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Journal:	*Polymer Chemistry*
Manuscript ID	PY-ART-08-2018-001217.R1
Article Type:	Paper
Date Submitted by the Author:	05-Oct-2018
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Photoresponsive Supramolecular Polymers Based on Quadruple Hydrogen-Bonding and a Photochromic Azobenzene Motif

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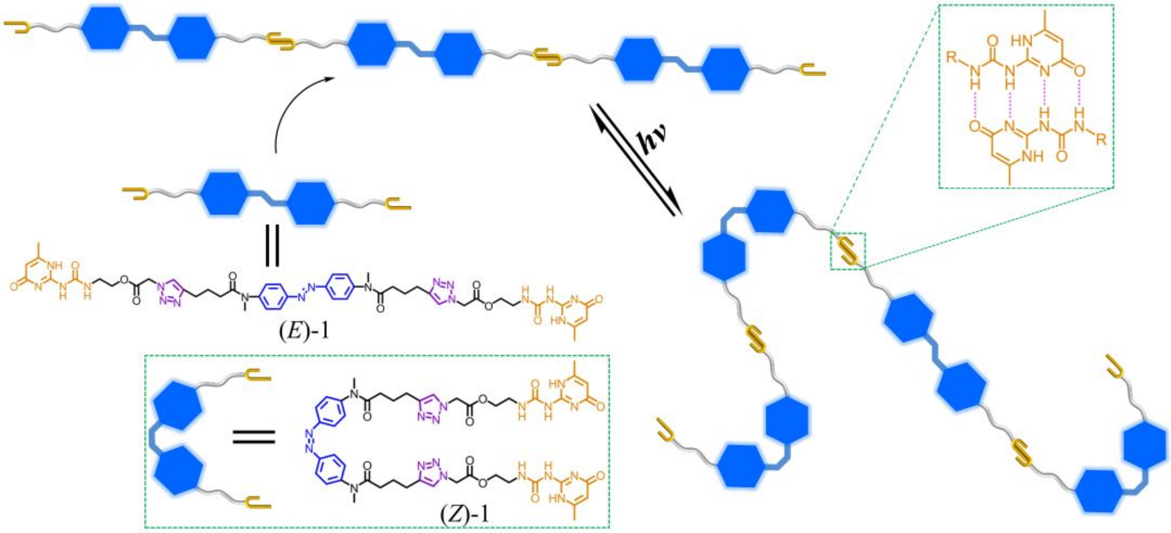
Abstract: A photoresponsive quadruple hydrogen-bonded supramolecular polymer was constructed using photochromic azobenzene and ureidopyrimidinone motifs. The *E*-isomer of azobenzene preferred to form linear supramolecular polymers and further aggregate as its concentration increased. After irradiation with UV light, *E*-isomer was converted into *Z*-isomer, and *Z*-isomer could also self-assemble into supramolecular polymers with relatively low degree of polymerization. Moreover, supramolecular polymer films were fabricated by a solution casting process. These supramolecular polymers showed highly reversible *trans*/*cis* photoisomerization in both solutions and films under alternating UV and visible light irradiation.

Introduction

Supramolecular polymers, in which the monomeric units are held together by hydrogen bonding, host-guest interactions, π-π stacking or other reversible noncovalent interactions, have attracted increasing attention in recent years owing to their fascinating properties such as stimuli-responsiveness, self-healing, and reversibility.[1-11] Among noncovalent interactions, hydrogen bonding has emerged as a powerful tool to construct supramolecular polymers due to its relatively high strength, directionality, and specificity.[12-15] The highly directional quadruple hydrogen bonding unit of ureidopyrimidinone (UPy) is a well-explored and robust building block in assembling supramolecular polymers because of its high association constant.[16-19]

Owing to the dynamic nature of noncovalent interactions, physical properties of supramolecular polymers could be controlled by external stimuli.[20-23] Among different kinds of stimuli, light is particularly favorable because it allows remote activation and control without introducing extra chemicals.[24-28] Previously reported supramolecular polymers showed a variety of properties such as dynamic switch between polymers and oligomers,[29] well-defined aggregated morphologies,[30] or reversibility between gel and solution,[31] upon irradiation. Azobenzene is one of the most explored photoswitchable molecules, which has been successfully used in the fabrication of photoresponsive functional polymers, because of the substantial structural difference between the *trans* and *cis* (or *E*/*Z*) isomers.[32-36]

Scheme 1. Chemical structures of (*E*)-**1** and (*Z*)-**1** containing azobenzene and ureidopyrimidinone, and their supramolecular assembly processes.



In this work, we prepare a monomer (*E*)-**1**, which combined photochromic azobenzene with two UPy moieties. It could self-assemble into supramolecular polymers in solution driven by quadruple hydrogen bonding between UPy groups at high concentrations (**Scheme 1**). When irradiated with 380 nm UV light, (*E*)-**1** can be converted into (*Z*)-**1**, which can also self-assemble into supramolecular polymers at such concentrations. The self-assembly behavior of these supramolecular polymers in solution was carefully investigated, and the photoresponsive properties of supramolecular polymers in films were also discussed.

Experimental Section

Materials

4,4'-Azodianiline (95%), ethanolamine (98%), bromoacetyl bromide (98%), sodium azide (99%), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl), sodium ascorbate (98%), and tetrabutylammonium hydrogen sulphate (98%) were purchased from VWR. 6-Methylisocytosine (98%), 1,1'-carbonyldiimidazole (97%), 5-hexynoic acid (97%), triethylamine (TEA, 99.5%), 4-(dimethylamino)pyridine (DMAP, 98%), methyl iodide (99%), and copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, 98%) were purchased from Sigma Aldrich. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone under N_2. All other chemicals were obtained from VWR and used without further purification unless otherwise noted.

Characterization

^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian Mercury 300 spectrometer using $CDCl_3$, CD_3OD or DMSO-d_6 as a solvent and tetramethylsilane (TMS) as an internal standard. 2D DOSY-NMR spectra were recorded on a Bruker Advance 400 spectrometer. High-resolution ESI mass spectra (HR-MS) were collected at the University of South Carolina mass spectrometry center. Fourier transform infrared spectroscopy (FTIR) was carried out on a PerkinElmer spectrum 100 FTIR spectrometer using an attenuated total reflection method. The UV-Vis spectra were recorded by a Shimadzu UV-2450 spectrophotometer. Dynamic light scattering (DLS) was performed on a Nano-ZS instrument, model ZEN 3600 (Malven Instruments).

Synthesis of UPy-OH (3)

1-(2-Hydroxyethyl)-3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea, in short, UPy-OH, was prepared according to literature.[37] A detailed synthesis procedure was given in the Supporting Information.

Synthesis of UPy-Br (4)

A solution of UPy-OH **3** (2.0 g, 9.44 mmol) and TEA (2 mL) in dry THF was cooled to 0 ^{o}C, then bromoacetyl bromide (2.1 mL, 23.6 mmol) was added dropwise via a syringe. The reaction mixture was allowed to reach room temperature and stirred for another 24 h. After reaction, water was added to the mixture, which was extracted with dichloromethane. The organic phase was washed with saturated $NaHCO_3$, 1 M HCl and brine. The organic layer was dried over Na_2SO_4 and evaporated to dryness. After dried under vacuum, the product **4** was obtained as a white solid without further purification (2.41 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.94 (s, 1H), 11.94 (s, 1H), 10.45 (s, 1H), 5.80 (s, 1H), 4.33 (t, 2H), 3.92 (s, 2H), 3.58 (m, 2H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 167.19, 163.64, 161.80, 155.23, 151.45, 104.42, 64.36, 38.10, 27.12, 22.91. HR-MS (ESI$^+$): *m*/*z* 333.0191 (calcd. 333.0193 for $C_{10}H_{14}BrN_4O_4^+$ $[M+H]^+$).

Synthesis of UPy-N_3 (5)

UPy-Br **4** (2.0 g, 6.0 mmol) was dissolved in 40 mL DMF in a 100 mL glass bottle. 4 mL distilled water and sodium azide (1.95 g, 30 mmol) were added to the mixture. The mixture was heated at 50 ^{o}C for 24 h under nitrogen. The solution was allowed to cool to room temperature and 20 mL water was added. The precipitate was filtered and washed with water. After dried under vacuum, the product **5** was obtained as a white solid (1.31 g, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.94 (s, 1H), 11.94 (s, 1H), 10.46 (s, 1H), 5.80 (s, 1H), 4.36 (t, 2H), 3.94 (s, 2H), 3.59 (m, 2H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.08, 168.59, 156.95, 154.63, 148.57, 106.89, 64.18, 50.49, 38.90, 19.10.

HR-MS (ESI$^+$): *m*/*z* 296.1099 (calcd. 296.1102 for $C_{10}H_{14}N_7O_4^+$ [M+H]$^+$).

Synthesis of (*E*)-N,N'-(diazene-1,2-diylbis(4,1-phenylene))bis(hex-5-ynamide) (6)

To a suspension of 4,4'-zaodianiline (1.0 g, 4.7 mmol) in dichloromethane (dehydrated, 60 mL) at 0 °C was added dropwise a solution of 5-hexynoic acid (1.3 g, 11.75 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) (2.97 g, 15.51 mmol) and 4-dimethylaminopyridine (DMAP) (2.01 g, 16.45 mmol) in dichloromethane (30 mL). The reaction mixture was allowed to reach room temperature before being stirred for a further 24 h. The yellow solid was collected by filtration and washed with dichloromethane, and dried in vacuum oven to afford a yellow powder (1.43, 76%). ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 10.27 (s, 2H), 7.82 (m, 8H), 2.84 (t, 2H), 2.25 (t, 4H), 1.78 (m, 4H). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 171.04, 147.51, 141.91, 123.34, 119.22, 83.98, 71.68, 35.20, 23.81, 17.37. HR-MS (ESI$^+$): *m*/*z* 401.1970 (calcd. 401.1972 for $C_{24}H_{25}N_4O_2^+$ [M+H]$^+$).

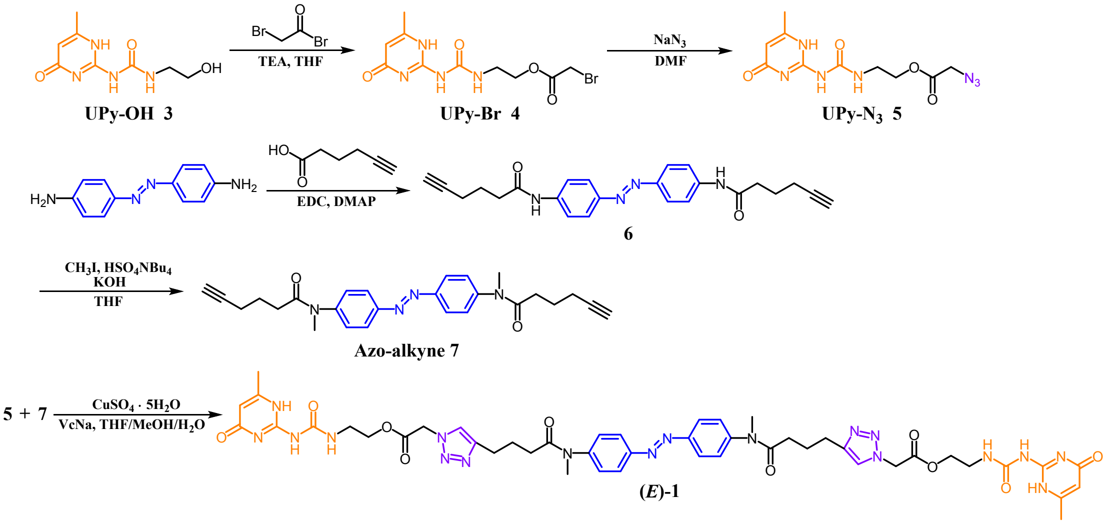
Synthesis of (*E*)-N,N'-(diazene-1,2-diylbis(4,1-phenylene))bis(N-methylhex-5-ynamide) (7)

Compound **6** (1.0 g, 2.5 mmol) was dissolved in 120 mL THF. Freshly ground potassium hydroxide (0.84 g, 15 mmol), tetrabutylammonium hydrogen sulfate (0.85 g, 2.5 mmol) and methyl iodide (0.78 mL, 12.5 mmol) were added and the solution was refluxed for 24 h. The solution was quenched with aqueous ammonia and then extracted with ethyl acetate. The organic phase was dried with Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography (ethyl acetate as elution) on silica gel to give a yellow solid (0.92 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, 4H), 7.38 (d, 4H), 3.33 (s, 6H), 2.32 (t, 4H), 2.20 (t, 4H), 1.87 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.18, 151.39, 146.60, 128.11, 124.34, 83.71, 69.03, 37.42, 32.90, 24.15, 17.93. HR-MS (ESI$^+$): *m*/*z* 429.2289 (calcd. 429.2285 for $C_{26}H_{29}N_4O_2^+$ [M+H]$^+$).

Synthesis of monomer (*E*)-1

UPy-N_3 **5** (200 mg, 0.68 mmol), azo-alkyne **7** (145 mg, 0.34 mmol), $CuSO_4·5H_2O$ (35 mg, 0.14 mmol), and sodium ascorbate (55.4 mg, 0.28 mmol) were dissolved in a mixture of THF (40 mL), methanol (8 mL), and H_2O (8 mL). The reaction mixture was stirred at 50 °C for 24 h. The solvents were removed in vacuum. The residue was poured into water, extracted with dichloromethane. The organic phase was washed with brine and dried over Na_2SO_4. After the solvent was removed under vacuum, the residue was purified by column chromatography (CH_2Cl_2/CH_3OH = 20/1) on silica gel to give a yellow solid (270 mg, 78%). ^1H NMR (300 MHz, $CDCl_3$): δ 12.87 (s, 2H), 11.89 (s, 2H), 10.40 (s, 2H), 7.90 (d, 4H), 7.30 (d, 4H), 7.27 (s, 2H), 5.82 (s, 2H), 5.15 (s, 4H), 4.32 (t, 4H), 3.51 (m, 4H), 3.31 (s, 6H), 2.69 (t, 4H), 2.25 (s, 6H), 2.19 (t, 4H), 1.96 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.14, 172.45, 166.79, 156.77, 154.51, 151.30, 148.97, 147.92, 146.53, 128.00, 124.32, 122.52, 106.80, 64.59, 50.83, 38.72, 37.41, 33.53, 33.14, 25.14, 19.05. HR-MS (ESI^+): *m*/*z* 1019.4311 (calcd. 1019.4343 for $C_{46}H_{55}N_{18}O_{10}^+$ $[M+H]^+$).

Scheme 2. Synthesis of monomer (*E*)**-1** by click chemistry between azo-alkyne and UPy-N_3.



Results and Discussion

Synthesis of monomer (*E*)-1

Monomer (*E*)**-1** was synthesized by copper-catalyzed click reaction between UPy-N_3 **5** and azo-alkyne **7** in a yield of 78% (**Scheme 2**). UPy-N_3 **5** was synthesized in two steps from UPy-OH **3**, which was synthesized according to literature.[37] Azo-alkyne **7** was obtained by amidation between 4,4'-zaodianiline and 5-hexynoic acid in a yield of 76%, and then methylation in a yield of 86%. The chemical structure of monomer (*E*)**-1** was confirmed by ^{1}H and ^{13}C NMR (see **Figures S15-S16** in the Supporting Information). The disappearance of absorption band of azide at 2105 cm^{-1} was observed in FTIR of (*E*)**-1** (**Figure S17**), indicating the successful click reaction. (*E*)**-1** was further confirmed by HR-ESI-MS, with a signal at m/z = 1019.4311, which corresponds to $[M+H]^+$ (**Figure S18**).

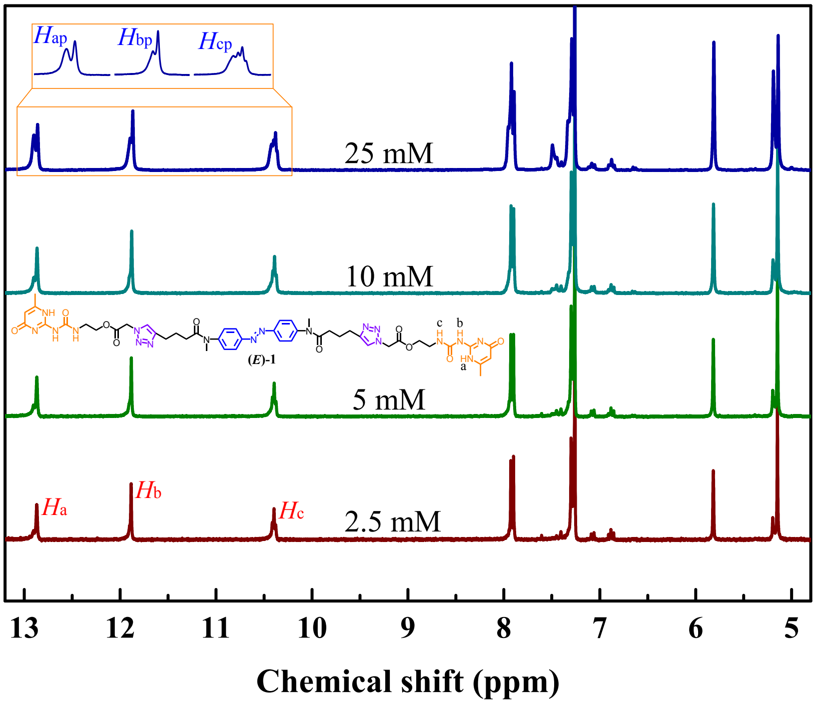


Figure 1. ^{1}H NMR spectra of monomer (*E*)**-1** at different concentrations in $CDCl_3$. Signals originating from polymeric aggregates are labeled “p”.

Self-assembly of (*E*)-1 in solution

The concentration-dependent ^{1}H NMR spectroscopy can be used to investigate the self-assembly behavior of supramolecular polymers.[38] As shown in **Figure 1**, ^{1}H NMR spectra of monomer (*E*)**-1** were collected at concentrations in the range of 2.5-25 mM. (*E*)**-1** at the concentration of 2.5 mM in $CDCl_3$ showed sharp N-H signals of UPy units with a large downfield shift to 10-13.5 ppm, indicating the formation of strong intermolecular hydrogen bonds.[38-41] With the increase of concentration, ^{1}H NMR spectra of (*E*)**-1** showed broadening of signals at 12.9, 11.9 and 10.4 ppm, suggesting the likely formation of linear supramolecular polymers at high concentrations, which was consistent with previous reports.[42-44] However, when the concentration was further increased, the supramolecular polymers had poor solubility in chloroform. This phenomenon revealed that the formed supramolecular polymers were highly aggregated.[45]

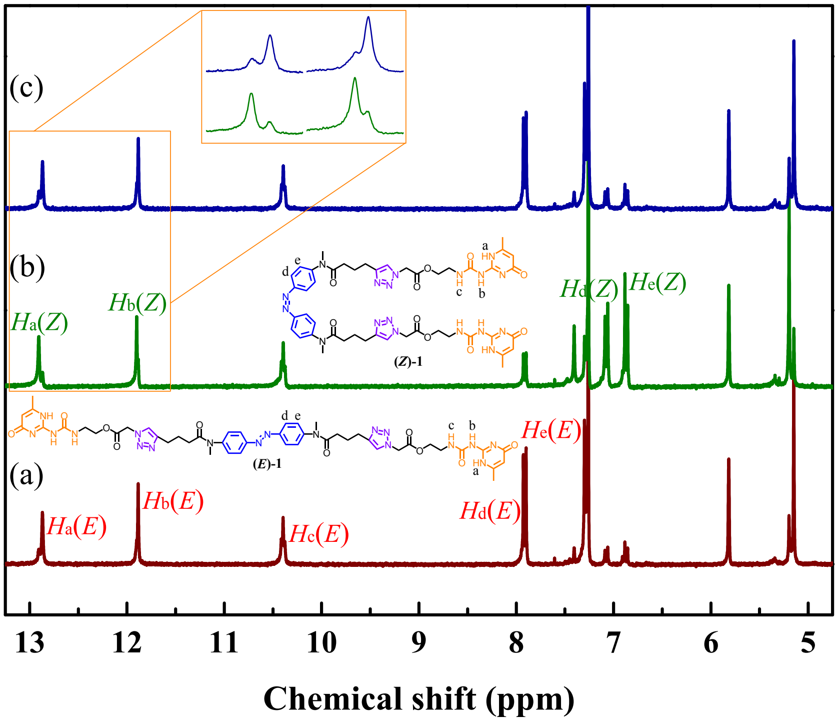


Figure 2. ^{1}H NMR spectra of (a) monomer (*E*)**-1** in $CDCl_3$ (5 mM); (b) irradiation with 380 nm UV light for 10 min; (c) irradiation with 450 nm visible light for 30 min.

Subsequently, we studied the photoisomerization of monomer (*E*)**-1** by ^{1}H NMR spectroscopy. After irradiation of (*E*)-**1** in $CDCl_3$ (5 mM) with 380 nm UV light for 10 min, the *E* to *Z* photoisomerization of azobenzene was observed by the urea NH signals of H_a (12.9 ppm) and H_b (11.9 ppm) in (*Z*)-**1** (**Figure 2b**). The NH signals in *Z*-isomers also appeared at high chemical shift, which overlapped with the signals from polymeric aggregates mentioned above. Meanwhile, the ratio of *Z*- to *E*-isomers in the photostationary state was determined to be 72:28, by integrating the peak areas of H_d (*Z*) and H_d (*E*) in the ^{1}H NMR spectrum. Furthermore, (*E*)-**1** could be regenerated when (*Z*)-**1** was irradiated with 450 nm visible light for 30 min, as determined by ^{1}H NMR spectroscopy (**Figure 2c**). The ratio of *Z*- to *E*-isomers in the photostationary state could also be determined to be 18:82, which was fairly close to the initial state (12:88). We also studied the photoisomerization of monomer (*E*)**-1** at different concentrations, as shown in **Figure S19**. After irradiation with 380 nm UV light for 3 min, the ratio of *Z*- to *E*-isomers was reduced with the increase of concentration, suggesting the formation of supramolecular aggregates at high concentrations, and the photoisomerization process is restricted.

2D diffusion-ordered ^{1}H NMR spectroscopy (DOSY) is a powerful tool to investigate the size distribution of supramolecular aggregates. Due to the relative low solubility of monomer (*E*)-**1** in chloroform, we first studied the DOSY spectra at a low concentration (5 mM) in $CDCl_3$, as shown in **Figure 3**. The DOSY spectrum of (*E*)-**1** solution showed two sets of well-defined signals (**Figure 3a**). The diffusion coefficients (*D*) were estimated to be 3.55×10^{-10} and 4.47×10^{-10} m^2 s^{-1}, respectively, indicating that a small fraction of supramolecular polymer was formed. However, after irradiation with 380 nm UV light, the signals corresponding to the lower *D* value disappeared, indicating that the degree of polymerization (DP) of supramolecular polymers decreased due to the *Z*/*E* photoisomerization process. This phenomenon becomes more pronounced when the concentration was increased to 20 mM, as shown in **Figure S20**.

In addition, the size distribution of supramolecular polymers was estimated by DLS measurement. As shown in **Figure S21**, the aggregation of monomer (*E*)**-1** in chloroform (2.5 mM) showed an average hydrodynamic size of 275 nm, indicating the formation of large supramolecular polymer aggregates. After irradiation with 380 nm UV light for 30 min, the size of aggregates decreased to 153 nm, suggesting the decrease in the molecular weight.

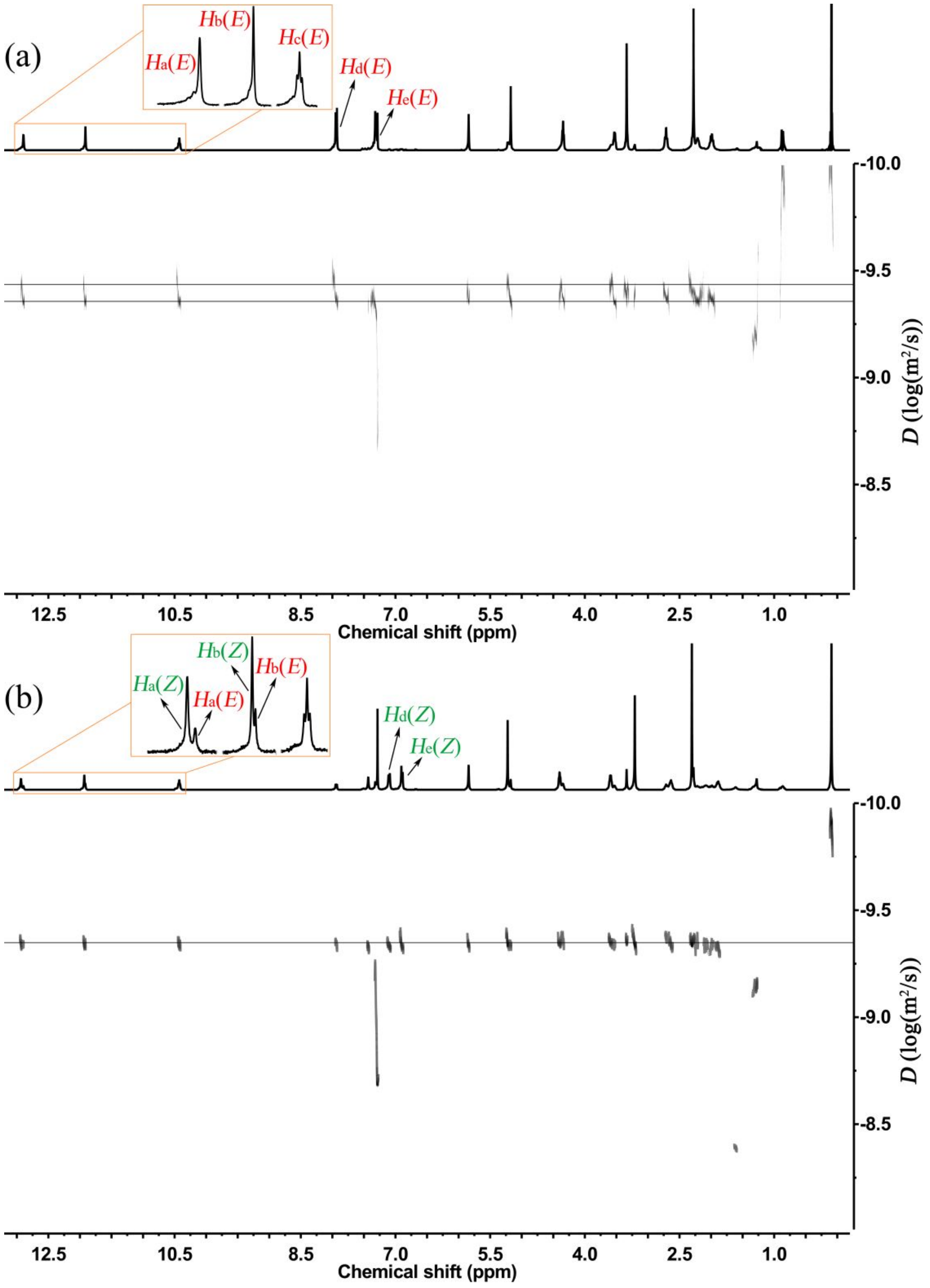


Figure 3. DOSY spectra of (a) solution (*E*)-**1** (5 mM); (b) the solution of (*E*)-**1** (5 mM) after irradiation with 380 nm UV light for 5 min.

The self-assembled supramolecular polymers from the quadruple hydrogen bonding motifs are significantly affected by the polarity of solvent. As observed in **Figure 4**, (*E*)-**1** in aprotic $CHCl_3$ at high concentrations (100 mg/mL) was turbid due to the formation of highly aggregated supramolecular polymers. However, after adding a small amount of protic solvent CH_3OH (50 μL), the system became clear. ^1H NMR spectra showed the significantly decreased NH intensities (between 10 and 13.5 ppm) after the introduction of protic solvent CD_3OD into the solution of (*E*)-**1** ($CDCl_3$, 10 mM), suggesting the intermolecular hydrogen bonds were largely disassembled (**Figure 5**).[46]

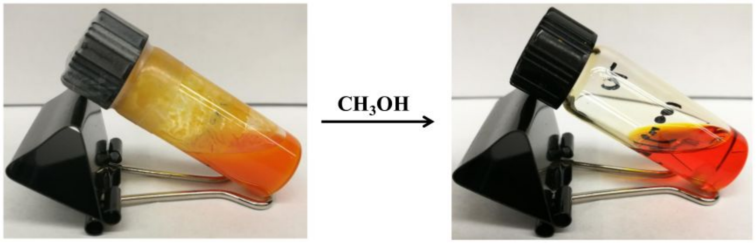


Figure 4. The photographs of (*E*)-**1** in $CHCl_3$ (100 mg/mL) and after addition of CH_3OH (50 μL).

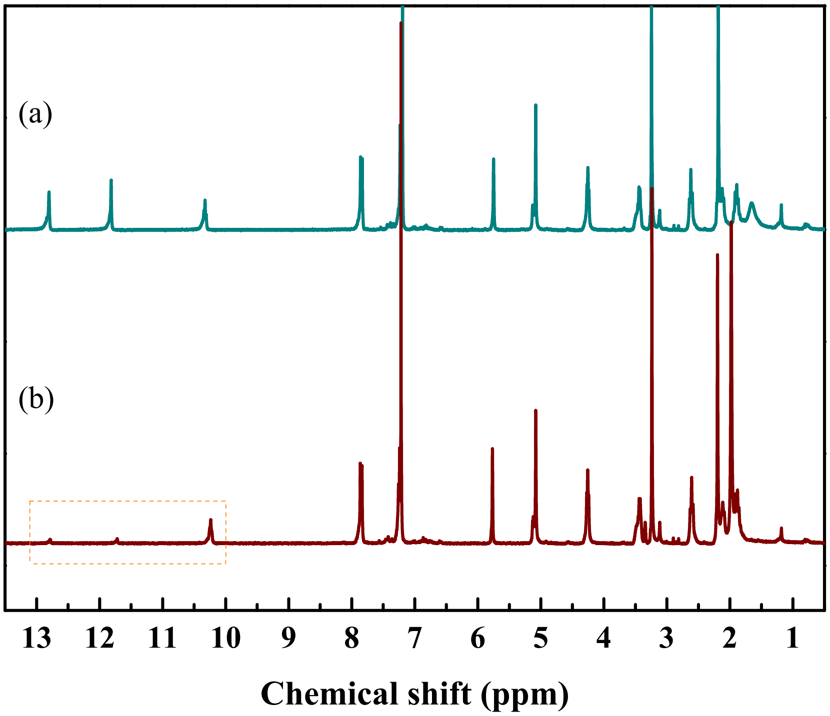


Figure 5. ^{1}H NMR spectra of (*E*)-**1** in different solvents (10 mM): (a) $CDCl_3$; (b) $CDCl_3/CD_3OD$ (4/1, v/v).

Supramolecular polymer films were also constructed by a solution casting process as follows. Monomer (*E*)-**1** was dissolved in chloroform and filtered through 0.45 μm PTFE syringe filter to obtain a solution with a concentration about 30 mg/mL. The film can be obtained by casting the solution onto a clear glass slide or a polyimide film and dried completely at room temperature for 24 h, as shown in **Figure S22**.

UV-Vis absorption studies

The photoresponsive properties of (*E*)-**1** were initially investigated in chloroform. By irradiation with 380 nm UV light, (*E*)-**1** solution underwent *trans* to *cis* photoisomerization until a photostationary state was eventually reached (**Figure S23a**). The intensity of the π→π* transition band around 342 nm gradually decreased as the irradiation time increased, whereas the n→π* transition band around 438 nm slightly increased. When irradiating the above solution at the photostationary state with visible light (450 nm), the *cis* to *trans* back-isomerization process occurred (**Figure S23b**). During this process, the π→π* transition band increased, and the n→π* transition band decreased. Moreover, the finally recovered absorbance of *trans*-azobenzene was almost the same as that before UV light irradiation with the recovery of the *trans*-isomer at ~99%. Furthermore, the photochemical isomerization became completely reversible upon the subsequent cycles of UV and visible light irradiation (**Figure S24**).

The photochemical isomerization of supramolecular films was also investigated. As shown in **Figure 6a**, the π→π* and n→π* transition bands in supramolecular polymer films were observed at 350 and 447 nm, respectively. Irradiation of the supramolecular polymer film with 380 nm UV light resulted in *trans* to *cis* photoisomerization, and a photostationary state was eventually reached in about 5 min. The supramolecular polymer film showed a lower level of *trans* to *cis* isomerization than that in solution due to the restricted movement of polymer chains in the film. In addition, the photochemical *cis* to *trans* back-isomerization was also observed upon irradiating the above film with 450 nm visible light (**Figure 6b**). However, the finally recovered absorbance of *trans*-isomer was lower than that before UV light irradiation and the recovery was about 93%, which might be resulted from the limited chain movement in the film. Furthermore, supramolecular polymer films also showed an excellent reversible light isomerization performance upon the alternating UV and visible light irradiation at least 15 times (**Figure 7**).

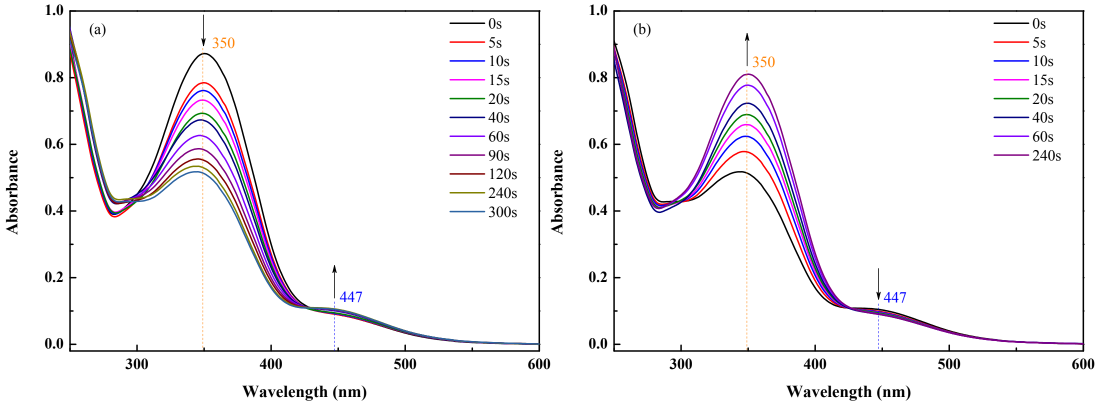


Figure 6. UV-vis spectral changes in dependence of time for supramolecular films at

25°C: (a) upon irradiation with 380 nm light and (b) upon irradiation of the film at the photostationary state with 450 nm visible light.

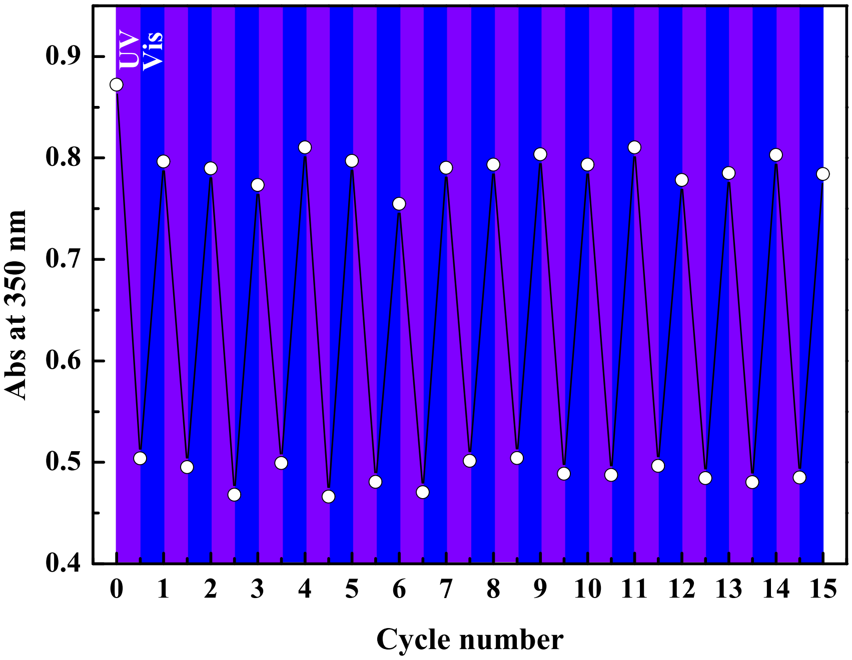


Figure 7. Absorption modulation under alternating UV irradiation (380 nm, 5 min) and visible light irradiation (450 nm, 4 min).

Conclusions

In summary, a photoresponsive quadruple hydrogen-bonded supramolecular polymer based on a bifunctional UPy bridged with an azobenzene motif was synthesized by copper-catalyzed click reaction. The supramolecular polymer was formed in chloroform due to the self-complementary recognition of the quadruple hydrogen bonds, and the self-assembly behavior of this supramolecular polymer was carefully investigated. The *E*-isomer preferred to form linear supramolecular polymers, and further formed highly aggregated supramolecular polymers as the concentration increased. After irradiation with UV light, *E*-isomer was converted into *Z*-isomer, and *Z*-isomer could also self-assemble into supramolecular polymers with relatively low degree of polymerization at such concentrations. In addition, supramolecular polymer films showed highly reversible *trans*/*cis* photoisomerization under alternating UV and visible light irradiation.

Electronic supplementary information (ESI) available: Experimental procedures, characterization data for all the materials. See DOI: 10.1039/

Acknowledgments

S.T. thanks the financial support from the China Scholarship Council (201706285068). This work was partially supported by the University of South Carolina.

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