A new self-assembling system is developed, based on dithienylcyclopentene photochromic switches, which forms extended aggregates in solution and for which the viscosity can be changed by light.

The self-assembly of small functional molecules into supramolecular structures comprises a powerful approach towards the development of new materials and devices of nanoscale dimensions, and the control of these organisational processes by chemical or physical elements is a major challenge. A promising approach towards such responsive or smart materials is the integration of an addressable function, e.g. photochromic moieties, into the supramolecular building blocks, which would offer the possibility to alter the self-assembly process of the individual molecules or change the properties of the supramolecular arrays by means of light.

Here we report on a new self-assembling system based on diarylethene photochromic switches, which forms extended aggregates in solution, and the viscosity of which can be changed by light. Diarylethene and particularly dithienylcyclopentene molecular switches are a distinct class of photochromic compounds that can undergo a reversible ring-closure reaction upon irradiation with UV- and visible-light, respectively, which is accompanied by a pronounced change of the individual molecules or change the properties of the supramolecular arrays. The gelation behaviour of diarylethene-switch has been extended with amide groups (Scheme 1). The 1,2-bis(5’[(alkylamino)carbonyl]-2’-methylthien-3’-yl)cyclopentenes (1o and 2o) were synthesised in a two-step procedure starting from 1,2-bis(5’-formyl-2’-methylthien-3’-yl)cyclopentene. Oxidation with Ag2O provided the corresponding diacid, which was next converted to amides by first activating the carboxylic acid with 2-chloro-4,6-dimethoxytriazine, followed by a reaction of the activated ester with the corresponding amine. Compounds 1o and 2o were obtained in 33 and 30% overall yield, respectively, after column chromatography starting from the diiodide.

The gelation behaviour of 1o was studied in various solvents of different polarity. It was found that 1o did not form gels with any of the solvents investigated, but with apolar solvents, like cyclohexane, dodecane and benzene, clear viscous solutions were formed at concentrations well above 5 mM, indicating that aggregation of 1o occurs. The $^1$H NMR spectra of 1o in C$_6$D$_6$ show a gradual down field shift of $\delta$NH from 5.26 to 5.56 ppm, and an increase of the line width with increasing concentration, indicating that 1o forms highly dynamic aggregates through hydrogen bonding between the amide groups at higher concentrations. Together with the observation that the results are not changed by prolonged aging of the samples, this also indicates that the aggregates formed by 1o are equilibrium structures. Fitting of the data to a cooperative aggregation model revealed that the dimerization constant $K_d = 81 \pm 3$ M$^{-1}$, and the association constant for the formation of higher order aggregates $K_N = 787 \pm 19$ M$^{-1}$. Apparently, the formation of higher order aggregates by bisamide 1o is highly favored over the formation of dimers in apolar solvents like benzene. Viscosity measurements of 1o were performed with a 14.6 mM solution of 1o in benzene at different shear rates. As is clear from the data shown in Fig. 1, the viscosity decreases with increasing shear rate, indicating that solutions of 1o behave as a non-Newtonian liquid. Although the molecular interpretation of this phenomenon is not yet clear, similar shear-thinning effects have been observed in helical self-assembled polymers consisting of small hydrogen bonding subunits. It should be noted that dissolution of 2o does not result in gel formation, nor does it cause a significant increase of the viscosity of the solvent. Moreover, the $^1$H NMR spectra of 2o in C$_6$D$_6$ show only minor...
showing any degradation. It is interesting to note that switching CH_3 signals, which can be assigned to the closed form 1_o at 313 nm caused the appearance of a second set of NH and carboxylic acid derivatives of diarylethene switches, 11 although initial state consisting of pure mixture of it was deduced that the photostationary state consists of a initial state consisting of pure 1_o, and this switching process between 1_o and 1_c could be repeated several times without showing any degradation. It is interesting to note that switching between 1_o and 1_c is not prohibited by formation of intra-molecular hydrogen bonds as has previously been reported for carboxylic acid derivatives of diarylethene switches, 11 although it cannot be excluded that such an intra-molecular hydrogen bond between the two amide groups is present. Also irradiation of a concentrated viscous solution of 1_o in benzene (11.7 mM) leads to the appearance of an absorption band at longer wavelength, characteristic for the formation of the closed form. The absorption maximum of 1_c shows a small red shift to 524 nm and is slightly broadened compared to the measurements at low concentrations, indicative of a weak exciton coupling between the chromophores in the aggregates. The switching process is also fully reversible in these concentrated solutions and can be repeated several times, although at very long irradiation times (> 20 h) some decomposition (< 5%) takes place. 12 The viscous solution needs, however, considerably longer irradiation times (6 h) to reach the photo-stationary state compared to monomeric solutions of 1_o (< 0.5 h), but quantitative analysis of the kinetics is not yet possible in our experiment set-up due to inner filter effects and an inhomogeneous optical field.

Most remarkably, even at relatively low conversions of 1_o to 1_c (1_o/1_c = 4) there is a clear decrease of the viscosity compared to benzene solutions of pure 1_o, demonstrating that the viscosity of solutions of 1 can be controlled by light (Fig. 1). 13 In order to determine whether this photo-induced viscosity change is due to a change of the aggregate properties like stiffness, or to a change of the extent of aggregation of 1, the photoconversion of viscous benzene solutions of 1_o (7.32 mM in C_6D_6) was followed by ^1H NMR. Irradiation of a solution of 1_o at 313 nm caused the appearance of a second set of NH and CH_3 signals, which can be assigned to the closed form 1_c. 13 After 50 min irradiation the NH signal of 1_c appears as a shoulder upfield from the NH signal of 1_o. After longer irradiation times both the NH signals of 1_o and 1_c are shifted upfield compared to the NH signal of pure 1_o (5.53 ppm) and after 6 h they have reached a constant position at 5.39 ppm. Although these results do not rule out any mesoscopic changes of the aggregates due to irradiation, they clearly indicate that photoconversion of 1_o to 1_c causes a decrease of the extent of aggregation. After 6 h irradiation a photostationary state was reached with the ratio 1_o/1_c = 0.5 (determined from the integration of the CH_3 signals of 1_o and 1_c at, respectively, 1.76 and 2.16 ppm), which is comparable to the photostationary state of monomeric 1. Irradiation at \( \lambda > 520 \) nm causes a complete conversion to 1_o with the NH signal again appearing at 5.53 ppm. Apparently, both the photoswitching and the aggregation of 1 are completely reversible. For comparison, similar experiments were carried out with C_6D_6 solutions of 2_o. Irradiation of 22 mM solutions of 2_o also resulted in two NH signals at 5.37 and 5.44 ppm, which can be assigned to 2_o and 2_c respectively, but for this compound the NH signals did not shift with increasing conversion of 2_o to 2_c. Also the viscosity measurements did not reveal a significant change of the viscosity due to photoswitching of 2.

In conclusion, the bis-amide photochromic switch 1_self-assembles in apolar solvents through a cooperative association mechanism, and forms extended aggregates, resulting in highly viscous solutions. Most remarkably, the reversible photoswitching of 1 from the open form to the closed form causes a change of the extent of aggregation, which is accompanied by a decrease of the viscosity. These changes can be attributed to different molecular properties like shape and conformational freedom of the open and closed form of diarylethene switch 1, and it is expected that this feature of diarylethene switches can be employed to control other macroscopic properties like gel formation by light as well.

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Notes and references

† Compounds 1_o and 2_o were fully characterised showing spectroscopic and analytical data in accordance with the structure shown.

‡ Viscosity measurements were performed on a Brabender Rheotran, with a cone/plate geometry (cone angle 3°), and 1_H NMR experiments were performed on a Varian VXR-300 spectrometer, using 0.15–22 mM benzene solutions of 1 or 2. All measurements have been carried out at room temperature. For a more detailed survey about viscosity measurements the following reference is recommended: A. Dinsdale and F. Moore, Viscosity and its Measurement, Chapman and Hall, London, 1962.

§ The samples were irradiated in a 1 mm quartz cuvet for UV–VIS measurements and in 5 mm pyrex tubes for NMR experiments, using a 200 W mercury lamp with a 313 nm band-pass or a 520 nm high-pass filter.

10 The viscosity of 2_o at shear rates 3 s^(-1) and 24 s^(-1) is 0.009 and 0.0002 Pas respectively; for 2_c 0.0012 and 0.0004 Pas respectively.