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New Light on the Ring–Chain Equilibrium of a Hydrogen-Bonded Supramolecular Polymer Based on a Photochromic Dithienylethene Unit and its Energy-Transfer Properties as a Storage Material

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Abstract: A novel, bifunctional, quadruple hydrogen-bonding ureido-pyrimidinone (UPy) unit bridged by photochromic dithienylethene (**1**) has been synthesized, which affords linear assemblies in solution and undergoes concentration-dependent ring-opening polymerization. The two UPy functional groups of **1** can dimerize intramolecularly to form a cyclic monomer with the two thienyl rings fixed in a parallel conformation, which prohibits its photocyclization. We exploited the photochemical reactivity and resonance difference of the linker of the bis-UPy derivative as well as using the more typical ^{1}H NMR, DOSY, and Ubbelohde viscometry methods to investigate for the first time the ring–chain polymerization mechanism. Moreover, we fabricated a mixed polymer film with a fluorescent dye noncovalently endcapping the linear photochromic assemblies through quadruple hydrogen bonds, which showed nondestructive fluorescent read-out ability for data storage by fluorescence resonance energy transfer (FRET) from the fluorescent dye to the closed form of the diarylethene.

Keywords: energy transfer · photochromism · polymers · ring-opening polymerization · supramolecular chemistry

Introduction

Supramolecular polymers[1,2] have attracted increasing attention in recent years as they not only possess many of the properties of traditional polymers, but also unprecedented distinct new material properties due to their dynamic reversible characteristics, which ensures their potential application in a broad range of fields. The noncovalent interactions[3] that are present in supramolecular polymers include hydrogen bonding, hydrophobic and hydrophilic forces, π–π stacking, ion-pairing, metal–ligand binding, and other host–guest interactions of which multiple hydrogen bonding is strong, directional, and with a high-fidelity that has unsurpassed potential for specificity, as shown by nucleic acids.[4] The ureido-pyrimidinone (UPy) moiety, discovered by Meijer and co-workers in 1997,[5] is one of the most used units in supramolecular polymer construction due to its high association constant ($K_{ass} > 10^7\,M^{-1}$ in chloroform) and synthetic accessibility.[6] In general, a monomer containing two of these self-complementary units can self-assemble into polymers. To date, many of the bifunctional UPy derivatives reported have 1) a short alkyl chain or long flexible polymer chain spacer to form linear supramolecular polymers,[5,7] 2) a rigid highly preorganized monomeric subunit to form cyclic dimers,[8] tetramers,[9] pentamers, or hexamers,[10] 3) 2- and 6-substituted bifunctional UPys to form the preferred cyclic heterodimers in solution,[11] and 4) several substituted alkyl spacers to form cyclic dimers in equilibrium with linear polymers in dilute solutions.[12] However, to the best of our knowledge, an AA-type bifunctional UPy derivative that exhibits a distinct concentration-dependent cyclic monomer–linear polymer equilibrium of the AB (UPy-Napy) type[13] has not yet been reported.

The ring–chain equilibrium is an important phenomenon in both covalent and supramolecular polymerization processes. It is vital for the construction of useful polymer materials to understand well the parameters related to the supramolecular polymerization mechanism. In the production of covalent polymers, ring formation is prevented as much as possible because rings usually form as byproducts. However, optimization of the yield of single rings in self-assembly supramolecular polymer systems is one of the goals of synthetic research. In all cases, understanding the parameters relating to the ring–chain equilibrium is useful for controlling the product distribution.[1a] Ring formation is inevitable in stepwise growth polymerization and the percentage

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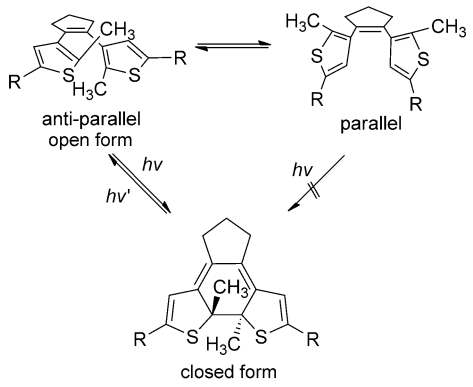
of ring formation increases with dilution of solutions because at low concentration the system favors intramolecular ring formation and not intermolecular chain extension. In general, viscometry, ^{1}H NMR, and DOSY NMR[12] methods are usually used to determine the critical concentration of the ring–chain equilibrium in supramolecular polymer systems. However, as far as we know, there has been no report of the investigation of ring–chain equilibria by photochromic methods. Moreover, the incorporation of certain functional subunits might enrich the methods used to investigate the supramolecular polymerization process and broaden the application of supramolecular materials.

Organic photochromic materials have attracted considerable interest due to their potential applications in photomemory and -switching devices. In particular, diarylethene, as an excellent photochromic compound, has proved to be the most promising switchable unit due to its excellent fatigue resistance and thermal stability.[14] Furthermore, the photochemical reactivity of diarylethene can be blocked when two thienyl rings are fixed in mirror symmetry in the molecule (Scheme 1),[15] and thus this property can be used to study the ring–chain equilibrium in supramolecular polymerization. In this work we have designed and synthesized a bifunctional UPy derivative **1** with a dithienylethene bridging unit and two flexible alkyl C_3 chains (Figure 1). Molecular modeling shows that the two UPy units of derivative **1** can dimerize intramolecularly to yield a cyclic monomer with two thienyl rings fixed in mirror symmetry. In 2005, Takeshita et al.[16] reported a similar structure in which the UPy group directly connected to the dithienylethene unit achieves a photoreversible, assembled system that can change its size, but the two UPy units could not dimerize intramolecularly and the chemical shifts of these protons in the ^{1}H NMR spectrum did not change upon changing their



Scheme 1. Photochromic reaction of diarylethenes.

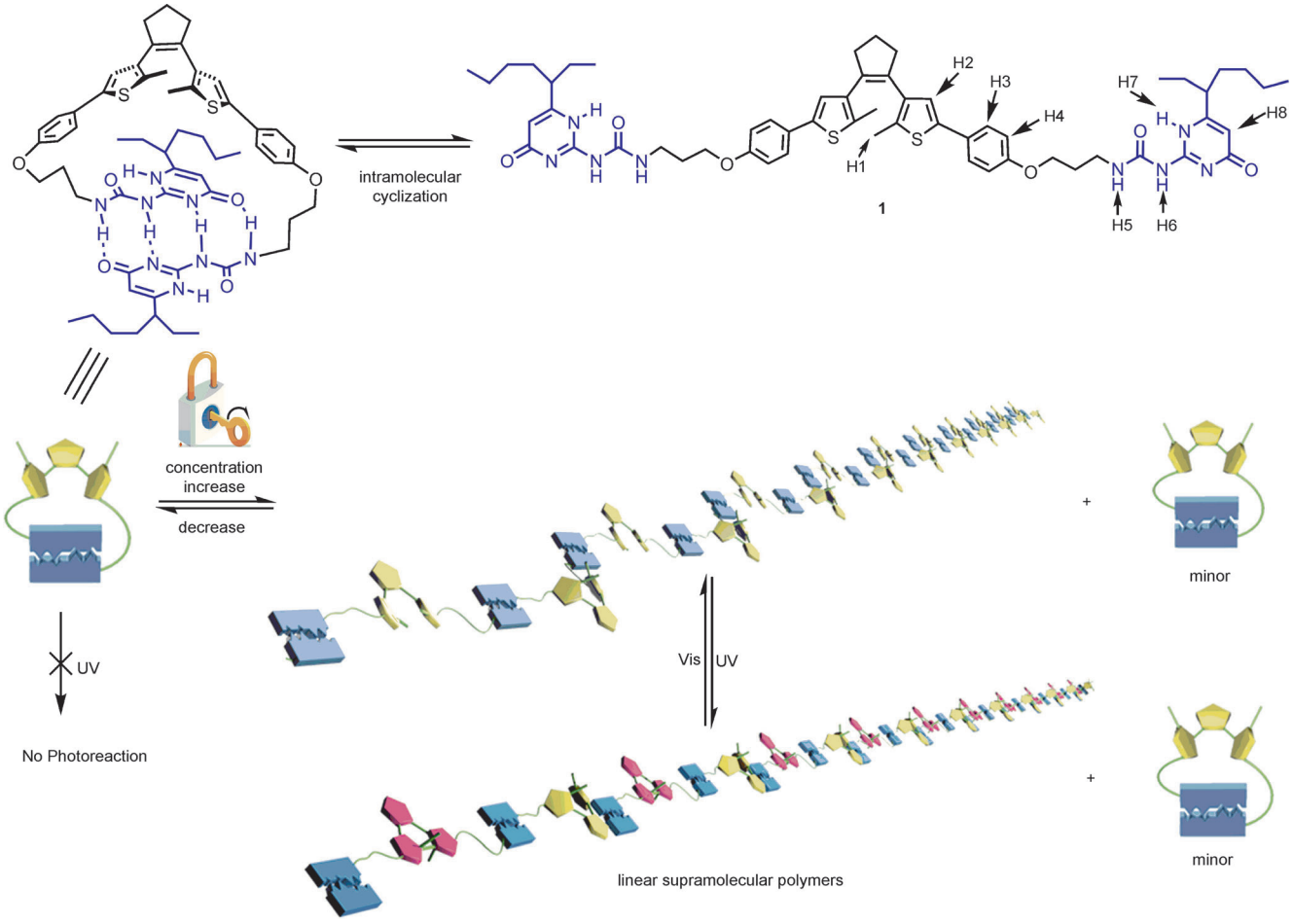
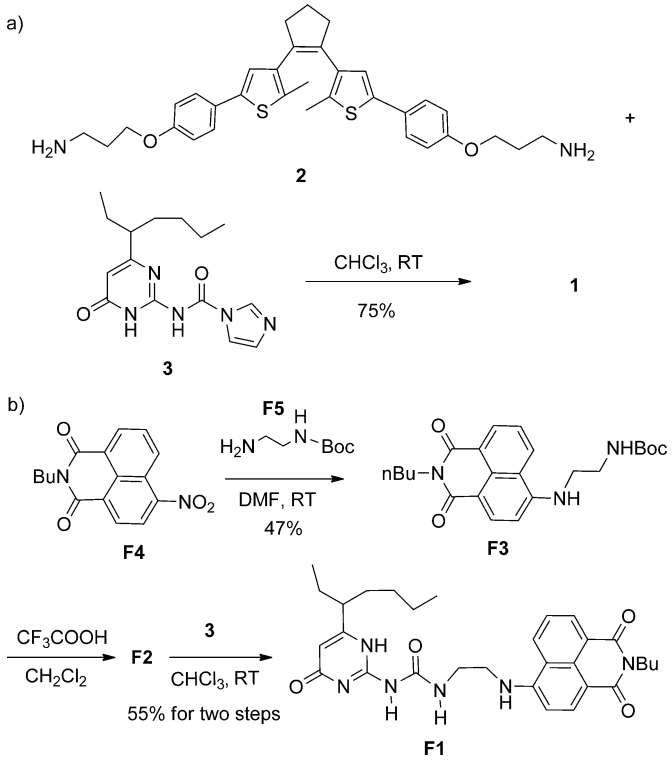


Figure 1. Proposed ring-opening polymerization of **1** and its photoreaction under UV or visible irradiation.

concentration in solution. In this work we sought 1) to use the photochemical reactivity of the diarylethene block, along with ^{1}H and DOSY NMR spectroscopy and Ubbelohde viscometry, to investigate the ring–chain equilibrium in the supramolecular polymerization process in solution, 2) to study the UPy dimer dissociation in DMSO/$CHCl_3$ by photochemical methods, and 3) to form a mixed polymer film with a fluorescent dye noncovalently endcapping the photochromic linear assemblies through quadruple hydrogen bonds. The film fluorescence could be switched by UV/Vis light and thus represents a fluorescent switch with nondestructive readout ability for data storage and high-resolution imaging technology.

Results and Discussion

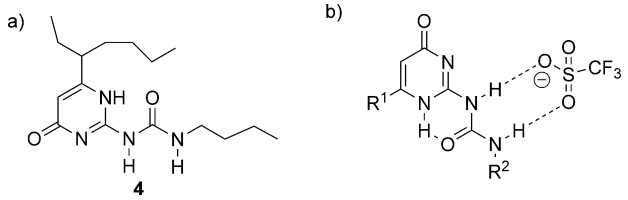
Synthesis of monomer 1 and mono-UPy fluorescent dye F1: The procedures for the synthesis of monomer **1** and mono-UPy fluorescent dye **F1** are depicted in Scheme 2. Bis-amine **2**[17] was treated with imidazolide **3**[18] in chloroform to readily give monomer **1** in a yield of 75%. The mono-UPy fluorescent dye **F1** was synthesized in three steps from naphthalimide derivative **F4**[19] via the intermediate **F3**. **F3** was obtained by nucleophilic substitution of the nitro group of compound **F4** by mono-*N*-Boc-protected ethylenediamine **F5**[20] in a yield of 47% and then *N*-deprotection of **F3** with CF_3COOH in CH_2Cl_2 afforded the free amine derivative **F2**. **F2** was then treated with imidazolide **3** to achieve **F1** in a yield of 55% based on **F3**.



Scheme 2. Synthesis of a) monomer **1** and b) mono-UPy fluorescent dye **F1**.

Self-assembly of the photochromic monomer 1: It is very convenient to "read" photoreaction processes with just the naked eye; color change is a well-known characteristic of photochromic molecules. A colorless 5 mM solution of **1** in DMSO turned pale purple immediately (<5 s) and gradually changed to a deep red-purple (2 min) under 313 nm light irradiation, which indicates the formation of the closed-ring isomer (the cyclohexadiene type) in the strongly polar solvent DMSO. However, the colors of 5 and 8 mM solutions of **1** in less polar $CHCl_3$ irradiated for 20 s did not change at all, which implies that the two thienyl rings of **1** are fixed in a parallel orientation in $CHCl_3$ by intramolecular hydrogen bonding, as shown by the CPK model. However, a 20 mM solution of **1** in $CHCl_3$ turned to a light red-purple under 313 nm irradiation (<5 s) and then gradually to a deep red-purple, which indicates that a concentration-dependent ring-opening polymerization process occurs to form linear assemblies that contain the anti-parallel-orientated diarylethene, as depicted in Figure 1. This is in accordance with the ^{1}H NMR experiments reported below.

The photoreactivity of diarylethene-based bifunctional UPy derivatives **1** in $CHCl_3$ (2×10^{-5} M) was also explored by the addition of the mono-UPy derivative and oxoanion salt as strong competitors for the urea hydrogen donors[8a] (Scheme 3). The addition of 200 equiv of mono-UPy **4**[18] led



Scheme 3. a) Structure of mono-UPy derivative **4** and b) the complex formed by a triflate ion and UPy unit.

to no obvious change in the color of the solution. When the proportion of **4** was increased to 500 equiv, the solution turned slightly red under 313 nm irradiation in the photostationary state (PSS). There was just a slight absorbance in the visible-light region (Figure S5), which shows that most of the bifunctional UPy derivatives **1** form cyclic monomers, even at very "high" relative concentrations of **4** in solution. It is notable that upon the addition of 500 equiv of tetrabutylammonium trifluoromethanesulfonate, bifunctional UPy derivatives **1** could not undergo photocyclization. These results all demonstrate that the two UPy units of **1** dimerize intramolecularly in $CHCl_3$ (2×10^{-5} M), and the cyclic monomer is much harder to destroy than the linear assemblies resulting from intermolecular dimerization (Scheme 3).

The photochemical reaction studied in this work was used to determine the dissociation ratio of the intramolecular UPy dimer at a lower concentration (2×10^{-5} M), although

^{1}H NMR spectroscopy is the universal tool for calculating the dissociation ratio of the UPy dimer in the mixed $CHCl_3$ and DMSO.[6b,8a] In this study, the unrestrained monomer should be the exclusive species in pure DMSO (λ_{max} = 528 nm, $\varepsilon = 15.2\times10^3\,M^{-1}cm^{-1}$ at the PSS) because DMSO is a strong hydrogen-bonding acceptor solvent for the UPy unit. Note, only the molecules in the antiparallel conformation can undergo the photocyclization reaction to give the closed form of **1**. In other words, the extent of dissociation of cyclic **1** is proportional to the amount of unrestricted molecules in DMSO/$CHCl_3$ mixtures at the absorbance of 528 nm (λ_{max} of the closed form of **1**) at the PSS. The apparent association constant at DMSO = 0.80 ($K^*_{ass} = 8150\,M^{-1}$ (±20%)) and at DMSO = 0.20 ($K^*_{ass} = 1.64\times10^5\,M^{-1}$ (±20%)) were determined from Figure 2.[8a] To the best of our knowledge, the photochemical reaction was firstly applied to determine the extent of dissociation of the UPy dimer at a very low concentration (2×10^{-5} M).

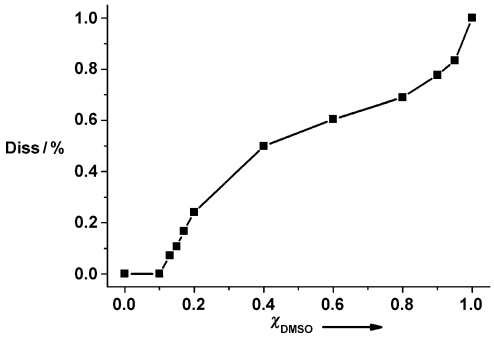


Figure 2. Plot of the extent of dissociation versus solvent composition for the intramolecular dimerization of **1** in $CHCl_3$/DMSO mixtures. The line connecting the data points serves to guide the eye.

NMR spectroscopy is a powerful tool for investigating the ring–chain transition. It is well known that a diarylethene with heterocyclic aryl groups has two conformations: The two rings with mirror or C_2 symmetry. The photocyclization reaction is prohibited when the compound is fixed in the conformation with mirror symmetry (Scheme 1). Moreover, the methyl protons at the 2-position of the thienyl rings give signals at different fields in the ^{1}H NMR spectrum depending on the conformation.[15b,21] In our system, the two thienyl rings are fixed in the mirror symmetry in the cyclic monomer but are free in linear assemblies, so there should be different resonance signals for the methyl protons in the cyclic and linear assemblies in solution. As a result, photochromic bifunctional UPy derivative **1** might be an ideal model compound for monitoring the ring–chain equilibrium in solution. ^{1}H NMR spectroscopy (300 MHz, $CDCl_3$, 24 °C) was performed at concentrations in the range of 3–150 mM (Figure 3). At low concentration (<15 mM), the methyl protons H1 appeared at 2.17 ppm and correspond to the cyclic oligomer. As the concentration was increased, a new peak appeared clearly at 1.95 ppm, which corresponds to the linear assemblies at 20 mM, and its relative intensity in-

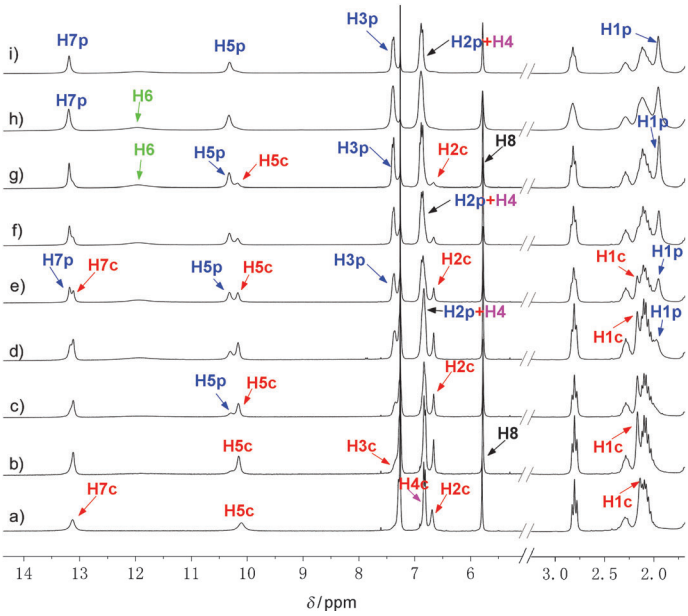


Figure 3. Partial ^{1}H NMR spectra (300 MHz, $CDCl_3$, 24 °C) of **1** at different concentrations: a) 5, b) 10, c) 15, d) 20,e) 30, f) 40, g) 60, h) 80, and i) 100 mM. Signals originating from cyclic aggregates are labeled "c", those from polymeric aggregates are labeled "p".

creased progressively, whereas the intensity of the former peak decreased. The assignment of H1 in the cyclic oligomer and the linear assemblies was based on published results,[15b,17,21] the following DOSY NMR results, and the photoreaction measurement. Meanwhile, we found that the thienyl and phenyl protons H2, H3, and H4 are also concentration-dependent. The 6.67 ppm signal of the thienyl protons H2 of the cyclic oligomer decreased gradually with increasing concentration (>15 mmol) and another signal appeared at 6.91 ppm, which gradually increased. There were similar changes observed for the phenyl protons (Figure 3). The higher field signals of the cyclic oligomer relative to the linear compound may be attributed to the shielding effect of the aromatic rings in the cyclic monomeric form in which the two thienyl rings and the two phenyl rings are close enough to influence the chemical environment of each other.

The ureido-pyrimidinone functionality has three tautomeric structures and exists as dimers of the pyrimidin-4(1*H*)-one and pyrimidinol tautomeric forms in solution (see Figure S6). The pyrimidinone tautomer with the alkyl substituent at the 6-position is highly favored over the pyrimidin-4-ol tautomer in $CHCl_3$. Although the presence of substantial amounts of the enol tautomer was confirmed for the bifunctional UPy derivatives bearing alkyl substituents at the 6-position based on a *m*-xylene linker or with several substituted linear alkyl spacers in dilute solutions,[8b,12a] the ureido-pyrimidin-4(1*H*)-one tautomer is the only one observed by FTIR (KBr, typical peak: 1701, 1656, 1583 cm^{-1}, absence of a 2500 cm^{-1} band for the enol tautomer) and ^{1}H NMR spectroscopy (only one signal of the pyrimidinone

proton H8 from 3 to 150 mM in $CDCl_3$) for the photochromic bifunctional UPy derivative **1**.

The hydrogen bonds typical of the UPy N–H protons have two sets of well-defined signals with a concentration-dependent relative intensity (Figure 2). Having excluded the presence of the enol tautomer, the resonances correspond to the different assemblies of the pyrimidinone tautomer. At low concentration, there was only one set of signals for the UPy N–H protons, whereas at higher concentrations, for instance, above 15 mM, an additional set of peaks showed up. Moreover, the relative intensities of the new peaks increased progressively and the original peaks decreased as the concentration was increased.

Diffusion-ordered ^{1}H NMR spectroscopy (DOSY) measurements provide useful information about the size of the assemblies in supramolecular aggregate systems.[9,10,12b,22] We performed the DOSY experiments on monomer **1** in $CDCl_3$ at different concentrations using heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin ($MW = 1429\ g\,mol^{-1}$) as an internal reference. We found out that the assembly diffusion constant of **1** decreased from 1.07 at 5 mM to 0.032 at 120 mM, which indicates the formation of much larger aggregates at "higher" concentrations (Figure 4). At 5 mM, the diffusion constant is slightly larger than that of the cyclodextrin, which implies that the assembly is smaller than that of the cyclodextrin; thus the monomer ($MW = 1028\ g\,mol^{-1}$) of **1** is the dominant species at this concentration. There was also only one set of signals for the UPy N–H protons; thus the $\delta = 10.12$ ppm (H5) peak should correspond to the cyclic monomer. This is consistent with the photochemical measurements. A small new peak appeared at $\delta = 10.33$ ppm at 12 mM, which has a smaller diffusion coefficient than the peralkylated β-CD and should correspond to the larger aggregates. As the concentration increased, the intensity of the peak at $\delta = 10.12$ ppm decreased, whereas that at $\delta = 10.33$ ppm increased progressively, which suggests the concentration dependence of the ring-opening linear supramolecular polymerization of monomer **1**. At higher concentrations, the diffusion constant of the assemblies corresponding to the peak at $\delta = 10.33$ ppm decreased progressively, but the diffusion constants of assemblies corresponding to the peak at 10.12 ppm were not less than the peralkylated β-CD, except at 5 and 12 mM (see Figures S7–S12). We deduced that this should be the reason that the linear polymer is the majority form at "higher concentration" and that the larger molecules can affect the small cyclic monomer by packing around it, and hence the reason for the apparent magnitude of the diffusion coefficient of the cyclic monomer in the DOSY spectra.

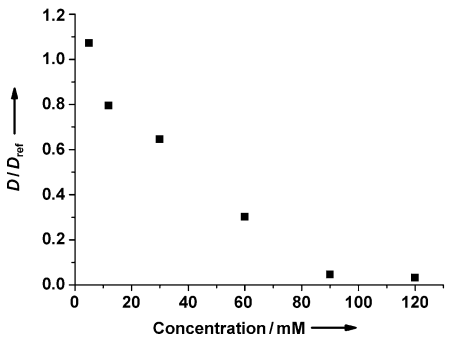


Figure 4. Concentration dependence of the diffusion coefficient D of **1** in $CDCl_3$ at 20 °C using heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin as an internal standard (when there were different assemblies in the system, we chose the larger one).

For ring–chain supramolecular polymerization mechanism systems, there exists a critical concentration below which the system is composed of cyclic products only and above which the concentration of cyclic species remains constant and excess monomer mainly produces linear species.[12a] The cyclic monomers and linear assemblies of our system can be distinguished by ^{1}H NMR spectroscopy. Therefore the partial monomer concentrations of cyclic monomers, calculated from the signals of H5, were plotted against the total monomer concentration (Figure 5a). There was a steady increase in the concentration of the cyclic monomer (slope of nearly 1) as the concentration increased and then a plateau; the results indicate a critical concentration of 13 mM (deduced from the graph).

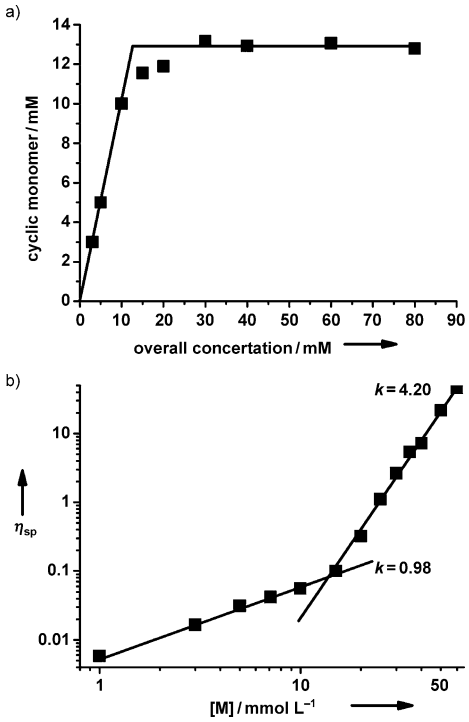


Figure 5. a) Partial concentration of cyclic monomers in $CDCl_3$ solutions of increasing concentration of monomer **1**, calculated from the ^{1}H NMR spectra (9.5–10.5 ppm range of H5) and b) specific viscosity (η_{sp}) of **1** ($CHCl_3$, 25 °C) versus monomer concentration.

To further test the validity of the ring–chain transition, viscosity measurements were taken at 25 °C in $CHCl_3$ by using a micro-Ubbelohde viscometer. A double-logarithmic plot of the specific viscosity versus concentration is shown in Figure 5b. The slope tended to 1 in the low-concentration

region, which is a characteristic of noninteracting assemblies of constant size and indicates the predominance of cyclic oligomers in dilute solutions. Upon increasing the concentration above 14 mM, a sharp rise in the slope to 4.20 was observed, which is consistent with the reported ureido-pyrimidone-based self-assembling systems (slopes of 2.8–6.1).[12a,13] This indicates the formation of linear polymers at high concentration, assemblies with increasing size concomitant with increasing concentration. The critical concentration is 14 mM, which is approximately in agreement with the ^{1}H NMR results (13 mM). Such a low critical concentration might be due to the ring strain in the cyclic monomer form, which is supported by the shift of 0.21 ppm of the H5 resonance signals for the cyclic and linear assemblies in the ^{1}H NMR spectra. The degree of polymerization (DP) of the polymeric fractions at 100 mM of **1** was estimated to be 3.7×10^3 at 298 K on the basis of the K_{dim} value of 5.7×10^7 for the UPy groups.[12b]

The viscosities of the 20, 25, and 40 mM solutions of **1** in $CHCl_3$ at 25 °C under 313 nm light irradiation were investigated. Although the solutions all turned a deep purple-red under 313 nm irradiation, there was little change in the viscosity of the solutions, which indicates that the assemblies do not change much. From the open form to the closed form, the increased rigidity of the monomer in the linear assemblies did not affect the ring–chain equilibrium. The quantity of the open form in the cyclic monomer remained unchanged, which is indicative of the innate character of the critical concentration. The closed form, to some extent, is also flexible and the assemblies are linear, so the solution viscosity remained almost unchanged.

Energy-transfer experiment of mixed film: Modulating luminescence intensity is one of the most attractive features of photomemory and -switching devices because of the high sensitivity, resolution, contrast, and fast response times of luminescence technology.[23] In addition, fluorescence on-off or fluorescence color switching can be applied in new high-resolution imaging techniques such as stochastic optical reconstruction microscopy (STORM).[24] Diarylethene is usually used to covalently connect a fluorescent dye or disperse the dye and diarylethene in a polymer matrix.[25] The luminescence of such systems can be quenched from the excited luminescent center to the colored state of the diarylethene through intra- or intermolecular resonance energy transfer (FRET). It is known that bis-UPy derivatives can be easily spin-coated to yield a smooth film and that energy transfer occurs effectively both in solution and in the solid state[26] because the donor and acceptor are hydrogen-bonded. Inspired by the above idea and to explore the potential applications of a prepared polymer, a small amount of mono-UPy-terminated fluorescent dye **F1** was added to a solution of **1** to endcap the linear polymer **1** and then the mixture was spin-coated to fabricate a smooth mixed film.

We chose **F1** as the fluorescent dye because the emission spectrum of the 4-aminonaphthalimide overlaps well the absorption of the closed form but not the open form of **1**, which can efficiently quench the fluorescent emission.[25a,27] In addition, the selected excitation wavelength (400 nm) causes little structural change in either the open or closed isomer of diarylethene, and thus it can act as a fluorescent switch with nondestructive readout ability. Monomer **1** (25 mM) mixed with 3% of **F1** in $CHCl_3$ was easily spin-coated on to silicon or quartz slides to give smooth films. In the film, no phase separation took place in the linear polymers of **1** endcapped with mono-UPy-functionalized **F1** because of the quadruple hydrogen bonds. The UV/Vis absorbance and energy-transfer properties of the thin films before and after irradiation with appropriate light are shown in Figure 6. The closed form of the diarylethene can absorb 4-aminonaphthalimide fluorescence emission, whereas the open form cannot. Nearly 90% of the fluorescence could be quenched by UV irradiation and regenerated by visible light irradiation of the thin film, concomitant with the color switching between yellow and purple-red.

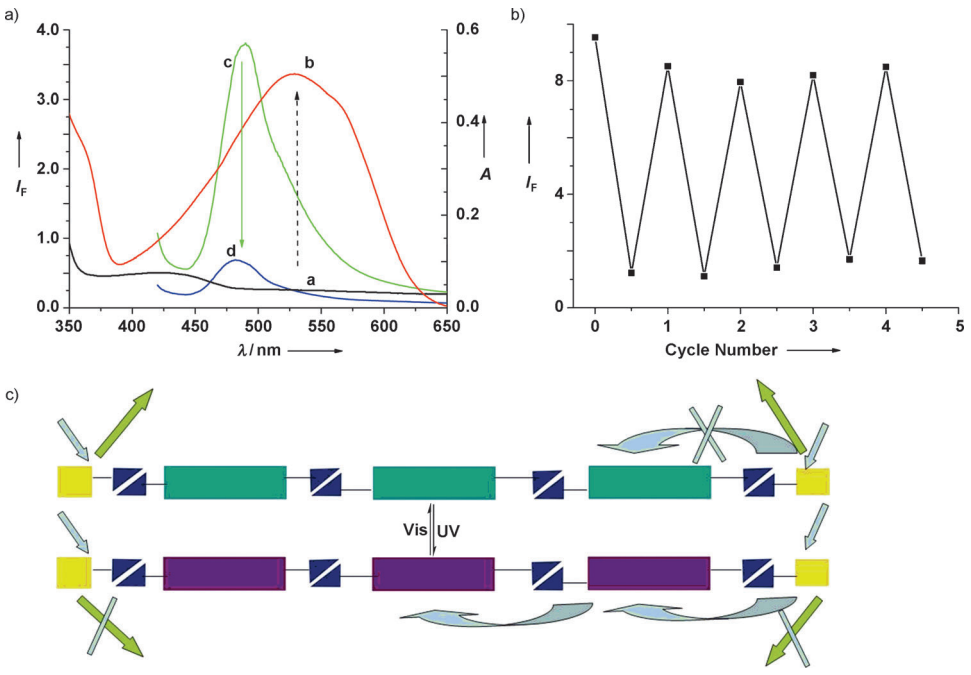


Figure 6. a) Absorption (a, b) and fluorescence (c, d) spectra, b) the fluorescence intensity at 490 nm of the film upon alternating irradiation at 313 nm for 3 min and at 530 nm for 15 min, and c) depiction of the energy-transfer (ET) process of the thin film spin-coated from solutions of 97:3 **1**–**F1** under UV/Vis irradiation.

Conclusion

We have prepared a novel, bifunctional, quadruple hydrogen-bonding ureido-pyrimidinone (UPy) unit bridged by photochromic dithienylethene **1**. It exists as a cyclic monomer at low concentrations and undergoes a concentration-induced ring-opening polymerization process. We exploited the photochemical reactivity and resonance difference of the linker of the bis-UPy derivative for the first time to investigate the ring–chain transition as well as using the more typical ^{1}H NMR, DOSY, and Ubbelohde viscometry methods, which provide new light on the ring–chain polymerization mechanism. We also used the photoreaction to study the UPy dimer dissociation in DMSO/$CHCl_3$. Moreover, we fabricated a mixed polymer film with a fluorescent dye noncovalently endcapping the linear photochromic assemblies through quadruple hydrogen bonds. The film fluorescence could be switched by UV/Vis light, presenting a fluorescent switch with nondestructive readout ability for data storage and high-resolution imaging technology. Further investigations of the supramolecular polymer based on ureido-pyrimidinone and its application as smart materials are in progress.

Experimental Section

General: All reactions were performed in air unless noted otherwise. The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literature. All yields are given as isolated yields. NMR spectra were recorded with a Bruker DPX 300 MHz spectrometer with tetramethylsilane (TMS) as internal standard and solvent signals as internal references. $CDCl_3$ was used as received. IR spectra were recorded on Bruker Vector 22 as KBr pellets. UV/Vis spectra were obtained with Perkin–Elmer Lambda 25 and Shimadzu UV-2401 spectrometers. Liquid-phase and solid-phase photoluminescence spectra (LEM and SEM) were recorded on Lambda 55 and Aminco Bowman Series 2 luminescence spectrometers. UV and visible irradiations were carried out with a CHF-XM500W power system (China) using a suitable band-pass filter. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded in positive-ion mode using an Autoflex III (Bruker Daltonics, Germany) time-of-flight mass spectrometer. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on a Finnigan Mat TSQ 7000 instrument. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6210 TOF LCMS instrument equipped with an electrospray ionization (ESI) probe operating in the positive ion mode with direct infusion. DOSY experiments were performed with a Bruker DPX 500 MHz spectrometer. Viscosity measurements were carried out with Ubbelohde micro-viscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 mm and 0.71 mm inner diameter) at 25 °C in chloroform.

Compound 1: 1,2-Bis[2-methyl-5-[*p*-(3-aminopropoxy)phenyl]-3-thienyl]-cyclopentene (**2**; 0.90 g, 1.53 mmol) and imidazolide (**3**; 1.07 g, 3.52 mmol) were dissolved in dry $CHCl_3$ (20 mL) and this solution was stirred overnight under nitrogen. Dry $CHCl_3$ (50 mL) was added to the reaction mixture and the organic layer was washed with 1 N HCl (20 mL), saturated $NaHCO_3$ (20 mL), and brine (20 mL). The organic layer was dried over Na_2SO_4 and the solvent was evaporated to dryness. Purification of the crude product by flash column chromatography (silica, $CHCl_3$) and then precipitation from CH_3OH gave a white powder (1.18 g, 75 %). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 24 °C): δ = 11.43 (brs, 2H), 9.63 (brs, 2H), 7.60 (brs, 2H), 7.43 (d, J = 8.7 Hz, 4H), 7.10 (s, 2H), 6.93 (d, J = 8.7 Hz, 4H), 5.73 (s, 2H), 4.02 (t, J = 6.5 Hz, 4H), 3.30 (t, 4H, J = 6.5 Hz, overlapped with water signals), 2.82 (t, J = 7.5 Hz, 4H), 2.19 (m, 2H), 2.03 (m, 2H), 1.92 (s, 6H), 1.89 (m, 4H), 1.50–1.36 (m, 8H), 1.25–1.07 (m, 8H), 0.82–0.70 (m, 12H) ppm; ^{13}C NMR (75 MHz, [D$_6$]DMSO, 24 °C): δ = 157.9, 154.7, 151.7, 138.9, 136.5, 134.1, 132.3, 126.6, 126.1, 123.0, 115.0, 105.0, 65.2, 47.8, 38.0, 36.2, 33.0, 29.1, 28.8, 26.6, 22.3, 22.2, 14.0, 13.9, 11.75 ppm; FTIR (KBr): $\tilde{\nu}$ = 3216, 2958, 2929, 2871, 1701, 1656, 1583, 1509, 1466, 1245, 1176, 1110, 1023, 823 cm^{-1}; MS (MALDI-TOF): m/z: 1029.98 $[M+H]^+$; HRMS (ESI): m/z: calcd for $C_{57}H_{72}N8O_6S_2Na$ $[M+Na]^+$: 1051.49139; found: 1051.49037, error 0.97 ppm.

Compound F3: A solution of **F4** (2.17 g, 7.3 mmol) and **F5** (1.52 g, 9.4 mmol) in DMF (50 mL) was stirred for 2 days. The resulting mixture was poured into water (400 mL) and the resulting solution extracted with $CHCl_3$ (4 × 100 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. Purification of the crude product by column chromatography (silica, CH_2Cl_2) gave **F3** as a yellow solid (1.42 g, 47 %). ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C): δ = 8.57 (d, J = 7.3 Hz, 1H), 8.43 (d, J = 8.3 Hz, 1H), 8.25 (d, J = 8.3 Hz, 1H), 7.61 (dd, J = 8.2, 7.5 Hz, 1H), 6.58 (d, J = 8.4 Hz, 1H), 5.13 (brs, 1H), 4.16 (t, J = 7.5 Hz, 2H), 3.81 (brs, 1H), 3.66–3.62 (m, 2H), 3.47–3.44 (m, 2H), 1.76–1.67 (m, 2H), 1.48 (s, 9H), 1.47–1.40 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C): δ = 164.9, 164.3, 158.7 , 150.2, 134.6, 131.1, 129.8, 127.1, 124.7, 122.9, 120.4, 109.9, 103.4, 80.7, 46.7, 40.0, 39.6, 30.4, 28.5, 20.5, 14.0 ppm.

Compound F1: Trifluoroacetic acid (15 mL) was gradually added to a solution of **F3** (1.42 g, 3.45 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred for 10 h. The solvent was evaporated in vacuo to afford a brown oil, which was dissolved in dry $CHCl_3$ (40 mL) and neutralized with *N*-methylmorpholine (NMM) to pH 7–8. Then imidazolide **3** (1.09 g, 3.61 mmol) was added to the solution under nitrogen and the reaction mixture was stirred for 12 h. Then dry $CHCl_3$ (50 mL) was added and the organic layer was washed with 1 N HCl (40 mL), saturated $NaHCO_3$ (40 mL), and brine (40 mL). After drying with Na_2SO_4 the organic layer was reduced to about 5 mL by evaporation in vacuo. The concentrated solution was slowly added to MeOH (30 mL) under vigorous stirring, which resulted in a yellow precipitate. The precipitate was filtered off and washed thoroughly with MeOH to obtain a yellow solid (0.98 g, 55 %). ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C): δ = 13.12 (brs, 1H), 11.89 (brs, 1H), 10.71 (brs, 1H), 8.55 (d, J = 7.2 Hz, 1H), 8.44 (d, J = 8.3 Hz, 2H), 7.51 (t, J = 7.7 Hz, 1H), 6.67 (d, J = 8.4 Hz, 1H), 5.94 (s, 1H), 4.15 (t, J = 7.4 Hz, 2H), 3.96 (brs, 1H), 3.75 (brs, 2H), 3.61 (brs, 2H), 2.46–2.35 (m, 1H), 1.82–1.55 (m, 6H), 1.50–1.18 (m, 6H), 0.98–0.86 (m, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C): δ = 173.2, 164.7, 164.1, 157.1, 156.3, 154.6, 149.8, 134.5, 130.8, 129.9, 127.1, 124.1, 123.0, 120.6, 110.2, 106.3, 103.8, 45.4, 44.0, 39.9, 38.8, 33.0, 30.3, 29.4, 26.7, 22.5, 20.4, 13.9, 11.8 ppm; LRMS (ESI): m/z (%): 547.25 (100) $[M+H]^+$, (28) 569.33 $[M+Na]^+$; HRMS (ESI): m/z: calcd for $C_{30}H_{38}N_6NaO_4$ $[M+Na]^+$: 569.2852; found: 569.2856, error 0.7 ppm; m/z: calcd for $C_{60}H_{76}N_{12}NaO_8$ $[2M+Na]^+$: 1115.5807; found: 1115.5813, error 0.5 ppm.

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