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A Supramolecular Polymer Blend Containing Two Different Supramolecular Polymers through Self-Sorting Organization of Two Heteroditopic Monomers

Shengyi Dong,^[a] Xuzhou Yan,^[a] Bo Zheng,^[a] Jianzhuang Chen,^[a] Xia Ding,^[b] Yihua Yu,^[b] Donghua Xu,^[c] Mingming Zhang,^[a] and Feihe Huang^{*[a]}

The creation of complex and highly-ordered structures with desired properties and novel functions has been fundamental to supramolecular chemistry and material science, and plays an essential role in high-tech and biorelated fields, such as drug delivery systems, molecular devices and photovoltaic applications.^[1] Nature, as the best example of precise and efficient self-assembly processes, promotes chemists to engage in developing highly-ordered artificial supramolecular assemblies, such as supramolecular polymers through the utilization of noncovalent interactions.^[2] Held together by reversible and highly dimensional interactions, such as host–guest interactions, hydrogen bonds, and metal coordination, supramolecular polymers have become one of the most active frontiers in the past two decades and have received a great deal of attention.^[3] Compared with conventional polymers, supramolecular polymers typically show many dynamic or precisely controllable properties arising from dynamic linking between the constituent monomers and have the ability to respond to their environment as adaptive materials.^[4]

The interest in supramolecular polymers has expanded in recent years, not only for their potential properties as functional materials, but also for their intriguing architectures and topologies that act as a basic aspect of potential applications.^[5] The simple blending of different polymers has produced new polymer blend materials with controllable and unique properties. Polymer blends have been widely studied in polymer chemistry and materials science,^[6,7] and as such supramolecular polymer blends, defined as mixtures of two or more different and mutually exclusive supramolecular

polymers, are an attractive topic.^[3m] There are beautiful examples of miscible polymer blends based on either multiple hydrogen-bonding,^[7a,c,d,h] π -stacking,^[7] carboxy–amine interactions,^[7j] or crown ether functionalized polymers with ammonium- or paraquat-functionalized polymers.^[7b,e–g] However, these blends were composed of high-molecular-weight, conventional covalently bonded polymers instead of noncovalently connected supramolecular polymers.^[7] It is still a big challenge for chemists to design and prepare supramolecular polymer blends completely from low-molecular-weight monomers without any conventional polymeric backbones.

Self-sorting systems, whereby different molecules or molecular aggregates can assemble themselves with corresponding recognition units, display a critical ability to efficiently distinguish between different recognition units even in a complex mixture or in a system with similar recognition units.^[8] For example, Harada et al. found that multiple noncovalent interactions including hydrophobic interactions, π – π stacking and hydrogen-bonding interactions can create a social-self-sorting system cooperatively.^[8] Crown ethers, as the first generation of supramolecular macrocyclic hosts, have been widely used as building blocks to construct various functional assemblies with different guest molecules.^[9] Based on the differences in binding affinity and binding selectivity between two crown ethers, dibenzo[24]crown-8 (DB24C8) and bis(*p*-phenylene)[34]crown-10 (BPP34C10), and their complementary guest moieties, dibenzylammonium salts (DBA) and paraquat derivatives, our group has successfully prepared an alternating supramolecular polymer by means of the self-sorting organization of two AB-type heteroditopic monomers.^[10] It is of considerable interest to investigate whether it is possible to combine a binary system consisting of a pair of supramolecular polymers through a self-sorting process into a supramolecular polymer blend from low-molecular-weight monomers. For example, if a supramolecular polymer gel is blended with a linear supramolecular polymer, the gelation and other properties of the supramolecular polymer gel can be tuned.

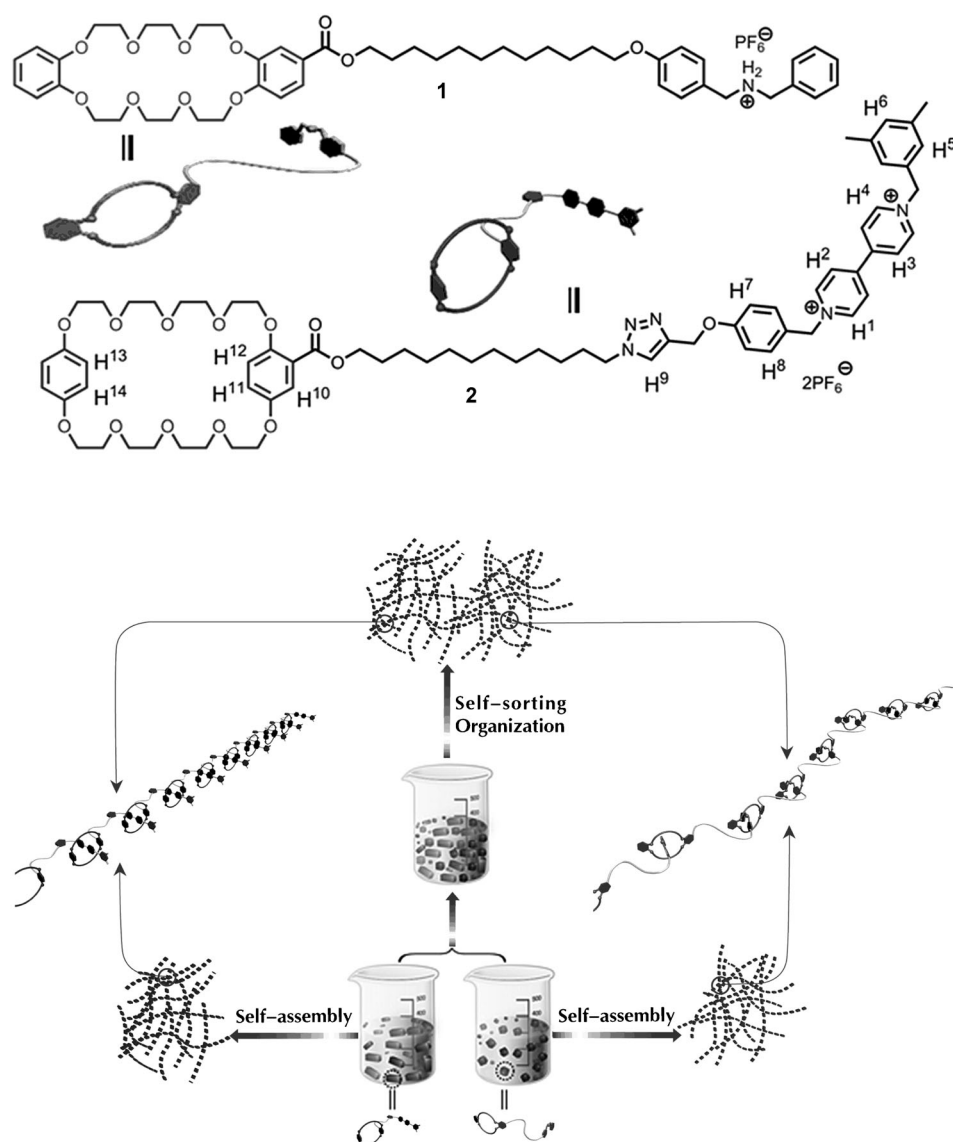
Herein we report on a supramolecular polymer blend, which is formed due to the self-sorting organization of two heteroditopic AB-type monomers, **1** and **2** (Scheme 1). Monomer **1** has a DB24C8 moiety and a DBA group, which are linked together by a long and flexible alkyl chain. Monomer **2** contains a BPP34C10-paraquat-based analogue and has

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Scheme 1. Formation of a supramolecular polymer blend containing two different linear supramolecular polymers **1** and **2** by means of the self-sorting organization of two heteroditopic monomers.

a similar structure to **1**. It is known that the DB24C8 and BPP34C10 moieties form 1:1 threaded structure with DBA and paraquat, respectively.^[11] Our approach is that 1) monomers **1** and **2** form linear supramolecular polymers independently due to the differences in binding affinity and binding selectivity between crown ethers (DB24C8 and BPP34C10) and their complementary guest moieties (DBA and paraquat) and 2) the utility of self-sorting assembly could favor the formation of a blend from a supramolecular polymer gel (constructed from monomer **1**) and a linear supramolecular polymer (built from monomer **2**).

The proton NMR spectrum of an equimolar blend of **1** and **2** revealed that the self-assemblies of monomers **1** and **2** were independent processes and did not interfere with each other, which could be defined as self-sorting organization. As we know, at high concentration, monomer **1** forms

a linear supramolecular polymer gel in CH₃CN,^[9p] and monomer **2** also favors the formation of an extended, high-molecular-weight supramolecular polymeric structure, which was confirmed by concentration-dependent ¹H NMR experiments and viscosity studies (see Figures S12a and S13 in the Supporting Information). When the concentration of the supramolecular polymer blend was progressively increased (an equimolar blend of monomers **1** and **2** with the concentrations from 27 to 100 mM), the two linear supramolecular polymers were gradually and independently formed (Figure 1), and neither new peaks nor evident chemical shift changes were observed compared with their individual NMR spectra.^[5d,8g,9p-r,10] Furthermore,

from the 2D NOESY spectrum of the blend, no correlation for the protons of monomer **1** with the protons of monomer **2** was observed (Figure S10 in the Supporting Information). For example, the pyridinium protons H¹–H⁴ of monomer **2** were only correlated with other protons of monomer **2**, but not correlated with any protons of monomer **1**. Therefore, from these NMR results it was shown that at high concentration, monomers **1** and **2** self-sort to form two different linear supra-

molecular polymers totally depending on their own host-guest interactions.

Viscosity is a direct method for the characterization of polymers. We propose that monomers **1** and **2** form a supramolecular polymer blend in an independent way. Therefore, a double logarithmic plot of specific viscosity versus concentration of an equimolar mixture of monomers **1** and **2** in CH₃CN was obtained to further investigate the supramolecular polymer blend in solution (see Figure S12 in the Supporting Information). The corresponding plots were also obtained for monomers **1**^[9p-r] and **2** alone. In the low-concentration range, the curves of monomers **1** and **2** had slopes of 1.02 and 0.85, respectively. As the concentrations increased, the curves approached slopes of 2.32 and 1.80 for monomers **1** and **2**, respectively. For the supramolecular polymer blend, the curve had a slope of 1.08 in the low concentration range.

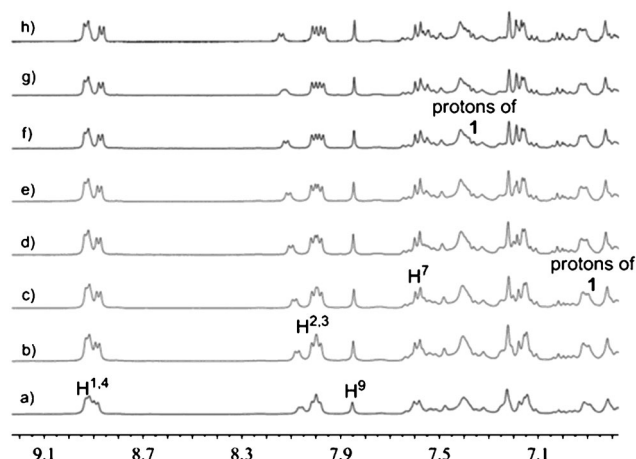


Figure 1. Partial ^1H NMR spectra (400 MHz, $[\text{D}_3]$ acetonitrile, 293 K) of equimolar supramolecular polymer blends from monomers **1** and **2** with each monomer at a) 100, b) 80, c) 67, d) 57, e) 50, f) 40, g) 33, and h) 27 mM.

This linear relationship indicated the presence of non-interacting assemblies of a constant size, which means that monomers **1** and **2** mainly formed low-molecular-weight cyclic oligomers in the blend at low concentration. As the concentration of the blend increased above the critical supramolecular polymerization concentration (about 100 mM), an exponential relationship (slope = 2.36) was observed. This slope value was close to that observed for monomer **1** (slope = 2.32), but higher than that observed for monomer **2** (slope = 1.80), indicating that both of monomers **1** and **2** form high-molecular-weight linear supramolecular polymers at high concentration. These specific viscosity data showed that the viscosity of the supramolecular polymer blend was derived mostly from the supramolecular polymer with a higher viscosity, that is, which was formed from monomer **1**. It was also demonstrated that in this supramolecular polymer blend, due to the self-sorting behavior, the self-assemblies of monomers **1** and **2** were two orthogonal processes.

Monomer **1** forms a supramolecular polymer gel; thus, by adjusting the molar ratio of monomers **1** and **2** during the preparation of the supramolecular polymer blend in CH_3CN , the gelation process can be manipulated to control a range of gel properties, such as the gelation time, color, transparency, morphology, and gel-sol transition. Five supramolecular polymer blends with different molar ratios of the two monomers were prepared for the concentration-dependent gelation test (Figure 2). By progressively increasing the molar ratio of monomers **1/2** from 1:9 to 9:1 in the blend, while their total molar concentration was kept constant at 60 mM, the samples transformed from a dark red homogeneous solution to a mixture of solution and gel, and finally to a reddish gel. Gelation took place when the concentration of monomer **1** was above the critical gel concentration and this gelation process was not interfered with by the addition of monomer **2**. When the molar percentage of monomer **1** was about 50%, the blend was a heterogeneous mixture

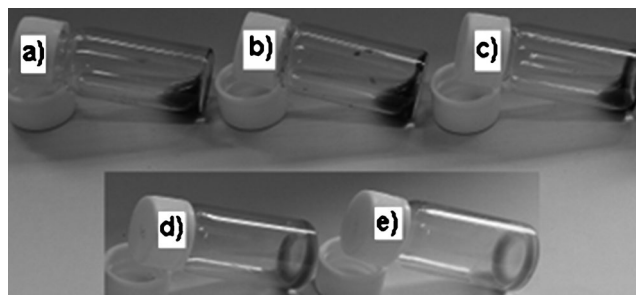


Figure 2. Supramolecular polymer blends with different molar ratios of two monomers (**1/2**): a) 1:9, b) 3:7, c) 5:5, d) 7:3, e) 9:1. The total molar concentration of **1** and **2** was kept as a constant at 60 mM. These samples were prepared from the corresponding supramolecular polymer blend solutions by cooling down to 278 K and then warming to 298 K.

containing both solution and gel phases. We propose that the self-sorting organization leads to the formation of a mixture of solution and gel.^[9p] Evidence for such a superstructure was derived from UV/Vis absorption spectroscopy. The absorption spectrum of the sol phase showed a strong band around 420 nm, which is characteristic for the charge-transfer interactions between the BPP34C10 host and paraquat guest units of monomer **2**.^[7i,8g] In contrast, no evident absorbance was observed for the gel phase from 350 to 500 nm, which meant that the gel was mostly constructed from monomer **1**. By comparison, we confirmed the self-sorting organization of these two host-guest recognition pairs. From the UV/Vis absorption spectra and the gelation test, it was clear that gelator **1** and monomer **2** can independently self-assemble to their own aggregates in the blend, with monomer **1** controlling the gel morphology. At a higher molar percentage of monomer **1**, due to the prevention of the flow of the supramolecular polymer based on monomer **2**, the aggregates from monomer **2** appeared to remain unchanged upon incorporation into the gel network. At a relatively lower molar percentage of monomer **1**, especially with the molar ratio of monomers **1** and **2** at 1:1, the supramolecular polymer constructed from monomer **2** could not be incorporated into the gel phase, leading to a separation between the gel and sol phases.

A supramolecular polymer blend formed by freeze-drying an equimolar mixture of monomers **1** and **2** in CH_3CN was then investigated by SEM (Figure 3 and Figure S11 in the Supporting Information). SEM images revealed that both monomer **1** and monomer **2** were indeed capable of self-sorting into their own independent aggregates. In these typical images of self-sorting organization, it was shown that monomer **1** acted as the gelator, forming long fibers and three-dimensional network structure, while monomer **2** favored the formation of a layer of porous structure. More importantly, these two independent aggregates showed a typical micro-phase separation by means of self-sorting, with the fiber network assembling at the bottom and the layer of porous structure covering the entire surface. This micro-phase self-sorting indicated that monomers **1** and **2** could

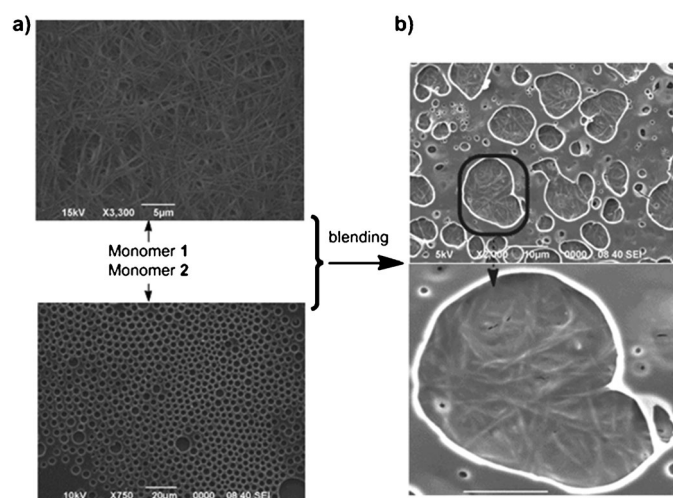


Figure 3. SEM images of aggregates: a) **1** and **2**; b) supramolecular polymer blend.

control their self-assembly processes in an independent way and did not interfere with each other.^[9p]

We also observed the self-sorting organization of monomers **1** and **2**, while preparing supramolecular polymer blend films (Figure S15 in the Supporting Information). Thin films of blends of monomers **1** and **2** with different molar ratios were cast by slowly evaporating the solvent on glass surfaces. As shown in Figure S15, monomers **1** and **2** favor independent self-assembly of their own macroscopic aggregates in the films. Further rheological measurements were also carried out to better characterize the supramolecular polymer blends with monomers **1** and **2**. First, the total concentration of **1** and **2** was kept as a constant at 100 mM, while the molar ratio between **1** and **2** was varied. It was observed that the storage and loss moduli of the supramolecular polymer blends increased with the increase of the molar percentage of gelator **1** (Figure S16 in the Supporting Information). The moduli of pure **2** were very low and near the measurement limitation of the rheometer (the concentration of **2** was 100 mM).^[12] For supramolecular polymer blends with different molar ratios of two monomers (**1/2** = 10:0, 8:2, 5:5 and 2:8), the storage moduli (G') of the samples were larger than the loss moduli (G'') of samples in the experimental range; no frequency dependence of G' and G'' was observed, indicating that network structures were formed in these samples. As the molar ratio between **1** and **2** was fixed as 5:5, the moduli of supramolecular polymer blends increased as the total concentration of **1** and **2** increased from 100 to 150 mM, and typical network characters were observed (Figure S17 in the Supporting Information). For the supramolecular polymer blends (**1/2** = 5:5) at concentrations of 10, 40, and 60 mM, moduli of the samples were very low and near the measurement limitation of the rheometer. This indicated that no network structure was formed in these samples.^[12] From these observations (Figures S16 and S17 in the Supporting Information), we found that the moduli of the supramolecular polymer blend were

derived mostly from the gelator **1**. This is in accordance with the above-mentioned viscosity measurements.

In conclusion, a novel and modular supramolecular polymer blend was prepared by means of self-sorting organization of two heteroditopic AB-type monomers. The blending experiments demonstrated that the self-assembly behavior was controlled by the self-sorting organization of monomers **1** and **2**. By blending these two different low-molecular-weight molecules, versatile and interesting micro- and macroscopic aggregates were prepared. This supramolecular polymer blend presented evidence that the self-sorting process not only takes place in solution, but also occurs in the gelation process and in the solid state. The work presented here provides a strategy to prepare complex and highly-ordered structures with desired properties and novel functions.

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Keywords: crown compounds • host–guest systems • molecular recognition • polymer blends • supramolecular chemistry

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