Photocontrolled self-assembly of molecular switches

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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,\textsuperscript{1,2} 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,\textsuperscript{3} 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.\textsuperscript{4}

Here we report on a new self-assembling system based on diarylethene photochromic switches,\textsuperscript{3} which forms extended aggregates in solution, and the viscosity of which can be changed by light. Diarylethene and particularly dithienylcyclopentene molecular switches\textsuperscript{3,5} 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 geometry of the molecules,\textsuperscript{1,2} 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,\textsuperscript{3} 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.\textsuperscript{4}

The 1,2-bis(5\textsuperscript{a}-(alkylamino)carbonyl)-2\textsuperscript{b}-methylthien-3\textsuperscript{c}-yl)cyclopentenes (10 and 20) were synthesised in a two-step procedure starting from 1,2-bis(5\textsuperscript{a}-formyl-2\textsuperscript{b}-methylthien-3\textsuperscript{c}-yl)cyclopentene.\textsuperscript{5} Oxidation with Ag\textsubscript{2}O provided the corresponding diacid, which was next converted to amides 10 and 20 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 10 and 20\textsuperscript{f} were obtained in 33 and 30% overall yield, respectively, after column chromatography starting from the dihalide.

The gelation behaviour of 10 was studied in various solvents of different polarity.\textsuperscript{2} It was found that 10 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 10 occurs.\textsuperscript{6} The \textsuperscript{1}H NMR spectra of 10 in C\textsubscript{6}D\textsubscript{6} show a gradual down field shift of \(\delta_{N}\) from 5.26 to 5.56 ppm, and an increase of the line width with increasing concentration, indicating that 10 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 10 are equilibrium structures. Fitting of the data to a cooperative aggregation model\textsuperscript{7} revealed that the dimerization constant \(K_d = 81 \pm 3\) M\textsuperscript{−1}, and the association constant for the formation of higher order aggregates \(K_N = 787 \pm 19\) M\textsuperscript{−1}. Apparently, the formation of higher order aggregates by bisamide 10 is highly favored over the formation of dimers in apolar solvents like benzene. Viscosity measurements\textsuperscript{8} were performed with a 14.6 mM solution of 10 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 10 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.\textsuperscript{9} It should be noted that dilution of 20 does not result in gel formation, nor does it cause a significant increase of the viscosity of the solvent.\textsuperscript{10} Moreover, the \textsuperscript{1}H NMR spectra of 20 in C\textsubscript{6}D\textsubscript{6} show only minor

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{scheme1.png}
\caption{Scheme 1 Photoswitching of diarylethene 10 and 20 and thereby controlling the extent of self-assembly of 1 by photochemical switching.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{Viscosity of 14.6 mM solution of 10 in benzene before (—) and after irradiation (---) (10/1c = 4).}
\end{figure}

In order to promote the formation of supramolecular assemblies in solution by hydrogen bonding, a dithienylcyclopentene-switch has been extended with amide groups (Scheme 1). The 1,2-bis(5\textsuperscript{a}-(alkylamino)carbonyl)-2\textsuperscript{b}-methylthien-3\textsuperscript{c}-yl)cyclopentenes (10 and 20) were synthesised in a two-step procedure starting from 1,2-bis(5\textsuperscript{a}-formyl-2\textsuperscript{b}-methylthien-3\textsuperscript{c}-yl)cyclopentene.\textsuperscript{5} Oxidation with Ag\textsubscript{2}O provided the corresponding diacid, which was next converted to amides 10 and 20 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 10 and 20\textsuperscript{f} were obtained in 33 and 30% overall yield, respectively, after column chromatography starting from the dihalide.

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shifts ( < 0.05 ppm) upon increasing the concentration from 2 to 22 mM, indicating that the sterically more demanding tert-butyl groups effectively prevent aggregation of 2o by intermolecular hydrogen bonding.

The photochromic behaviour§ of a dilute solution of 1o in benzene (0.29 mM) was followed by UV spectroscopy as is depicted in Fig. 2. Upon irradiation of the solution of 1o at 313 nm, a new absorption band at 514 nm appeared due to the formation of the conjugated closed form 1c. From 1H NMR data it was deduced that the photostationary state consists of a mixture of 1o and 1c in a molar ratio of 1o/1c = 0.43. Irradiation at > 520 nm causes a complete conversion to the initial state consisting of pure 1o, and this switching process between 1o and 1c could be repeated several times without showing any degradation. It is interesting to note that switching between 1o and 1c 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 1o 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 1c 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.11

The viscous solution needs, however, considerably longer irradiation times (6 h) to reach the photo-stationary state compared to monomeric solutions of 1o (<0.5 h), but quantitative analysis of the kinetics is not yet possible in our experimental set-up due to inner filter effects and inhomogeneity of the sample.

Most remarkably, even at relatively low conversions of 1o to 1c (1o/1c = 4) there is a clear decrease of the viscosity compared to benzene solutions of pure 1o, demonstrating that the viscosity of solutions of 1 can be controlled by light (Fig. 1).12 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 1o (7.32 mM in C8D8) was followed by 1H NMR. Irradiation of a solution of 1o at 313 nm caused the appearance of a second set of NH and CH2 signals, which can be assigned to the closed form 1c.§ After 50 min irradiation the NH signal of 1c appears as a shoulder upfield from the NH signal of 1o. After longer irradiation times both the NH signals of 1o and 1c are shifted upfield compared to the NH signal of pure 1o (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 1o to 1c causes a decrease of the extent of aggregation. After 6 h irradiation a photostationary state was reached with the ratio 1o/1c = 0.5 (determined from the integration of the CH3 signals of 1o and 1c at, respectively, 1.76 and 2.16 ppm), which is comparable to the photostationary state of monomeric 1. Irradiation at λ > 520 nm causes a complete conversion to 1o 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 C8D8 solutions of 2o. Irradiation of 22 mM solutions of 2o also resulted in two NH signals at 5.37 and 5.44 ppm, which can be assigned to 2o and 2c respectively, but for this compound the NH signals did not shift with increasing conversion of 2o to 2c. 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 1o and 2o were fully characterised showing spectroscopic and analytical data in accordance with the structure shown.

‡ Viscosity measurements were performed on a Brabender Rheotron, 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 1o or 2o. 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 2o at shear rates 3 s−1 and 24 s−1 is 0.0009 and 0.0000 Pas, respectively; for 2c 0.0012 and 0.0004 Pas, respectively.