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Electrospun nanofibers and multi-responsive supramolecular assemblies constructed from a pillar[5]arene-based receptor†

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Multi-responsive supramolecular polymers have been constructed from pillar[5]arene-based receptors. Significantly, nanofibers, nanosized supramolecular polymers based on pillararenes, have been successfully fabricated employing an electrospinning technique for the first time.

Stimuli-responsive disassembly and reassembly of supramolecular assemblies play a significant role in realizing their biological functions, for example, the reversible conversion of tubulin dimer and microtubules.[1] Inspired by this, considerable effort has been devoted to the design and development of structurally well-defined assemblies with fascinating properties and intriguing functions for their diverse applications in chemistry, biology, and materials science.[2] Among them, supramolecular polymers, self-assembled from low molecular weight monomeric entities through reversible noncovalent interactions,[3] have attracted great attention.[4] Host–guest complexation, as an intriguing noncovalent driving force, has proven to be essential for constructing macrocyclic host-based supramolecular polymers. Due to the dynamic and reversible nature of noncovalent interactions, supramolecular polymers undergo stimuli-responsive disassembly–reassembly transitions in response to the external environment, including temperature, pH, counter ion, redox, solvent composition, *etc*.

Nanofibers, owing to their fascinating properties and multi-functionalities, have been applied in many research fields, *i.e.*, tissue engineering, controlled release system, textiles, membranes/filters, *etc*.[5] Electrospinning has attracted great attention since this versatile technique provides a powerful tool to fabricate nanoscale fibers from various polymers, polymer blends, composites and ceramics. However, electrospinning has been limited to pre-formed polymers and has been barely used to fabricate fibrous materials from low molecular weight materials, especially synthetic macrocycles.[6]

Pillar[*n*]arenes represent a new family of supramolecular hosts and have stimulated great interest with significant advances in recent years.[7] Monofunctionalized pillar[*n*]arenes have extended the versatility of pillar[*n*]arenes and provided an appropriate platform for the construction of various supramolecular assemblies. Until now, some block-based co-pillar[*n*]arenes have been employed in the fabrication of supramolecular polymers.[8] However, these reported supramolecular polymers have not been shown to disassemble/reassemble reversibly and efficiently in response to external stimuli.

Herein, we report the fabrication of stimuli-responsive supramolecular polymers based on pillar[5]arene/tertiary ammonium salt recognition motifs, and investigate the reversible multi-responsive transition between supramolecular polymers and disassembled monomers. Significantly, nanofibers were constructed for the first time from the nanosized supramolecular polymers by an electrospinning technique, paving a new way to the fabrication of novel fibrous organic materials.

Employing a facile catalytic system that we developed and combined with "click" chemistry,[9] we designed and synthesized monomer **1**, a monofunctionalized pillar[5]arene carrying a tertiary ammonium-ended alkyl chain (Fig. 1 and Scheme S1†).

The aggregation behavior[8b,10] of monomer **1** at low concentrations in solution was firstly investigated. Concentration dependent ^{1}H NMR titration is a powerful method to monitor and quantify aggregation. To investigate the self-aggregation ability of monomer **1**, ^{1}H NMR measurements were carried out over a concentration range from 1.0×10^{-4} to 1.2×10^{-3} M in $CDCl_3$. The effective aggregation constant K_{agg} and the aggregation number n were calculated to be $1.86 \pm 0.22 \times 10^3$ M^{-1} and 2, respectively (Fig. S17–S20†). This indicates that monomer **1** forms dimers in the determined concentration range, which further revealed the general rule of the formed dimers in the self-assembly process of monofunctionalized pillar[5]arenes. The dimerization is the first step in the formation of linear supramolecular assemblies.

Furthermore, variable temperature ^{1}H NMR spectra (1 mM of monomer **1** in $CDCl_3$) corroborated that there existed two dimeric aggregates of monomer **1** at low concentrations (Fig. S21†).

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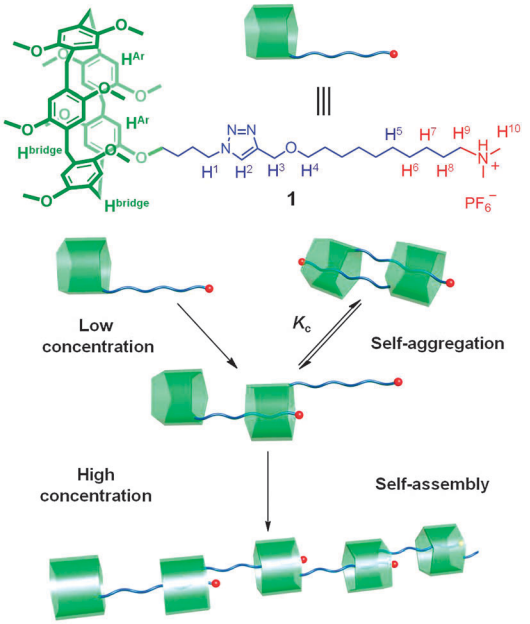

Fig. 1 Representation of self-aggregation at low concentration and self-assembly at high concentration in solution of monomer **1**. At low concentrations, monomer **1** forms a head to tail dimer and a [c2]daisy chain dimer through self-aggregation.

In principle, monomer **1** can potentially form two different dimeric structures including a head to tail form and an interpenetrated [c2]daisy chain form. Formation of the [c2]daisy chain is often a thermodynamically stable aggregation step preventing the formation of longer oligomers,[11] whereas formation of an acyclic head to tail dimer is usually the first propagation step towards supramolecular polymers (Fig. 1).

Subsequently, the self-assembly of monomer **1** at high concentrations in solution was investigated, revealing the change of the assembly form of the pillar[5]arene-based receptor from a dimer to a linear supramolecular polymer. The process was confirmed by means of a combination of various techniques, *i.e.*, ^{1}H NMR, ROESY experiments, two-dimensional diffusion-ordered NMR spectroscopy (DOSY) and viscometry study (Fig. S22–S26†). The critical polymerization concentration (CPC, *ca.* 59.6 mM) was determined as well. Moreover, a rod-like fiber with a regular diameter of *ca.* 17 μm was drawn from monomer **1** at a high concentration of chloroform solution and observed by scanning electron microscopy (SEM), which provided direct insight into the formation of supramolecular polymers with high molecular weight (Fig. 2a).

Electrospinning is a convenient and versatile technique for fabricating functional nanofibers from a variety of materials. However, pillararene-based nanofibers have not yet been described until now. As a very fascinating class of supramolecular hosts, pillararenes are envisioned to form electrospun nanofibers upon fine-tuning their molecular structures and functionalities. In this work, the supramolecular polymer self-assembled from monomer **1** (300 mM in chloroform) was overlaid during the electrospinning process, producing a mat of supramolecular polymer fibers. Representative SEM images of the resulting fibers show that their diameters span a range from 50 to 800 nm, most of which are between 100 and 500 nm (Fig. 2b–d). As suggested by the

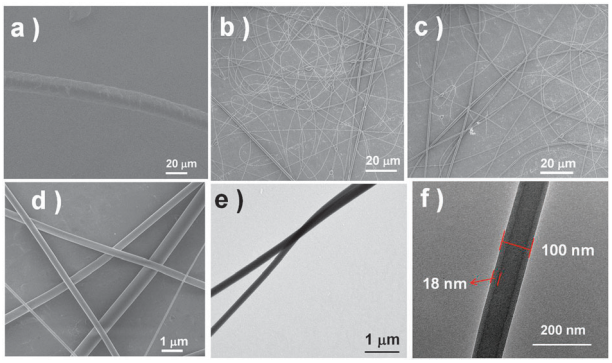

Fig. 2 (a) SEM image of a rod-like fiber drawn from a high concentration chloroform solution of monomer **1**; (b–d) SEM images of the electrospun supramolecular polymer nanofibers from monomer **1**; (e and f) TEM images of the electrospun supramolecular nanofibers.

micrographs, the nanofibers with larger diameters possess rigid structures, whereas the smaller ones (the fibers showing high curvatures) are more flexible.

The structure of supramolecular polymer fibers was further investigated by transmission electron microscopy (TEM), demonstrating that the diameter of supramolecular nanofibers is *ca.* 100–300 nm (Fig. 2e and Fig. S27e/f†), consistent with SEM data. Significantly, the hollow nature of the supramolecular polymer nanofiber has been observed by TEM; the wall thickness of the nanofiber is *ca.* 18 nm (Fig. 2f and Fig. S27g†).

Atomic force microscopy (AFM) as one of the foremost tools for reflecting and measuring the surface morphology of the matter at the nanoscale has also been used to analyze the fiber structure. The electrospun nanofibers exhibited the morphology of 1D linear nanostructures with a height of 250 nm (Fig. 3a and b) and 286 nm (Fig. 3c and d), respectively.

Fabrication of externally addressable supramolecular polymers is particularly fascinating, because responsiveness to external stimuli would give rise to a more flexible and adaptable supramolecular structure and smart materials (Scheme S2†). As expected, the supramolecular polymer constructed from monomer **1** is responsive to pH owing to the reversible deprotonation and protonation of the tertiary ammonium moiety. Therefore, triethylamine (Et_3N) and trifluoroacetic acid (TFA) were used as the operating base–acid pair to obtain reversible disassembled monomer and reassembled

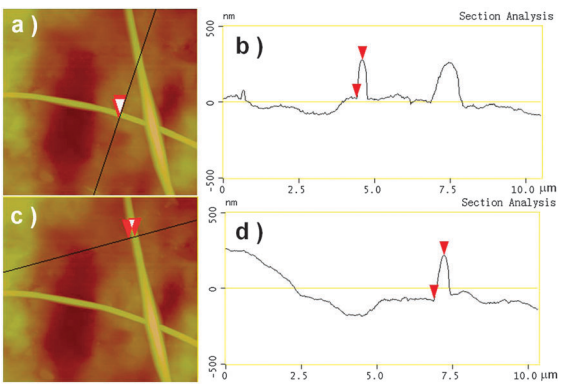

Fig. 3 (a and c) AFM images of the electrospun supramolecular polymer nanofibers; (b and d) section analysis for (a) and (c).

polymer transition. The reversible disassembly–reassembly transition was efficiently realized even though the NMR peaks of supramolecular assemblies, *e.g.*, H^7 and H^6, shifted downfield slightly (Fig. S28†). This slight difference was ascribed to the integrative interactions of mixed hexafluorophosphate and trifluoroacetate counter anions.

More interestingly, the reversible disassembly–reassembly of supramolecular assemblies could also be realized by the addition of tetrabutylammonium chloride (TBACl) and silver trifluoromethanesulfonate (AgOTf). Upon addition of 1.2 equivalent of TBACl to the solution of monomer **1**, disassembly between the pillar[5]arene moiety and the tertiary ammonium moiety was observed (Fig. S29, ESI,† spectrum b). This is due to the formation of the close-contact ion pair[12] between the tertiary ammonium moiety and chloride (Cl^-) through counter anion exchange, preventing the complexation of pillar[5]arene and tertiary ammonium side-chain. Afterwards, upon addition of 1.5 equivalent of AgOTf to the above solution, the upfield chemical signals reappeared, indicating that the supramolecular polymer reassembled through the removal of chloride counter anions by adding excess Ag^+ (Fig. S29, ESI,† spectrum c). Meanwhile, excess Ag^+ can coordinate with triazole in monomer **1**, resulting in the broadening of the NMR peaks of H^2, H^3 and H^4 adjacent to triazole and the downfield shift of the H^2 peak.

Solvent composition-responsive supramolecular polymers are a class of degradable materials obtained by means of gradually adjusting the polarity of the mixed solvent.[13] The reversible disassembly–reassembly transition can also be switched by varying the volume fraction of acetone in the mixed solvent system ($\chi_{acetone}$). As the solvent polarity increased, the tertiary ammonium chains included in the pillar[5]arene cavity started moving out of the cavity gradually, which was confirmed by the large downfield-shifts of the NMR proton signals of tertiary ammonium chains (Fig. S30†). These results indicated that the formation of supramolecular polymers took place in chloroform but not in acetone. This might be due to the cation–π interaction that depends on different kinds of solvents, *e.g.*, in a polar solvent acetone, the cation–π interaction becomes very weak.

These reversible assembly–disassembly transitions between supramolecular polymers and disassembled monomers were verified by means of DOSY analysis as well (Fig. S25 and S31†).

In conclusion, we have successfully fabricated supramolecular polymer nanofibers from a pillar[5]arene-based receptor **1** employing the electrospinning technique. Significantly, the linear supramolecular assemblies from **1** exhibited responsiveness to three stimuli: pH, counter ion, and solvent composition. These stimuli induce an efficient and reversible assembly–disassembly of the pillar[5]arene-based monomer into/from linear polymers. The present study provides an alternative method for the topological control and stimuli-responsiveness of macromolecules, which will benefit the fabrication of novel fibrous organic materials and the construction of stimuli-responsive smart materials.

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