Photoresponsive dithienylethene-urea-based organogels with "reversed" behavior†

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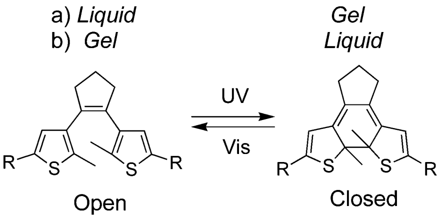
Dithienylperhydrocyclopentene-bisurea-based low molecular weight gelators are described that function as photoresponsive organogels that show a remarkable gel-to-liquid transition upon irradiation. The two series of derivatives, with and without alkyl spacers between the urea hydrogen bonding groups and the photochromic unit, show different gelation behavior. Upon UV irradiation of the gels, a gel liquified at only 1.4% conversion of the photochromic unit. Transmission electron microscopy (TEM) shows that the gel fibres consist of thin ribbons. Semi-empirical (PM3) calculations indicate that the hydrogen bonding between the open-ring isomer (o) molecules is weak, and that formation of the closed-ring isomer (c) destabilises the hydrogen bonding further. The results indicate that a small amount of the closed-ring isomer will disrupt the intermolecular hydrogen-bonding, leading to disintegration of the gel fibre ribbons and hence reversible liquification.

Photochromic behaviour, the reversible unimolecular transformation between two states having different absorption spectra, holds considerable potential towards application in molecular switching, as control elements in molecular devices and in the development of smart materials.[1] Diarylethenes are amongst the most promising of photochromic compounds,[2] not only as memory materials but also as switching unit components in molecular devices and supramolecular systems.[3] Recently, we have shown that a dithienylcyclopentene disubstituted with chiral (*R*)-*N*-phenylethylamide groups forms gels through self-assembly due to the formation of multiple intermolecular hydrogen bonds between the amide functionalities. The supramolecular chirality of the gel governed the dynamic molecular chirality through the hydrogen bonding networks formed, and upon photochemical ring closure of the dithienylethene allows for locking of the molecular chirality of the gel molecules stereoselectively.[4] Furthermore, it was shown that switching between gels of different aggregate (fibre) stability could be achieved with the gel-to-liquid transition being achieved by photochemical ring opening of gelator molecules (Scheme 1a). Indeed, photochemical control of supramolecular aggregation was used to achieve dynamic holographic pattern formation.[5]



Scheme 1

We report here new dithienylethene-based bis-urea gelators that, in sharp contrast to the light-switchable gelator systems described earlier, show reversible gel-to-liquid phase transitions upon ring closure of the photochromic unit (Scheme 2). Furthermore, it is demonstrated that liquification takes place even with only 1.4% conversion of the dithienylethene gelator molecules to the closed state.

Urea moieties have proven to be versatile functional groups in driving gelation of low molecular weight gelator systems. In particular, compounds that contain two urea groups have been demonstrated to be very potent and versatile gelating agents for a wide range of organic solvents.[6,7] Cyclohexane bis-urea compounds are well known gelators not only of organic solvents but for aqueous solutions also.[8] The introduction of photochromic responsiveness to urea-based gelators was reported previously in the use of the azobenzene unit in conjunction with two urea groups to produce thermoreversible gels.[9]

We report herein the synthesis and characterisation of a series of dithienylcyclopentene-urea-based organogelators **1o**–**6o**, and explore the effect of the spacer between the urea group and diarylethene moiety and the chain length of terminal alkyl groups, together with the photo-responsiveness of the gelators. Diarylethenes **1o**–**6o** were prepared from 1,2-bis(5-chloro-2-methylthien-3-yl)perfluorocyclopentene[10] (see ESI†) and show reversible photochromism in solution (Fig. 1 and Fig. 2).

Fig. 1 and Fig. 2 illustrate the changes in the absorption spectra for compounds **1** and **4** in ethanol upon photo-irradiation. Upon irradiation at $\lambda_{exc} = 312$ nm, the colourless solution turned red and absorption bands assigned to **1c** appeared at 523 nm (ε: 1.3×10^4 M^{-1} cm^{-1}). Concomitantly the absorption of **1o** at 283 nm (ε: 2.8×10^4 M^{-1} cm^{-1}) decreased in intensity. Upon irradiation at $\lambda > 500$ nm, the red colour was bleached and **1o** was regenerated, as confirmed by UV/Vis absorption spectroscopy. Isosbestic points were maintained at 206, 232, and 299 nm. The absorption maxima

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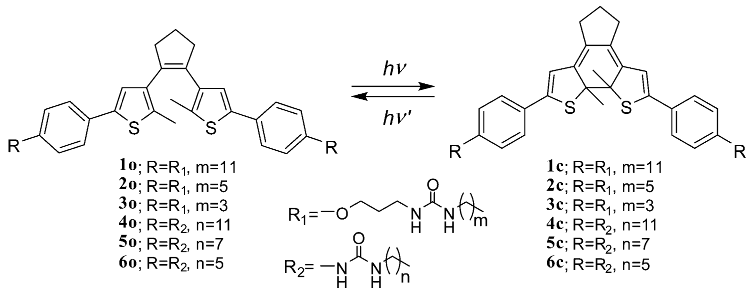

Scheme 2 Diarylethene derivatives having propylene spacers (**1o**–**3o**), and derivatives without spacers (**4o**–**6o**). The corresponding closed-ring isomers **1c**–**3c** and **4c**–**6c** are generated by UV irradiation. (o = open, c = closed).

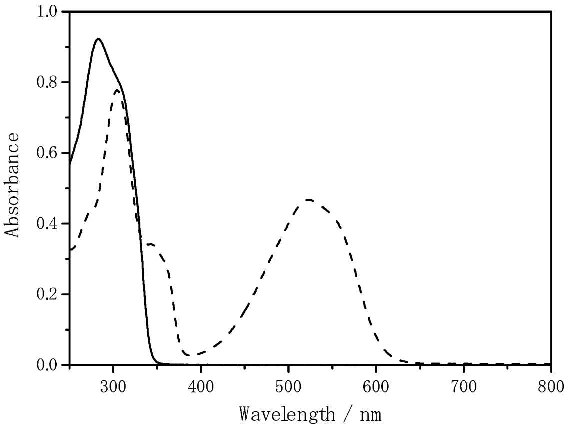

Fig. 1 Absorption spectral changes of **1** in ethanol (0.33 mM), **1o**: solid line; photostationary state under 312 nm light: dashed line.

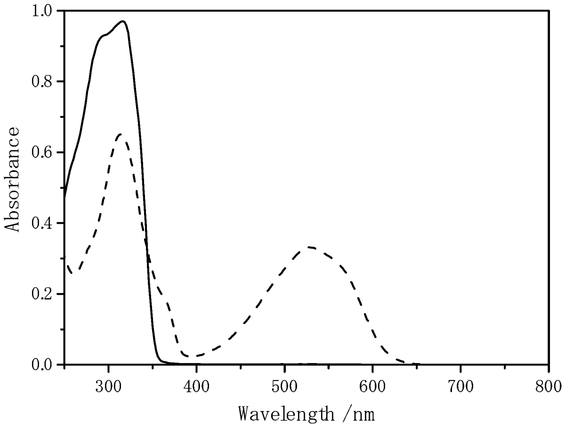

Fig. 2 Absorption spectral changes of **4** in ethanol (0.31 mM), **4o**: solid line; photostationary state under 312 nm light: dashed line.

of **4o** and **4c** in ethanol are 315 nm (ε: 3.10 × 10^4 M^{-1} cm^{-1}) and 530 nm (ε: 1.4 × 10^3 M^{-1} cm^{-1}), respectively, as shown in Fig. 2.

The gelation properties were studied by first dissolving the compounds by heating in the appropriate solvent, followed by cooling to room temperature. For some of the solid–solvent combinations, the formation of a gel was observed. The results are shown in Table 1, in which the solvents are arranged in order of increasing polarity according to their $E_T(30)$-values. From Table 1, in the compounds which incorporate propylene spacers, only compound **1o** showed gelation behaviour, while **2o** and **3o** do not gelate any of the solvents tested but form precipitates instead.

Table 1 Gelation properties of compounds **1o**–**6o** in organic solvents[a]

Solvent	**1o**	**2o**	**3o**	**4o**	**5o**	**6o**
Hexane	I	P	P	I	I	I
Cyclohexane	I	I	I	I	I	I
P-Xylene	—	—	—	I	I	I
Benzene	P	S	S	I	I	P
Toluene	P	P	P	I	I	I
Tetralin	D	P	P	I	P	I
1,4-Dioxane	D	P	P	P	P	P
N-Butyl acetate	I	I	I	G (19.2)	I	P
Di-*N*-butyl ether	I	I	I	I	I	I
Cyclohexanone	—	—	—	S	S	S
Chloroform	G (25.0)	S	S	P	I	P
Dichloromethane	G (25.0)	P	P	G (25.0)	P	P
Diphenyl ether	G (25.0)	P	P	S	P	I
1,2-Dichloroethane	P	P	P	P	P	G (12.5)
O-Dichlorobenzene	P	P	P	G (12.5)	P	G (12.5)
Chlorobenzene	P	P	I	G (15.6)	P	P
THF	G (25.0)	P	P	S	S	D
DMF	S	S	S	S	S	S
DMSO	P	S	S	S	S	P
1-Octanol	—	—	—	S	S	P
2-Propanol	—	—	—	P	P	S
1-Propanol	P	S	P	S	P	S
Ethanol	P	P	P	P	I	I
Acetonitrile	P	P	P	I	P	I
Water	I	I	I	I	I	I

[a] G: gelation, P: precipitation, I: insoluble, S: soluble, D: decomposition. The gelation concentrations (mg ml^{-1}) are shown in parentheses.

For the gelators in which the urea moiety is attached directly to the phenyl rings of the switching unit, only compound **5o** did not show gelation behaviour in any of the solvents tested, instead forming precipitates. The minimum gelation concentrations for **4o** and **6o** were almost half of that of **1o**, indicating their superior gelation abilities. The changes in gelation behaviour induced by light were investigated in the THF gel of **1o** and the *o*-dichlorobenzene gels of **4o** and **6o**. The gel-to-sol transition temperature was measured by the tilt tube method in an air oven with a heating rate of 0.5 °C min^{-1}.

The melting temperature of the THF gel (25 mg ml^{-1}) of **1o** was 40–42 °C, while that of the photostationary state (PSS) mixture (**1o**:**1c** = 6 : 4) after UV irradiation showed a very modest increase to 44–47 °C. The gel–sol temperature of *o*-dichlorobenzene gel (12.5 mg ml^{-1}) of **4o** was 113–116 °C, while that for the mixture (**4o**:**4c** = 98.6 : 1.4) formed after UV irradiation for 30 s was 96–102 °C. The *o*-dichlorobenzene gel (12.5 mg ml^{-1}) of derivative **6o**, which bears shorter terminal alkyl chains, undergoes the sol–gel transition at 116–119 °C, while that of the mixture (**6o**:**6c** = 98.2 : 1.8) formed after UV irradiation for 30 s was 108–115 °C. The temperature differences obtained by DSC were not clear due to the low content of closed-ring isomers (see ESI†). The most dramatic sol–gel transition change was observed for **4**. Upon UV irradiation (312 nm, 30 s) of the *o*-dichlorobenzene gel of **4o**, a photoinduced gel–sol transition was observed in the temperature range between 105–110 °C, forming a transparent solution as a consequence of photochemical ring closure of the gelator molecules. Visible light irradiation to the sol at that temperature leads to re-formation of the initial turbid gel. TEM image of the *o*-dichlorobenzene gel of **4o** was obtained to further understand the origin of this dramatic change. The gel fibres show a thin ribbon structure (Fig. 3).

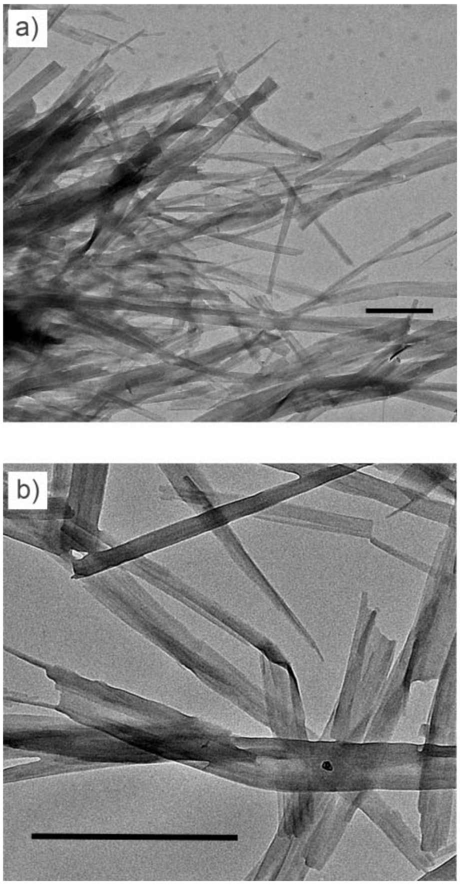

Fig. 3 TEM images of the *o*-dichlorobenzene gel of **4o** (12.5 mg ml^{-1}) (scale bar: 1.0 µm).

Additionally, semi-empirical (PM3) calculations[11] were carried out[12] to suggest a possible array of the molecules. Fig. 4 shows the results for the optimized structures of **4o**–**4o** assembly (a, b), **4o**–**4c** assembly (c, d), and **4c**–**4c** assembly (e, f), respectively. It is remarkable that the hydrogen bond length in the complexes was found to be between 2.5 and 3 Å; while the reported value for a hydrogen bond is about 2 Å.[13] There may be a significant contribution from the interaction of the alkyl chains; however, intermolecular H-bonding through the urea moieties is expected to be the dominant interaction. The calculated distance of the C_{12} chains is the same for all three complexes. This suggests that the differences in energy of the intermolecular interactions of the complexes **4o**–**4o**, **4o**–**4c** and **4c**–**4c** are due to the switch and urea moieties only. From the longitudinal views shown in Fig. 4, a significant change in the relative position of the switch moieties is indeed visible going from **4o**–**4o** to **4c**–**4c**.[14]

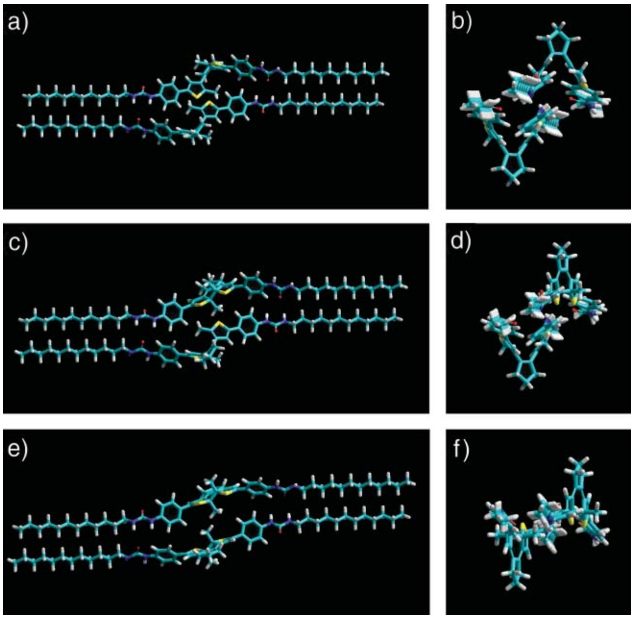

Fig. 4 Dimer assemblies of **4o**–**4o** (a, b), **4o**–**4c** (c, d), and **4c**–**4c** (e, f) obtained by PM3 calculations (left: lateral view; right: longitudinal view).

From the calculations, the interaction energies of **4o**–**4o**, **4o**–**4c**, and **4c**–**4c** are 30.86, 28.20, and 31.62 kcal mol^{-1}, respectively. From these numbers, it can be seen that the energy of interaction of **4o**–**4c** is 2.66 kcal mol^{-1}, which is lower than that for **4o**–**4o**. The results of the calculations suggest that the hydrogen bonding between **4o** molecules is weak, and that photo-induced formation of **4c** slightly destabilizes the intermolecular interaction. The experimental results indicate, in agreement with calculations, that the small amount of **4c** formed decreases the intermolecular interactions, leading to break-up of the ribbons and eventual liquification of the gel.[12]

In summary, we have described photo-switchable organogelators consisting of a diarylethene and urea units. The gel-to-liquid transition occurs even at very low conversion from the open colourless state to the closed coloured state. This is attributed to the weakness of the molecular level interactions and the thin ribbon-like gel structure of the gel fibres. Visible light irradiation recovers the gel. Compared with earlier switchable gelators, which show gel-to-liquid phase changes upon ring opening, the present system allows gel-to-liquid transitions triggered by photochemical ring closure. This system is an excellent demonstration of the delicate balance in supramolecular behaviour that can be achieved in photo-reversible supramolecular systems and the possibility of addressing aggregation with light.

Acknowledgements

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14 These results, however, have to be taken only as qualitative, as two molecules only might be not adequate for an accurate description of the system. By contrast, the **4c**–**4c** assemblies, which were estimated (on the basis of the calculations) to have the strongest intermolecular interactions, were not observed because of low fatigue resistance of the molecule. Prolonged UV irradiation decomposed the switch (see ESI†).