Supramolecular Polymers

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Supramolecular Polymerization Promoted and Controlled through Self-Sorting**

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Abstract: *A new method in which supramolecular polymerization is promoted and controlled through self-sorting is reported. The bifunctional monomer containing p-phenylene and naphthalene moieties was prepared. Supramolecular polymerization is promoted by selective recognition between the p-phenylene group and cucurbit[7]uril (CB[7]), and 2:1 complexation of the naphthalene groups with cucurbit[8]uril (CB[8]). The process can be controlled by tuning the CB[7] content. This development will enrich the field of supramolecular polymers with important advances towards the realization of molecular-weight and structural control.*

Supramolecular polymers are of great interest because the nature of the noncovalent interactions holding them together imparts dynamic, reversible, and degradable characteristics to these materials.[1] There are two methods that can be used to fabricate supramolecular polymers. One is to design and synthesize bifunctional monomers, which subsequently assemble through directed noncovalent interactions. In this method, supramolecular polymerization can be driven by multiple hydrogen-bonding,[2] metal-coordination,[3] host–guest,[4] and π–π interactions.[5] Another route is to first fabricate supramonomers through noncovalent interactions. These supramonomers then undergo traditional covalent bond-forming polymerization.[6] Although significant advances have taken place, it remains a challenge in the field to realize control over supramolecular polymerization.[7]

Herein, we introduce a new method in which supramolecular polymerization is promoted and controlled through self-sorting. Self-sorting is a self-assembly process in which molecules are endowed with the ability to selectively and specifically form complexes with their own recognition units within a complex mixture.[8] While it has been used successfully to fabricate alternating supramolecular polymers,[9] we employed self-sorting to promote and control the process of supramolecular polymerization. The key point is the design and preparation of a bifunctional monomer with the ability to self-sort, the rigidity of which can be modulated through reversible and dynamic assembly. By modulating the rigidity of the bifunctional monomers, cyclization and dimerization, two factors that are unfavorable for the formation of linear supramolecular polymers, can be suppressed. Hence, linear supramolecular polymers can be readily obtained and control over the molecular weight can be simply adjusted through the rigidity of the structures in an in situ self-sorting process.

To this end, we designed a monomer (Naph-Phen-Naph) that contains one *p*-phenylene moiety in the middle flanked by two naphthalene moieties as end groups (Scheme 1). We envisioned that the *p*-phenylene moiety would selectively bind to cucurbit[7]uril (CB[7]) through a self-sorting process, thus allowing free access to the naphthalene end groups for 2:1 complexation with cucurbit[8]uril (CB[8]). An aqueous equimolar mixture containing Naph-Phen-Naph, CB[7], and CB[8] should result in the formation of a strong host–guest complex between CB[7] and the *p*-phenylene moiety, to give a rigid and bulky 'linker' between the two naphthalene units, thus serving to prohibit monomer cyclization and dimerization and facilitate the linear supramolecular polymerization mediated by 2:1 CB[8] host–guest complexation.

We prepared two model compounds bearing only the *p*-phenylene moiety (Phen) or only the naphthalene moiety (Naph) to confirm a self-sorting process as shown in Scheme 1. As indicated clearly by 1H NMR spectroscopy, Phen (Figure 1 a) and Naph (Figure 1 g) were both capable of forming host-guest complexes with the macrocyclic host molecules CB[7] or CB[8]. Upon host–guest complexation, significant upfield shifts of the aromatic ring protons were observed (Figure 1 b, c, e, f). Interestingly, when Naph, Phen, CB[7], and CB[8] were mixed at a ratio of 2:1:1:1, only the complexation between Naph and CB[8] and the complexation between Phen and CB[7] were observed. The peak at 6.7 ppm in Figure 1 d, which is identical to the peak in Figure 1 e, as well as the absence of a peak at 6.8 ppm (as in Figure 1 f), strongly indicates that the *p*-phenylene group only complexes with CB[7]. CB[7] preferentially binds the *p*-phenylene moiety while CB[8] selectively complexes the naphthalene moieties, thus indicating that self-sorting indeed occurs.

The mechanism behind the self-sorting process was elucidated from extensive isothermal titration calorimetry

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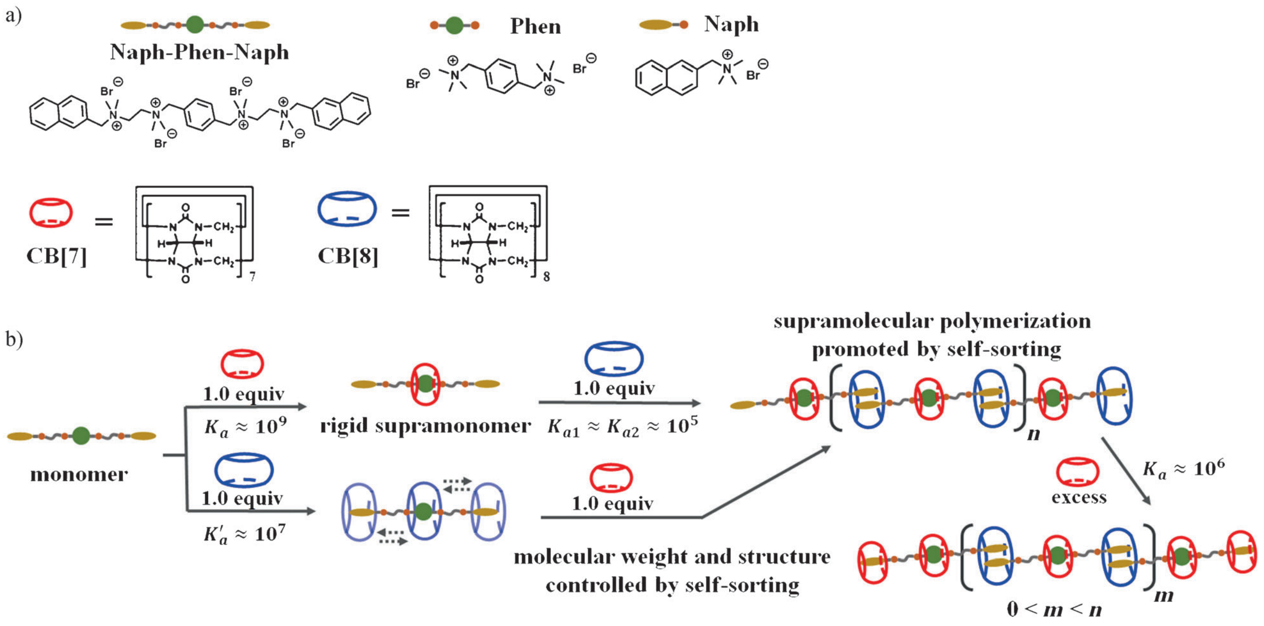

Scheme 1. a) Chemical structures of the designed monomer Naph-Phen-Naph, CB[7], CB[8], and the two model compounds Phen and Naph; b) a schematic diagram of cucurbituril-based supramolecular polymerization promoted by self-sorting upon equimolar mixing of CB[7], CB[8], and Naph-Phen-Naph; and controlled depolymerization of the supramolecular polymers in an excess of CB[7].

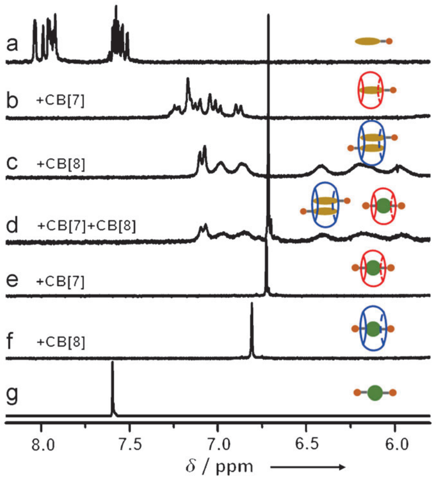

Figure 1. Partial ^{1}H NMR spectra (300 MHz, D_2O, 25.0 °C) of a) Naph (2.0 mм); b) Naph–CB[7] (2.0 mм); c) Naph–0.5CB[8] (2.0 mм); d) a mixture of Naph (2.0 mм), Phen (1.0 mм), CB[7] (1.0 mм), and CB[8] (1.0 mм); e) Phen–CB[7] (1.0 mм); f) Phen–CB[8] (1.0 mм); and g) Phen (1.0 mм).

(ITC) experiments (see Figures S1 and S2 in the Supporting Information). As shown in Scheme 1, the binding constant for Phen–CB[7] was as high as 10^9 м$^{-1}$, while the stepwise binding constants for each of the Naph derivatives in the 2:1 homoternary complex were only around 10^5 м$^{-1}$. Therefore, a plausible mechanism would involve CB[7] strongly binding to the *p*-phenylene moiety on account of its remarkably high binding constant, thus allowing the CB[8] macrocycles easy access to the naphthalene end groups.

We wondered whether the self-sorting process observed in the model compounds could be exploited for supramolecular polymerization. ITC was employed to explore this question. When a solution of monomer Naph-Phen-Naph (0.625 mм) was added dropwise into an sodium acetate buffer solution of CB[7] (0.11 mм), an abrupt change was observed at a molar ratio of 0.33 as shown in the ITC titration curve (Figure 2a). This result suggests that all of the *p*-phenylene moieties and the naphthalene end groups of the Naph-Phen-Naph monomer were complexed by CB[7] at the beginning of the titration when there was an excess of CB[7] around. With continued addition of Naph-Phen-Naph into the CB[7] solution, a second transition appeared in the ITC titration curve (Figure 2a), thus indicating that a 1:1 complex was formed. Taking the NMR complexation data into account, the

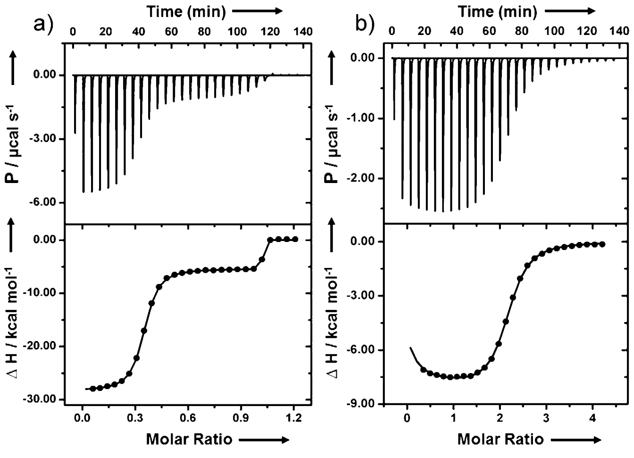

Figure 2. ITC titration data and fitting curves (sodium acetate buffer pH 4.75, 25.0 °C) of a) Naph-Phen-Naph (0.625 mм) titrated into CB[7] (0.11 mм) and b) Naph-Phen-Naph–CB[7] (0.5 mм) titrated into CB[8] (0.05 mм).

substantially higher binding constant of CB[7] with the *p*-phenylene moiety of Naph-Phen-Naph resulted in selective binding. This led to a transition from the 1:3 Naph-Phen-Naph–3CB[7] complex to the 1:1 Naph-Phen-Naph–CB[7] complex. Subsequently, on titrating the 1:1 Naph-Phen-Naph–CB[7] complex (0.5 mM) into a sodium acetate buffer solution of CB[8] (0.05 mM), a typical ITC curve for CB[8] complexation with two naphthalene moieties was obtained (Figure 2b), thus indicating that the self-sorting process indeed occurs as expected in the linear supramolecular polymerization.

The formation of the supramolecular polymer is clearly indicated by diffusion-ordered NMR spectroscopy. As shown in Figure S4, the diffusion coefficient of the supramolecular polymer Naph-Phen-Naph–CB[7]–CB[8] was dramatically reduced to $4.0\times10^{-11}\,\text{m}^2\text{s}^{-1}$ compared with the monomer Naph-Phen-Naph ($2.85\times10^{-10}\,\text{m}^2\text{s}^{-1}$) and individual cucurbiturils (CB[7]: $2.75\times10^{-10}\,\text{m}^2\text{s}^{-1}$, CB[8]: $2.95\times10^{-10}\,\text{m}^2\text{s}^{-1}$). Furthermore, no end-group signals were detected in the ^{1}H NMR spectra of the supramolecular polymers, which indicates that relatively high-molecular-weight polymeric species had been successfully formed (Figure S3).

The formation of the supramolecular polymers was further confirmed by asymmetric flow field flow fractionation (AsF-FFF). AsF-FFF belongs to a family of field flow fractionation techniques that are suitable separation methods for the characterization of macromolecules and particles. Unlike gel-permeation chromatography, the lack of a stationary phase makes AsF-FFF a very mild technique and significantly reduces the possibility of supramolecular polymer degradation as a result of shear forces and enthalpic interactions between the sample and the stationary phase. These advantages make AsF-FFF a powerful technique for characterizing supramolecular assemblies. The AsF-FFF apparatus was connected in-line to ultraviolet, differential refraction, and multi-angle light scattering (MALS) detectors and was demonstrated to be an efficient method for molecular-weight and distribution characterization of supramolecular polymers. Typical elution curves of supramolecular polymers prepared with different molar ratios of CB[7] and Naph-Phen-Naph–CB[8] were obtained with a MALS detector (Figure 3). As the molar ratio approached 1.0, the intensity of the MALS signal increased and the peak also shifted to the right, thus indicating a higher-molecular-weight polymer. The highest molecular weight of the supramolecular polymers was calculated to be $9.7\times10^4\,\text{g}\,\text{mol}^{-1}$ with a polydispersity of 1.5, and the average degree of polymerization was about 28. It should be mentioned that no MALS signal was detected when the molar ratio was lower than 0.5 because the molecular weight of any polymer produced was lower than the detection limit of the instrument.

To understand whether the self-sorting process is indeed critical to realizing controlled supramolecular polymerization, we explored molecular-weight control as a function of monomer rigidity. As expected, the rigidity of the central *p*-phenylene units complexed with CB[7] along the polymeric chain structure is an important factor for promoting linear polymerization. By simply adjusting the amount of the rigid linker present during the self-sorting process, the linear supramolecular polymerization can be controlled. To demonstrate this point, CB[7]-titration experiments were performed and measured by AsF-FFF. When CB[7] was gradually added into the solution of Naph-Phen-Naph–CB[8], more and more of the rigid linker unit consisting of *p*-phenylene complexed with CB[7] was formed, and the molecular weight of the supramolecular polymers increased dramatically (Figure 4). When the ratio of CB[7] reached 1.0 equivalent, the supramolecular polymers with the highest molecular weight were obtained. Therefore, without the aid of self-sorting, the linear supramolecular polymerization would not have been promoted.

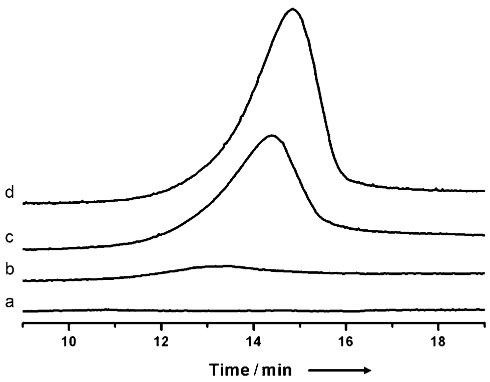

Figure 3. Ratio-dependent AsF-FFF elution curves of a) Naph-Phen-Naph–0.5CB[7]–CB[8]; b) Naph-Phen-Naph–0.6CB[7]–CB[8]; c) Naph-Phen-Naph–0.8CB[7]–CB[8]; d) Naph-Phen-Naph–1.0CB[7]–CB[8] obtained by the MALS detector.

When the ratio of CB[7] exceeds 1.0 equivalent the molecular weight of the supramolecular polymer decreases (Figure 4). This suggests that an excess of CB[7] can also act as a disassembling agent to depolymerize the supramolecular polymers, likely through the competitive binding of naphthalene end groups to CB[8]. As shown in Scheme 1, the binding constant for the naphthalene moiety with CB[7] is higher than the stepwise binding constants for the naphthalene moieties with CB[8], a difference that is responsible for the competitive binding process. The degree of polymerization for supramolecular polymers can thus be tuned to give a range of species from oligomers ($1.0\times10^4\,\text{g}\,\text{mol}^{-1}$) to polymers ($9.7\times10^4\,\text{g}\,\text{mol}^{-1}$).

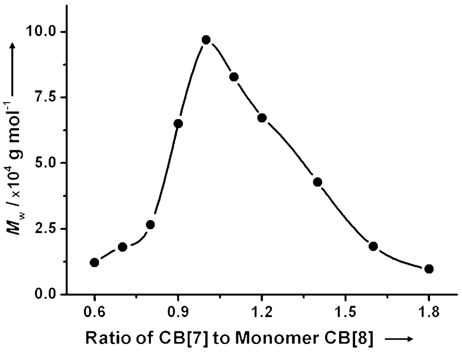

Figure 4. A plot showing the ratio-dependence of the molecular weights of the supramolecular polymers in the CB[7]-titration experiments as measured by AsF-FFF.

In conclusion, we have developed a new method for controlled supramolecular polymerization through self-sorting. A similar methodology could be employed to fabricate supramolecular polymers exhibiting not only linear topology, but also alternating, branched, and hybrid structures. Furthermore, different self-sorting systems based on host–guest chemistry or other reversible chemistry could be utilized to achieve supramolecular polymerization in a controlled manner. It is anticipated that this line of research will enrich the field of supramolecular polymer chemistry with important advances towards the realization of molecular-weight and structural control.

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