Supramolecular Polymers

DOI: 10.1002/anie.201405025

Effective Integrative Supramolecular Polymerization**

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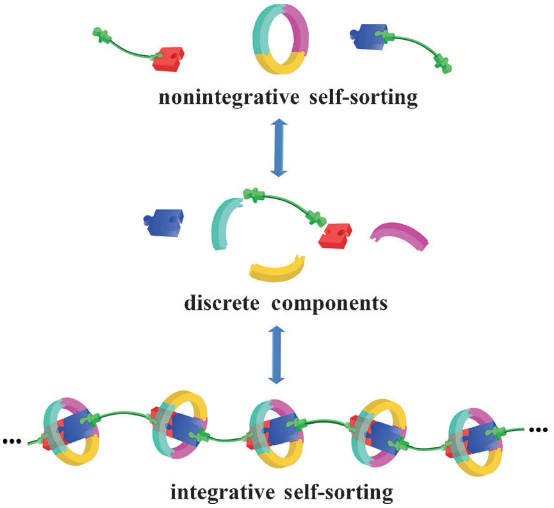
host–guest systems · self-assembly · self-sorting · supramolecular polymers

Supramolecular self-assembly, which is ubiquitous in biological systems, is a vast source of inspiration for chemists.[1] Supramolecular polymers represent a fascinating class of polymer materials with highly directional and ordered structures.[2] In general, they can be readily prepared from monomeric units by reversible noncovalent interactions, such as hydrogen bonding,[3] metal–ligand coordination,[4] donor–acceptor interaction,[5] host–guest recognition,[6] π–π stacking,[7] and so forth. Because of their intriguing structures and stimuli-responsive properties, the investigation of supramolecular polymers has attracted considerable interest and they have been applied in various fields, such as drug delivery systems, self-healing, and shape-memory materials. Although various strategies have been developed for the assembly of supramolecular polymers, it remains an important challenge to organize structure-controllable and stimuli-responsive supramolecular polymers from discrete and complex components. Inspired by the fact that nature successfully accomplishes intricate functions under extremely complex conditions by using the principles of noncovalent self-assembly together with self-sorting phenomena, chemists have developed some controllable supramolecular polymers by taking advantage of self-sorting.

Self-sorting,[8] a concept that is based on a suggestion of Isaacs and Wu,[9] can be defined as high fidelity recognition between molecules and ions within a complex system. It is divided into narcissistic self-sorting (self-recognition) and social self-sorting (self-discrimination) according to the affinity for itself or for others, respectively.[10] Recently, Schalley et al. classified self-sorting further into nonintegrative and integrative self-sorting, in accordance to the result that there is more than one final complex and only one global complex, respectively (Scheme 1).[11] In general, self-sorting processes, which are used to prepare supramolecular polymers, can occur among diverse functional building blocks and can be directed by various noncovalent recognitions, including host–guest interactions.



Scheme 1. Schematic representation of the different types of social self-sorting processes: nonintegrative and integrative.

The host–guest complexation is one of the most thoroughly investigated noncovalent interaction, and has been used to prepare supramolecular polymers through self-sorting processes as a result of their high affinity and selectivity.[12] For example, Huang and co-workers[13] have employed self-sorting organization to prepare a linear supramolecular alternating copolymer in an organic solvent based on the host–guest interactions between two AB-type heteroditopic monomers. On the other hand, complexes of cucurbit[*n*]urils[14] (CB[*n*]s) and cyclodextrins[15] with different guests were extensively studied in aqueous solution. Recently, our group constructed micromorphology-changeable supramolecular aggregates by utilizing the self-sorting process between γ-cyclodextrin, bis-sulfonatocalix[4]arene, and a ditopic monomer in aqueous solution.[15f] With regard to cucurbit[*n*]urils, Isaacs and co-workers have extensively studied the binding ability of CB[*n*] ($n = 6,7,8$) with different guests.[16] The results show a high level of selectivity and affinity between the CB[*n*] family and their guests, which shows their potential in complex self-sorting systems.

Although significant progress has been made, the effective control of the supramolecular polymerization remains a great challenge. Herein, we highlight an effective method for promoting the supramolecular polymerization and controlling the molecular weight by taking advantage of self-

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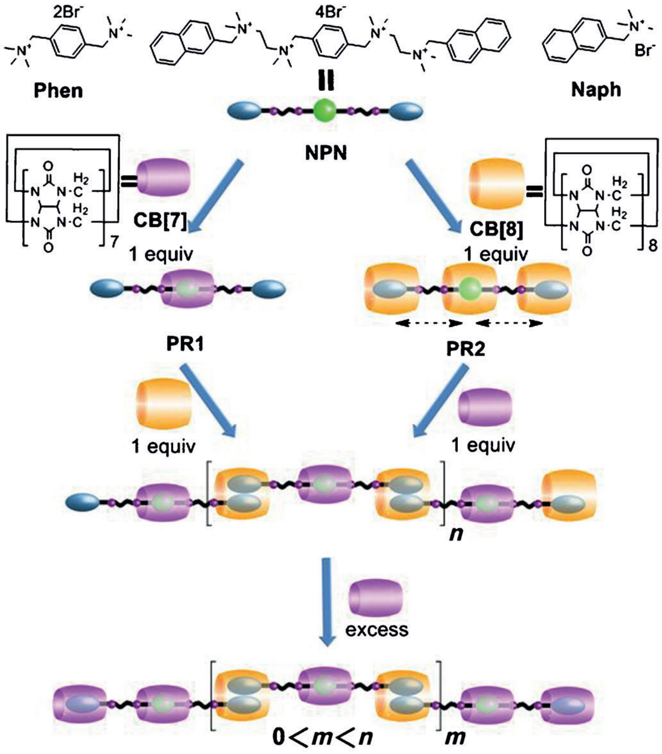
[**] This work was supported by the National Basic Research 973 Program (2011CB808400) and NSFC. Q.Z. thanks Dr. X. Ma and Dr. D.-H. Qu for their helpful discussions.

sorting, which has recently been reported by Scherman, Zhang, and co-workers.[17]

The two primary competitive processes that occur during supramolecular polymerization are cyclization and dimerization, both of which are unfavorable for the formation of a linear polymer with a high degree of polymerization. In their work, Scherman, Zhang, and co-workers synthesized a bifunctional monomer (**NPN**) that contained two naphthalene moieties at the ends, separated by a *p*-phenylene group in the center (Scheme 2). By taking advantage of the host–guest self-sorting between CB[7], CB[8], and **NPN**, a linear supramolecular polymer was readily obtained, and what is most exciting, the molecular weight of this polymer could be simply and effectively adjusted.

By employing ^{1}H NMR spectroscopy, the group demonstrated not only the capability of the model compounds **Phen** and **Naph** to form host–guest complexes with macrocyclic hosts CB[7] and CB[8], but also their different binding abilities. When they were mixed at a molar ratio of [**Phen**]:[**Naph**]:[CB[7]]:[CB[8]] = 1:2:1:1, only (**Phen**)-(CB[7]) and 2(**Naph**)-(CB[8]) complexes were formed. This result strongly indicates that in the mixture, CB[7] preferentially binds to **Phen**, while CB[8] selectively binds two **Naph** molecules into its cavity, showing that a self-sorting process can indeed occur in such a mixture (Scheme 2). Additional and quantitative evidence for the driving force of the self-sorting process was obtained by an extensive isothermal titration calorimetry (ITC) experiment. The binding constant for **Phen**-CB[7] was $10^{9}\,\text{M}^{-1}$, while the stepwise binding constant for each **Naph** molecule with CB[8] in a 2:1 ternary complex was only about $10^{5}\,\text{M}^{-1}$. Hence, the authors deduced that in the mixture, CB[7]s first bind to **Phen**, thus leaving bare **Naph**, which is then easily bound by CB[8]s.



Scheme 2. Schematic representation of the structures of the monomer **NPN**, CB[7], CB[8], and the controlled linear supramolecular polymers obtained through host–guest self-sorting processes.

ITC measurements were also employed to verify that self-sorting processes can occur in supramolecular polymerization. From the titration results, the following dynamic transition processes could be deduced. When **NPN** is mixed with CB[7] in a ratio of 1:1, the high binding constant of the CB[7]-**Phen** complex results in the preferential binding of the macrocycle to the *p*-phenylene moiety of the rod-like monomer **NPN** and the formation of a pseudorotaxane (**PR1**; Scheme 2). This supramonomer[18] **PR1** is more rigid than the monomer **NPN** and can easily form a linear supramolecular polymer, when one equivalent of CB[8] is subsequently added to the solution (Scheme 2, left route). On the other hand, such a self-sorting process could also occur, when one equivalent of CB[8] is added to the **NPN** solution (**PR2** formed, Scheme 2), followed by the addition of one equivalent of CB[7] (Scheme 2, right route). Through this integrative host–guest self-sorting, a linear supramolecular polymer with a highest molecular weight of $9.7\times10^{4}\,\text{g}\,\text{mol}^{-1}$ is obtained. Furthermore, its polydispersity index (PDI) is 1.5, which is relatively low compared with other supramolecular polymer systems.

The most amazing phenomenon appears when an excess of CB[7] is added to the existing supramolecular-polymer solution. That is, as the amount of CB[7] increases from 0.5 to one equivalent (compared with the molar amount of monomers), the molecular weight of the self-sorted supramolecular polymer increases gradually and reaches a maximum (at 1 equivalent of CB[7]); when the amount of CB[7] exceeds one equivalent, the molecular weight begins to decrease again. Thus, an excess of host molecule CB[7] can act as a disassembling agent through the competitive binding of the end groups of monomer **NPN** with CB[8] (Scheme 2). In summary, CB[7] acts as an adjuster of the molecular weight in this self-sorting system, as observed in the transition process.

In addition, Scherman, Zhang, and co-workers made an extremely important advancement in the characterization of supramolecular polymers. As is known, the dynamic nature and reversibility of supramolecular polymers makes their in situ characterization by conventional polymer techniques difficult. The group thus used the asymmetric flow field flow fractionation (abbreviated as AsF-FFF) experiment to confirm the formation of supramolecular polymers and measure their molecular weight. AsF-FFF belongs to the family of field flow fractionation techniques, which are usually employed to separate and characterize polymers, nanoparticles, proteins, colloidal materials, and biomaterials.[19] AsF-FFF is suitable for the characterization of samples with a molar-mass range starting from about $5000\,\text{g}\,\text{mol}^{-1}$ and no upper limit. Because of its mild test conditions, it can provide a more reliable description of the distribution of high molar masses and more reliable values of weight-average and Z-average molecular weights (M_{w} and M_{z}), unaffected by shearing degradation. Therefore, it is highly anticipated that the AsF-FFF technique will find wide use in characterization of supramolecular polymers.

As supramolecular polymerization mechanisms were gradually investigated, a variety of strategies have been developed for the assembly of supramolecular polymers. However, important challenges beyond conventional polymer chemistry, such as the improvement of the mechanical strength and thermodynamic stability, still remain. An example is the controlled polymerization: The synthesis of covalent copolymers with well-defined architectures by using living polymerization has become straightforward and the PDI of the covalent polymer can be controlled in a quite narrow range. However, the controlled supramolecular polymerization is still challenging. Fortunately, some encouraging progress has been made, namely the successful living supramolecular polymerization through a biomimetic approach[20] and the controlled supramolecular polymerization through a host–guest self-sorting process. It should be noted that the supramolecular polymer reported in reference [17] has a PDI value of 1.5, which strictly speaking indicates, that the polymer is not in equilibrium and thus not a real "controlled supramolecular polymer".[21] Although there is room for improvement, the results reported by Scherman, Zhang, and co-workers can still be considered a significant step forward in the field of controlled supramolecular polymerization. The results will inspire the design of other highly ordered stimuli-responsive supramolecular polymers through integrative host–guest self-sorting. Furthermore, we are convinced that this exploratory research will help us to develop other controlled polymerization processes and thus to prepare supramolecular polymers for different applications in materials science.

Received: May 6, 2014
Published online: July 30, 2014

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[21] We would like thank the referees of this Highlight for helpful suggestions and valuable comments.