ChemComm

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Journal:	*ChemComm*
Manuscript ID	CC-COM-02-2019-001660.R1
Article Type:	Communication

Journal Name

COMMUNICATION

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Supramolecular Network Derived by Rotaxane Tethering Three Ureido Pyrimidinone Groups

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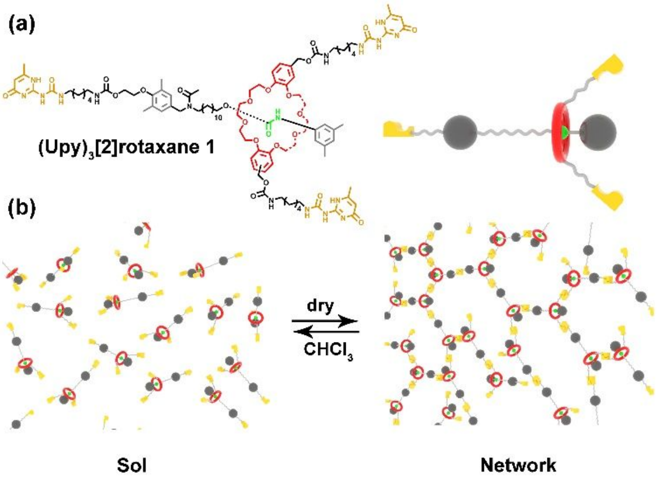
A supramolecular network and its film were prepared *via* intermolecular hydrogen bonding of a [2]rotaxane with three ureido pyrimidinone groups. Adding less polar solvents such as $CHCl_3$ to the rotaxane afforded a swollen rotaxane-cross-linked network. The properties of the film obtained by drying were evaluated to chracterize it.

Supramolecular polymers[1] attracted much research attention during the last decades because of their fascinating characteristics, including stimuli-responsiveness, self-healing ability, and antimicrobial properties.[2] Compared with traditional polymers, supramolecular polymers can be easily and conveniently constructed through non-covalent interactions.[3] Host–guest,[4] hydrogen bonding,[5] and π–π stacking interactions[6] and metal coordination[7] are significant non-covalent interactions. These have been extensively employed to construct various topological supramolecular polymer structures, such as linear[8] and cross-linked supramolecular polymers.[9]

Usually, cross-linked supramolecular polymers are constructed by introducing an additional cross-linker to linear supramolecular polymer structures.[10] Cross-linked supramolecular polymers exhibit higher molecular weights and viscosity, and sometimes unique performances.[9c,10,11] Cross-linked supramolecular polymers always form gel-type aggregates because of the introduction of additional cross-linking sites, such as low-molecular-weight cross-linking reagents and polymer backbones. Cross-linked supramolecular polymers were also shown to form elastic polymer gels,[9c,10a] exhibiting self-healing properties[11] and shape memory.[12] However, developing strong and stretchable supramolecular polymeric networks will be challenging. To the best of our knowledge, there has been insufficient research on preparing strong and stretchable supramolecular polymeric networks without introducing additional cross-linking sites.

Hydrogen bonding interactions have occupied a central position in constructing supramolecular polymers because of their high strength, directionality, and specificity.[5] Importantly, the 2-ureido-4-pyrimidinone (Upy) moiety,[13] designed and developed by Meijer's group, can dimerize *via* quadruple hydrogen bonding with a large dimerization binding constant ($K_{dim} > 10^6$ M^{-1} in $CHCl_3$)[13a] and is a well-investigated and important building block.[14]



Scheme 1 (a) Schematic illustration of the molecular structure and cartoon picture of **$(Upy)_3$[2]rotaxane 1**. (b) The formation of supramolecular network based on **$(Upy)_3$[2]rotaxane 1** and reversible, solvent-induced dissociation.

Meanwhile, rotaxanes as important mechanically interlocked molecules (MIMs) have attracted considerable attention because of their potential application in molecular machines.[15] Ito's and our groups independently reported a series of polymeric rotaxane-cross-linkers and revealed the significance of the rotaxane moiety in cross-linker polymers; for example, it endows polymers with a wide mobility range and improved mechanical strength.[16] Our aim is to combine [2]rotaxane with traditional Upy moieties to produce a stretchable rotaxane-cross-linked network. Herein, we report

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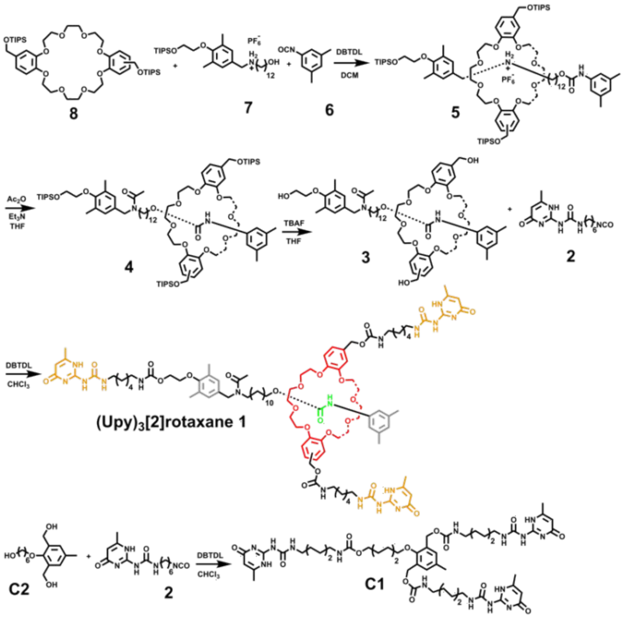
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x the design and preparation of a rotaxane-cross-linked network *via* intermolecular hydrogen bonding of a trifunctional [2]rotaxane having three ureido pyrimidinone groups.

As shown in Scheme 1, we designed a crown ether-based rotaxane having three ureido pyrimidinone moieties (**(Upy)$_3$[2]rotaxane 1**). **(Upy)$_3$[2]rotaxane 1** bears a dibenzo-24-crown-8 (DB24C8) macrocyclic ring with two Upy groups on one side of its axle and a Upy group on the other side. Adding a less polar solvent, such as CHCl$_3$, to the rotaxane afforded a swollen rotaxane-cross-linked network. A film was obtained by drying the supramolecular network.



Scheme 2 Preparation and chemical structures of key intermediate [2]rotaxane **3**, target compound **(Upy)$_3$[2]rotaxane 1**, and control compound **C1**.

To achieve the above-mentioned rotaxane-cross-linked network, key intermediate [2]rotaxane **3** and target compound **(Upy)$_3$[2]rotaxane 1** were designed, as shown in Scheme 2. Key intermediate [2]rotaxane **3** bears a DB24C8 macrocyclic ring with two hydroxyl groups on one side of its axle and one hydroxyl group on the other side. Compound **5** was obtained from compounds **8** and **7** in the presence of stopper **6** *via* classical threading-followed-by-stoppering and one-pot strategy. After producing dibenzylammonium compound **5**, deprotonation and a protection process yielded compound **4**. Compound **3** was obtained by deprotecting hydroxyl groups of compound **4**. The structure of [2]rotaxane **3** was confirmed with various characterization tools, including ^{1}H NMR (Figure S16), ^{13}C NMR (Figure S17), HR-ESI mass spectrometry (Figure S18), ^{1}H-^{1}H COSY (Figure S19), and ^{1}H-^{1}H ROESY (Figure S20). [2]Rotaxane **3** and compound **2** were dissolved in dry CHCl$_3$, and DBTDL was added and stirred at room temperature under Ar atmosphere. Target compound **(Upy)$_3$[2]rotaxane 1** was obtained as a white solid with a moderate yield of 41%. **(Upy)$_3$[2]rotaxane 1** was also confirmed with various characterization tools, including ^{1}H NMR (Figure S21), ^{13}C NMR (Figure S22), HR-ESI mass spectrometry (Figure S23), ^{1}H-^{1}H COSY (Figure S24), and ^{1}H-^{1}H ROESY (Figure S25). The major peaks in the HR-ESI mass spectrum of **(Upy)$_3$[2]rotaxane 1** were found at m/z 1980.0584 and 1001.5279, which correspond to $[M + Na]^+$ and $[M + 2Na]^{2+}$, respectively.

Concentration-dependent ^{1}H NMR spectroscopy was used to investigate the aggregation of **(Upy)$_3$[2]rotaxane 1** in CDCl$_3$ (Figure S32). As the **(Upy)$_3$[2]rotaxane 1** concentration increased from 0.2 to 30 mM, the major signals gradually became broader, with no significant chemical shift changes.

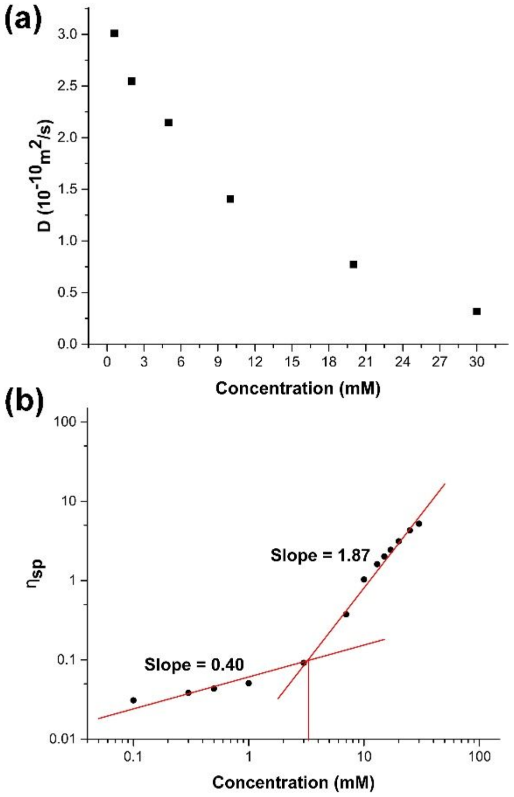


Figure 1 (a) Variation of diffusion coefficient *D* with concentration (500 MHz, CDCl$_3$, 298 K). (b) Specific viscosity (η_{sp}) of **(Upy)$_3$[2]rotaxane 1** (CHCl$_3$, 298 K) *versus* the monomer concentration.

Variable-concentration 2D diffusion-ordered ^{1}H NMR spectroscopy (DOSY; Figures S33–S38) is a convenient and reliable method for measuring the size distribution of supramolecular polymer aggregates. As the **(Upy)$_3$[2]rotaxane 1** concentration increased from 0.6 to 30 mM, the diffusion coefficient (*D*) decreased from 3.010×10^{-10} to 3.172×10^{-11} m^2/s (Figure 1a). The result showed that the size distribution of rotaxane-cross-linked supramolecular polymer gradually increased with the **(Upy)$_3$[2]rotaxane 1** concentration.

To study the properties of the rotaxane-cross-linked supramolecular polymer in detail, concentration-dependent viscosity experiments were performed. The specific viscosity (η_{sp}) of **(Upy)$_3$[2]rotaxane 1** in CHCl$_3$ at 298 K was measured, and a double-logarithmic plot of η_{sp} *versus* concentration is shown in Figure 1b. The rotaxane-cross-linked supramolecular polymer assembled from the monomer exhibited a viscosity transition. At low concentrations, a linear plot with a slope of 0.40 was observed, demonstrating a linear relationship between the specific viscosity and concentration. When the concentration exceeded the critical polymerization concentration (CPC: approximately 3.2 mM), a sharp increase in the viscosity was observed, with a slope of 1.87, illustrating a transition from monomer to cross-linked supramolecular polymer with increased size.

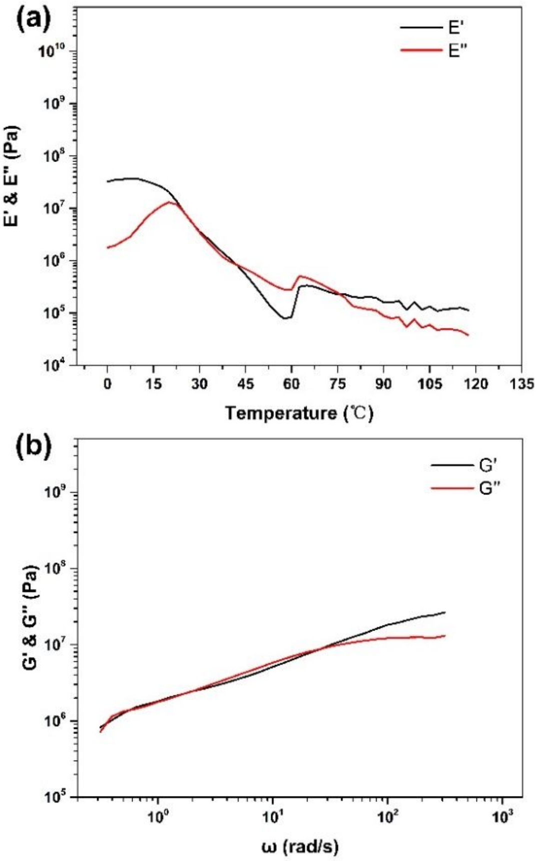


Figure 2 Mechanical and rheological properties of rotaxane-cross-linked film. (a) Representative dynamic mechanical analysis (DMA, 2.5°C/min) trace of film; shown are the storage (*E′*) and loss moduli (*E′′*). (b) Storage (*G′*) and loss moduli (*G′′*) of film versus scanning frequency (ω) at 298 K.

Thermogravimetric analysis (TGA; Figure S39) and differential scanning calorimetry (DSC; Figure S40) were used to evaluate the thermal properties of **(Upy)$_3$[2]rotaxane 1**. The TGA of **(Upy)$_3$[2]rotaxane 1** shows a 2% weight loss at 217°C; above this temperature, the decomposition rapidly accelerates. The DSC heating trace of **(Upy)$_3$[2]rotaxane 1** shows a endothermic transition at 86°C, which is associated with the glass transition. The cooling scan shows a glass transition around 79°C and is devoid of any other transitions, illustrating that, upon melting and cooling, **(Upy)$_3$[2]rotaxane 1** is an amorphous solid. Meanwhile, powder X-ray diffraction (Figure S41) experiments demonstrated that **(Upy)$_3$[2]rotaxane 1** is an amorphous solid before heating and after heating to 185°C and cooling to room temperature.

As shown in Scheme 1b, a rotaxane-cross-linked supramolecular polymeric film can be obtained through a slow solvent evaporation strategy. First, the film surface was investigated using scanning electron microscopy (SEM; Figure S42). The SEM image revealed the film surface as a relatively complete plane, except for some air holes caused by solvent evaporation.

The thermomechanical properties of the film were investigated by dynamic mechanical analysis (DMA), as shown in Figure 2a. The DMA trace of the film shows a glassy regime up to 27.5°C with a 7.5°C storage modulus (*E′,* black line) of 37.5 MPa, reflecting high stiffness.

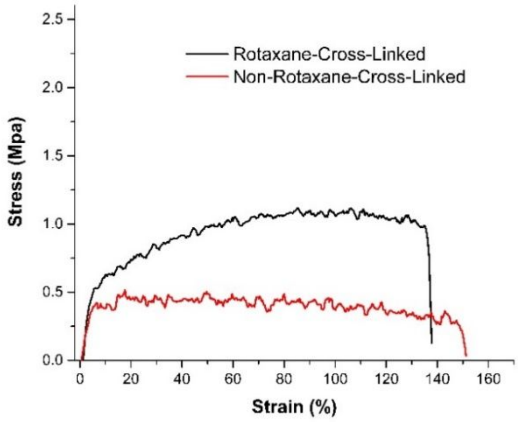


Figure 3 Tensile strength test for rotaxane-cross-linked film and non-rotaxane-cross-linked film (sample size: 12 mm × 12 mm × 0.20-0.25 mm, elongation rate: 50 mm/min, 298K).

To investigate the mechanical properties of the film, rheological characterization was performed. Figure 2b shows the changes in storage modulus (*G′*, black line) and loss modulus (*G′′*, red line) as a function of frequency during a dynamic frequency sweep at 298 K. During the frequency sweep, both *G′* and *G′′* increased with frequency, but *G′* showed higher values than *G′′* above 2.495 rad/s. The *G′* plateau value is 26.5 MPa at 314.2 rad/s. This is compared with a host–guest-based supramolecular polymer network gel system (plateau modulus ≈ 10–10^4 Pa) reported by Huang and co-workers.[10a] Therefore, the rotaxane-cross-linked supramolecular polymer network based on hydrogen bonding interactions exhibits better mechanical properties.

To deeply demonstrate the mechanical properties of the film, the tensile strength of the film was examined (Figure 3, black line). A tensile stress–strain curve indicated that the film could be stretched to 1.3 times its original length. From the low-strain region (2% to 8%) of the tensile strength curve, the Young's modulus was calculated as 8.46 ± 0.21 MPa, illustrating the high strength of the hydrogen bonds.

To illustrate the effects of the rotaxane framework on the mechanical properties, control compound **C1** was synthesized (Scheme 2). The structure of compound **C1** was confirmed by ^{1}H NMR (Figure S29), ^{13}C NMR (Figure S30), and HR-ESI mass spectrometry (Figure S31). A non-rotaxane-cross-linked supramolecular polymeric film can also be obtained from a solution of control compound **C1** through a slow solvent evaporation strategy. The mechanical properties of the non-rotaxane-cross-linked film were evaluated using DMA (Figure S43), rheological characterization (Figure S44), and tensile strength testing (Figure 3, red line). The DMA trace (Figure S43) of non-rotaxane-cross-linked film shows a glassy regime up to 25°C with a 0°C storage modulus (E'_{C1}, black line) of 20.8 MPa, indicating that the non-rotaxane-cross-linked film has a lower stiffness. Rheological examination of the non-rotaxane-cross-linked film was also performed as shown in Figure S44.

The storage modulus plateau value is 10.9 MPa at 314.2 rad/s, illustrating that the rotaxane-cross-linked film has better mechanical properties (the storage modulus plateau value is 26.5 MPa at 314.2 rad/s). From the low-strain region (2% to 8%) of the tensile strength curve (Figure 3, red line) of non-rotaxane-cross-linked film, the Young's modulus was calculated as 3.91 ± 0.26 MPa. Compared with the Young's modulus of the rotaxane-cross-linked film (8.46 ± 0.21 MPa), this result demonstrated that the non-rotaxane-cross-linked film has poorer mechanical properties. These results illustrated that the film based on the rotaxane framework exhibits better mechanical properties than the non-rotaxane-cross-linked film.

In summary, we successfully prepared a novel rotaxane-cross-linked supramolecular network with good mechanical property resulting from **(Upy)$_3$[2]rotaxane 1** *via* intermolecular hydrogen bonding interactions without introducing additional low-molecular-weight cross-linking reagents or polymer backbones. The polymerization process of the rotaxane-cross-linked supramolecular polymer was monitored by ^{1}H NMR, DOSY, and viscosity measurements. The mechanical properties of rotaxane-cross-linked and non-rotaxane-cross-linked films were carefully investigated using DMA and rheological and tensile strength testing, which indicated that the film based on a rotaxane framework exhibited better mechanical properties. We not only successfully developed and constructed a novel rotaxane-cross-linked film but also provided insight into supramolecular polymerization.

We are grateful for the support of the JST CREST Grant Number JPMJCR1522, Japan, JSPS KAKENHI Grant Number JP16K17955. The authors would like to thank Dr Tadashi Tsukamoto, Dr Jun Sawada, and Prof. Satoshi Uchida for the valuable discussions and suggestions on the experimental work.

Conflicts of interest

There is no conflict to declare.

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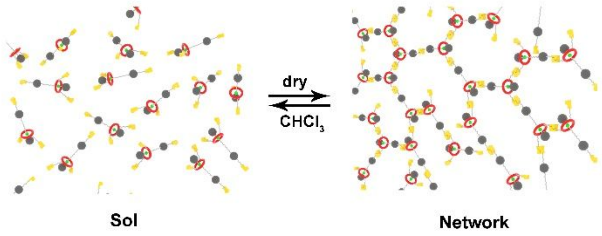

Rotaxane-cross-linked supramolecular network with good mechanical property resulting from a trifunctional [2]rotaxane *via* intermolecular hydrogen bonding interactions.