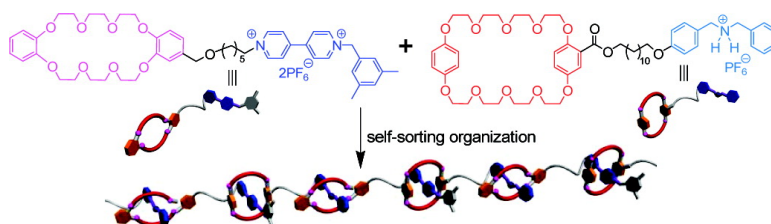


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Self-Sorting Organization of Two Heteroditopic Monomers to Supramolecular Alternating Copolymers

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Self-sorting,¹ whereby molecules can find and self-assemble their corresponding recognition units within a complex mixture with high affinity and fidelity, is commonplace and critical in biological systems. For example, the self-sorting hydrogen bond recognition between relatively few nucleic acid bases results in an enormous amount of information stored in DNA, which further lead to its replication and transcription. However, few examples were reported to construct synthetic polymeric systems, analogues to the biopolymers such as DNA and RNA, using the principle of self-sorting.^{1c} Alternating copolymers have unique properties different from those of random copolymers, and some have been shown to be useful materials.² Supramolecular polymers (suprapolymers) can form when repeating units in traditional polymers are connected via noncovalent interactions instead of covalent interactions.^{3,4} Although there is considerable interest in supramolecular alternating (block) copolymers,⁴ to the best of our knowledge, supramolecular alternating copolymers based on self-sorting organization of low-molecular-weight monomers have not been reported yet. Herein, we demonstrate that when self-sorting organization is applied to two AB-type heteroditopic monomers, linear supramolecular alternating copolymers can be obtained driven by host-guest interactions.

For the successful preparation of supramolecular alternating copolymers from self-sorting organization of two heteroditopic monomers H1-G2 and H2-G1 (H1, G2, H2, and G1 represent host or guest moieties on the two monomers) driven by host-guest interactions, it is required that the complexations between H1 and G1 and between H2 and G2 should be much stronger than the complexations between H1 and G2 and between H2 and G1 and have 1:1 stoichiometries. We designed and prepared heteroditopic monomers **1** and **2**, from which we want to get supramolecular alternating copolymer **3** by self-sorting organization. It is well-known that bis(*p*-phenylene)-34-crown-10 (BPP34C10) and dibenzo-24-crown-8 (DB24C8) form 1:1 complexes with paraquat derivatives and dibenzylammonium salts, respectively.^{5,6} Furthermore, the self-sorting studies on model compounds **4**–**7** demonstrated that the complexations between BPP34C10 and paraquat derivative moieties and between DB24C8 and dibenzylammonium moieties are much stronger than the complexations between BPP34C10 and dibenzylammonium moieties and between DB24C8 and paraquat moieties.⁷ Therefore, the self-sorting organization of monomers **1** and **2** should lead to alternating arrangement of the two monomers, which further self-organize into linear supramolecular alternating copolymers **3** (Scheme 1). Here the two linkers between host and guest moieties on the two monomers were designed to have totally more than 20 atoms in anticipation for a relatively low critical suprapolymerization concentration (CPC).^{3a,8}

The concentration-dependent ¹H NMR spectra of equimolar solutions of **1** and **2** are complicated (Figures 1 and S7) due to the coexistence of the slow- and fast-exchange complexations of host

Scheme 1. Formation of Supramolecular Alternating Copolymers **3** from Self-Sorting Organization of Heteroditopic Monomers **1** and **2**



and guest units. At low concentration (below 103 mM), protons, such as the pyridinium protons and benzyl protons H₅, on the fast-exchanging units have two sets of well-defined signals standing for the cyclic and linear species, respectively. This phenomenon is quite different from reported supramolecular polymers assembled by fast-exchange complexations,^{3h} for which only one set of signals was observed. This can attribute to the presence of slow exchanging interactions exerting significant effects on the fast ones. As the concentration increased, the signals of pyridinium protons H₂ and H₃ shifted upfield while those of benzyl protons H₅ moved downfield. At high concentration (232 to 650 mM), the signals for the cyclic species are no longer observed and all signals become broad, confirming the formation of high-molecular-weight aggregates.

Moreover, values of the fraction *p* of complexed crown ether moieties⁹ at different initial concentrations were obtained (Table S1) from the chemical shift change Δ₀ of the fully complexed paraquat unit, which was estimated to be 0.113 ppm for benzyl protons H₅.⁷ Then maximum possible polymerization degrees at

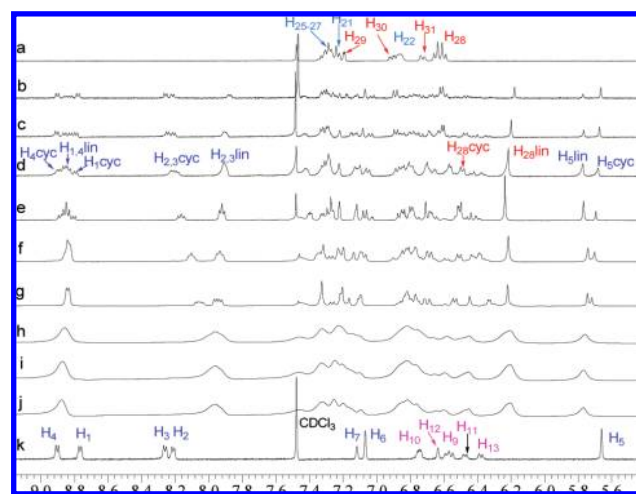


Figure 1. Partial ¹H NMR spectra (400 MHz, 1:1 CDCl₃/CD₃CN, 20 °C) of (a) **2**; equimolar mixtures of **1** and **2** at different crown unit concentrations: (b) 2, (c) 8, (d) 20, (e) 40, (f) 60, (g) 103, (h) 232, (i) 464, and (j) 650 mM; and (k) **1**.

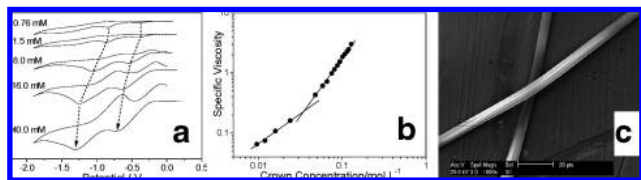


Figure 2. (a) Cyclic voltammograms (chloroform/acetonitrile (1/1, v/v), 298 K, scan rate 100 mV/s) of equimolar mixtures of **1** and **2** at different crown concentrations. (b) Specific viscosity of chloroform/acetonitrile (1/1, v/v) solutions of equimolar mixtures of **1** and **2** versus the crown concentration (298 K). (c) Scanning electron microscopy of (gold-coated) fibers drawn from a high concentration solution of **1** and **2**.

different initial concentrations were calculated using the Carothers equation (Table S1).¹⁰ As the concentration increases, the calculated size of aggregates increases to truly large values and supramolecular alternating copolymers are formed. For example, at 650 mM, $p = 98.2\%$ and $n = 56.5$, corresponding to a polymer with a molar mass of 126.1 kDa.

The influence of the self-assembly process on the electrochemical properties of equimolar solutions of **1** and **2** was analyzed through cyclic voltammetry (CV) performed at different concentrations (Figure 2a). The electrochemistry reduction process shows two clear voltammetric waves of viologen groups. Upon concentration the reduction processes become more energetic and irreversible with both of the first and second reduction potentials of the viologen shifting toward more negative values.^{3i,11} These indicated that the fraction of encircled viologen units by crown ether units becomes larger as the concentration increases,¹¹ in accordance with the proton NMR results. The formation of supramolecular alternating copolymers **3** was also supported by dynamic light scattering (DLS) experiments.^{7,12} A 40 mM equimolar solution of **1** and **2** in chloroform/acetonitrile (1/1, v/v) has a hydrodynamic radius of 7.2 nm. However, no aggregate could be detected for a 10 mM equimolar solution of two monomers as well as the solutions of either of two monomers under the same conditions.

The concentration dependence of the solution viscosity gives important information on the aggregation behavior. Therefore, a double logarithmic representation of specific viscosity versus the concentration of equimolar solution of **1** and **2** in chloroform/acetonitrile (1/1, v/v) was obtained (Figure 2b). In the low concentration range, the curve has a slope of 1.02, which is characteristic for noninteracting assemblies of constant size.¹³ As the concentration increases, the curve approaches a slope of 2.05.⁷ The clear change in slope at approximately 40 mM indicates a transition from cyclic species to linear supramolecular polymers of increasing size. By contrast, the curves for the aggregation of monomer **1** and **2** have a slope of 1.15 and 1.10, respectively. This also supported the formation of supramolecular alternating copolymers **3**.

In addition, amorphous, flexible, and transparent films, obtained by evaporation of an equimolar solution of **1** and **2**, were characteristic for entanglement of linearly connected macrosized aggregates.^{3a} Furthermore, rodlike fibers with a regular diameter of 6.25 μm were drawn from a high concentration solution and observed by scanning electron microscopy (SEM) (Figure 2c), providing direct evidence of the formation of supramolecular polymers with high molecular weight.

In summary, we demonstrated that self-sorting organization of two AB-type heteroditopic monomers **1** and **2** could result in the

formation of supramolecular alternating copolymers **3** in solution as confirmed by ¹H NMR, CV, DLS, viscosity measurements, and SEM. The degree of polymerization was dependent on the initial concentrations of two monomers. Morphology control of suprapolymers is essential for their future applications,¹⁴ and the construction of various architectures in the self-sorting manner will be reported in our future publications.

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Supporting Information Available: Experimental details, syntheses of **1** and **2**, self-sorting organization of model compounds (**4–7**), and other materials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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