocyclic monomer was polymerized into a hexagonal cavity-cored supramolecular polymer network (SPN) upon the addition of bisammonium salt cross-linker **13** due to the formation of [2]pseudorotaxane host–guest linkages between the crown ether and ammonium moieties (Fig. 5). At high concentration, the viscosity of SPN showed a dramatic increase, resulting in the formation of a metallo-hexagonal supramolecular gel. Such novel cavity-containing metallogels possess potentional functionalities such as host–guest recognition, catalysis, absorption, separation, *etc*. This work encompasses hierarchical orthogonal self-assembly with metal-coordiantion, host–guest interactions, and supramolecular polymerization. Given the high efficiency of constructing the SCCs and favorable properties induced by host–guest interactions, the hierarchical polymerization of metallacycles represents a promising route to access fascinating supramolecular materials.

2.2 Dibenzo-24-crown-8-based molecular recognition

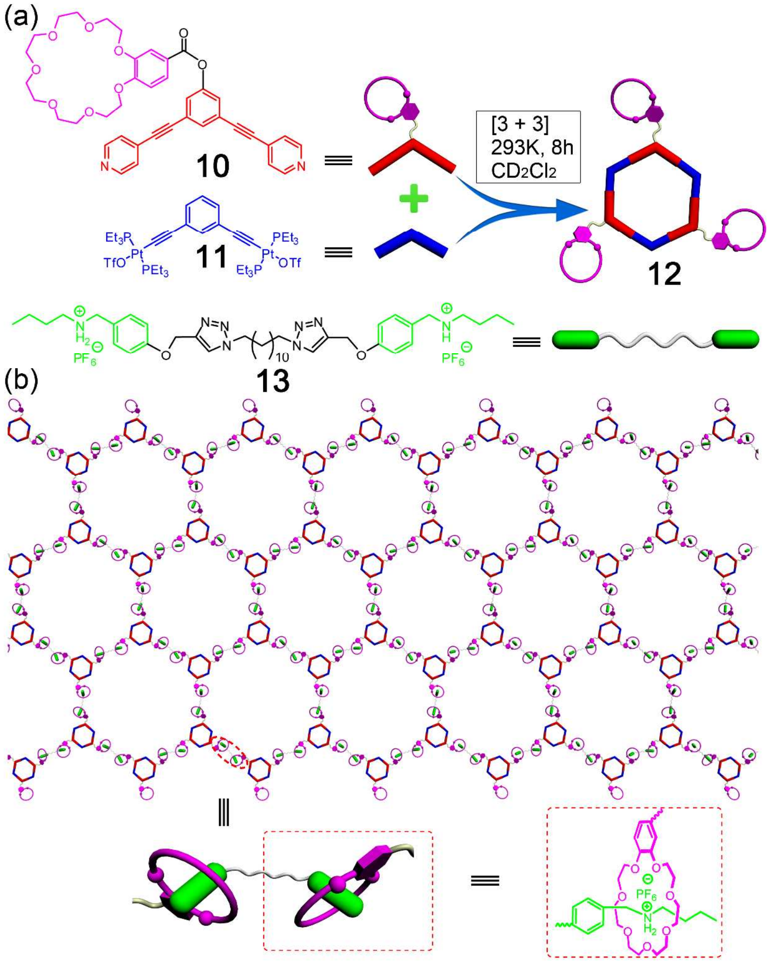

Fig. 5 (a) Self-assembly of B21C7-functionalized discrete metallacyclic hexagon **12** and (b) cartoon representation of the formation of a cross-linked 3D supramolecular polymeric network from self-assembly of hexagon **12** and bisammonium salt **13** (reproduced with permission of American Chemical Society from ref. 33).

It is well-known that dibenzo-24-crown-8 (DB24C8) can form a steady yet responsive 1:1 threaded structure with its complementary dibenzylammonium salt (DBA) guest through a cooperative combination of [N^+-H···O] and [C-H···O] hydrogen bonds and π-π stacking.[34,35] Bu and co-workers reported a metallosupramolecular polymer by coordinating Zn^{2+} with a conjugated bis-tpy ligand **14** bearing DB24C8 arms.[36] This conjugated bis-tpy ligand formed long-chain polymers with a high degree of polymerization at high concentration (Fig. 6). Interestingly, the metallosupramolecular polymer showed concentration-dependent emissions from cyan to white to yellow in the concentration range of 1.25–125 μM. Upon addition of **15** to a solution of the linear metallosupramolecular polymer, the resulting changes of ^{1}H NMR and fluorescence spectra indicated the formation of a cross-linked supramolecular polymeric network. Subsequent alternative addition of 2.4 equiv of base (*N-tert-butyl-N′,N′,N′′,N′′,N′′′,N′′′*-hexamethylphosphorimidic triamide) and 2.8 equiv of CF_3COOH resulted in the dethreading and rethreading of DBAs in the host moieties and thus reversible fluorescence emissions. Such dual responsive metallosupramolecular polymer is expected to hold promise for applications in light-emitting materials and optoelectronic devices. Recently, Yin and coworkers have also reported excellent responsive supramolecular polymer networks by the orthogonal self-assembly of the DB24C8/DBA and metal-tpy motifs.[37,38]

By an elegant combination of a tailored bistable DB24C8-based [*c*2]daisy chain rotaxane and metal-coordination driven supramolecular polymerization, Giuseppone and coworkers realized the goal of linear amplification of muscle-like translational molecular motions by orders of magnitude.[39,40] These polymer chains were long and soluble enough so that micrometric changes of their contour length could be measured upon synchronization of many of contractions and extensions. The different binding constants of the secondary ammonium and the triazolium ions with the DB24C8 motif endow monomer **16** with efficient pH-responsive translational motion at the molecular scale (Fig. 7). ^{1}H NMR and UV-vis spectra experiments well confirmed the metal-coordination

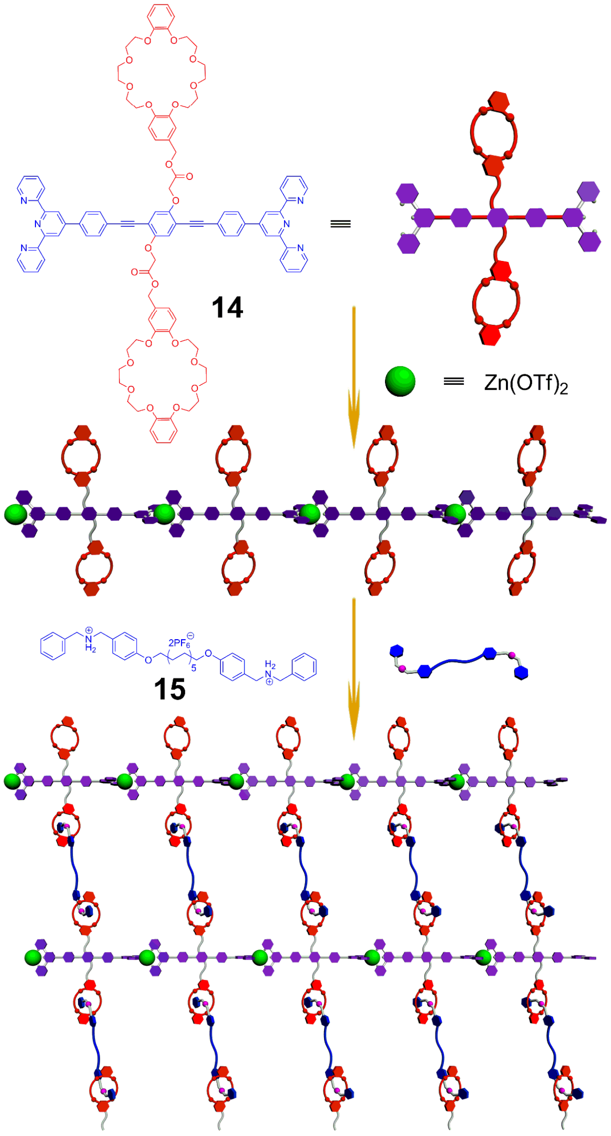

Fig. 6 Cartoon representation of the formation of linear and cross-linked metallosupramolecular polymers based on monomers **14** and **15**.

driven supramolecular polymerization processes of **16** with either $Zn(OTf)_2$ or $FeCl_2$. Meanwhile, light scattering (DLS and SLS) and small-angle neutron scattering (SANS) experiments were used to obtain the lengths and conformations of the expected metallosupramolecular polymers. This work showed that the capacity to integrate molecular motions of molecular machines produced an amplification effect by orders of magnitude within a single supramolecular polymeric chain based on an elegant combination of molecular synthesis, supramolecular engineering, and supramolecular polymerization.

The discovery of facile and efficient methods to control the topologies of polymeric assemblies is no easy matter. Cryptands have been proved to be much better hosts than the corresponding simple crown ethers because of better preorganization of structural conformations and the incorporation of additional binding sites.[41] Unifying the themes of coordination-driven self-assembly and *cis*-DB24C8 cryptand-based molecular recognition in an orthogonal fashion, supramolecular polymers with linear and cross-linked topological structures can be constructed easily and efficiently by just changing angular orientation of the metal acceptors. We designed and synthesized a *cis*-DB24C8-based cryptand **17** with its pyridine nitrogen atom outside the third arm which facilitated its further self-assembly into bis-cryptand and tri-cryptand by metal-coordination. After mixing cryptand **17**, bisparaquat **18**, and bis-arm or tri-arm organoplatinum(II) acceptors (**19** or **20**) together, linear or cross-linked supramolecualr polymers (LSP or CSP) were obtained in concentrated solutions, respectively (Fig. 8),.[42,43] By contrast, the CSP showed better polymeric characteristics than that of the LSP, such as the formation of long, macroscopic fibers with several centimeters drawn from a concentrated CSP solution. More importantly, an alternative stepwise strategy, such as changing the self-assembly sequence, could also result in the formation of LSP and CSP based on the noninterfering orthogonal nature of coordination-driven self-assembly and host–guest interactions. Moreover, cryptand-based molecular recognition endowed the two polymers with cation-induced dynamic assembly/disassembly properties, making them promising candidates for applications in degradable materials. Considering the rich combinatorial molecular library consisting of complementary building blocks and the high efficiency of constructing SCCs, this work provides an easy way to control the topologies and exploit intriguing macroscopic properties of the functional supramolecular assemblies.

2.3 Bis(*m*-phenylene)-32-crown-10-based molecular recognition

Bis(*m*-phenylene)-32-crown-10 (BMP32C10) and its derivatives, which have symmetric chemical structures, can form taco or threaded host–guest complexes with paraquat derivatives with good binding ability, exhibiting fascinating geometries. Gibson, Huang, and others have contributed many outstanding studies based on this recognition motif during the past two decades.[44] If we want to efficiently prepare metallosupramolecular polypseudorotaxanes *via* BMP32C10-based molecular recognition, two factors should be considered: (1) the introduction of Lewis basic donors on BMP32C10 to coordinate with metal acceptors and (2) the formation of threaded complexes instead of taco structures. Bearing these two points in mind, our group synthesized two BMP32C10 derivatives with different lengths of pyridyl groups, which had well-defined taco and threaded conformations when complexed with guest **23**, as confirmed by single-crystal X-ray analysis.[45] BMP32C10 derivative **21** with short pyridyl groups formed a taco complex, while **22** functionalized with π-extended pyridyl groups formed a [2]pseudorotaxane-type threaded sturcture with the pyridine nitrogen atoms located outside which would endow this complex with post-self assembly ability by metal-coordination (Fig. 9). Subsequently,

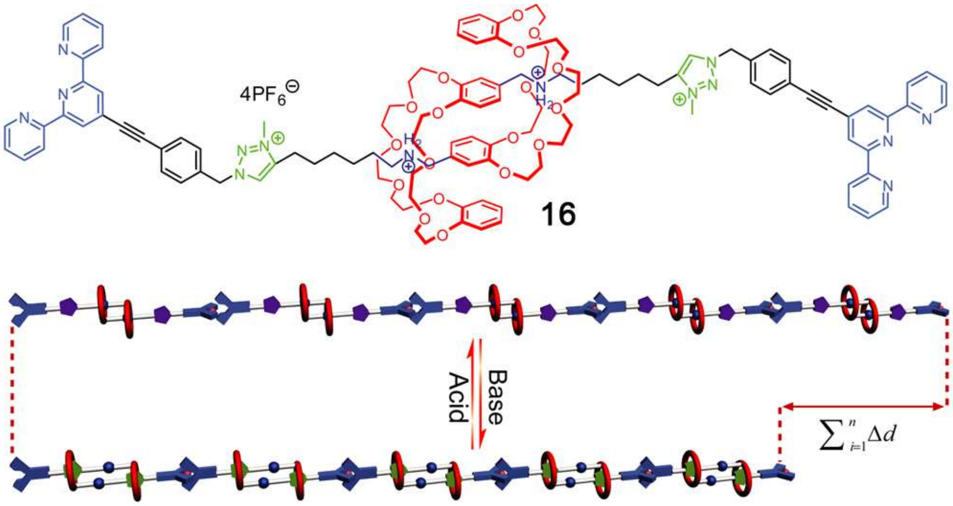

Fig. 7 Chemical structure of the difunctional [*c*2]daisy chain **16** and cartoon representation of the acid–base switching contraction–extension process of the resultant metallosupramolecular polymers (reproduced with permission of John Wiley & Sons, Inc. and The Royal Society of Chemistry from ref. 39 and 40).

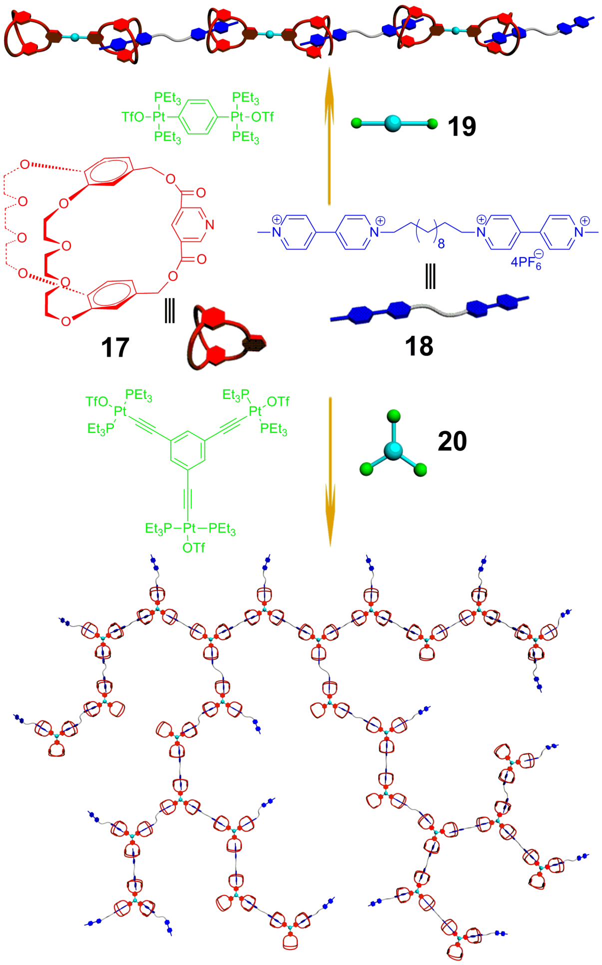

Fig. 8 Cartoon representation of the formation of linear and cross-linked supramolecular polymers by orthogonal self-assembly strategy based on monomers **17**–**20** (reproduced with permission of The Royal Society of Chemistry from ref. 42 and 43).

a main-chain poly[2]pseudorotaxane with metallosupramolecular polymer backbone was constructed by metal-coordination between 180° diplatinum(II) acceptor **19** and [2]pseudorotaxane **22**⊃**23**, as evidenced comprehensively by various techniques (Fig. 9). Resulting from the dynamic and reversible supramolecular polymer backbone, the polypseudorotaxane structure would show adaptive properties.

Orthogonal noncovalent interactions not only facilitate the design of complicated supramolecular assemblies, but also make it easy to prepare supramolecular polymers with different topologies. For example, Huang and co-coworkers reported responsive supramolecular polymers that have linear and cross-linked topological structures by orthogonal self-assembly of metal-coordination and cryptand-based host–guest chemistry.[46] From the self-assembly of a heteroditopic monomer **24** which was incorporated with a 1,2,3-triazole group between a BMP32C10-based cryptand host and a paraquat guest, a linear supramolecular polymer formed in acetonitrile at high concentration driven by hydrogen bonding and face-to-face π-stacking interactions between the cryptand host unit and the paraquat guest moiety (Fig. 10). Then the addition of a cross-linker, [PdCl$_2$(PhCN)$_2$], which coordinated with the triazole ligand, afforded a cross-linked supramolecualr polymer network, which was confirmed by remarkable changes in viscosity and diffusion coefficient values compared with the linear analogue. Destruction and reconstruction of the supramolecular polymer network was readily realized by the alternative addition of the competitive ligand and cross-linker. This work represents a new method for the topological control of supramolecular polymers by orthogonal self-assembly.

2.4 Bis(*p*-phenylene)-34-crown-10-based molecular recognition

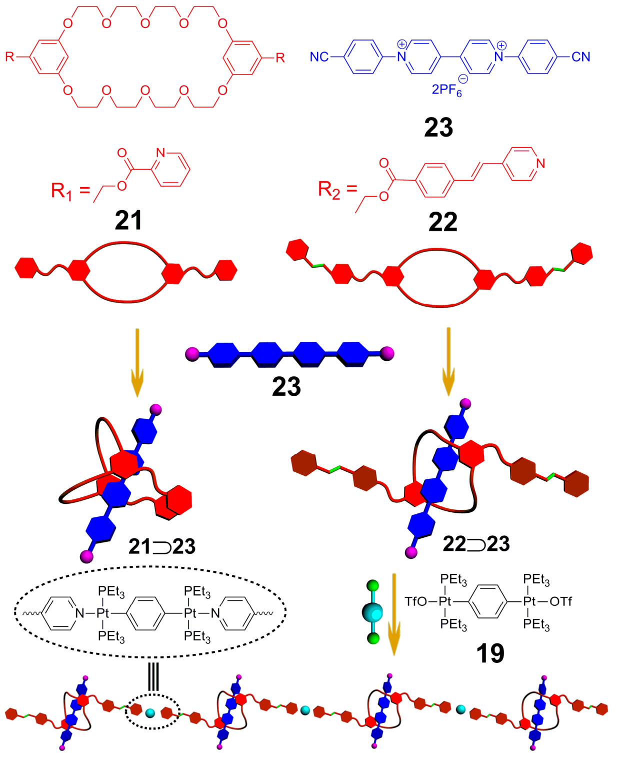

Fig. 9 Cartoon representations of the formation of a metallosupramolecular poly[2]pseudorotaxane driven by metal-coordination from compounds **19**, **22**, and **23** and the formation of taco complex **21**⊃**23** (reproduced with permission of American Chemical Society from ref. 45).

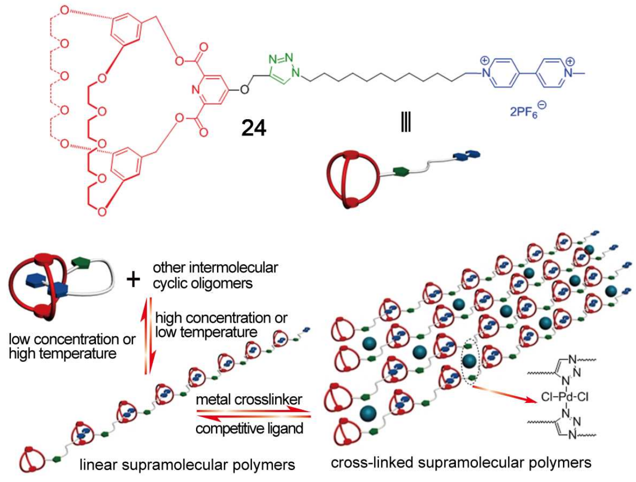

Fig. 10 Cartoon representation of the formation of supramolecular polymers with different topologies based on monomer **24** (reproduced with permission of John Wiley & Sons, Inc. from ref. 46).

Bis(*p*-phenylene)-34-crown-10 (BPP34C10) derivatives can form threaded complexes with paraquat derivatives with good binding ability. Meanwhile, they show much higher association constants with more electron-deficient organic guest molecules, such as 2,7-diazapyrenium derivatives (DAPs). On the basis of such recognition motifs, we reported an efficient approach to construct responsive supramolecular polymers. Our strategy involved the unification of BPP34C10-based host–guest interactions and metal-coordination in an orthogonal way to afford desired supramolecular side-chain poly[2]pseudorotaxanes.[47] Specifically, by Suzuki coupling, we could obtain a BPP34C10 derivative **25** bearing two pyridyl groups (Fig. 11). Notably, the X-ray crystal structure showed that the pyridine *N*-atoms are oriented in the opposite directions of the same phenyl ring of **25**, which offers the pyridyl ligands to coordinate with di-Pt(II) acceptor **26**, thereby forming the paraquat-based side-chain polypseudorotaxane with a metallosupramolecular polymer backbone. Moreover, this paraquat-based polypseudorotaxane could be readily transformed into a DAP-based polypseudorotaxane by competitive host–guest complexation because more electron-deficient DAP could expel paraquat from the cavity of BPP34C10. This design principle benefited the construction of complexed supramolecular materials with reversibility and adaptability.

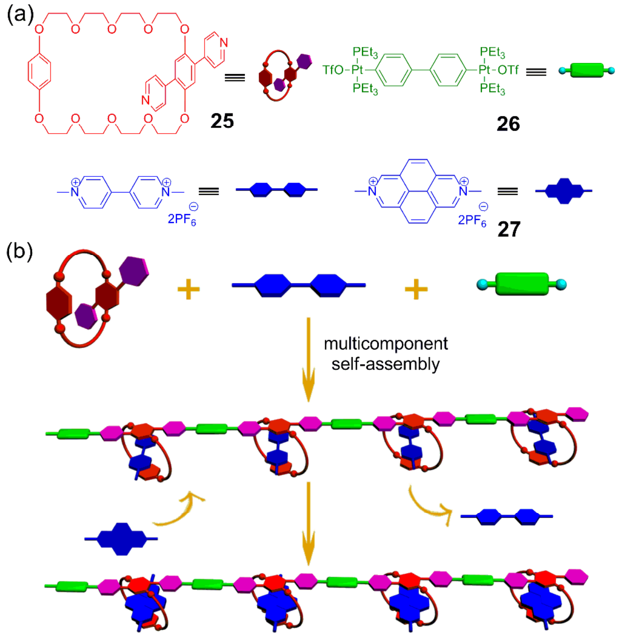

Fig. 11 (a) Chemical structures of paraquat and compounds **25**–**27** and (b) cartoon representation of the formation of side-chain metallosupramolecular poly[2]pseudorotaxanes (reproduced with permission of American Chemical Society from ref. 47).

3. Supramolecular polymers constructed by orthogonal metal-coordination and cyclodextrin-based host–guest motifs

Cyclodextrins (CDs) consisting of six, seven, or eight glucose entities are called α-, β-, or γ-CDs, respectively. CDs assume a toroidal shape with the primary hydroxyl groups at the narrow side and the secondary hydroxyl groups at the wide side, showing prominent host–guest interactions with various organic and inorganic molecules. The relatively hydrophobic interior and hydrophilic exterior make them ideal hosts for the formation of stable inclusion complexes in aqueous solution which are quite different from crown ether-based supramolecular assemblies.[48] Interestingly, by modifying guest molecules or cyclodextrins themselves with different metal-coordination sites, scientists can easily construct water-soluble metallosupramolecular polymers by coordination-driven self-assembly.

By successful combination of host–guest and metal-ligand interactions, Liu and co-workers developed a polypseudorotaxane.[49] As shown in Fig. 12, supramolecular assembly **29** from *β*-CD and 4,4'-dipyridine **28** was firstly obtained, as evidenced by its head-to-head channel structure in the solid state. Then, Ni^{2+} was introduced as a linker to deliver a metal-coordinated supramolecular polypseudorotaxane, which was fully confirmed by ^1H NMR and infrared spectra (IR). The induced circular dichroism (ICD) spectra of the inclusion complex and polypseudorotaxane revealed different photophysical behaviors which might be caused by different binding modes of **28** with *β*-CD in different assemblies. The thermal stabilities of **28** and **29** measured by thermogravimetric (TG) experiments and differential thermal analysis (DTA) demonstrated that the coordination of Ni^{2+} ions stabilized the molecular aggregation of **29**. Scanning tunneling microscopy (STM) and transmission electron microscopy (TEM) provided the most convincing evidence for the formation of supramolecular aggregates. The current investigation might serve as guidance for the development of electroactive organic materials that contain CDs and coordination linkages.

The same group had extended their work by preparing a series of inclusion complexes of *α*-, *β*-, and *γ*-CDs with **28** and comprehensively investigated their assembly behaviors of resulting linear polypseudorotaxanes through the coordination linkage of metal cations in both solution and the solid state.[50] The combination of various characterization methods manifested that the size of the CD cavity could not only determine the complexation stoichiometry between the CD ring and **28** but also have a big influence on the morphology of the resultant polypseudorotaxanes. The approach using simple CD and metal cations to construct nanometer-scaled functional assemblies furnished an easy way for designing molecular devices and molecular machines.

Liu and co-workers have also reported the synthesis of novel nanosized bis(polypseudorotaxane)s by possessing the bridged bis(*β*-cyclodextrin)s **30** with multiple coordinated metal centers, in which *β*-CD acted as the host, amino-terminated polypropylene glycol (PPG) as the guest, and nickel(II) complexes as templating moieties.[51] The two PPG chains were separately threaded into the cavities of metallo-bridged bis(*β*-CD)s forming the double-strand structures, and they also played a stabilizing role in the aggregation process (Fig. 13). Fluorometric titrations were performed in a mixture of acetonitrile/water to calculate the effective binding constants and to gain insight into the molecular assembly behavior of **31** with amino-terminated PPG from the thermodynamic point of view. The results manifested that the assembly process was absolutely driven by favorable entropic contributions accompanying a large positive enthalpic change. This work provided a simple way to understand the mechanism of molecular self-assembly and control the aggregation behavior of CDs. Following this work, they successfully converted the preorganized bis(polypseudorotaxane) (~20 nm long) to a lengthened bis(molecular tube) (~200 nm long) through the intramolecular and intermolecular joining of ~10 discrete bis(polypseudorotaxane) units and the subsequent removal of the polymer templates.[52] This bis(molecular tube) can efficiently capture C_{60} within the holes formed by adjacent metallobridged bis(*β*-cyclodextrin) units, which might be further used to selectively recognize organic/inorganic/biological substrates.

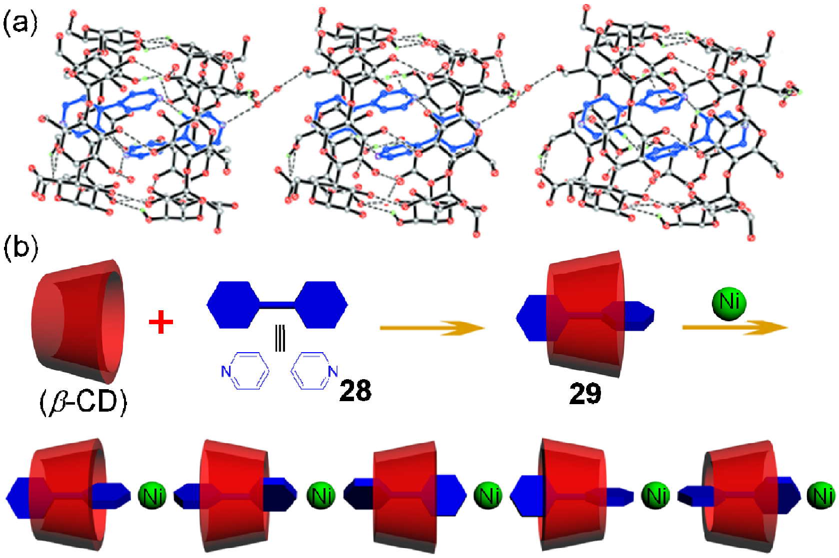

Fig. 12 (a) X-ray crystal structure showing the head-to-head channel structure of **29**. (b) Cartoon representation of the formation of *β*-CD-based metallosupramolecular polymers (reproduced with permission of John Wiley & Sons, Inc. from ref. 49).

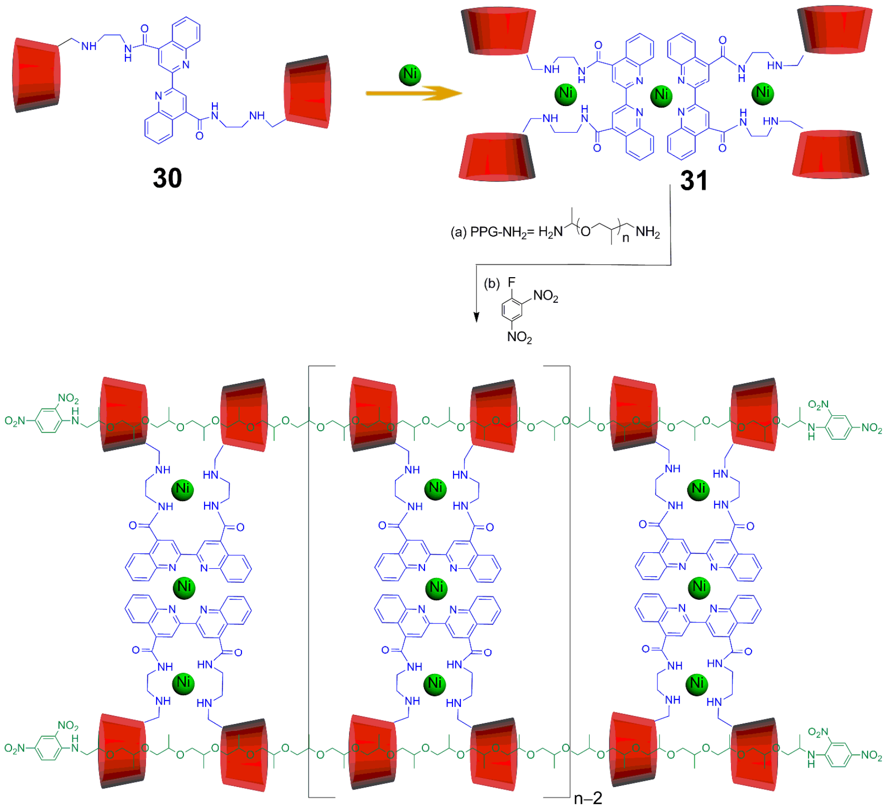

Fig. 13 Cartoon representation of the formation of bis(polypseudorotaxane)s by multiple metallo-bridged *α*-cyclodextrins based on compound **30**.

Another supramolecular polymerization based on orthogonal self-assembly of CD-based host–guest chemistry and metal-coordination was contributed by Tian and co-workers.[53] An active ligand **34** modified with 4,4'-bipyridine moiety at the 6-position of the *β*-CD was prepared. This ligand could coordinate with ethylenediamine palladium(II) nitrate **33** which was confirmed to be a strong and quantitative didentate acceptor for pyridine derivatives in water. Also, a rod-like guest compound **32** containing two azobenzene groups in the two ends linked by viologen units was designed and prepared. The azobenzene motif is able to be well encapsulated by *β*-CD *via* hydrophobic host–guest interaction. Based on these two kinds of orthogonal recognition motifs, supramolecular polymers could form *via* three different ways. As shown in Fig. 14, one route for constructing the polypseudorotaxane was to create an intermediate complex $\mathbf{34_2{\supset}32}$ followed by metal-ligand coordination with **33**. Then changing the self-assembly sequence also afforded the desired polymer. Similar to the case of that prepared by the stepwise fashion, as expected, the well-controlled precise structure of the polypseudorotaxane could be still kept *via* a one-pot route by mixing **32**, **33**, and **34** together. What is more, the introduction of host–guest interaction between azobenzenyl moieties and *β*-CD rings to the main-chain endowed this system with photoresponsive assembly/disassembly behaviors as evidenced by the obvious specific viscosity change. This work provides a synthetic methodology for intelligent design and construction of novel stimuli responsive supramolecular polymers.

Through the coordination polymerization of a Ru(II) porphyrin with an insulated bridging ligand, a one-dimensional transition metal-containing molecular wire with desirable properties for molecular electronics materials was designed and prepared.[54] This molecular wire combined the advantages of organic insulated molecular wires (IMWs) with those of transition metal complexes. The quantitative self-inclusion of precursor **35** resulted in the formation of the inclusion complex **36**, which further reacted with *p*-iodopyridine *via* Sonogashira coupling to afford **37** containing pyridyl coordinating sites at both ends (Fig. 15). A fixed [3]pseudorotaxane structure in the solid state was used as a model to illustrate that **37** possessed the desirable properties for wiring materials. By UV irradiating the mixture of **37** and Ru(II) carbonyl porphyrin **38**, a one-dimensional metal-containing insulated molecular wire was formed *in situ*. Just as expected, this wire displayed not only rigidity, linearity, and structural stability, but also high intramolecular charge mobility. More interestingly, this coordination polymer could undergo the interconversion between monomer and polymer under specific conditions, such as CO or UV irradiation. Such processabilities derived from the unique reversible nature of the coordination bond is not feasible for the conventional covalently bonded molecular wires. These results indicated that metal-containing insulated molecular wires had wide potential for applications in molecular electronics.

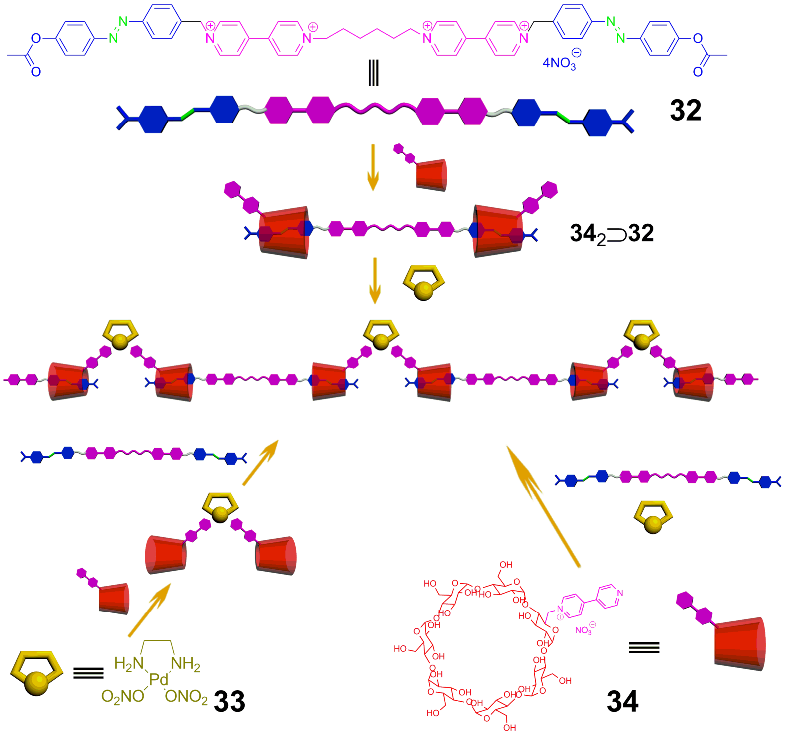

Fig. 14 Cartoon representation of the stepwise and one-pot construction processes with three different self-assembly pathways for the functional polypseudorotaxane based on compounds **32**–**34**.

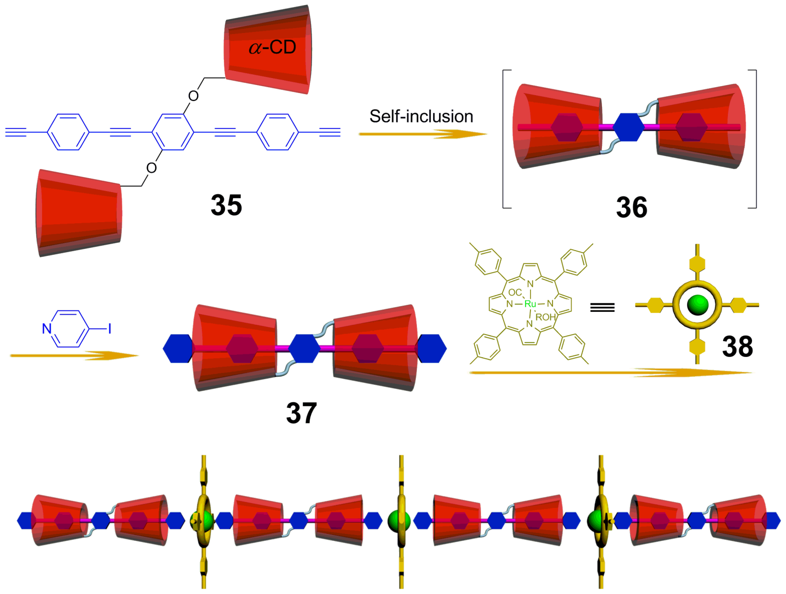

Fig. 15 Cartoon representation of the formation of a polymeric insulated molecular wire *via* orthogonal self-assembly based on compounds **37** and **38**.

4. Supramolecular polymers constructed by orthogonal metal-coordination and cucurbituril-based host–guest motifs

Cucurbit[*n*]urils (CB[*n*], *n* = 5–8, 10) are macrocyclic oligomers comprising six or more glycoluril units. The structural features of CB[*n*]s are the hydrophobic cavity and the polar carbonyl groups surrounding the portals. The supramolecular chemistry of CB[*n*]s has captured wide attention of the scientific community. During the last two decades, a large variety of stimuli-responsive self-assemblies with interesting properties have been constructed based on the unique host–guest recognition behaviors.^{55} As a representative, CB[8] displays remarkable binding affinity towards positively charged and relatively large guests. Kim and co-workers have reported that CB[8] can form stable 1:1:1 ternary complexes with paraquat and 2,6-dihydroxynaphthalene, which resulted in enhanced charge-transfer interaction within the assembly. The unique binding features make CB[*n*]-based host–guest chemistry a good platform for the construction of supramolecular polymers by elegant combination with metal-coordination.

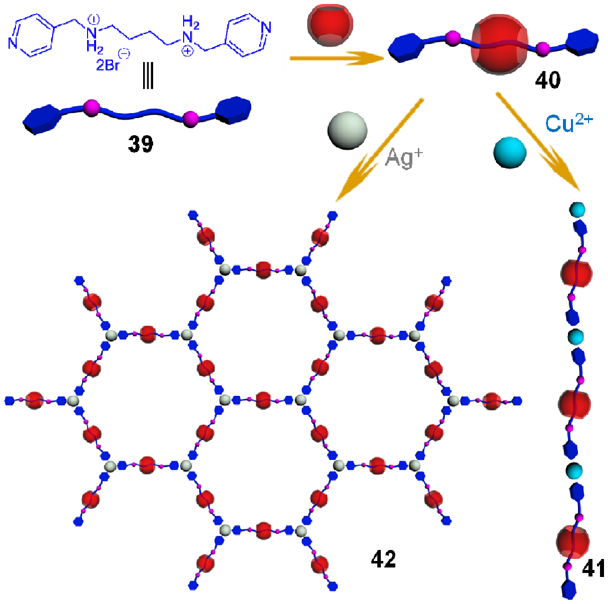

Fig. 16 Cartoon representation of the formation of 1D and 2D coordination polymers based on CB[6] and compound **39**.

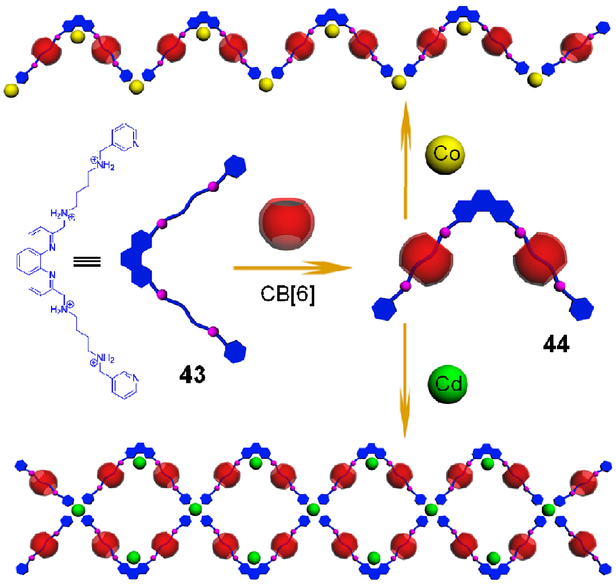

Fig. 17 Cartoon representation of the formation of a double-chained one-dimensional polyrotaxane and a zigzag-shaped one-dimensional polyrotaxane.

By utilizing the principles of host–guest chemistry and coordination chemistry, Kim and co-workers presented a novel one-step approach to synthesize 1D polyrotaxanes with high structural regularities.[56] A pseudorotaxane **40** containing CB[6] as a "bead" and spermine **39** as a "string" by taking advantage of the strong binding ability of the cucurbituril to aliphatic diammonium ions was first prepared. The end functional pyridine groups of the pseudorotaxane could coordinate to Cu^{2+} to form a coordination polymer **41** which was confirmed by its X-ray crystal structure (Fig. 16). This is the first coordination polymer containing a cyclic component in each repeating unit and the first one to be structurally evidenced by single-crystal X-ray crystallography. However, when $AgNO_3$ was added into a solution of the pseudorotaxane, an unprecedented polycatenated 2D polyrotaxane net **42** formed, in which cyclic CB[6]s were threaded onto 2D coordination polymer networks that were in turn fully interlocked with themselves (Fig. 16).[57] By using carboxylate and cyano as the terminal groups and binuclear lanthanide metal ions as the linkers which have larger ionic radii and higher coordination numbers than transition metal ions, the same group have also obtained a 3D polyrotaxane network.[58] Extending this orthgonal approach, they reported a double-chained one-dimensional polyrotaxane and a zigzag-shaped 1D polyrotaxane assembled from L-shaped pseudorotaxane **44** and metal ions Cd^{2+} and Co^{2+}, respectively (Fig. 17).[59] In conclusion, topologically intriguing supramolecular species can be orthogonally assembled from carefully designed CB-based host–guest interactions and properly chosen metal-ligand interactions.

The ability of CB[8] to bind two guests simultaneously has been widely utilized for the construction of supramolecular assemblies. The combination of this ability with coordination-driven self-assembly will undoubtedly promote the formation of metallosupramolecular polymers. For example, Zhang and co-workers reported a linear cucurbit[8]uril-based supramolecular polymer in aqueous solution by employing cucurbit[8]uril-based host–guest interaction and tpy-Fe coordination as the driving forces.[60] They synthesized a heteroditopic molecule **45**, consisting of a naphthalene moiety and a tpy moiety (Fig. 18). The tpy moiety could bind with the metal ion Fe^{2+} to deliver a monomer **46** with two naphthalene moieties at the head and tail. An isothermal titration calorimetry (ITC) experiment indicated the CB[8]-naphthalene host–guest interaction is strong enough for the formation of supramolecular polymers. More importantly, the introduction of tpy-Fe linker could not only remarkably enhance the solubility of monomers but also suppress cyclization, thus facilitating efficient supramolecular polymerization. AFM-based single-molecule force spectroscopy was employed to convince the formation of supramolecular polymers. They could also control the supramolecular polymerization by tuning the molar ratio of **46** and CB[8]. This supramolecular polymerization promoted by metal-coordination provides a new approach to construct water-soluble polymeric materials based on CB[8].

5. Supramolecular polymers constructed by orthogonal metal-coordination and pillararene-based host–guest motifs

Pillar[*n*]arenes, a new class of macrocyclic hosts with symmetrical pillar architectures and rigid electron-donating cavities, have stimulated the development of supramolecular chemistry.[61–64] Due to their intrinsic characteristics, not only cationic molecules but also neutral guests can be used to investigate pillararene-based host–guest complexation. By taking advantage of these hosts, we can functionalize pillararenes and guests to deliver the expected supramolecular polymers based on orthogonal coordination-driven self-assembly and pillararene-based host–guest recognition motifs. Based on an amino-modified copillar[5]arene [*c*2]daisy chain with tpy stoppers, we prepared a solvent driven muscle-like metallosupramolecular polymer.[65] Firstly, we obtained a doubly threaded rotaxane dimer **47** in chloroform, driven by van der Waals forces (mainly dispersion force) between the *exo* cavity parts of the long alkyl groups (Fig. 19). Monomer **47** could change its length continuously instead of step-by-step by changing the polarity of the solvent as monitored by ^{1}H NMR spectroscopy, similar to the molecular spring based on an amino-modified copillar[5]arene previously reported by us.[66] Consequently, the introduction of Fe^{2+} would result in the formation of muscle-like metallosupramolecular polymers based on the individual contraction or extension of each daisy chain

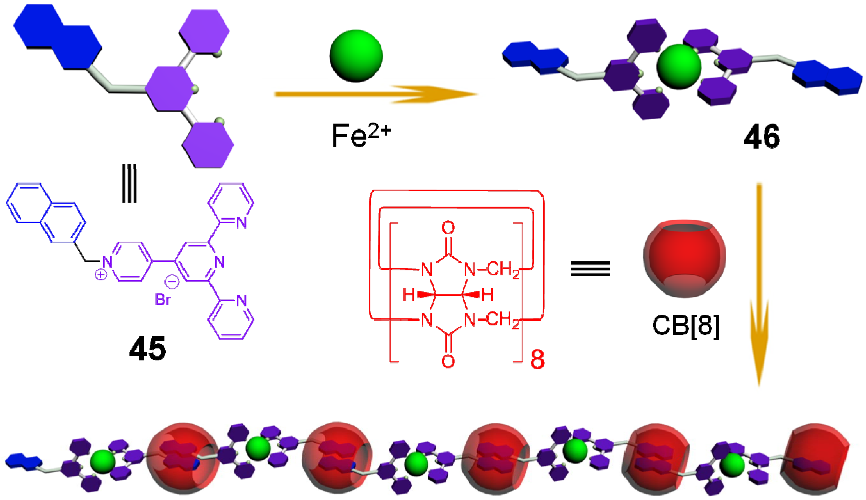

Fig. **18** Cartoon representation of the orthogonal supramolecular polymerization based on CB[8] and metal-coordination.

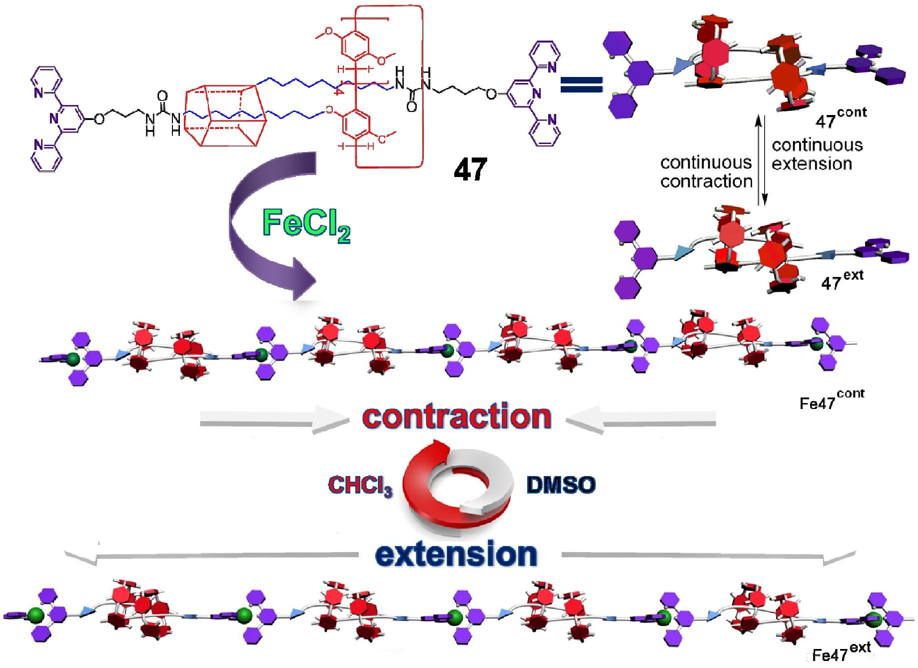

Fig. **19** Cartoon representation of the formation of supramolecular polymers and the corresponding integrated translational motion based on the individual contraction and extension of each daisy chain repeating unit (reproduced with permission of The Royal Society of Chemistry from ref. 65).

repeating unit. UV-vis absorption spectroscopy, dynamic light scattering, TEM, and scanning electron microscopy were performed to understand the self-assembly behavior of the resulting coordination polymer. This work could be considered as a new platform for designing artificial molecular machines to mimic living systems.

Based on discrete hexakis-pillar[5]arene metallacycles, Yang and co-workers elegantly prepared multiple stimuli-responsive cross-linked supramolecular polymers *via* hierarchical self-assembly involving metal–ligand coordination and host–guest recognitions.[67] Specifically, by selecting a suitable monofunctionalized pillar[5]arene, a 120° pillar[5]arene containing dipyridyl precursor **48** was successfully prepared, which was further combined with the corresponding complementary 180° di-Pt(II) acceptors to deliver the desired multi-pillar[5]arene-based hexagonal metallacycle **49** in nearly quantitative yield (Fig. 20). After addition of neutral ditopic dinitrile guest **50**, cross-linked supramolecular polymers formed at high concentration based on host–guest interactions. Furthermore, these supramolecular polymers could transform into stable supramolecular polymer gels at higher concentrations. Considering the dynamic nature of metal-ligand bonds and host–guest interactions, these polymer gels could undergo reversible multiple stimuli-responsive gel–sol phase transitions under different stimuli, such as temperature, halide, and competitive guest, *etc*. These transitions could be illustrated by *in situ* multinuclear NMR and more importantly, macroscopic visualization. This work represents a new method for preparing pillararenes-based “smart” soft materials, which can respond to environment changes in a predictable way, allowing scientists to control their physical properties for applications in materials science.

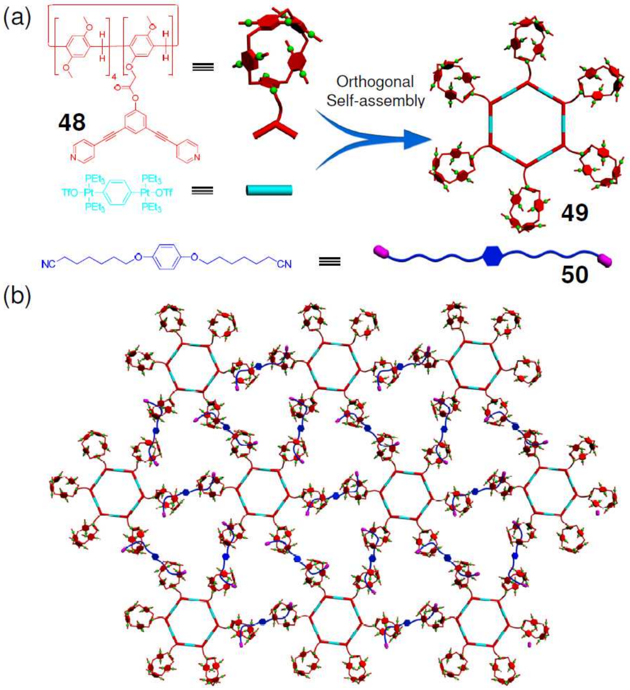

Fig. 20 Cartoon representation of the formation of a cross-linked supramolecular polymeric network from self-assembly of hexagon **49** and complementary guest **50**.

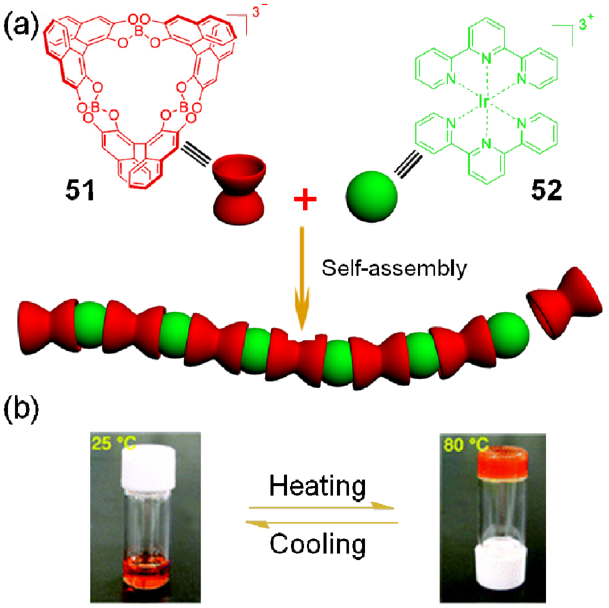

Fig. 21 (a) Cartoon representation of the formation of a supramolecular polymer by iterative clathration of twin-bowl-shaped cyclophone **51** with guest molecule **52**; (b) Illustration of the thermal reversibility of a gel based on this supramolecular polymer (reproduced with permission of American Chemical Society from ref. 68).

6. Supramolecular polymers constructed by orthogonal metal-coordination and non-classical host–guest motifs

As mentioned above, traditional macrocyclic hosts have been widely used for the construction of host–guest compounds, which further self-assemble into more complicated supramolecular polymers *via* metal-coordination. Meanwhile, there were also some elegant examples constructed by non-classical host–guest motifs. By rationally designing the hosts or the guests, scientists could obtain expected structures that exhibit molecular recognition behavior and coordination ability, which is very important for further organizing them into advanced structures, such as metallosupramolecular polymers. For example, Yamaguchi and coworkers designed a supramolecular polymer gel that exhibited the lower critical solution temperature (LCST) based on a back to back twin bowls of D_3-symmetric tri(spiroborate)cyclophanes **51**.[68] Compared with the standard calix[4]arene (*ca.* 12.5 Å × 6 Å), **51** has wider cavities (*ca.* 17 Å × 11 Å) on both sides of the symmetry plane, which facilitated its binding for large guest molecules. ^{1}H NMR and cold spray ionization mass spectrometry (CSI-MS) study revealed that the host **51** could encapsulate the ditopic guest molecule **52** ([Ir(2,2’:6’,2’-terpyridine)$_2$](PF$_6$)$_3$) iteratively in solution *via* π–π stacking and electrostatic interactions, resulting in the formation of supramolecular metallo-copolymers (Fig. 21a). Interestingly, this supramolecular chain system exhibited reversible thermo-responsive gel–sol transition behavior. When a mixture of **51** (10 mM) and **52** (10 mM) in *N,N,NN′,N″,N″*-hexamethylphosphoric triamide was heated above the LCST, which was estimated to be 78.5 °C at this concentration, the phase transition occurred to form an organogel (Fig. 21b). After cooling to ambient temperature, the gel recovered to the solution phase within 15 min.

Royal and coworkers reported a novel class of coordination polymers with redox-responsive phase-transition behaviors based on the multitopic cyclam (1,4,8,11-tetraazacyclotetradecane) bis-tpy platform (CHTT) ligand.[69,70] This ligand contained two chelating tpy terminal units linked through a coordination cyclam macrocycle which allowed the insertion of additional metal ions in the polymeric chains. The metallation of **53** in DMF with $Co(ClO_4)_2$ in a 1:1 molar ratio afforded a red solution, indicating the formation of a $(tpy)_2Co^{2+}$ derivative in which the cyclam unit remained metal-free confirmed by cyclic voltametry (CV) (Fig. 22). Upon addition of another equiv of $Co(ClO_4)_2$ to the previous solution, an additional and irreversible oxidation wave appeared which was attributed to the formation of the cyclam-Co^{2+} unit, leading to the formation of a metallosupramolecular polymer **55** confirmed by viscosity measurements. Stepwise electro-oxidation of the solution made the color change from red to orange-yellow, and then to green, resulting from the oxidation of $(tpy)_2Co^{2+}$ to $(tpy)_2Co^{3+}$ and then cyclam-Co^{2+} to cyclam-Co^{3+}. By reduction of the oxidized green solution, the initial red solution was readily restored. When the metallation of **53** was performed in DMF by addition of two molar equiv of Co^{2+}, red gels were spontaneously formed from the metallosupramolecular polymer at a concentration lower than 1.0 wt%. What is more, by electrolyzing the gel at +1.0 V, the remarkable gel-to-sol transition was observed, along with the red to green color change. By reduction at –0.4 V of the Co^{3+} to Co^{2+} units, the red gel recovered again. This gel-to-sol transition may be due to the introduction of more positive charges in the polymer chains upon oxidation, which possibly affected the solubility of the system and destabilized the gel. This electrochromic responsive system is a promising candidate for the elaboration of heterometallic and organized architectures.

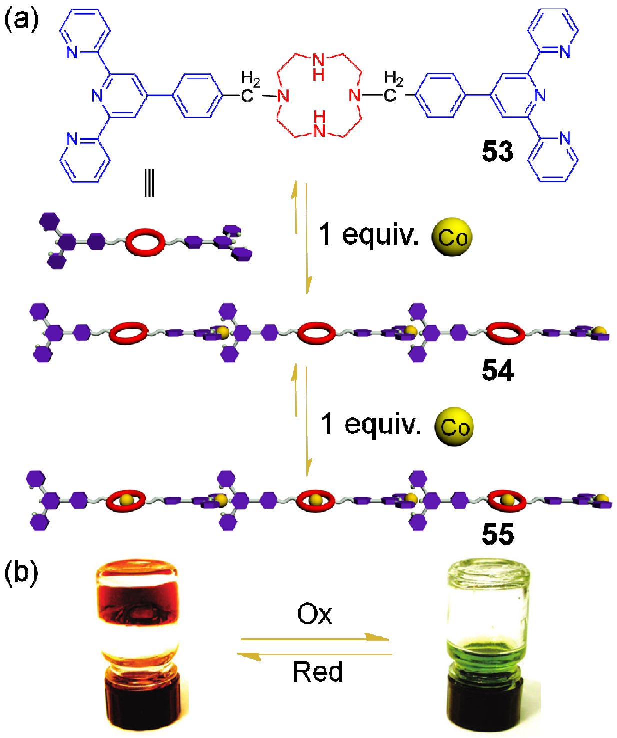

Fig. 22 (a) Cartoon representation of the formation of metallosupramolecular polymers by self-assembly of ligand **53** and $Co(ClO_4)_2$; (b) Illustration of redox-responsiveness of a gel based on metallosupramolecular polymer **55** (reproduced with permission of American Chemical Society from ref. 69).

Weck and coworkers reported a methodology for the synthesis of supramolecular ABC triblock copolymers[71] based on orthogonal host–guest (Hamilton-cyanuric acid interaction) and metal-ligand interactions (Fig. 23).[72] A heterotelechelic poly(norbornene imide) polymer **56** containing two terminal supramolecular motifs was synthesized *via* ring-opening metathesis polymerization (ROMP) through the employment of *N*,*N*′-bis[6-(alkanoylamino)pyridin-2-yl] isophthalamide (often referred to as the Hamilton receptor or Wedge) initiator and a pyridine-based chain-terminator. The authors confirmed that metal coordination did not affect the hydrogen-bonded complex in the telechelic polymers. The target supramolecular triblock copolymers were then prepared in one pot by simply adding complementary cyanuric acid terminated poly(norbornene imide) **57** and carboxylic acid terminated PEO **58** to a solution of the heterotelechelic polymer **56**. This work realized straightforward incorporation of orthogonal recognition motifs at either chain end with the use of functionalized ruthenium initiators and chain terminators, which promoted the development of supramolecular block copolymers.

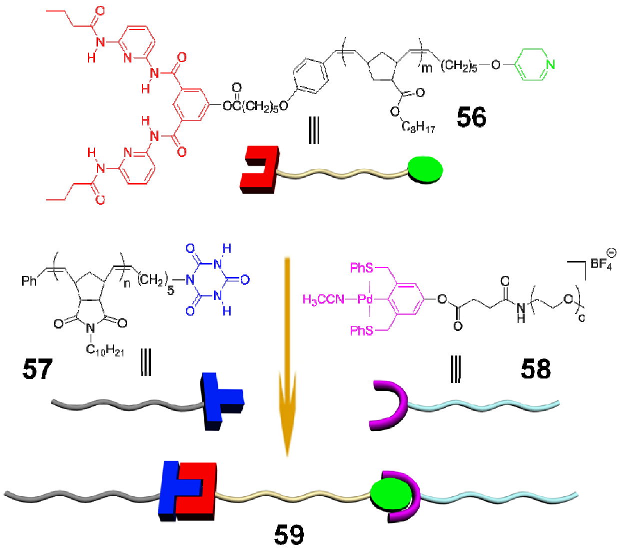

Fig. 23 Cartoon representation of the formation of a supramolecular ABC triblock copolymer **59**.

7. Summary and outlook

The marriage of macrocycle-based host–guest interactions and coordination-driven self-assembly brings many opportunities for the preparation of new multi-functional supramolecular polymeric materials with various responsivenesses. Supramolecular polymers based on host–guest interactions, benefiting from good selectivity, convenient enviro-responsiveness, and highly directional and self-complementary properties of host–guest interactions, are advantageous for the development of materials with unprecedented macroscopic properties. For the metal–ligand coordination polymers, various coordination geometries, strong yet tunable coordination binding ability, as well as magnetic, redox, photophysical, and electrochromic properties from metal ions and ligands, lead to a variety of metallosupramolecular architectures and promising applications in the field of heterocatalysis, electronics, gas storage, *etc*. In this review, we have summarized recent advances in the fabrication and application of supramolecular polymers based on the orthogonal coordination-driven self-assembly and dynamic host–guest chemistry. A series of macrocycles, including traditional macrocyclic hosts involving crown ethers, cyclodextrins, cucurbiturils, and pillararenes, and non-classical host–guest motifs have been used to prepare metallosupramolecular polymers with diverse topological structures by elegantly tailoring the dynamically reversible host–guest and metal–ligand interactions at the most fundamental level. However, the current research in this field is far from sufficient and there are still many uncharted terrains for chemists to explore, and some basic challenges remain to be solved before much more extensive practical applications. With these considerations in mind, we would like to highlight some future directions that may produce pronounced effects in this field. Firstly, most of the functionalities of these kinds of supramolecular polymers derived from the host–guest units, while the unique characteristics of metal ions, such as optical and catalytic properties, are often overlooked. From the perspective of more specific applications, efforts should be devoted to excavating the advantages of metal ions. Secondly, though the responsiveness represents the most obvious characteristic for metallosupramolecular polymers, the chemical/physical/mechanical properties still need to be enhanced by tuning the relationship between these two orthogonal interactions and the structures of the building units for better mimicking the naturally existing polymeric systems or the covalently bonded polymers. Thirdly, developing more biocompatible supramolecular polymers that can be integrated into biological systems is a large unexplored area, from which we can study, comprehend, replicate, and even amplify biological processes. Fourthly, it is urgent to develop metallosupramolecular polymeric materials based on host–guest interactions in the bulk or in the gel state and exam their performance in devices. We envisage that this review will stimulate new ideas and encourage continued endeavors in this emerging area and further put forward the development of supramolecular polymeric materials.

Acknowledgements

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Key learning points

(1) Importance of host−guest and metal-ligand interactions in supramolecular polymeric chemistry.

(2) Superiorities of orthogonal self-assembly.

(3) Design strategies for macrocycle-based metallosupramolecular polymers.

(4) Control of stimuli-responsivenesses and topologies of supramolecular polymers.

(5) Diverse applications and possible future hotspots of macrocycle-based metallosupramolecular polymers.

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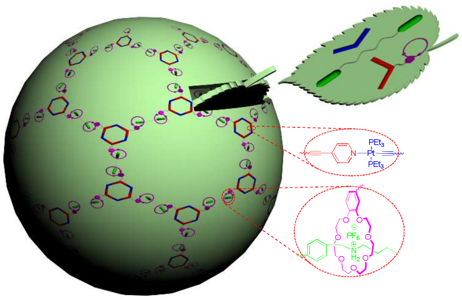

This review describes recent progress in the orthogonal construction of supramolecular polymers based on host−guest and metal-coordination interactions.

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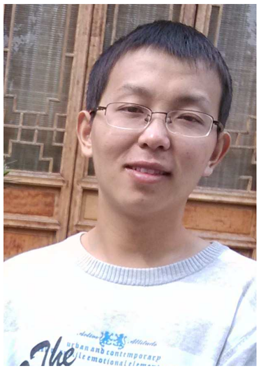

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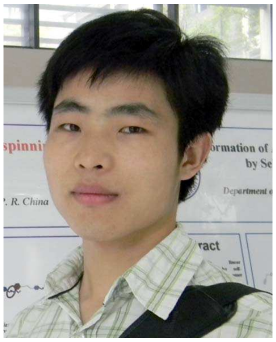

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