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Hydrogels

A Dithienylethene-Based Rewritable Hydrogelator

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Abstract: Dithienylethene photochromic switching units have been incorporated into a hydrogelating system based on a tripeptide motif. The resulting hybrid system provided both a photochromic response and the ability to gelate water under acidic and neutral conditions. Fluorescence spectroscopy shows that the dithienylethene units are in sufficient proximity to each other to stack in gel fibers, with the tripeptide unit determining solubility. TEM measurements provided insight into the microscopic structure of the fibers formed.

Introduction

The development of responsive hydrogels is of importance for several fields of research, including controlled release of drugs, cell growth, and adaptive materials. Light-induced transformations, in particular, are of great interest because they are non-invasive, allow high temporal and spatial control, and have potentially fast response times.[1] This is an important advantage over other triggers, such as pH changes, chemical reactions, and even temperature changes, which will have response times considerably longer than the initial trigger event. Because of their tunable spectroscopic properties, high thermostability, good closed to open ratios in the photostationary state, high fatigue resistance, and the possibility to address several distinct (chiral) states,[2] dithienylethene photoswitches are primary candidates for incorporation as functional units into hydrogels.[3] However, owing to their hydrophobicity, the application of dithienylethene photoswitches in gels has, so far, to the best of our knowledge, only been achieved in organic solvents. Nonetheless, dithienylethene switches have seen successful application in systems that form aggregates in water, including vesicles,[4] DNA complexes,[5,6] guest–host complexes,[7] nanospheres,[8] and one-dimensional fiber-like aggregates.[9] Herein, we report the incorporation of a dithienylethene switch into a hydrogelator system and the characterization of the function and structure of the resulting gels.

Dithienylethene switches are amongst the more-hydrophobic photoswitchable moieties reported in the literature and their incorporation into a hydrophilic system is nontrivial. Several approaches have been taken towards the production of light-sensitive (hydro)gel systems. Molecular switches have been added as dopants to hydrogels,[10] covalently attached to known gelator motifs and incorporated into known gelators, replacing parts of the original gelator.[11] Dithienylethene switches do not show large changes in molecular geometry or dipole moment upon switching, in contrast to azobenzenes ($\Delta\mu \approx 3$D)[12] and spiropyrans ($\Delta\mu \approx 12$D),[13] and, therefore, the effects of switching-dithienylethene dopants are relatively minor. This feature has limited their use as dopants to highly organized supramolecular structures, such as liquid crystals.[14] Covalent attachment or incorporation of a dithienylethene switch to a known gelator would result in a substantial increase in hydrophobicity and, hence, would be detrimental to the gelation properties. Therefore, we took the approach to redesign a known hydrogelator that already bears an aromatic group of similar size.[15]

In recent years the ability of fluorenyl-functionalized oligopeptides, especially dipeptides, to gelate water, has received attention for many hydrogel-related functionalities.[16] It has already been shown that for oligopeptide-based gelators, the fluorenyl moiety can be replaced by other aromatic groups, such as pyrenes,[17] naphthalenes,[18] and coumarines,[19] inducing highly organized stacking and resulting in hydrogelation.[20] Because the dithienyl switch can bare some similarity in size and shape to the fluorenyl group, we focussed on introducing a new maleimide-based dithienylethene switch (Figure 1).

Maleimide-based dithienyl switches were first reported by Irie and Mohri in 1988.[3b,21] A glycine moiety provides the carboxylic acid functionality necessary to couple the switch to the dipeptide, in effect, rendering the system a tripeptide. The maleimide motif was used because it allows for functionalization of the switch in a symmetric manner, instead of functionalization at the thienyl groups, as would be the case for the conventional cyclopentene-based dithienyl switches.[3] This approach results in the switch resembling the fluorene moiety more closely, but more importantly, also increases the polarity of the switch, thereby increasing the water solubility of the

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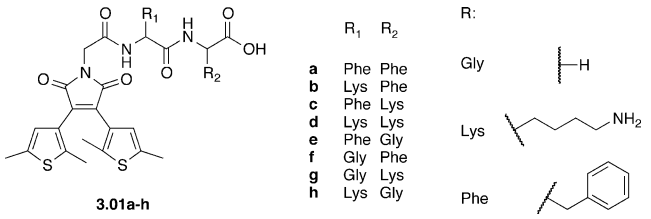


Figure 1. Dithienylethene-functionalized tripeptide hydrogelators **1 a**–**1 h**.

entire system. Because gels are a metastable phase and need to be soluble enough to dissolve, but also insoluble enough to aggregate anisotropically afterwards, the polarity of the molecules was adapted using dipeptides attached to the switch. Eight dipeptides were used, including apolar (phenylalanine), neutral (glycine), and polar (lysine) amino acids, to tune the polarity of the molecules.

Results and Discussion

Dithienylethene-based tripeptides **1 a**–**h** were synthesized according to the route depicted in Scheme 1.

Maleic anhydride was brominated by using a modified literature procedure.[22] Imide formation with methyl 2-aminoacetate was followed by transhalogenation, affording compound **4**, which was then coupled to compound **6** in a double Suzuki coupling reaction. Compound **6** was obtained in two steps from commercially available 2,5-dimethylthiophene.[23] Both the use of a methoxy-protected carboxylic acid, rather than a free carboxylic acid, and the iodination of the dibromo compound proved to be essential for the Suzuki coupling reaction to proceed in good yields. Ester hydrolysis of compound **7** was found to proceed best by using lithium-ion-coordinated iodide-based dealkylation.[24] This yielded a free carboxylic acid that was then used to couple the switch to a series of *O*-*tert*-butyl-protected dipeptides, which were prepared in two steps from commercially available protected amino acids. A final deprotection step yielded the desired compounds. For synthetic details and full characterization see the Supporting Information.

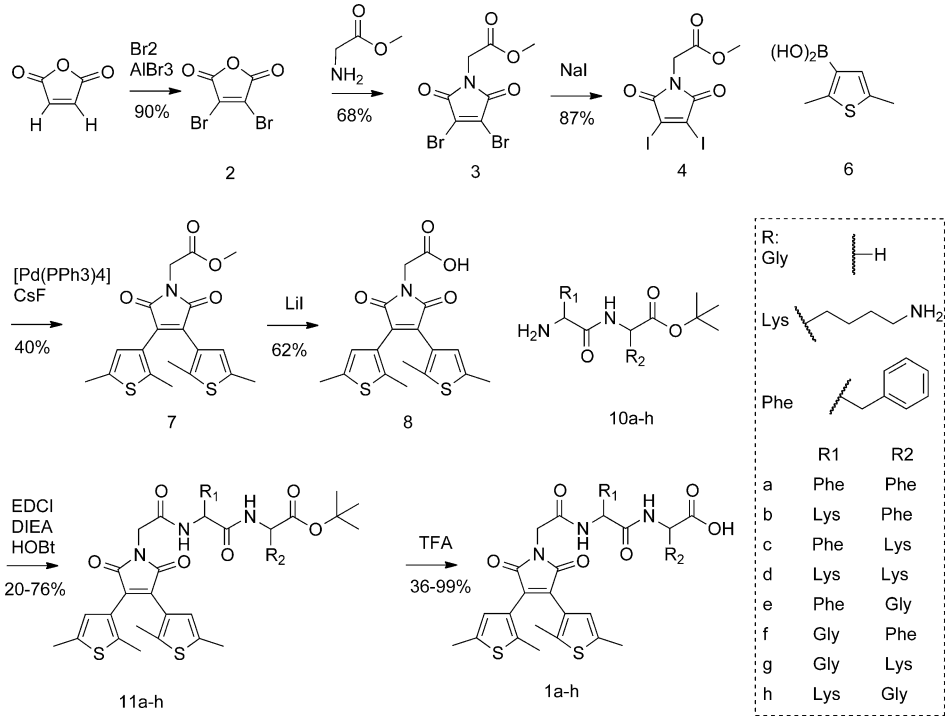
The hydrogelation properties of **1 a**–**h** were tested (Table 1) by using several different gelation methods, as described in the Supporting Information. It was found that most compounds formed gels in water with a critical gelation concentration (cgc) in the range of 20–40 mg mL^{-1}. The incorporation of lysine increased the cgc, and the dilysine compound (**1 d**) remained in solution even at concentrations above 100 mg mL^{-1}. Phenylalanine, as anticipated, has an opposite effect, exemplified by the insolubility of the diphenyl compound (**1 a**). The lysine–phenylalanine compound (**1 b**) was also found to be insoluble or formed precipitates, depending on the preparation method applied. Differences in gelation behavior between compounds with similar structures, in which only the order of the amino acids is varied, for example, **1 b** and **1 c**, have been reported before.[15,25] This is an illustrative example of the subtle changes in interactions that can enhance and disrupt anisotropic aggregation.

Table 1. Hydrogelation of **1 a**–**h** (deionized water).[a]

	1 a	1 b	1 c	1 d	1 e	1 f	1 g	1 h
cgc [mg mL^{-1}]	p	p	34	s	21	24	38	40

[a] p = precipitate, s = solution at 100 mg mL^{-1}.

Rheology was performed when the compound provided a gel. Frequency sweeps (as shown for **1 h** in Figure 2) revealed that the gels possess a plateau region over a wide frequency range. In this region the gels still show some frequency dependence and $G'/G'' < 10$ (G' = storage modulus, G'' = loss modulus). This result classifies the samples as weak gels or, more precisely, viscoelastic systems (Figure 2).[26,27] Owing to its synthetic accesibility and good gelation properties, **1 h** was used for further analysis.



Scheme 1. Synthesis of **1 a**–**1 h** (EDCI = 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, DIEA = *N*,*N*-diisopropylethylamine, HOBt = 1-hydroxybenzotriazole, TFA = trifluoroacetic acid).

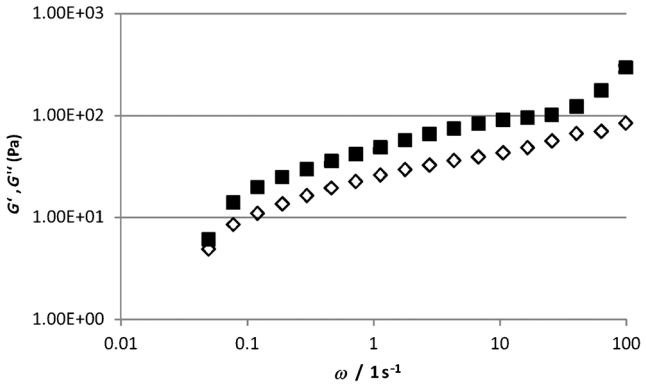


Figure 2. Frequency dependence of a hydrogel of **1h** (40 mg mL^{-1}), measured at. $\gamma = 0.5\,\%$ ■ = G′(storage modulus), ◇ = G″ (loss modulus).

The switching units were found to be stable at acidic and neutral pH, but at pH > 7 the disappearance of the original switch and the appearance of a new species was observed by fluorescence (Figure S3, see the Supporting Information) and UV/Vis absorption spectroscopy (Figure 3a). FTIR and NMR spectroscopy (see the Supporting Information) indicated that under basic conditions (pH > 7.5), hydrolysis of the imide functionality occurred, yielding, for example, **12h** (Figure 3b). This base-catalyzed hydrolysis of the cyclic imide was also observed in the synthesis of compound **8**, in which attempts to hydrolyze the methyl ester under basic, aqueous conditions yielded the corresponding hydrolyzed imide (amide). The newly formed species were found to be more water soluble than the original switch, as expected from their structure.

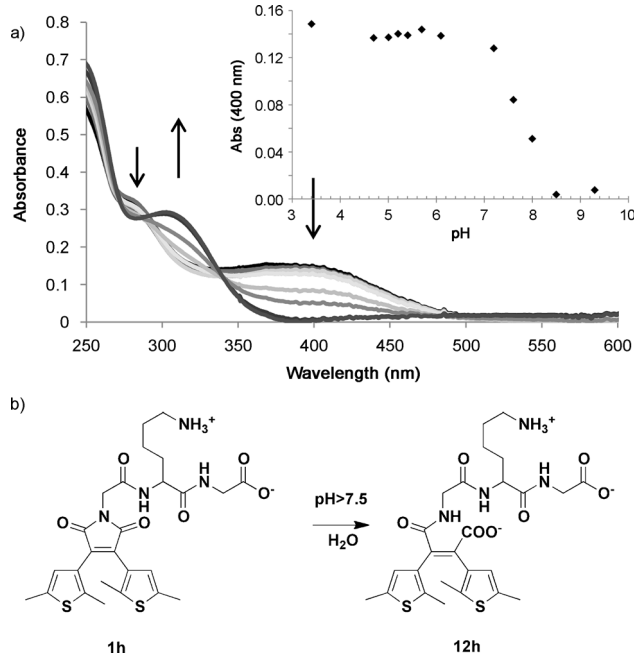


Figure 3. a) pH-dependent UV/Vis absorbance of **1h** (0.04 mg mL^{-1}) in a 10 mM sodium phosphate buffer. Inset: Absorbance at 400 nm. b) Ring-opening hydrolysis of the imide under basic aqueous conditions.

The hydrolyzed compound was found to undergo reversible photoswitching, with a ratio of open/closed switch, at the photostationary state ($\lambda_{exc} = 360$ nm), of 62:38. Irradiation at 360 nm generated new absorbance maxima at 316 and 471 nm, whereas irradiation above 450 nm resulted in recovery of the original spectrum (Figure 4).[28]

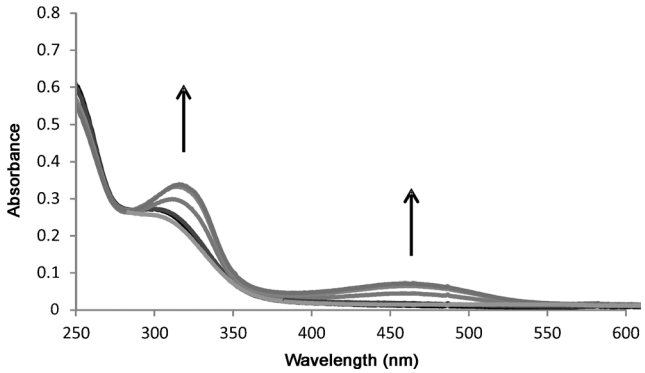


Figure 4. Change in UV/Vis absorbance of **12h** (pH 10) upon irradiation (360 nm).

Changes to the UV/Vis absorption spectrum of **1h** below the critical gelation concentration (0.10 mg mL^{-1}), at pH 7, were observed upon irradiation at 312 nm (Figure 5). New absorbance bands appeared at 360 and 530 nm, with a decrease in absorbance at 290 nm.[29] An isosbestic point was maintained at 326 nm, indicating that side reactions, for example, hydrolysis or degradation, did not occur. The ratio of open/closed form at the photostationary state was determined to be 92:8 for solutions of the gelator.[30] The changes were fully reversed upon irradiation at longer wavelengths (> 500 nm).

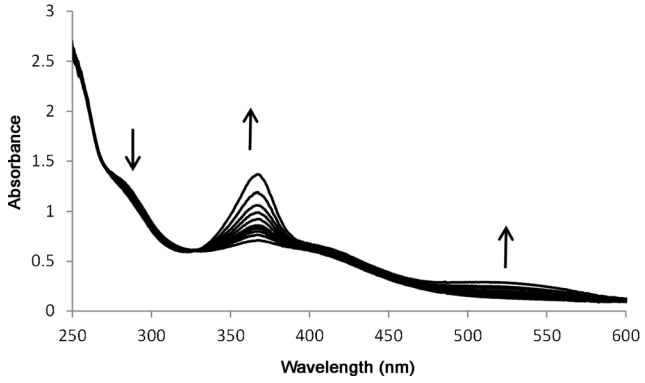


Figure 5. Ring closing of **1h** in water (0.10 mg mL^{-1}) at 312 nm, followed by UV/Vis absorption spectroscopy.

Irradiation of **1h** in the gel state at 312 nm resulted in a change in color, turning the samples from bright yellow to red. However, the macroscopic appearance and mechanical properties of the gel itself remained unchanged (Figure 6). When the gelators were dissolved in methanol and ring closing was carried out by irradiation at 312 nm, a photostationary-

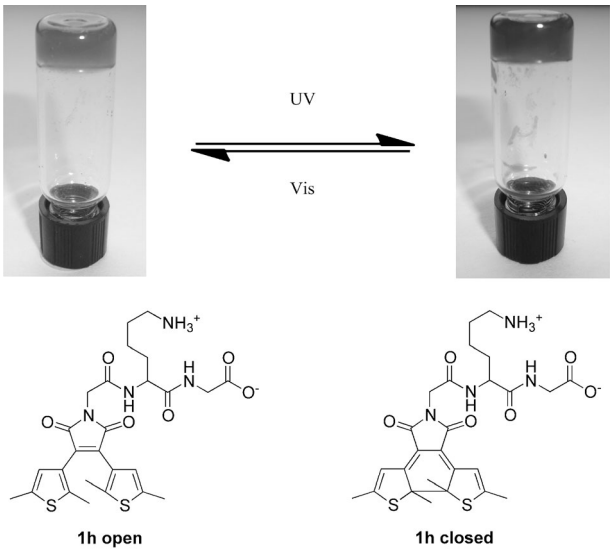


Figure 6. Ring closing/opening in a hydrogel of **1h** (44 mg mL^{-1}) by using irradiation at 312 nm and >500 nm, respectively.

state ratio of 52:48 (open/closed) was reached. Removal of methanol in vacuo and attempts to form hydrogels by using the obtained partially closed sample gave rise to suspensions, indicating that there is an intrinsic difference in the aggregating properties of the open and closed states.

UV/Vis absorption spectroscopy, above gelation concentrations, was only possible at wavelengths longer than 500 nm. A new absorption maximum at ≈530 nm appeared for all gelators upon irradiation at 312 nm (Figure 7), which is similar to the maximum observed at lower concentrations. Irradiation with visible light (>500 nm) recovered the original spectrum, without indication of fatigue, over several cycles (Figure 7, inset).

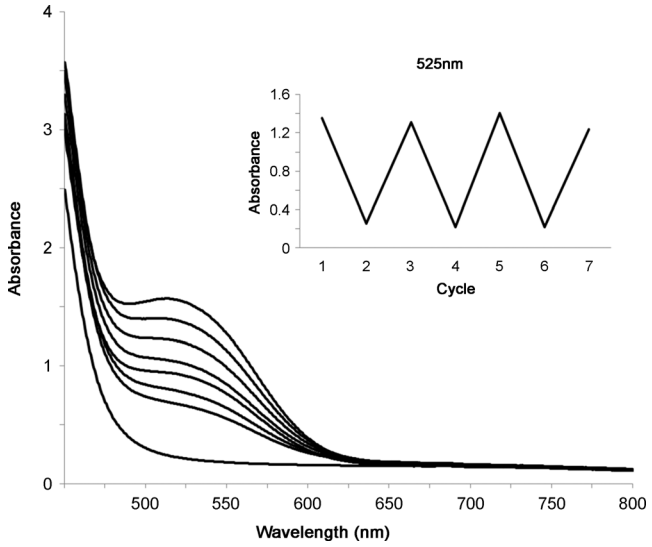


Figure 7. Ring closing/opening of a hydrogel of **1h** followed by UV/Vis absorption spectroscopy. Insert: Ring opening and closing followed at 525 nm over several cycles.

Diffuse reflectance absorption spectroscopy was performed on the gelators, both in the open and the photostationary states, showing much higher closed to open ratios in the photostationary state at the glass–gel interface.[31] Comparison of the ratio of diffuse reflectance values at the isosbestic point and at 550 nm revealed that there is a qualitative increase in the pss (pss = photostationary state) when the concentration of the switch is increased (Figure S4, see the Supporting Information). This result could be rationalized by the consideration that at higher concentrations, higher amounts of gelator are present in an aggregated state instead of in solution. In this aggregated state, the switches experience a less-polar environment, which makes the photocyclization reaction more efficient, as was shown in earlier reports on similar switches in organic solvents with increasing polarity.[32] The lower photocyclization efficiency in polar solvents is attributed to a shift in the equilibrium of the open switch from the planar conformer, rapidly undergoing photocyclization into the twisted conformer, which cannot ring close. Aggregation of the gelators not only provides a more apolar environment for the switches (see below), but most likely also forces the switches into a more planar conformation, as this would create flatter structures, which are known to benefit the aggregation of dipeptide gelators.[16]

Given the low penetration depth of the irradiated light and the clear differences in absorbance between the ring-open and ring-closed states, it was possible to use the gel for writing by using a mask, UV light, and visible light to address the desired state. The gel could be "written" and erased over several cycles without indications of instability (Figure 8).

Figure 8. Writing of initials "JvH" in a hydrogel by using visible light (>500 nm) and a mask. See the Supporting Information for the complete procedure.

All water-soluble hydrogelators examined provided similar UV absorption spectra, as expected. The circular dichroism (CD) spectra, however, showed significant variation between the gelators. Although CD spectra could not be obtained from as-formed gel samples because of their opacity, dilution of the gels to approximately 2.6 mM[33] could be carried out without dissolution of the gel fibers. In this way, CD spectra could be obtained. As the dipeptide moieties show no absorption or CD signal at wavelengths longer than 250 nm, signals at longer wavelengths can be assigned to the dithienylethene switch unit (Figure 9). The switch moieties by themselves are achiral and do not exhibit a CD signal at concentrations at which aggregation is not observed. Therefore, a CD signal at these wavelengths is indicative of supramolecular aggregation of

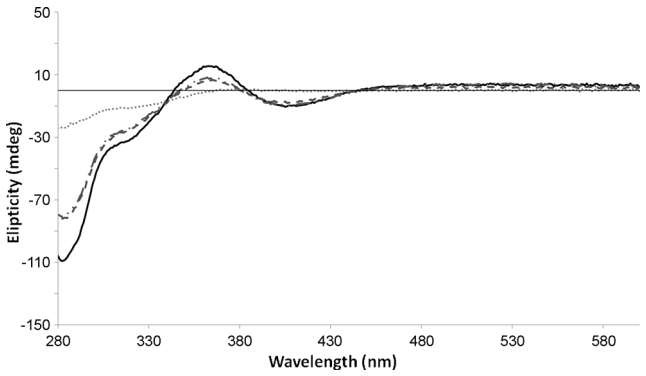


Figure 9. Gel of **1 h** diluted to 2.6 mM. — = original spectrum (**1 h** open), ---- = after irradiation at 312 nm, - - - = after subsequent irradiation with visible light (> 470 nm), ···· = after heating and subsequent cooling of the 2.6 mM solution.

a type that forces the switch preferentialy into one of the two chiral conformations.

When the diluted gel samples were irradiated at 312 nm, closure of the switch ocurred to some extent, manifested in the appearance of an absorption band at 530 nm. The closing of the switch was accompanied by a decrease in the CD signal, indicating that the closed switch does not maintain its aggregation state in the same manner as the open switch. Irradiation with visible light subsequently caused the system to ring open fully again, without further change to the CD spectrum. Finally, heating and subsequent cooling of the sample caused almost complete disappearance of the CD signal, owing to the dissolution of the gelators from their aggregated state.

Most gels showed a negative Cotton effect around 410 nm (Figure S6, see the Supporting Information), coinciding with their UV/Vis absorption. As expected, **1 d** does not show a CD signal at this wavelength because it does not form aggregates. The lack of a CD signal for **1 g** is due to dissolution of the fibers upon dilution.[34] This finding could be attributed to the high polarity of **1 g**; however, **1 h**, containing the same amino acids, but in a different order, remains in an aggregated state, demonstrating the fine balance of interactions responsible for the aggregation (see above). The lack of signal for **1 e** cannot be explained by dissolution, as the samples still show turbidity upon dilution. A possible explanation is that **1 e** stacks in an achiral manner.

The fluorescence spectra of **1 h**, which forms a gel in water, and **1 d**, which is completely soluble in water at high concentrations, were measured in both ethanol and water (see Figure 10). In ethanol, switch **1 h** and **1 d** behave similarly, showing fluorescence at 400 nm.[35] On increasing the concentration, a new emission band appears at 560 nm. This emission was red-shifted from the original emission and suggests the formation of aggregates. In water, **1 h** and **1 d** behave very differently. **1 h** shows a broad emission peak at 580 nm, even at low concentrations, whereas the emission of **1 d** appears to be completely quenched (Figure 10 b).[36]

The lack of emission from compound **1 d** in water is consistent with quenching. By contrast, for **1 h** the 560 nm emission is typical of emission from aggregates and, thus, is consistent

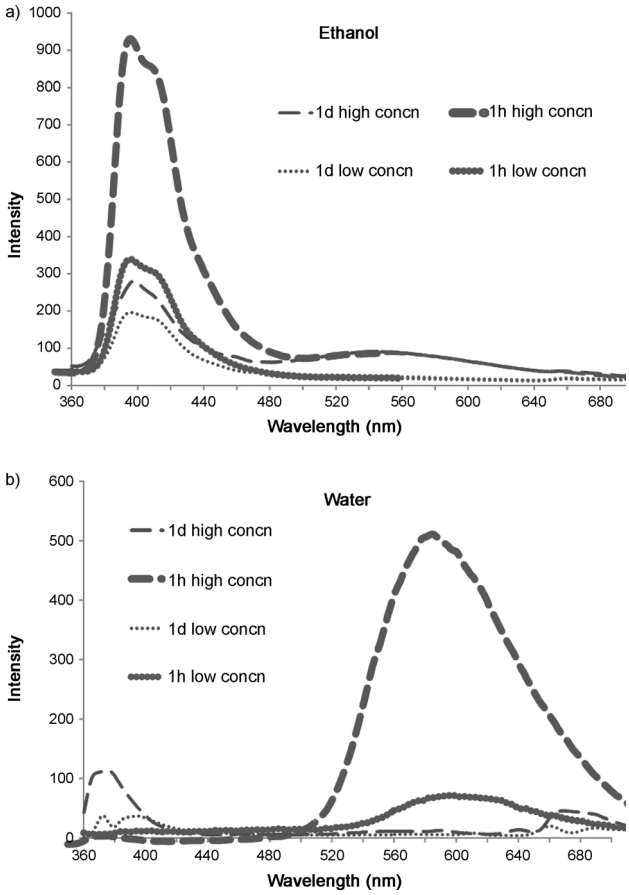


Figure 10. a) Fluorescence of **1 d** and **1 h** (λ_{exc} = 265 nm) in ethanol at high (4×10^{-3} mM) and low (4×10^{-5} mM) concentrations. b) Fluorescence spectrum of **1 d** and **1 h** in water (pH 6.5) at high (4×10^{-3} mM) and low (4×10^{-5} mM) concentrations.

with substantial intermolecular interaction, such as stacking of the dithienylethene units in the gel state.

Cryo-transmission electron microscopy (cryo-TEM) imaging of the gels revealed that they do not possess a fibrilar or ribbon-like structure, unlike the corresponding Fmoc- (9-fluorenylmethoxycarbonyl) functionalized gelators.[25] Instead, tube-like structures, which appeared to be formed by curled sheets, were observed (Figures 11 and 12).[37] This provides a rationalization as to why relatively high gelator concentrations are necessary to provide gelation. Formation of a three-dimensional network with sufficient entanglement to provide rigidity is most efficient with thin long fibers that have substantial supramolecular interaction with other fibers (junctions). The tube-like structures found for the present gels, however, mainly demonstrate intrastructural interactions, accounting for the rolled-up-sheet shape. To have enough interaction between these supramolecular structures, a high concentration is necessary.

Interestingly, the structures observed for all gelators are similar, showing that the aggregation mode is dictated by the switch, with the dipeptide moiety functioning mainly as a solubilizing group. The lack of signals assignable to hydrogen bonding in the IR spectra (Figure S2, see the Supporting Infor-

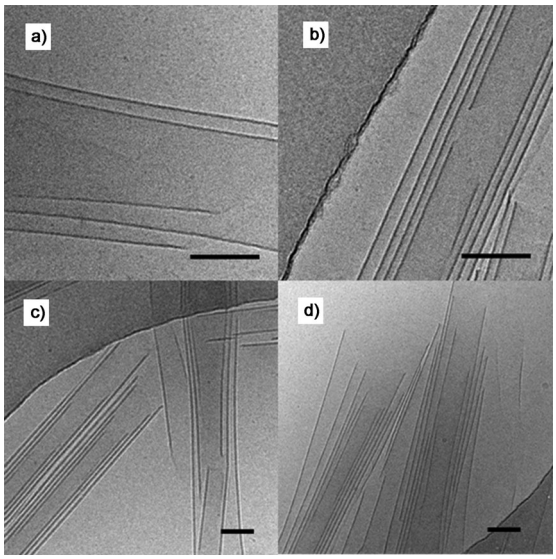


Figure 11. Cryo-TEM images of hydrogels a, b) **1 f** and c, d) **1 h** (scale bar 200 nm). For higher magnification images see Figure S8 in the Supporting Information.

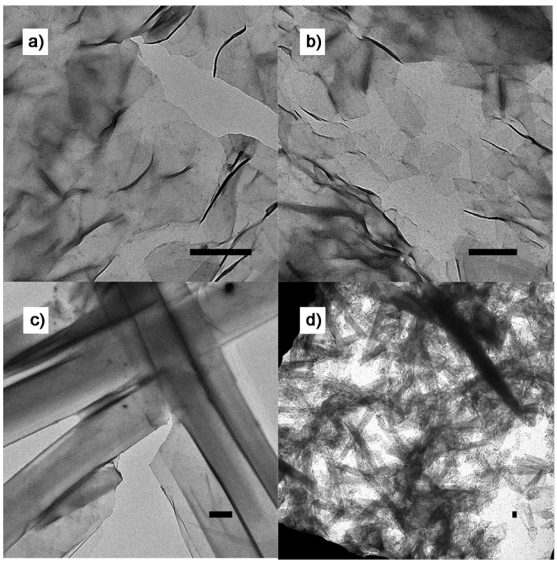


Figure 13. TEM images of a, b) **1 c** in a closed and c, d) **1 c** in an open state, in water (scale bar 1 μm).

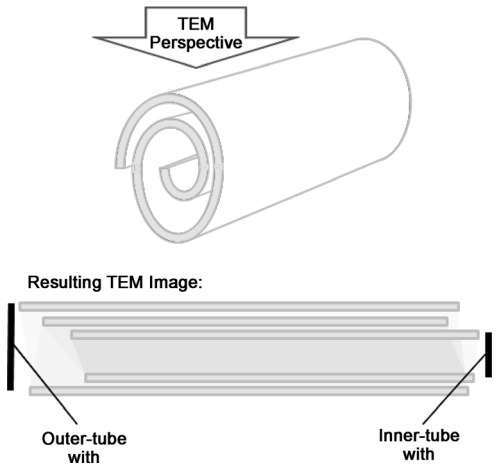


Figure 12. Schematic representation of curled sheets and their resulting image when imaged from a TEM perspective.

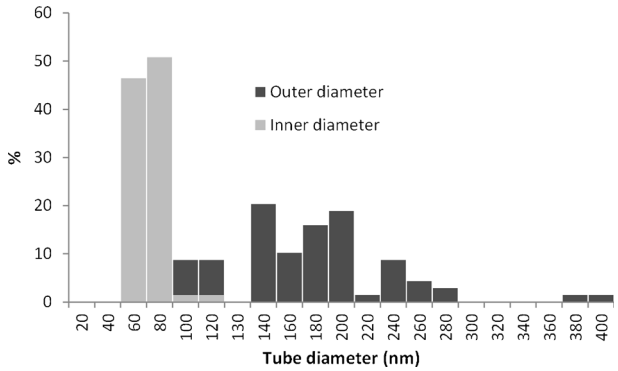


Figure 14. Histogram of inner and outer diameters of the tubes observed in the cryo-TEM samples of **1 h**.

mation), and the relative insensitivity towards changes in the composition and concentration of the buffers used (see the Supporting Information), support this conclusion.[38] It should be noted, however, that both the inability of **1 b** to gelate water and the structure dependence of the CD signal show that the dipeptides also influence the stacking of the gelators to some extent.

As with the mechanical properties, the microscopic structure observed by cryo-TEM microscopy does not seem to undergo significant change upon irradiation with UV light. Attempts to obtain cryo-TEM images of the suspensions formed when the closed switch was used in the gel formation were unsuccessful. Regular TEM images did, however, reveal clear differences between the aggregates of the closed switch (Figure 13 a and b) and the open switch (imaged in the same manner for comparison, Figure 13 c and d).[39]

As can be concluded from the histogram of the inner and outer diameters of the tubes (Figure 14), the inner diameter has a more defined size, suggesting that aggregation is probably starting from the inside of the tube and extending outwards, with the tubes growing to different outer diameters. It appears that the decreased curvature required for the outer layers of the tubes is energetically unfavorable because the major part of the outer widths remains below 300 nm in diameter.

Aggregates of the closed (pss) compounds do not possess this curvature, as becomes evident from the TEM images. As a direct consequence, there is no limitation to the size of the aggregates and, therefore, they can cover surfaces of multiple square micrometers.

Conclusion

We have shown that it is possible to incorporate dithienylethene switches into hydrogels. The gelators form stable gels

under acidic and neutral conditions, and are hydrolyzed under basic conditions to the corresponding amide, which forms solutions in water. The hydrogels seem to obtain their stability from large rod-like structures, formed by steeply curved sheets.

The high concentration of light-absorbing switch in the sample prevents the light from penetrating the gel completely, allowing the gelator to maintain its macroscopic and mechanical properties, whereas the spectral properties can be altered photochemically.

The gelating behavior of the compounds, as determined by cryo-TEM microscopy, and CD and IR spectroscopy, suggests that the switch moiety is mainly responsible for the aggregation mode, whereas the dipeptide moiety provides solubility.

Further studies towards the nature of the aggregation, as well as more efficient gelation, are ongoing.

Acknowledgements

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Keywords: electron microscopy · gels · photochromism · switching

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