Supramolecular Polymers

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Metal Coordination Mediated Reversible Conversion between Linear and Cross-Linked Supramolecular Polymers**

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The topology of a polymer has a significant influence on its properties and functions, both in bulk and in solution. Therefore, the discovery of efficient methods to control polymer topology is very important.[1] The introduction of non-covalent interactions into traditional covalent polymers represents a novel approach for the control of polymer topologies, and has allowed the incorporation of reversible and switchable functionality into different macromolecular architectures.[2] However, this strategy usually requires the integration of specific molecular recognition motifs into polymer chains; such an approach suffers from problems such as the availability of suitable monomers and the poor efficiency of polymerization techniques that are tolerant to functional groups on the polymer. Conversely, supramolecular polymers that are assembled from low molecular weight monomers by non-covalent interactions, such as hydrogen bonding,[3] metal coordination,[4] and host–guest interactions,[5] have demonstrated traditional polymeric properties and are an important resource in the development of stimuli-responsive dynamic materials.[6]

Until now, efforts to control the topology of supramolecular polymers have mainly been concerned with the conversion between the large-sized species and their corresponding monomers/oligomers; comparatively little effort has been devoted to the transformation between supramolecular polymers of different topologies. The desired recognition motifs can be conveniently introduced into the low-molecular-weight-monomers, thus avoiding the problems commonly associated with covalently linked polymer backbones, and thus leading to a more effective method for switching between different architectures. Herein, we present reversible switching between linear and cross-linked supramolecular polymers.

That biological systems utilize multiple-interaction self-assembly to afford hierarchical and multifunctional systems[7] has inspired the development of multiple-code artificial supramolecular analogues.[8] In particular, we have assembled dynamic supramolecular polymers that have linear or cross-linked topologies using bimodal non-covalent recognition motifs, host–guest and metal–ligand interactions. As bis(*meta*-phenylene)-[32]crown-10-based cryptands form complexes with paraquat derivatives much more strongly than bis(*meta*-phenylene)-[32]crown-10 (BMP32C10),[9] the cryptand–paraquat complementary interaction was incorporated into monomer **1** for the efficient construction of its linear supramolecular polymer (Scheme 1). BMP32C10–paraquat-based analogue **2** was also synthesized to compare the effect of the host–guest binding ability on the properties of the resulting supramolecular aggregates.

The role of 1,2,3-triazole as a ligand for coordination with transition metals has been well reported.[10] Recently, Astruc et al. reported that when $[PdCl_2(PhCN)_2]$ (**3**) acts as the metal precursor, palladium(II) complexes could be formed with two *trans* triazole ligands (Scheme 1).[10c] The strategy was successfully utilized here by the introduction of the 1,2,3-triazole group into monomers **1** and **2**. Therefore, a reversible conversion between multiple supramolecular assemblies, such as cyclic oligomers and linear and cross-linked supramolecular polymers, could be triggered by external stimuli, for example, concentration change, temperature change, or metal–coordination (Scheme 1).

Heteroditopic monomers **1** and **2**, which consisted of 1,2,3-triazole groups between the BMP32C10-based host and paraquat guest units, were efficiently synthesized from compounds **4** and **5** using copper(I)-catalyzed 1,3-dipolar click cycloaddition reactions (see the Supporting Information, Scheme S1). Although the presence of flexible aliphatic spacer groups between the host and guest moieties can result in the formation of intramolecular cyclic assemblies at low concentration, we anticipated a relatively low critical polymerization concentration (CPC) for the aggregation of both heteroditopic monomers into supramolecular polymers,[3d] owing to the unrestricted complexation conformations and the avoidance of entropic costs usually encountered with rigid analogues.[5b]

We then carried out host–guest complexation studies of the heteroditopic monomers. Both the UV/Vis absorption

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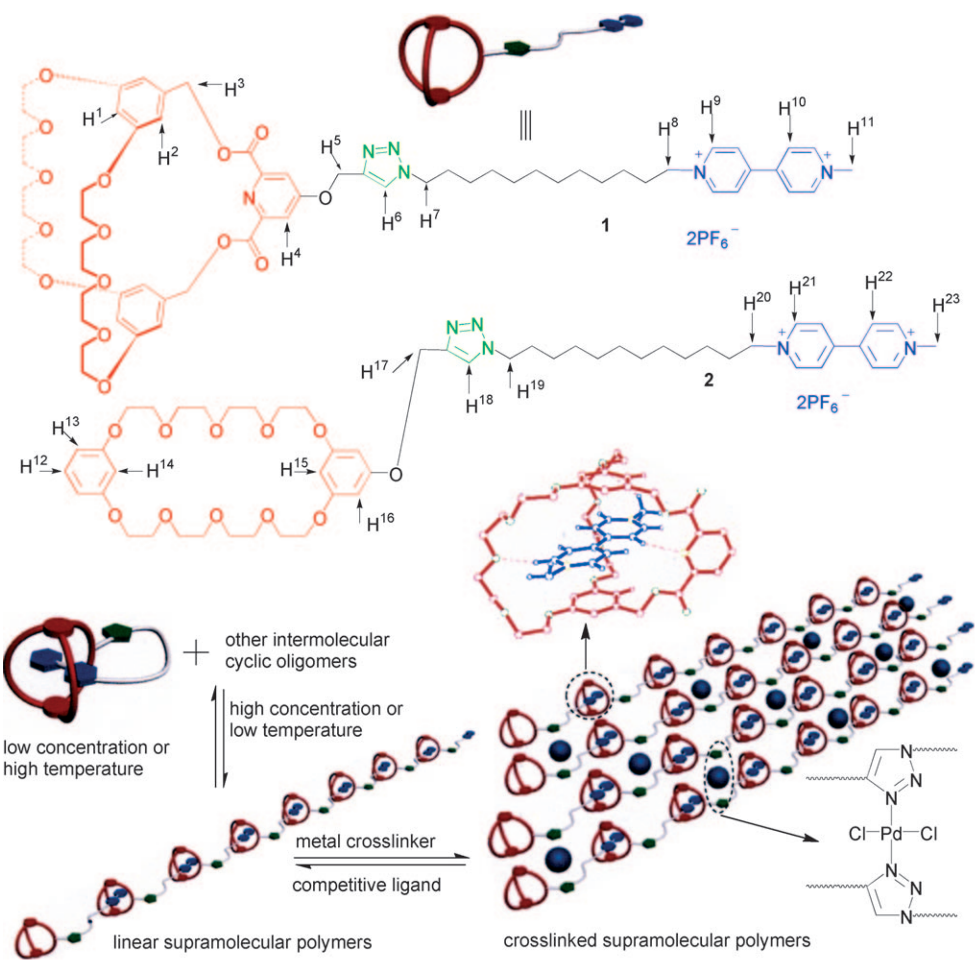

Scheme 1. Bottom: Controlling supramolecular polymer topology from heteroditopic monomer **1**; Middle: Part of a reported cryptand/paraquat complex crystal structure[9d] showing host–guest interactions in the supramolecular polymers.

spectrum (Supporting Information, Figure S1) and the NOESY NMR spectrum (Supporting Information, Figure S2) of **1** suggested that the paraquat group was deeply threaded into the cavity of the cryptand moiety. Furthermore, variable-temperature ^{1}H NMR experiments were also performed (Supporting Information, Figure S3). The ^{1}H NMR spectrum at 348 K showed well-defined sharp signals, indicating that cyclic oligomers dominated. When the solution was gradually cooled to 298 K, the aromatic H^2 protons and pyridinium H^9 protons exhibited upfield shifts ($\Delta\delta = -0.08$ and -0.05 ppm, respectively), and H^4 and H^{10} exhibited downfield shifts ($\Delta\delta = 0.02$ and 0.04 ppm, respectively; Supporting Information Figure S3a). The most significant feature was the shielding of the ethyleneoxy protons, which appeared characteristically upfield at $\delta = 3.40$ ppm ($\Delta\delta = -0.27$ ppm). These shifts confirmed the temperature-dependent aggregration of monomer **1**. Moreover, the energy barrier for the host–guest threading/dethreading process was also calculated ($\Delta G^{\neq} = 16.8$ kcal mol^{-1}),[5d] based on the two pyridinium H^9 protons ($\delta = 8.887$ and 8.876 ppm) that broadened and coalesced at 318 K (Supporting Information, Figure S3b). The relatively high value of $\Delta G^{\neq}$ also suggested the formation of large-size assemblies, which imposed a larger hindrance on the rapidly exchanging host–guest interactions in solution on the ^{1}H NMR timescale.

^{1}H NMR spectroscopy of monomer **1** ([D$_3$]acetonitrile, 400 MHz, 298 K) at concentrations in the range 2.72–203 mm provided further insight into the competition between linear chain extension and cyclic oligomerization of monomer **1** (Figure 1). Compared with the model compounds (Supporting Information, Figure S4), the protons on both the host and guest moieties exhibited unusual behavior; for example, at low concentration, the pyridinium proton H^9 underwent a significant upfield chemical shift ($\Delta\delta = -0.17$ ppm; 2.72 mm versus **4**), and at higher concentration there was an accompanying slight downfield shift. This trend is quite different from those previously reported for supramolecular polymers that are assembled from rigid monomers,[5b] in which the protons shifted continuously as the monomer concentration increased. This phenomenon indicates that the flexible spacer group contributes to the intramolecular

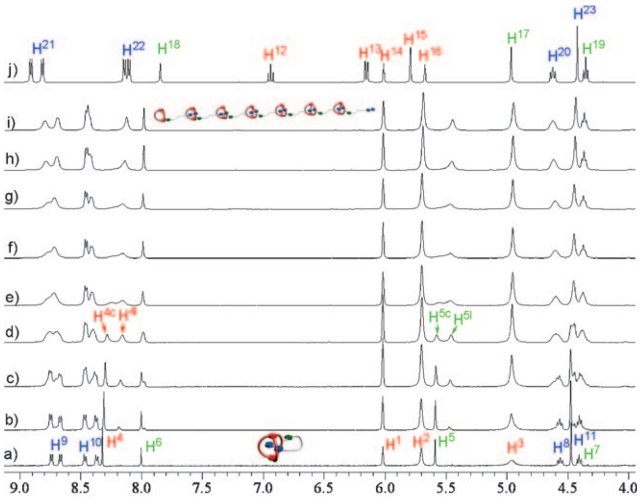

Figure 1. Partial ^{1}H NMR spectra (400 MHz, [D$_3$]acetonitrile, 20 °C) of **1** at different concentrations: a) 2.72, b) 17.4, c) 34.1, d) 61.4, e) 77.4, f) 89.3, g) 96.8, h) 141, i) 203 mm; j) monomer **2** at 203 mm. "c" and "l" denote cyclic and linear species, respectively.

formation of cyclic species at low concentrations. In the ^{1}H NMR spectra at concentrations between 17.4 and 89.3 mM (Figure 1, spectra b–f), the pyridinium H^4 and the benzyl H^5 protons were resolved into two sets of signals, representing the cyclic and linear species, respectively. The main reasons for the peak splitting in these fast-exchange systems were presumably the different chemical environments for the extended linear chains and the cyclic oligomers, and also the relatively high energy barrier for the pseudorotaxane threading/dethreading process (demonstrated in the variable-temperature ^{1}H NMR experiment). When the monomer concentration exceeded 96.8 mM, the signals for the cyclic species were no longer observed, along with a broadening of all signals, which confirmed the formation of high molecular weight aggregates driven by hydrogen bonding, face-to-face π-stacking and charge-transfer interactions between the cryptand–host and paraquat–guest moieties (see the crystal structure in Scheme 1).[9d] Furthermore, the signals in concentrated solutions of monomer **1** were broader than those of monomer **2** under the same conditions (203 mM; Figure 1, spectrum i versus j). This result shows that monomer **1** is more prone to aggregate into higher molecular weight polymer, because the signals are indicative of the reduced mobility of the polymer chains. Therefore, it is evident that both the temperature and monomer concentration had a significant impact on the reversible transformation between the cyclic oligomers and linear supramolecular polymers.

We then investigated the transition from linear to cross-linked supramolecular polymers, which was accomplished by replacing the PhCN ligands of $[PdCl_2(PhCN)_2]$ (**3**) with 1,2,3-trizole moieties to form a disubstituted palladium(II) complex. To investigate the feasibility of this approach, we studied the feed-ratio effect of $[PdCl_2(PhCN)_2]$ on the formation of the cross-linked supramolecular polymer (Figure 2). The initial concentration of monomer **1** was chosen to be 140 mM because the linear species plays a prominent role at this concentration (Figure 2, spectra a–g). Upon progressive addition of $[PdCl_2(PhCN)_2]$, the triazole H^6 proton and the neighboring protons $H^{4,5,7}$ (assigned by NOESY NMR spectroscopy) underwent substantial downfield shifts, indicating preferential complexation between the triazole ligands and the palladium atom (Supporting Information, Figure S7). Increasing the amount of $[PdCl_2(PhCN)_2]$ favored the cross-linking process, which was manifested by a progressive decrease in the original signals, and a gradual strengthening of the newly formed coordinated proton signals (Figure 2). Complete disappearance of the original signals of uncomplexed H^{5-7} was achieved when 0.5 equivalent of $[PdCl_2(PhCN)_2]$ was added to the solution, which is direct evidence for the formation of the triazole-disubstituted palladium(II) complex.

Deconstruction of the supramolecular polymer networks was triggered by the addition of a competitive ligand, PPh_3. The competition reaction for coordination at the metal center, to form the $[Pd(PPh_3)_2Cl_2]$ complex, was visually confirmed by the precipitation of a white solid from the acetonitrile solution. When one equivalent of PPh_3 was added to the solution, the original linear supramolecular species, derived from monomer **1**, was quantitatively restored upon filtration (Figure 2, spectrum i). Therefore, successive addition of the metal cross-linker $[PdCl_2(PhCN)_2]$ and use of the competitive ligand PPh_3 provide a convenient method for the reversible transition between linear and cross-linked supramolecular polymers.

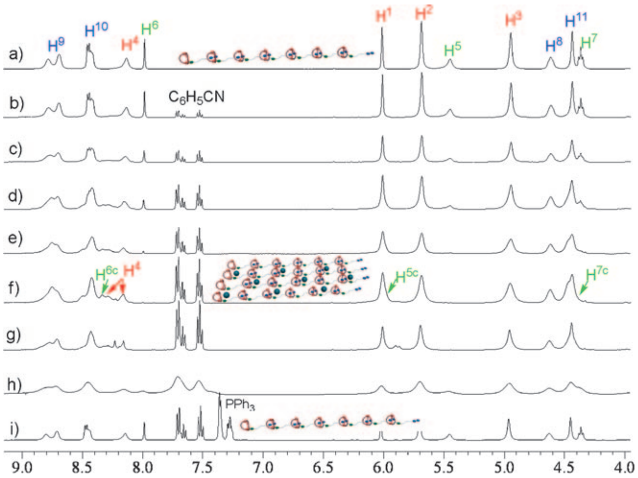

Figure 2. Partial ^{1}H NMR spectrum (400 MHz, $[D_3]$acetonitrile, 20 °C) of **1** at a concentration of 140 mmol L^{-1} with successive addition of $[PdCl_2(C_6H_5CN)_2]$ and PPh_3: a) 0 equiv; b) 0.1 equiv; c) 0.2 equiv; d) 0.3 equiv; e) 0.4 equiv; f) 0.5 equiv; g) 0.8 equiv of $[PdCl_2(C_6H_5CN)_2]$ (**3**); h) 0.8 equiv of **3** and 1.2 equiv of PPh_3; i) 0.8 equiv of **3** and 1.6 equiv of PPh_3, after filtration.

Two-dimensional diffusion-ordered NMR (DOSY) experiments were performed to investigate the self-aggregation of monomer **1** to form linear or cross-linked supramolecular polymers. As the monomer concentration was increased from 10 to 120 mM, the measured weight average diffusion coefficients decreased considerably from 8.58×10^{-9} to $2.57\times10^{-10}\,m^2\,s^{-1}$ (Figure 3), suggesting the concentration dependence of the linear supramolecular polymerization of monomer **1**. When 0.5 equivalent of $[PdCl_2(PhCN)_2]$ was added to a 100 mM solution of monomer **1**, a decrease in the diffusion coefficient from 3.53×10^{-10} to $2.69\times10^{-10}\,m^2\,s^{-1}$ was observed, which indicates an increase in the average aggregation size owing to cross-linking of the linear supramolecular polymer.

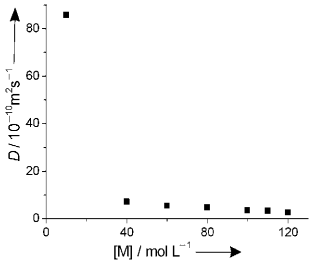

Figure 3. Concentration dependence of diffusion coefficient *D* (500 MHz, $[D_3]$acetonitrile, 20 °C) of **1**.

To further compare the supramolecular aggregations derived from the two heteroditopic monomers **1** and **2**, viscosity measurements were carried out in acetonitrile using a micro-Ubbelohde viscometer. The linear supramolecular polymers, assembled from monomers **1** and **2**, both exhibited viscosity transitions, and were characterized by a change in slope in the double logarithmic plots of specific viscosity versus concentration (Figure 4a). At low concentrations, the slopes of both curves tended to 1, which is characteristic for cyclic oligomers with constant size.[5c] When the concentration exceeded the CPC (approximately 75 mM for both monomers **1** and **2**,[11] in agreement with the ^{1}H NMR results), the weak association between the crown ether host and paraquat guest units afforded a slope of 1.43 for monomer **2**. In contrast, a sharp increase in the viscosity for monomer **1** was observed (slope = 3.54) which is consistent with the theoretically predicted value (3.5–3.7) using the reptation model of a telechelic polymer.[12] Moreover, this value is comparable to the ureidopyrimidone-based self-assembling systems reported by Meijer et al. (slopes of 3–6),[3b,d,h] which implies an extremely strong association between the cryptand host and paraquat guest units in solution.

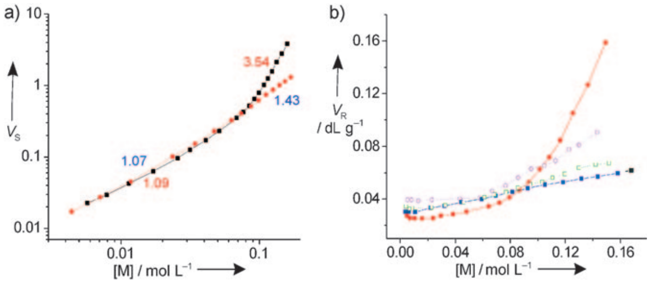

Figure 4. a) Specific viscosity V_S (acetonitrile, 25 °C) of **1** (■), and **2** (●), versus the monomer concentration; (b) reduced viscosity V_R (acetonitrile, 298 K) of **1** (●), **2** (■), 1 equiv of **1** plus 0.5 equiv of $[PdCl_2(C_6H_5CN)_2]$ (○), and 1 equiv of **2** plus 0.5 equiv of $[PdCl_2(C_6H_5CN)_2]$ (□), versus the monomer concentration.

The formation of supramolecular polymer networks was also confirmed using viscosity studies (Figure 4b). The reduced viscosity increased nonlinearly with concentration for the palladium-cross-linked supramolecular polymers, indicating growth of the cross-linked supramolecular polymer chain length with increasing concentration. When the concentration was increased above the CPC, both the linear and cross-linked solutions of monomer **1** had relatively higher viscosity values than those of monomer **2**; this observation further supports the formation of larger polymeric aggregates of **1** owing to the higher association constant between the cryptand and paraquat units. On the other hand, the cross-linked polymers exhibited higher viscosities than their linear counterparts at low concentration, which partially results from the polyelectrolyte effect.[13] It is known that ionic species on polyelectrolyte chains repel each other, thus resulting in the expansion of the polymer coil and consequently an increase in the viscosity in dilute solutions. However, at high concentration, cross-linking of monomer **1** led to a dramatic decrease in the reduced viscosity. This can be attributed to two factors: 1) the extensive cross-linking between the polymer chains, shown by the fact that all of the triazole groups are complexed when 0.5 equivalents of $[PdCl_2(PhCN)_2]$ was added to solutions of monomer **1** (Figure 2), and 2) the influence of metal–ligand interactions on the host–guest aggregation; the linker in monomer **1** becomes more rigid after coordination, which is disadvantageous for the entanglement of the supramolecular polymers.[14] However, for monomer **2**, cross-linking led to a small increase in the reduced viscosity at high concentrations (Figure 4b). One possible reason for this is that the polyelectrolyte effect is more important than the extensive cross-linking and monomer rigidification effects, given the lower association constant between the BMP32C10 and paraquat units.

In conclusion, the topologies of supramolecular polymers can be efficiently controlled by utilization of orthogonal noncovalent recognition motifs, host–guest and metal–ligand interactions. Using a combination of various techniques, such as ^{1}H NMR, variable-temperature ^{1}H NMR, NOESY, UV/Vis spectroscopy, DOSY, and Ubbelohde viscometry, the formation of linear supramolecular polymers was shown to be highly dependent on the temperature, monomer concentration, and the association constants, all of which exert significant influence on the reversible conversion between the cyclic oligomeric and linear supramolecular polymer forms. Moreover, the convenient inclusion of the 1,2,3-trizole unit in the monomer allows for the efficient transition between linear and cross-linked supramolecular polymers, and subsequently reversal by the successive addition of a metal cross-linker $[PdCl_2(PhCN)_2]$ and a competitive ligand PPh_3. This study provides an alternative method for the topological control and stimuli responsiveness of macromolecules, which benefits the construction of smart materials that will be investigated in our future work.

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[11] It is expected that CPC values for the two systems would be nearly the same, as the CPC corresponds to the ratio of equilibrium concentrations of linear versus cyclic species, which are equal. Therefore, because $[\mathrm{L}] = K_{\mathrm{linear}}[\mathrm{M}'][\mathrm{M}]$ and $[\mathrm{C}] = K_{\mathrm{cyclic}}[\mathrm{M}']$, when $[\mathrm{L}]/[\mathrm{C}] = 1$, $[\mathrm{M}]_{\mathrm{CPC}} = K_{\mathrm{cyclic}}/K_{\mathrm{linear}}$, in which [L] is the concentration of the linear species, [M′] is the concentration of the growing species, [M] the concentration of monomer, and [C] is the concentration of cyclic species. The absolute values of K are immaterial in determining $[\mathrm{M}]_{\mathrm{CPC}}$, the CPC value; only the geometry of the system comes into play, and thus the identical linkers lead to essentially identical CPC values. See: N. Yamaguchi, H. W. Gibson, *Chem. Commun.* **1999**, 789 – 790.

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