Photocontrolled self-assembly of molecular switches

Linda N. Lucas,[a] Jan van Esch,*[a] Richard M. Kellogg[b] and Ben L. Feringa*[a]

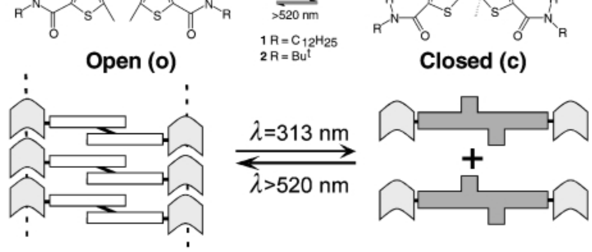
[a] *University of Groningen, Organic and Molecular Inorganic Chemistry, Stratingh Institute, Nijenborgh 4, 9747 AG, Groningen, The Netherlands. E-mail: Esch@chem.rug.nl; Feringa@chem.rug.nl*
[b] *Syncom BV, Kadijk 3, 9747 AT, Groningen, The Netherlands*

Received (in Liverpool, UK) 1st February 2001, Accepted 1st March 2001
First published as an Advance Article on the web 3rd April 2001

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,[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,[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.[4]

Here we report on a new self-assembling system based on diarylethene photochromic switches,[3] which forms extended aggregates in solution, and the viscosity of which can be changed by light. Diarylethene and particularly dithienylcyclopentene molecular switches[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 electronic properties and conformational flexibility: in the open form (**1o**) the two thienyl moieties are not conjugated and can rotate around the bond connecting them with the cyclopentene ring, whereas in the ring-closed form (**1c**) the conjugation extends throughout the molecule and the rotational freedom is lost (Scheme 1). In this study, the geometrical change accompanying the photochemical transformation is exploited to change the self-assembling properties of **1**, and hence the macroscopic properties of the system. The dithienylcyclopentenes used here offer two distinct features when compared to the commonly used azostilbenes:[4] (i) the photochemically induced ring-closure reaction of dithienylcyclopentenes involves geometrical transformation which is clearly different from the *cis*–*trans* isomerization, and (ii) the activation energy for thermal interconversion between the open and closed form is large.[3] The use of dithienylcyclopentenes in switchable supramolecular systems will therefore expand the scope of available transformations and will lead to thermally bistable systems (Scheme 1).



Scheme 1 Photoswitching of diarylethene **1o** and **2o** and thereby controlling the extent of self-assembly of **1** by photochemical switching.

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′[(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.[6] Oxidation with Ag_2O provided the corresponding diacid, which was next converted to amides **1o** and **2o** 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 dialdehyde.

The gelation behaviour of **1o** was studied in various solvents of different polarity.[7] 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.[8] The ^1H NMR spectra of **1o** in C_6D_6 show a gradual down field shift of δ_{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[9] revealed that the dimerization constant $K_2 = 81 \pm 3\ M^{-1}$, 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‡ 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.[8] 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.[10] Moreover, the ^1H NMR spectra of **2o** in C_6D_6 show only minor

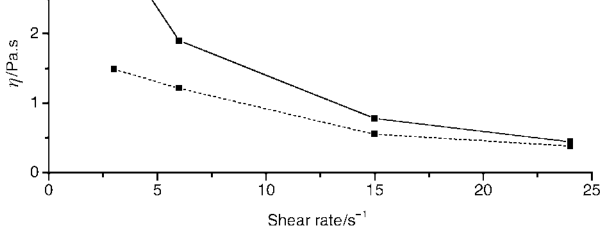


Fig. 1 Viscosity of 14.6 mM solution of **1o** in benzene before (—) and after irradiation (···) (**1o**/**1c** = 4).

DOI: 10.1039/b101231m

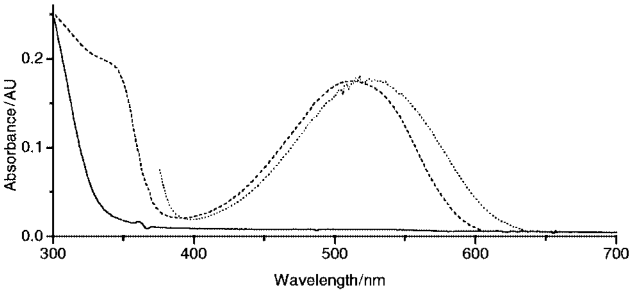


Fig. 2 UV–VIS spectra of a solution of **1o** in benzene (0.29 mM) before (—) and after irradiation (---) at 313 nm for 20 min and of a viscous solution of **1o** in benzene (11.7 mM) after irradiation (···) for 10 min at 313 nm.

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 ^{1}H 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 $\lambda > 520$ 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.[12] 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 an inhomogeneous optical field.

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).[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 **1o** (7.32 mM in C_6D_6) was followed by ^{1}H NMR. Irradiation of a solution of **1o** at 313 nm caused the appearance of a second set of NH and CH_3 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 CH_3 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 $\lambda > 520$ 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 C_6D_6 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 extented 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.

We are grateful for a fellowship to J. van Esch from the Royal Academy of Science of the Netherlands (KNAW), and we thank ir. V. W. A. Verhoeven for this help with the viscosity measurements.

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 **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*, Chapmann 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.

1 J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1154.

2 J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley, Chichester, 2000.

3 *Photochroism: Memories and Switches*, guest editor M. Irie, *Chem. Rev.*, 2000, **100**, 1683.

4 F. Würthner and J. Rebek Jr., *J. Chem. Soc., Perkin Trans. 2*, 1995, 1727; F. Würthner and J. Rebek, Jr., *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 446; J. Rosengaus and I. Willner, *J. Phys. Org. Chem.*, 1995, **8**, 54; K. Murata, M. Oaki, T. Nishi, A. Ikeda and S. Shinkai, *J. Chem. Soc., Chem. Commun.*, 1991, 1715; M. S. Vollmer, T. D. Clark, C. Steinem and M. R. Ghadiri, *Angew. Chem., Int. Ed.*, 1999, **38**, 1598.

5 L. N. Lucas, J. van Esch, R. M. Kellogg and B. L. Feringa, *Chem. Commun.*, 1998, 2313.

6 S. L. Gilat, S. H. Kawai and J.-P. Lehn, *Chem. Eur. J.*, 1995, **1**, 275; J. M. Endtner, F. Effenberger, A. Hartschuh and H. Port, *J. Am. Chem. Soc.*, 2000, **12**, 3037.

7 P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133; J. H. van Esch and B. L. Feringa, *Angew. Chem., Int. Ed.*, 2000, **39**, 2263.

8 J. H. K. K. Hirschberg, L. Brunsveld, A. Ramzi, J. A. J. M. Vekemans, R. P. Sijbesma and E. W. Meijer, *Nature*, 2000, **407**, 167.

9 J. Jadżyn, M. Stockhausen and B. Żywucki, *J. Phys. Chem.*, 1987, **91**, 754; M. Akiyama and T. Ohtari, *Spectrochim. Acta, Part A*, 1994, **50**, 317; M. de Loos, J. van Esch, R. M. Kellogg and B. L. Feringa, *Angew. Chem., Int. Ed.*, 2001 **40**, 613.

10 The viscosity of **2o** at shear rates 3 s^{-1} and 24 s^{-1} is 0.0009 and 0.0000 Pa.s, respectively; for **2c** 0.0012 and 0.0004 Pa.s, respectively.

11 M. Irie, O. Miyatake, K. Uchida and T. Eriguchi, *J. Am. Chem. Soc.*, 1994, **116**, 9894.

12 See also: M. Irie, T. Lifka, K. Uchida, S. Kobatake and Y. Shindo, *Chem. Commun.*, 1999, 747.

13 M. Irie, A. Menju and K. Hayashi, *Macromolecules*, 1979, **12**, 1176; M. Irie, Y. Hirano, S. Hashimoto and K. Hayashi, *Macromolecules*, 1981, **14**, 262.