

A supramolecular polymer formed by the combination of crown ether-based and charge-transfer molecular recognition †

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Crown ether-based supramolecular polymers have been widely studied. The driving forces for their formation were usually focused on host–guest interactions and only very limited other supramolecular interactions are utilized to build crown ether-based supramolecular polymers. Here we report a supramolecular polymer constructed from two heteroditopic monomers driven by the combination of crown ether-based and charge-transfer molecular recognition. From our experiments, it is feasible and reasonable to introduce charge-transfer interactions into the field of supramolecular polymers constructed from crown ethers. In addition, we successfully demonstrated that this supramolecular polymer can be used in the preparation of nanofibers *via* electrospinning. The successful fabrication of nanofibers and supramolecular polymer films shows the versatility of this kind of low molecular weight supramolecular asymmetric AB-type monomers.

Introduction

Supramolecular polymers, defined as polymeric arrays of many repeating units held together by reversible and weak noncovalent interactions, are considered as the result of the combination of supramolecular chemistry and polymer science.¹ Noncovalent interactions, such as multiple hydrogen bonding, host–guest interactions and metal-coordination, have been introduced to fabricate supramolecular polymers, and these reversible and highly directional secondary interactions endow supramolecular polymers with novel topological structures and unique functions.^{1g,h,2} Charge-transfer complexes, prepared by the association between an electron acceptor and an electron donor, have been proved to be important and attractive building blocks for the construction of multiple supramolecular aggregates.³ Some groups have studied the

supramolecular polymerization process driven by charge-transfer interactions, while their attention was mainly focused on the supramolecular polymerization process at a relatively low monomer concentration.^{3a,b,d} Supramolecular polymers formed by charge-transfer interactions are still rare^{3a,b,d} and their macroscopic conventional polymer-like properties have not been mentioned yet.

Among the supramolecular macrocyclic hosts, crown ethers are one of the most commonly used building blocks to prepare supramolecular polymers with complementary guest salts *via* host–guest interactions.^{2a,2b,4} For example, an AB-type heteroditopic monomer (A: dibenzo[24]crown-8 (DB24C8), B: dibenzylammonium salt (DBA)) has the ability to self-assemble into a linear supramolecular polymer *via* the host–guest interactions between DB24C8 and DBA.^{4m} One of the features of crown ether-based supramolecular polymers is that the polymerization shows obvious concentration-dependent properties and macroscopic properties, such as high viscosity, macroscopic aggregates and other conventional polymer-like properties at high concentration of monomers can also be observed.⁴

Electrospinning, a well-known and very convenient technique, is widely applied for the generation of nanofibers which have a wide range of applications in many fields.⁵ Though electrospinning is very commonly used in the field of conventional polymer science, the application of electrospinning in supramolecular chemistry is very limited and only a few examples were reported.^{5b–e} Inspired by the nature of crown ether-based supramolecular polymers, we wonder whether we can introduce charge-transfer interactions into crown ether-based supramolecular polymers and prepare nanofibers *via* electrospinning from these supramolecular polymers. However, this concept is very challenging, due to difficulties in the reasonable design of monomers and the lack of detailed information of charge-transfer complexes at high monomer concentration.

Pyrene derivatives and paraquat derivatives are one of the most common charge-transfer molecular pairs, and have been used in the formation of different kinds of supramolecular complexes.^{3a,c,e} Therefore, it is feasible to introduce pyrene units and paraquat moieties into crown ether-appended supramolecular monomers. However, the incorporation of the structures of pyrene, paraquat,

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crown ether and crown ether-based complementary guest into one molecule is quite difficult and is unfavorable for further investigation of polymerization. Furthermore, from our previous work, we found that long flexible linkers not only increased the solubility of monomers but also improved the polymerization at a high concentration range of monomers.^{2a,b,4b,m,5c,6} Hence, we designed and synthesized two asymmetric supramolecular monomers **1** and **2**. Monomer **1** has a pyrene unit and a DB24C8 moiety (Scheme 1), while monomer **2** contains a DBA group and a paraquat derivative, which are linked together by a long flexible alkyl chain.^{4b} It is known that DB24C8 and DBA moieties form 1 : 1 threaded structures.^{4a} Our approach is that (1) the pyrene group and the crown ether group in monomer **1** can recognize the paraquat derivative and the DBA unit in monomer **2**, respectively, and (2) the formation of a supramolecular polymer could be driven by the combination of host-guest interactions between the DB24C8 and DBA groups and charge-transfer interactions between the pyrene and paraquat units.

Results and discussion

The formation of a charge-transfer complex between the pyrene moiety and the paraquat unit plays a crucial role in the occurrence of supramolecular polymerization. After the addition of pyrene to a solution of paraquat in acetonitrile, a change in the color of the solution was observed from colorless to yellow, indicating the formation of the charge-transfer complex. Further strong evidence for the existence of charge-transfer interactions between pyrene and paraquat groups was obtained from ¹H NMR spectroscopy. As shown in Fig. S7,[†] after mixing pyrene and paraquat together, proton signals of both pyrene and paraquat moved upfield. For example, the α -pyridinium protons on paraquat shifted upfield from 8.84 ppm to 8.74 ppm, which was in accordance with the changes in a similar system.^{3a} Then concentration-dependent ¹H NMR spectra of monomers **1** and **2** (in CD₃CN) in the range from 30.0 mM to 200 mM were obtained to provide an important insight into the complexation behavior of monomers **1** and **2** in solution and to investigate the polymeric aggregation process (Fig. 1). After mixing, proton signals on the paraquat unit all moved upfield, while proton signals on the pyrene moiety showed downfield movements, indicating the existence of charge-transfer interactions. Then we further investigated the concentration-dependent supramolecular polymerization process. The NMR spectra of equimolar solutions of monomers **1** and **2** were complicated due to the slow-exchange

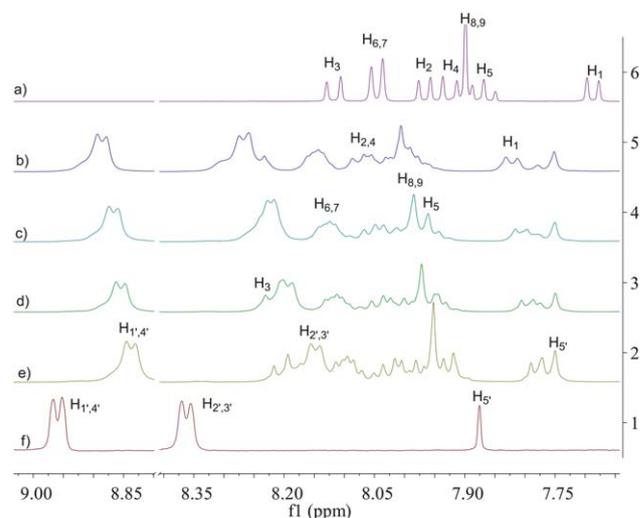
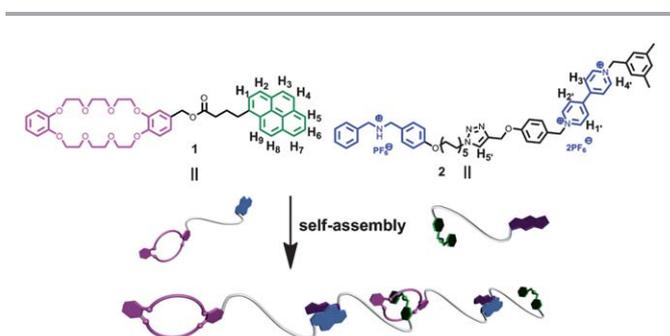


Fig. 1 Partial ¹H NMR spectra (400 MHz, CD₃CN, 298 K) of equimolar solutions of **1** and **2** at different concentrations: (a) **1** only; (b) 200 mM; (c) 150 mM; (d) 80.0 mM; (e) 30.0 mM; and (f) **2** only. The concentration is for each monomer.

complexation of the DB24C8 and DBA units on the proton NMR time scale. With the increase of monomer concentrations, proton signals of both **1** and **2** became broad and smooth, which were consistent with the formation of high molecular weight supramolecular aggregates. We also observed that H_{2',3'} (monomer **2**) moved downfield from 8.15 ppm (30.0 mM) to 8.27 ppm (200 mM), which indicated a concentration-dependent supramolecular polymerization process. Similar changes were also found for the other protons. For example, protons H_{8,9} of the pyrene unit (monomer **1**) moved downfield from 7.95 ppm to 8.00 ppm, while protons H₃ moved downfield from 8.20 ppm to 8.30 ppm. All these changes were in accordance with characteristic changes occurred in the field of crown ether-based supramolecular polymeric systems.^{2h,4m,6}

As a convenient and reliable method to confirm the propensity of monomers to self-assemble into high molecular weight aggregates, a double logarithmic plot of specific viscosity *versus* the concentration of monomers **1** and **2** in equimolar CH₃CN solutions was obtained to further investigate the nature of supramolecular polymers (Fig. 2a). In the low concentration range, the slope of the curve



Scheme 1 Schematic representation of the formation of a supramolecular polymer *via* self-assembly of monomers **1** and **2**.

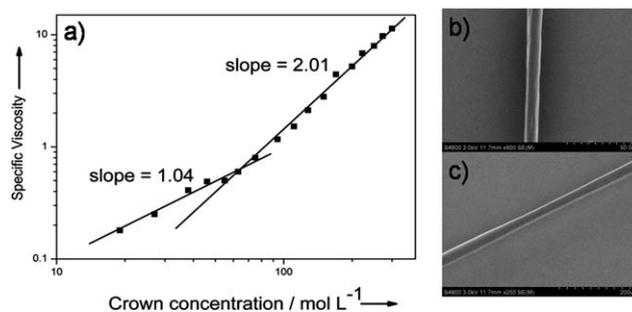


Fig. 2 (a) Log-log plot of specific viscosity of equimolar solutions of monomers **1** and **2** *versus* the monomer concentration at 298 K; (b and c) scanning electron micrographs of (gold-coated) fibers obtained from a high concentration solution of **1/2** in CH₃CN.

was 1.04, indicating the presence of cyclic oligomers or monomers with constant sizes. As the concentration increased, a slope of 2.01 was observed, which meant the existence of high molecular weight polymers and a concentration-dependent polymerization process. The CPC (critical polymerization concentration) for monomers **1** and **2** was about 75 mM as evidenced by the clear change of the slope occurring at this concentration, and indicated a ring-chain transition from low molecular weight oligomers to supramolecular polymers.^{2h,4k,6}

Long rod-like fibers with diameters of 20 μm were obtained from a concentrated CH_3CN solution of monomers **1** and **2** and investigated by scanning electron microscopy (SEM), which gave us direct evidence of the existence of high molecular weight supramolecular polymers (Fig. 2b and c).^{2,4m,6a}

Acting as a powerful and convenient tool for generating nanofibers which show a variety of applications, electrospinning has been widely used in many research fields.⁵ Though nanofibers electrospun from conventional polymers are well investigated in polymer science, supramolecular polymer nanofibers *via* electrospinning from low molecular weight monomers are quite rare.⁵ Here, a mat of supramolecular polymer fibers was overlaid on the surface of clean glass by electrospinning a high concentration solution of monomers **1** and **2** (200 mM for each monomer in acetonitrile). We further investigated these nanofibers by SEM (Fig. 3b–f). SEM images showed supramolecular polymer nanofibers with diameters of 0.1 μm and lengths of hundreds of micrometers. These nanofibers further formed an entangled spinning network. We also observed that most of the surfaces of nanofibers were quite smooth, indicating a good rheological property and processability of this host-guest/charge transfer-based supramolecular polymer. The formation of nanofibers electrospun from two complementary

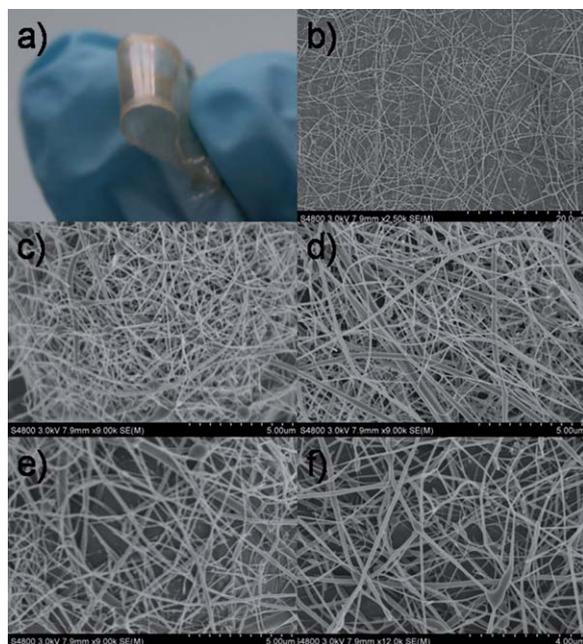


Fig. 3 A supramolecular polymer film (a) and scanning electron microscopy images of nanofibers *via* electrospinning ((b) a lower magnification; (c–f) a higher magnification).

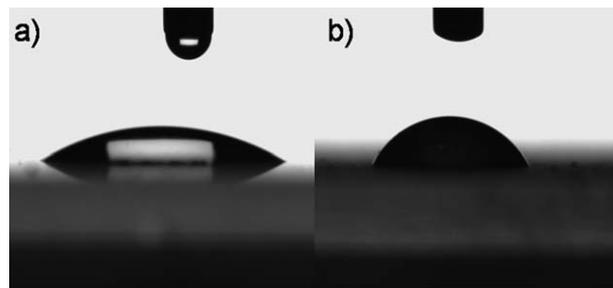


Fig. 4 Contact angles of the glass surface (a) and the glass surface covered with nanofibers (b).

monomers demonstrated the existence of supramolecular polymers with high viscosity and high molecular weight.^{5c}

Water repellency, one of the common natural phenomena, originates from the intrinsic hydrophobic properties and microstructures of solid materials. By extending the idea of highly ordered microstructures, such as a honeycomb pattern in the micron range of the supramolecular polymers, here we measured the contact angle of water droplets deposited on the glass surface and the glass surface covered with nanofibers produced *via* electrospinning. As shown in Fig. 4, the contact angle of the glass surface was about 29° . After covering with nanofibers *via* electrospinning the contact angle of the modified glass surface increased to about 60° . The transition in the contact angles originated from the extensive nanofiber network, which increased the surface area and changed the surface structure of the intrinsically hydrophilic glass surface to a less hydrophilic surface.⁷

It was worth noting that with the increase of the concentrations of monomers **1** and **2** in the equimolar acetonitrile solution, macroscopic aggregates were observed. Glue-like viscous liquids could be obtained by dissolving monomers **1** and **2** in acetonitrile at concentrations higher than 1.0 M. While by evaporation of an equimolar acetonitrile solution of monomers **1** and **2** at room temperature, a flexible, transparent and smooth film was formed (Fig. 3a), which was also the direct evidence of the formation of high molecular weight aggregates. The formation of supramolecular polymer films is quite rare in the field of supramolecular polymers constructed from low-molecular-weight monomers.^{2h}

Conclusions

In conclusion, we reported the design and preparation of a novel supramolecular polymer *via* the self-organization of two AB-type monomers. The supramolecular polymerization of two heteroditopic monomers was driven by the combination of host-guest interactions and charge-transfer interactions. Though crown ether-based host-guest interactions and charge-transfer interactions are widely applied in various fields of supramolecular chemistry, the combination of these two kinds of supramolecular interactions is still limited. Hence the investigation of the combination of these two kinds of supramolecular interactions is full of challenge and is worth doing. From our experiments, it is feasible and reasonable to introduce charge-transfer interactions into the field of supramolecular polymers constructed from crown ethers. We also demonstrated that high molecular weight supramolecular polymers can be

formed by complexation between crown ethers and secondary ammonium salts, and paraquat derivatives and pyrene derivatives, respectively. This kind of supramolecular polymers exhibit the ability to construct nanofibers *via* electrospinning technology. The successful fabrication of nanofibers and supramolecular polymer films shows the versatility of this kind of low molecular weight supramolecular asymmetric AB-type monomers. With the introduction of different supramolecular interactions during the preparation of supramolecular polymers, we can enrich this class of assembly monomers and could endow supramolecular assemblies with more unique structures and specific functions. This study is also helpful for understanding supramolecular polymerization driven by crown ether-based molecular recognition and charge-transfer interactions and for investigating the potential applications of supramolecular nanofibers formed by electrospinning technology.

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