Supramolecular Polymers

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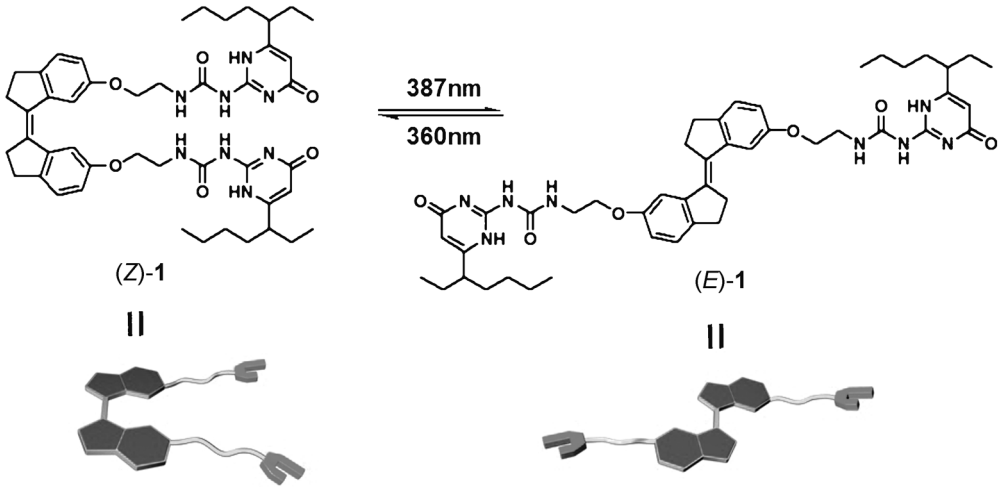
Photoresponsive Hydrogen-Bonded Supramolecular Polymers Based on a Stiff Stilbene Unit**

*Jiang-Fei Xu, Yu-Zhe Chen, Dayong Wu, Li-Zhu Wu, Chen-Ho Tung, and Qing-Zheng Yang**

Supramolecular polymers are arrays of low-molecular-weight building blocks held together by hydrogen bonding or other reversible noncovalent interactions.[1] They have attracted increasing attention recently because of their potential applications in the fabrication of smart functional materials whose physical properties and functions could be controlled by external stimuli.[2] Among such stimuli, light is especially attractive as it allows remote activation and control with sub-micrometer spatial and sub-millisecond temporal resolution without generating waste chemicals.[3] Previously reported supramolecular polymers have been shown to polymerize/depolymerize[4] as well as switch between well-defined aggregation states[5] or gel and solution[6] upon irradiation. Azobenzene (**AB**) is the most commonly used chromophore in photoresponsive polymers because of the large structural difference between its *E* and *Z* isomers. However, the half-life of most (*Z*)-**AB** derivatives at room temperature is a few hours,[7] which makes polymers of pure (*Z*)-**AB** hard to prepare and study. This has so far made it difficult to exploit the (probable) differences in the physical properties and polymerization mechanisms between the two isomeric states of **AB** polymers.

A stiff stilbene (1,1-biindane, Scheme 1) moiety offers considerable advantages over **AB** as a chromophore for photoresponsive supramolecular polymers. Similar to **AB**, stilbene exists as structurally distinct *E* and *Z* isomers. Unlike **AB**, the isomers are separated by an activation barrier of about 43 kcal mol^{-1} (i.e., a half-life of ca. 10^9 years at 300 K), thus making thermal isomerization negligibly slow at temperatures below about 420 K.[8a] The photoisomerization of either isomer of the stiff stilbene derivative proceeds with 50% quantum yield,[8d] compared to about 20% ($\lambda < 320$ nm) or 35% ($\lambda > 400$ nm) for the photoisomerization of (*E*)-azobenzene to the *Z* isomer.[8e] The stiff stilbene offers greater opportunities for peripheral substitution than **AB** while being generally more inert. Boulatov et al. has used the stiff stilbene moiety extensively as a molecular force probe to mimic the strain generated in diverse functional groups when they are part of a stretched polymer.[8] Herein, we report a photoresponsive supramolecular polymer comprised of quadruply hydrogen-bonded monomers of stiff stilbene with two ureidopyrimidinone moieties (Scheme 1). The self-assembly behavior and physical properties of the supramolecular polymers can be regulated by photoisomeirization of stiff stilbene. (*Z*)-**1** and (*E*)-**1** polymerize by ring-chain and isodesmic growth mechanisms, respectively. The polymer of



Scheme 1. Photoisomerization of the UPy-linked stiff stilbene derivates (*Z*)-**1** and (*E*)-**1**.

[*] J.-F. Xu, Dr. Y.-Z. Chen, Prof. Dr. L.-Z. Wu, Prof. Dr. C.-H. Tung, Prof. Dr. Q.-Z. Yang
Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences
Beijing 100190 (P. R. China)
E-mail: qzyang@mail.ipc.ac.cn
J.-F. Xu
University of the Chinese Academy of Sciences
Beijing 100049 (P. R. China)
Prof. Dr. D. Wu
National Engineering Research Center of Engineering Plastics, Technical Institute of Physics and Chemistry
Chinese Academy of Sciences
Beijing 100190 (P. R. China)

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(*Z*)-**1** yielded fluorescent nanofibers by electrospinning, while (*E*)-**1** analogues formed a multi-responsive gel.

The quadruple hydrogen-bonding unit 2-ureido-4[1*H*]-pyrimidinone (UPy) is one of the most commonly used building blocks in supramolecular polymer because of its high association constant ($K_{ass} = 6 \times 10^7\,\text{M}^{-1}$ in $CHCl_3$) and synthetic accessibility.[9] Molecules containing two UPy moieties often form long supramolecular polymer chains, either by isodesmic or ring-chain polymerization mechanisms, as studied thoroughly by Meijer and co-workers.[10] However, photocontrol of the polymerization mechanisms of bifunctional UPy compounds remains unexplored.

The *Z* isomer of the stiff stilbene bearing two UPy moieties ((*Z*)-**1**) was synthesized in 30% yield in 7 steps[11] and characterized by NMR spectroscopy and high-resolution ESI-MS (see Figure S1 in the Supporting Information). The UV/Vis and fluorescence spectra of (*Z*)-**1** show a broad absorption band at approximately 350 nm and an emission band at 420 nm, respectively, which we ascribed to the *Z*-configured stiff stilbene chromophore (see Figures S3 and S4 in the Supporting Information).

The ^{1}H NMR spectrum of (*Z*)-**1** in $CDCl_3$ showed a large downfield shift (between 10 and 14 ppm) for the UPy NH signals, thus giving direct evidence for the formation of quadruple hydrogen-bonded supramolecular aggregates. Diffusion-ordered ^{1}H NMR spectroscopy (DOSY) is a useful technique to investigate the size distribution of such supramolecular aggregates.[12] A DOSY spectrum of a 50 mM solution of (*Z*)-**1** in $CDCl_3$ with polystyrene (M_n = 1770 g mol^{-1}) as the standard revealed two sets of signals (Figure 1a) which correspond to two types of species in solution. The diffusion constant of the more intense set of signals was similar to that of the polystyrene standard. The molecular weight of (*Z*)-**1** is 821 g mol^{-1}, and thus we assume that the dominant species at 50 mM is the dimer of (*Z*)-**1** (M_w = 1642 g mol^{-1}). We assigned the set of signals of lower intensity and larger diffusion constant to the monomer. The formation of the dimer was further confirmed by high-resolution ESI-MS, with the signal at m/z = 1641.9377 (100%), which corresponds to $[2M+H]^+$, being clearly observed (see Figure S1c in the Supporting Information).

Irradiation of (*Z*)-**1** at 387 nm, produced (*E*)-**1** in > 99% yield, as determined by ^{1}H NMR spectroscopy. The reverse isomerization was achieved by irradiation at 360 nm. The ready accessibility of photostationary states dominated by a single isomer facilitates detailed studies of the self-assembly of **1**. A DOSY spectrum of (*E*)-**1** in $CDCl_3$ at 50 mM (Figure 1b) revealed a broad distribution and smaller diffusion constants than those of (*Z*)-**1**, thus indicating that (*E*)-**1** forms supramolecular polymers even at modest concentrations. Thus, while (*Z*)-**1** appears to form cyclic dimers at 50 mM, (*E*)-**1** polymerizes. Repeated cycles of 387 nm and 360 nm irradiation of a solution of **1** induced the reversible transitions between low-molecular-weight cyclic dimers ($D > 3.6 \times 10^{-11}$ m^{2}s^{-1}) and supramolecular polymers ($D < 2.2 \times 10^{-11}$ m^{2}s^{-1}, Figure 1c).

Viscosity measurements on solutions of (*Z*)-**1** and (*E*)-**1** in $CHCl_3$ were consistent with the results of the NMR studies. The double-logarithmic plot of specific viscosity versus concentration of (*Z*)-**1** was linear with a slope of 1.01 at concentrations < 0.1 M, thus indicating the presence of solutes whose size was concentration-independent (e.g., cyclic dimer; Figure 2). A slope of 2.85 was observed at concentrations > 0.1 M, which indicates an increase in the degree of polymerization of (*Z*)-**1** with concentration.[13] In contrast to (*Z*)-**1**, the slope of the graph for (*E*)-**1** was constant at 2.55 over the whole concentration range. This result indicates the propensity of (*E*)-**1** to polymerize even at very low concentrations, which further confirms the DOSY experiments.

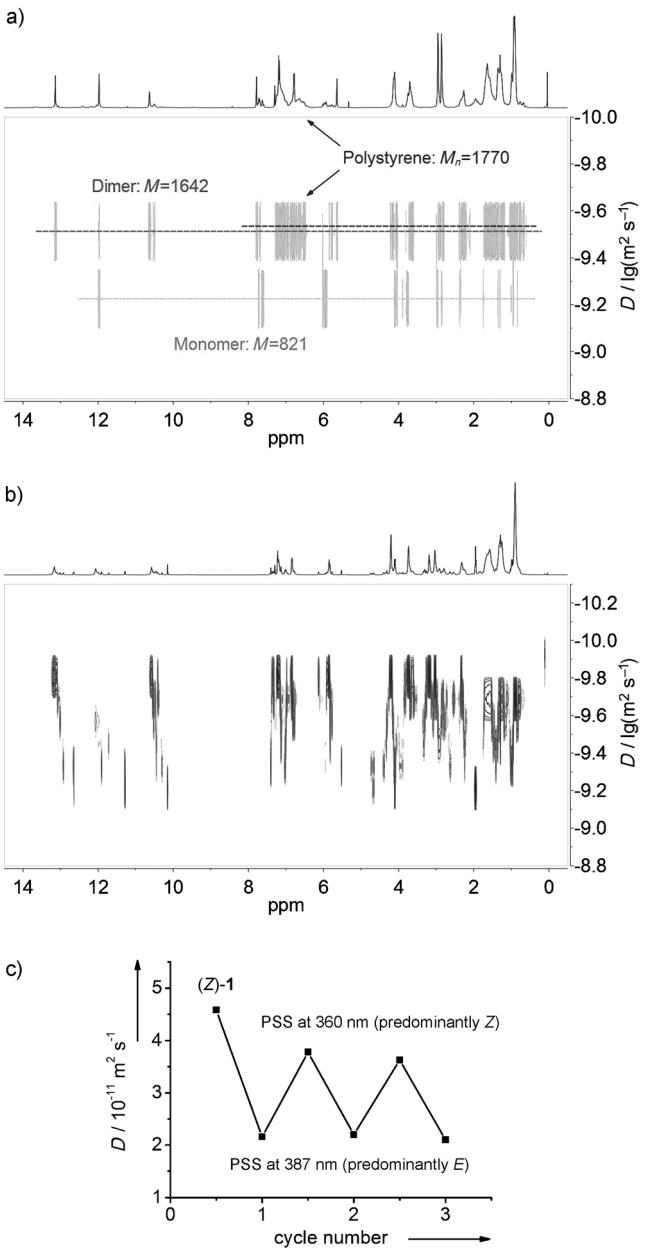


Figure 1. DOSY spectra (600 MHz, $CDCl_3$, 298 K) of a) (*Z*)-**1** in 50 mM with the addition of polystyrene (M_n 1770 g mol^{-1}) as an internal standard, b) (*E*)-**1** in 50 mM solution (no internal standard). c) Cyclic changes in the measured weight-average diffusion coefficients (600 MHz, $CDCl_3$, 298 K) of (*Z*)-**1** (50 mM) upon irradiation at 387 nm and 360 nm .

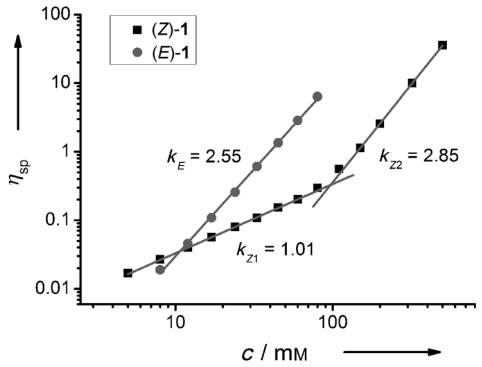
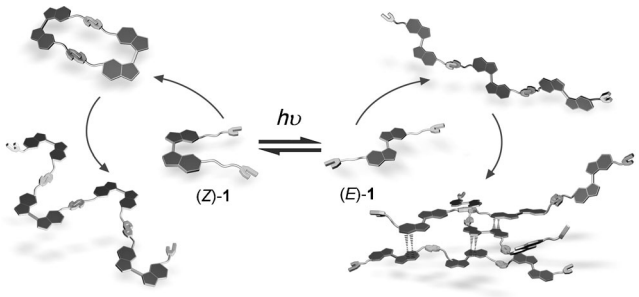


Figure 2. Specific viscosity of (*Z*)-**1** and (*E*)-**1** in $CHCl_3$ solutions versus the concentration (298 K). The values by the lines indicate the slopes.

The results of the NMR spectroscopy and viscosity measurements indicate the *Z* and *E* isomers of stiff stilbene derivatives polymerize by distinct mechanisms.[1b,14] The existence of a critical polymerization concentration, evident from the discontinuity in the slopes of the viscosity graphs for (*Z*)-**1**, is consistent with the ring-chain polymerization mechanism. The *Z* geometry of the stiff stilbene in (*Z*)-**1** enforces the two UPy moieties into an orientation that is particularly favorable for cyclic dimerization.[10] The linear viscosity curve with a constant slope for (*E*)-**1** suggests that it polymerizes by the isodesmic growth mechanism. Such a mechanism is likely facilitated by the linear conformation of (*E*)-**1**, which suppresses the tendency to form cyclic oligomers. This illustrates how photoisomerization can modulate self-assembly behavior (Scheme 2).

Concentrated solutions of (*Z*)-**1** in $CHCl_3$ have high viscosity, which facilitates the formation of fibers by electrospinning. Although electrospinning is a well-known and convenient technique for the fabrication of nanofibers, very few examples of supramolecular polymer nanofibers obtained by electrospinning have so far been reported.[15] Electrospinning a 0.4 M solution of (*Z*)-**1** in $CHCl_3$ produced a mat of nanofibers, thus confirming that (*Z*)-**1** forms supramolecular polymers with high molecular weights. SEM images of these fibers showed them to have diameters between 0.3 and 3 μm



Scheme 2. Schematic presentation of the supramolecular assembly processes of (*Z*)-**1** and (*E*)-**1**. (*Z*)-**1** forms cyclic dimers at low concentrations and polymerizes to supramolecular polymers at high concentrations. (*E*)-**1** forms linear supramolecular polymers and is further aggregated into three-dimensional fiber networks driven by π–π interactions between stiff (*E*)-stilbenes as the concentration increased.

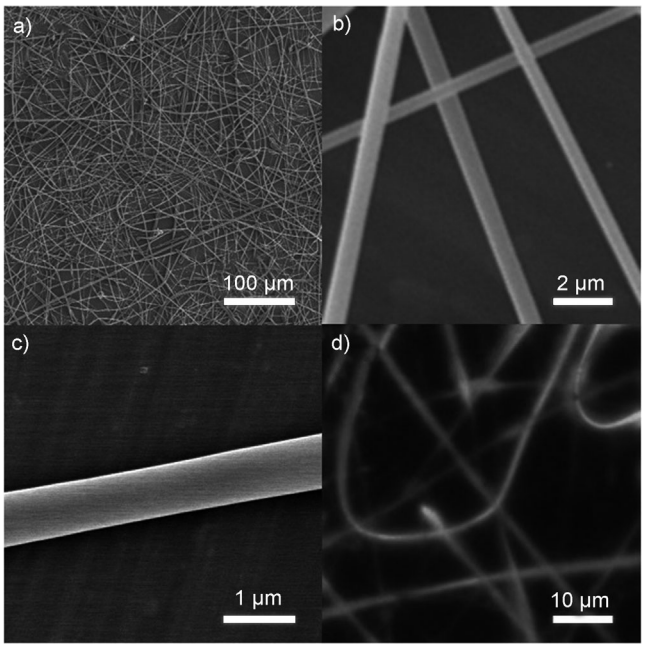


Figure 3. SEM images (a, b, and c) and fluorescence microscopy image (d) of nanofibers formed by (*Z*)-**1** by electrospinning; λ_{ex} = 365 nm.

and lengths of hundreds of micrometers (Figure 3 a–c). To the best of our knowledge, this is the first example of electrospun fibers constructed from quadruple hydrogen-bonded supramolecular polymers. The fibers generate blue fluorescence upon irradiation at 365 nm (Figure 3 d), which we attribute to emission of the stiff stilbene unit. Such fluorescent supramolecular polymeric nanofibers may have applications in material science for the fabrication of optoelectronic devices.

In contrast to (*Z*)-**1**, (*E*)-**1** forms a gel. Such supramolecular gels constructed from small molecules by reversible noncovalent interactions can respond to external stimuli, for example, changes in temperature, pH value, solvent, electronic field, and light.[16] Supramolecular gels have attracted increasing attention because of their potential applications in controlled release, as drug carries, molecular devices, and functional membranes. Irradiation of a 0.2 M solution of (*Z*)-**1** in $CHCl_3$ at 387 nm yielded a gel of supramolecular polymer (*E*)-**1**. The critical gel concentration was approximately 150 mM. A possible mechanism for the gel formation is that linear supramolecular polymers with a high degree of polymerization were first generated, and subsequently aggregated into three-dimensional fiber networks, as their concentration increased during irradiation, driven by π–π interactions between the stiff (*E*)-stilbenes (Scheme 2). This hypothesis is supported by the formation of a supramolecular gel in $CHCl_3$, CH_2Cl_2, and 1,2-$C_2H_4Cl_2$, but not in aromatic solvents such as benzene and toluene, which could interfere with π–π interactions between stiff (*E*)-stilbene moieties. The nonplanar geometry of the *Z*-configured stiff stilbene precludes intermolecular π–π interactions, thus accounting for the lack of gelation of (*Z*)-**1**. Indeed, irradiation of a gel of (*E*)-**1** at 360 nm to photoisomerize the stiff (*E*)-stilbene unit to its *Z* analogue, resulted in gel dissolution (Figure 4). Reversible

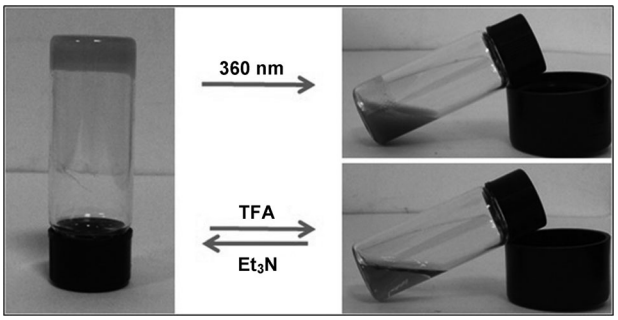


Figure 4. Supramolecular gel formed by (*E*)-**1** in $CHCl_3$ (0.2 M) and its response to stimuli (light and pH).

dissolution of the gel was also observed upon addition of CF_3COOH (TFA),[17] as previously observed for other supramolecular gels. Addition of excess Et_3N reformed the gel. Analysis of the xerogels by scanning electron microscopy (SEM) revealed an interconnected porous gel network (see Figure S8 in the Supporting Information), which may be useful for applications in material science.[18]

In summary, we described a photoresponsive quadruple hydrogen-bonded supramolecular polymer based on a stiff stilbene moiety. The polymerization mechanism and properties of the resulting materials depend strongly on the isomeric state of the chromophore. (*Z*)-**1** follows a ring-chain supramolecular polymerization and (*E*)-**1** forms a supramolecular polymer by an isodesmic growth mechanism. The electrospun fluorescent nanofibers were fabricated from the *Z* isomer, and a pH- and photoresponsive supramolecular polymer gel was formed from the *E* analogue. We speculate that the stiff stilbene chromophore will prove to be at least as useful as, and probably more useful than, azobenzene for the construction of various photoresponsive supramolecular assemblies and smart supramolecular materials with switchable properties.

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