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COMMUNICATION

Responsive cross-linked supramolecular polymer network: hierarchical supramolecular polymerization driven by cryptand-based molecular recognition and metal-coordination

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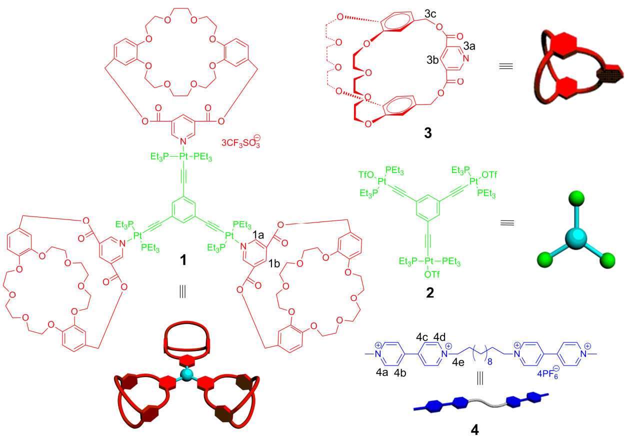
Facile and efficient design and control of the topologies of polymers are important in the field of supramolecular polymers. Different pre-organized supramolecular coordination complexes with secondary recognition moieties in various directions can be easily obtained by just changing the number or orientation of the coordination sites. Herein, a responsive cross-linked supramolecular polymer network was constructed in an orthogonal way by unifying the themes of coordination-driven self-assembly and cryptand-based molecular recognition. Two stepwise self-assembly behaviors as well as a one-pot interaction for the preparation of this advanced supramolecular polymer were addressed. Notably, cation-induced dynamic properties make the resulting polymer promising candidate for application in degradable materials.

Introduction

Scientists are always motivated by the nature to seek new methods to obtain elaborate and functional ordered polymeric analogues by integrating various permanent, irreversible bonds or non-covalent physical interactions. Supramolecular polymers, the combination of supramolecular chemistry and polymeric science, are held together through reversible noncovalent interactions such as hydrogen bonding,[1] host−guest interaction,[2] π−π interaction,[3] and metal coordination.[4] We have witnessed their superiority in recent years for their characteristics of stimuli-responsiveness, self-healing, and degradability.[5] As we know, supramolecular polymers with various chain topologies such as linear, cross-linked, star-type, and dendronized, have been extensively studied.[6] However, it is no easy matter to realize the topological conversion of supramolecular polymers. Therefore, the discovery of facile and efficient methods to control the topologies of polymers is important in the field of supramolecular polymers.[7]

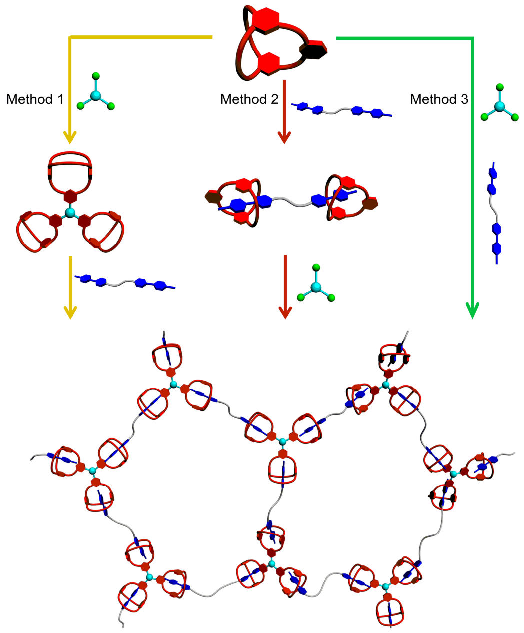
The spontaneous formation of metal–ligand bonding has been proven to be a well-established method to direct the construction of molecular precursors through strategies such as coordination-driven self-assembly.[8] Undoubtedly, the programmed organization of mechanically linked molecular components into unified entities using directional metal–ligand approachs will give the resultant architectures considerable stability and hierarchical complexity. This rational design strategy allows for a combinatorial molecular library consisting of complementary building blocks that allows us to think reasoningly on how best to achieve the geometry of a particular assembly. By carefully combining selected precursors with predefined bite angles and appropriate stoichiometric ratio, discrete supramolecular coordination complexes (SCCs) with secondary recognition moieties in different directions can be obtained.[9] Cryptand has been proven to be much better host for paraquat derivative than the corresponding simple crown ether.[10] Very recently, a AA-BB-type linear supramolecular polymer was constructed by us *via* the orthogonal self-assembly of a bisparaquat derivative and a *cis*-dibenzo-24-crown-8 (DB24C8)-based biscryptand prepared by the directional metal–ligand approach.[11] Herein, by just changing angular orientation of the metal acceptor, we can very easily change the the topology of the supramolecular polymer from linear to cross-linked. Furthermore, this cross-linked supramolecular polymer network (CSPN) showed better material properties than that of the linear supramolecular polymer.

Results and discussion



Scheme 1. Compounds used in this study and their cartoon representations.

In our previous work, we synthesized a novel *cis*-DB24C8-based cryptand (**3**) with its pyridine nitrogen atom outside the third arm based on the consideration of its further self-assembly by metal coordination. The symmetry and number of binding sites of the acceptors guide the shape of the pre-organized assembly. Herein, a mixture of cryptand ligand **3** (15.0 mM) and tri-arm organoplatinum(II) acceptor **2** (5.00 mM) with a 3:1 ratio in CD_2Cl_2 was stirred for 30 min at room temperature to result in the formation of the self-assembled tri-cryptand host **1** (Scheme S1, ESI†). Multinuclear NMR (^{1}H and ^{31}P) analyses of the reaction mixtures demonstrated the formation of desired discrete species (Figs. S3–S4, ESI†). The $^{31}P\{^1H\}$ NMR spectrum of **1**, for example, revealed a single sharp singlet at ~15.57 ppm with concomitant ^{195}Pt satellites (J_{Pt-P} = 2284.6 Hz), consistent with a single phosphorus environment (Fig. S4, ESI†). This peak is shifted upfield relative to that of acceptor **2** by *ca.* 6.40 ppm (Fig. S7, ESI†). In addition, in the ^{1}H NMR spectrum of **1**, the protons of the pyridyl groups (H_{3a} and H_{3b}) showed downfield shifts compared to those of ligand **3** (Fig. S6, ESI†), consistent with coordination of the *N*-atoms to platinum centers. Electrospray ionization time of flight mass spectrometry (ESI-TOF-MS) provided evidence for the formation of tri-cryptand host **1**. In the mass spectrum of **1**, two peaks were found to assign a [3 + 1] assembly. The peak at m/z = 1754.56 corresponding to $[M - 2OTf]^{2+}$ and the peak at m/z = 1120.05 corresponding to $[M - 3OTf]^{3+}$ (Fig. 1). Both of the peaks were isotopically resolved and agreed very well with the calculated theoretical distributions.



Scheme 2. Cartoon representation of the formation of CSPN by hierarchical orthogonal strategies.

We have demonstrated that *cis*-DB24C8-based cryptand **3** can form a stable complex with paraquat, we wonder whether it is possible to construct CSPN using the molecular recognition of host **1** to a homoditopic bisparaquat derivative **4**. The formation of CSPN was first investigated by ^{1}H NMR experiment. The solution of **1** and **4** with a molar ratio of 2:3 in CD_2Cl_2/CD_3CN (1:1, *v*/*v*) was deep-yellow as a result of the charge-transfer interaction between the electron-rich aromatic rings of tri-cryptand **1** and the electron-poor pyridinium rings of bisparaquat **4**, which is good evidence of complexation. ^{1}H NMR spectra recorded at concentrations in the range of 0.500–200 mM shows concentration-dependent nature of the CSPN (Fig. 2). Large chemical shift changes of both the host and guest and the splitting of signals of biparaquat derivative **4** demonstrated that the percentage of complexed species was concentration-dependent, and the formation of supramolecular polymer was favored at high concentration. In addition, all the proton signals became broad at high concentrations, further indicating the formation of high-molecular-weight polymeric species.

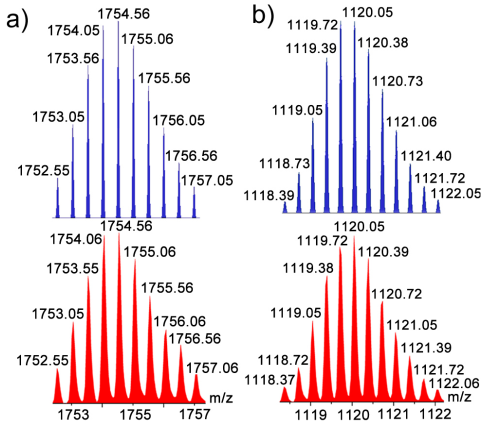


Fig. 1 Experimental (red) and calculated (blue) ESI-TOF-MS spectra of (a) **1** $[M - 2OTf]^{2+}$, and (b) **1** $[M - 3OTf]^{3+}$.

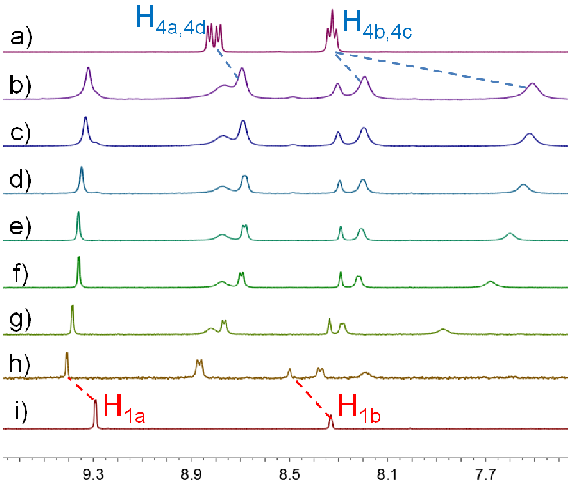


Fig. 2 Partial ^{1}H NMR spectra [500 MHz, CD_3CN/CD_2Cl_2 (1:1, *v*/*v*), 293 K]. (a) **4**; (b–h) solutions of **1** and **4** with 1:1 molar ratio at concentrations of (b) 200, (c) 150, (d) 80.0, (e) 25.0, (f) 6.25, (g) 2.00, and (h) 0.500 mM; (i) **1**.

2D diffusion-ordered ^{1}H NMR spectroscopy (DOSY) was used to probe the dimensions of polydispersed supramolecular aggregates. As the concentration of solution of **1** and **4** with a molar ratio of 2:3 increased from 25.0 to 200 mM, the measured weight average diffusion coefficient *D* decreased from 5.33×10^{-10} to 1.50×10^{-10} m^2s^{-1} (Fig. 3a). The supramolecular entity has narrow dispersities in this concentration range. This result is consistent with the above concentration-dependent ^{1}H NMR result, indicating that concentration exerts a significant influence on the supramolecular polymerization process. Moreover, dynamic light scattering (DLS) measurements were also performed to investigate the size distributions of the polymer at different concentrations. As the concentration increased from 12.5 to 50.0 mM, the average hydrodynamic diameter (D_h) increased from 210 to 1282 nm, further indicating a concentration dependence on CSPN size (Fig. 4a).

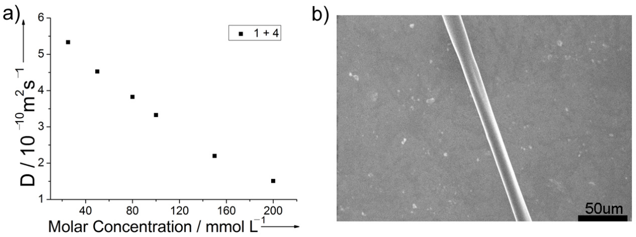


Fig. 3 (a) Concentration dependence of diffusion coefficient D [500 MHz, CD_3CN/CD_2Cl_2 (1:1, *v*/*v*), 298 K)] of CSPN and (b) SEM image of (gold coated) fiber drawn from concentrated solution of CSPN in CH_3CN/CH_2Cl_2 (1:1, *v*/*v*).

Although the polymeric material was sufficiently soluble to allow for the solution-based characterization methods described above, rod-like fibers could be mechanically drawn from high viscosity CH_3CN/CH_2Cl_2 (1:1, *v*/*v*) solutions of CSPN (Fig. 3b). As we all know, fiber formation is a typical feature of polymer chains with high molecular weight. What is more interesting here is that even long macroscopic fibers with several centimeters could easily be drawn from the concentrated solutions (See attached movie, ESI†), while no fibers could be drawn from the individual highly concentrated solutions of monomers **1** and **4**. Through orthogonal cryptand-based host–guest interaction and coordination-driven self-assembly, the chain can spread to generate the desired 3D cross-linked network which shows good polymeric characteristics.

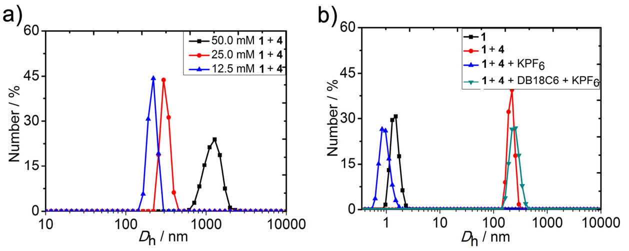


Fig. 4 Size distributions of (a) CSPN at different concentrations and (b) CSPN before and after addition of KPF_6 (c = 12.5 mM).

The nature of DB24C8-based cryptand makes it easy to control the reversible self-assembly process of CSPN by adding or removing K^+ cation. When KPF_6 is added, cryptand **1** can form a more stable complex with K^+, which can cause the disassembly of CSPN. Subsequently, the CSPN can form again when enough DB18C6 is added to trap the added K^+. This reversible process can be demonstrated by the proton NMR experiment (Fig. 5). Upon adding K^+ to the equimolar solutions of **1** and **4**, almost all complexed signals corresponding to $H_{4a–d}$ on **4** restored to their uncomplexed states and the color of the solution changed from yellow to colorless, indicating that the complexation between **1** and bisparaquat salt was essentially quenched (Fig. 5, spectra a and c). However, after addition of DB18C6 (2.00 equiv) to this solution, the complexation between **1** and **4** was recovered; large chemical shift changes and splits of the peaks corresponding to the protons on **4** were observed again (Fig. 5, spectra a, d, and e) and accordingly the yellow color of the solution recovered, representing the reformation of CSPN. DLS further confirmed this reversible conversion. By adding and removing potassium cation, the average D_h of CSPN (12.5 mM) decreased from 220 nm to 0.96 nm and then recovered (Fig. 4b). What is more, DOSY experiments with the addition of K^+ ions further substantiated that the polymers fall apart and then reassembled (Fig. S10, ESI†).

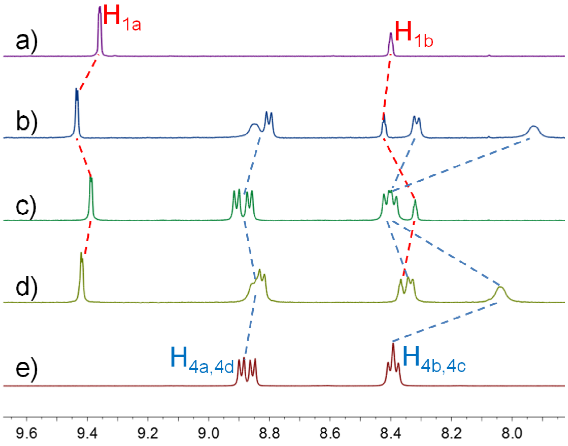


Fig. 5 Partial ^{1}H NMR spectra [400 MHz, CD_3CN/CD_2Cl_2 (1:1, *v*/*v*), 293 K)]: (a) 5.00 mM **1**; (b) 5.00 mM **1** + 5.00 mM **4**; (c) after addition 2.00 equiv of KPF_6 to b; (d) after addition 2.00 equiv of DB18C6 to c; (e) 5.00 mM **4**.

Considering the noninterfering orthogonal nature of organoplatinum(II) coordination-driven self-assembly and cryptand-based host–guest interactions, the CSPN can be also constructed by using another stepwise method by exchanging the self-assembly sequence or a one-pot reaction. The construction of CSPN *via* route 2 underwent another intermediate [3]pseudorotaxane $\mathbf{3}_2\supset\mathbf{4}$ which was obtained by stirring a 2:1 mixture of host **3** and guest **4** in CD_2Cl_2/CD_3CN (1:1, *v*/*v*) (Scheme 2, method 2). Upfield shifts revealed by protons on cross-linker **4** and the splitting of $H_{4b,4c}$ together with the appeared yellow color of the solution demonstrated the complexation between **3** and **4** (Fig. S8, ESI†). Electrospray ionization mass spectrometry (ESI-MS) further confirmed the existence of intermediate $\mathbf{3}_2\supset\mathbf{4}$: *m*/*z* 1039.3 (100%) for $[\mathbf{3}_2\supset\mathbf{4} - 2PF_6]^{2+}$ (Fig. S9, ESI†). Then, 0.667 equiv of **2** was added into the above mixture. The formation of CSPN was evidenced by the same characteristics of multinuclear NMR (^{1}H and ^{31}P). Except for the two stepwise strategies, we also explored the one-pot reaction for examing the fine structure of CSPN. We mixed components **2**, **3**, and **4** at a ratio of 6:3:2 together in CD_2Cl_2/CD_3CN (1:1, *v*/*v*) at room temperature (Scheme 2, method 3). Similar to the case of that prepared by stepwise fashion, the well-controlled superstructure could be also obtained according to its multinuclear NMR (^{1}H and ^{31}P) analyses. Thus, these three methods provide sufficient proof to demonstrate the feasibility and the power of this noninterfering orthogonal strategy.

Conclusions

In summary, it was demonstrated that the topologies of supramolecular polymers could be efficiently controlled by just changing the orientation of platinum(II) acceptor. We first designed and synthesized a *cis*-DB24C8-based cryptand with its pyridine nitrogen atom outside the third arm which can further post-self-assemble into tri-cryptand by metal-coordination with very high efficiency. Upon interacting with a bisparaquat **4**, this tri-arm acceptor was demonstrated to fabricate CSPN at high concentration. With the combination of various techniques, such as ^{1}H NMR, DOSY NMR, DLS, and SEM, this supramolecular polymer was well studied. More importantly, the CSPN showed better material properties than that of linear supramolecular polymer, such as the formation of long, macroscopic fibers from CSPN. In addition, another stepwise strategy and one-pot method also resulted in the formation of CSPN based on the consideration of the spontaneous and orthogonal self-assembly behaviors of metal coordination and host–guest interactions. Assembly/disassembly behaviour with cation responsiveness was also observed in this system. Given the rich combinatorial molecular library consisting of complementary building blocks and the high efficiency of constructing SCCs, this work provides a facile and efficient way to control the topologies and exploit intriguing macroscopic properties of the functional supramolecular assemblies.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Synthetic procedures, characterizations, and other materials. See DOI: 10.1039/b000000x/

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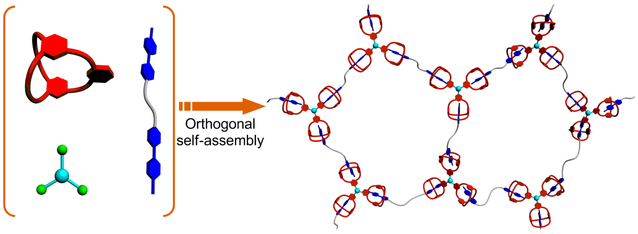

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