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The enhancement of photoswitching in a diarylethene derivative by the incorporation of cyanobiphenyl groups

Michel Frigoli and Georg H. Mehl*

Department of Chemistry, University of Hull, Hull, UK. E-mail: g.h.mehl@hull.ac.uk; Fax: (44) 1482 466411; Tel: (44) 1482 465590

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A photochromic liquid crystal system based on a diarylethene functionalised in the 2,2′-positions and linked to 4-cyano-4′-hydroxybiphenyl groups *via* alkyl spacers as chromophores was synthesised and its photochromic and mesomorphic behaviour was investigated.

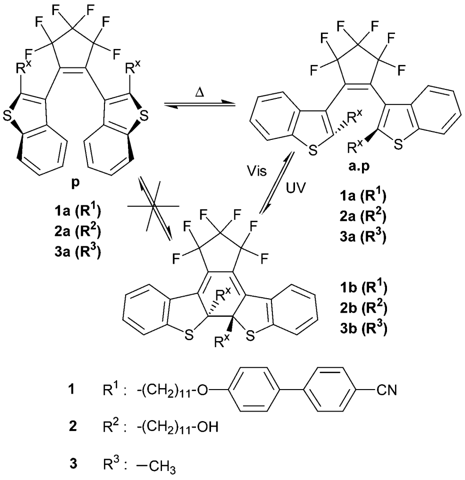
The combination of self-assembly and photochromic behaviour, the modulation of chemical structure and physical properties in molecular systems by light, promises to be very useful in optical technological devices.[1] Diarylethene based photochromes, notably bis(dibenzothien-3-yl) systems, are very suitable for this purpose, due to the remarkable thermal stability of both colourless and coloured forms and their high photo-resistance.[2] Functionalisation of bis(dibenzothien-3-yl) or bis(dithien-3-yl) systems with mesogens has so far been in positions at the long axis of the molecules.[3,4] However the functionalisation of the 2,2′-positions of a diarylethene unit allows for a controlled modulation of the absorption spectra and of the electrochemical properties, the introduction of chirality and the addressing of the equilibrium between open and closed forms.[5,6] Also, the substituents introduced in 2,2′-positions influence strongly the distribution between the parallel (p) and antiparallel (ap) conformers (active form for electrocyclisation) present in diarylethene derivatives (Scheme 1).[6]

We report the first photochromic liquid crystal **1**, which is connected to two mesogens *via* a spacer of eleven methylene groups in 2,2′-positions, based on the novel photochromic diol **2** shown in Scheme 1. The reactive alcohol functions are separated from the photochromic core by an alkyl spacer, decoupling of the aromatic groups is required for the formation of LC behaviour. Cyanobiphenyl groups were used as mesogens, due to their fluorescence properties and for comparison with other functional hybrid oligomeric liquid crystal systems.[3,4]

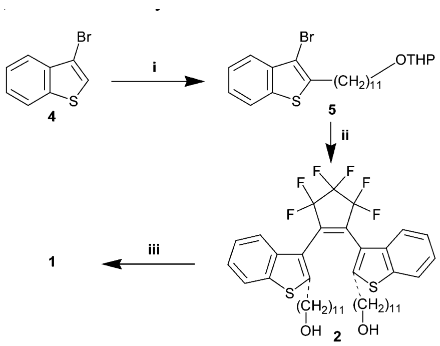
The photochromic liquid crystal **1** was prepared following the synthetic route shown in Scheme 2. The approach takes advantage of the acidity of the hydrogen in the α-position to the sulfur atom of the benzothiophene core prefunctionalised in the 3-position by a bromo group **4**. The lithiation in the 2-position using LDA in THF at −60 °C allowed the conversion of **4** to the product **5** by reacting the lithiated derivative with 2-(11-bromoundecyloxy)tetrahydropyran (78%), containing the protected alcohol function. The photochromic diol **2** was prepared by reacting the lithiated derivative of **5** obtained by an bromide/lithium exchange using *n*-BuLi in THF at −78 °C with a semi-equivalent of octafluorocyclopentene, followed by the removal of the protective group, carried out in ethanol at reflux in the presence of a catalytic amount of PPTS (overall yield 58%). Diol functions of photochromic compound **2** were reacted with 4-cyano-4′-hydroxybiphenyl by a Mitsunobu reaction in the presence of DIAD and PPh$_3$ in dichloromethane yielding the target molecule **1** (29%). The molecular structure and purity of **1a** were confirmed by ^{1}H-NMR, elemental analysis and HPLC.[7]

The photochromic properties of **1** and **2** are compared with those obtained for bis(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene **3**.[6] The introduction of cyanobiphenyl groups that absorb strongly in the UV region increases considerably the extinction coefficient at the wavelength of irradiation, shown in Fig. 1. At 313 nm, the extinction coefficient for **1a** (25000) is more than seven times higher than that of **2a** (3500). When photochromic solutions of **1a** and **2a** were irradiated with 313 nm light, all the compounds turned from colourless to red-purple. The change of colour is due to the formation of the closed forms **1b** and **2b**. The presence of the cyanobiphenyl groups does not affect the maximum absorption in the visible region. For both molecules **1b** and **2b**, the visible band is centred at 538 nm. A bathochromic shift of 21 nm is observed when compared with the maximum absorption value of molecule **3a** (517 nm). Similar results have been also reported for structurally related dithienylethene derivatives when methyl groups are replaced by hexyl groups.[8] The original absorption spectrum can be recovered by irradiation with visible light at 546 nm. Fig. 1 shows also the calculated absorption spectra of the pure closed-ring forms **1b** and **2b**.[3] The value of the extinction coefficient (ε) at 538 nm for **1b** is 8600 and 8400 mol^{-1} L cm^{-1} for **2b**, similar to the value obtained at 517 nm for **3b** (9100). The photochromic properties are listed in Table 1.

The replacement of the methyl group by the undecyloxyl group in the 2,2′-positions reduces the quantum yield of cyclisation from 0.35 (**3**) to 0.23 (**2**). This decrease is directly correlated to the ratio



Scheme 1 Photochromic interconversion in diarylethene series.



Scheme 2 *Reagents and conditions*: i, LDA/THF, −60 °C, 1.5 h, 2-(11-bromoundecyloxy)tetrahydropyran, −78 °C to r.t., 78%; ii, BuLi/THF, 30 min, −78 °C, $\frac{1}{2}$ eq of octafluorocyclopentene, −78 °C to r.t., ethanol, PPTS, reflux, 4 h, 58%; iii, 4-cyano-4′-hydroxybiphenyl, DIAD, PPh$_3$, CH$_2$Cl$_2$, r.t., 3 h, 29%.

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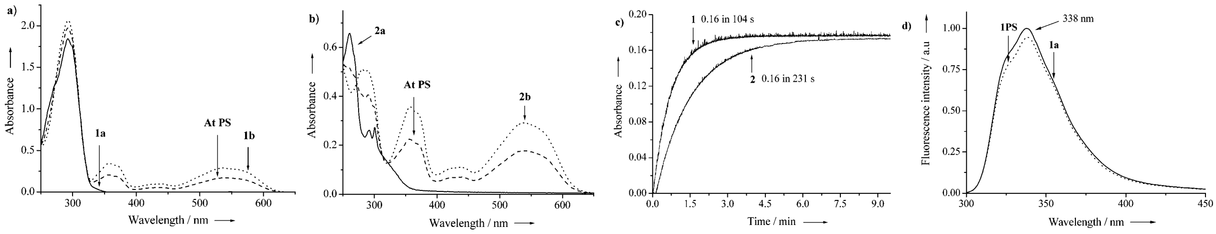

Fig. 1 (a) and (b) Absorption spectral changes of **1** and **2** in cyclohexane solution. (c) Rate of photocolouration (absorbance (538 nm) *vs.* time of irradiation) for **1** and **2**. (d) Fluorescence spectra (excitation wavelength 313 nm) of **1** and **1PS** in cyclohexane solution.

between the active antiparallel (ap) and parallel (p) conformers. ^{1}H NMR signals for the CH$_2$ groups in α-position (2.21 ppm for ap and 2.55 ppm for p) at 25 °C of **2a** indicate that the ratio between the active antiparallel and parallel conformers is 44/56. For **3a**, the relative population is 65/35. As expected, this decrease in the relative population of the antiparallel conformer reduces the quantum yield of electrocyclisation (colouration reaction).[6] The value for the conversion (the concentration of open or closed molecules) obtained at the photostationary (PS) state (equilibrium conditions) determined by HPLC[9] is 0.60 for **2**, higher than the conversion value obtained for the parent molecule **3** (0.43). The conformer ratio of **1** (43/57 ap/p)[7] is similar to that of **2**, the quantum yield of photocyclisation for **1** (**1a** to **1b**) is 0.12, lower than for **2** (0.23). However, on irradiation (313 nm), the photostationary state is reached at least two times faster for **1** than for **2** and **3**, shown in Fig. 1c, and a conversion of 62% at the PS state was detected. The enhancement in the rate can be explained by active participation of the cyanobiphenyl groups in this process. Comparing the emission quantum yield of the fluorescence found for the cyanobiphenyl group (0.75)[10] with those for **1a** (0.13) and for system **1** at the PS state (0.125), Fig. 1(d), indicates that strong quenching of the fluorescence of the cyanobiphenyl groups (donor) takes place.[11] This process of quenching of fluorescence and the energy transfer through space to a functional group with a lower excited state energy (Förster or FRET effect) has been used in diarylethene series to modulate the fluorescence of the donor without its participation in the photochromic process.[12] For **1**, following excitation with light (313 nm), fluorescence resonance energy transfer (FRET) from the cyanobiphenyl groups to the photochromic core occurs, and additionally the rate of the photoswitching is increased. This result demonstrates for the first time that suitably selected mesogens can be employed as donors for the optimisation of FRET assisted photoswitching. For all of the investigated systems the quantum yield values of cycloreversion by irradiation with 546 nm light are broadly similar, ranging from 0.35 to 0.30.

The LC behaviour of the open-ring isomers **1a** and the system at photostationary conditions **1PS** was investigated using differential scanning calorimetry (DSC) and optical polarising miscoscopy. The results are given in Table 2.

Table 1 Photochromic properties of compounds **1**, **2** and **3**[a]

	Cyclisation (313 nm)			Cycloreversion[b] (546 nm)
	$\Phi_{a\rightarrow b}$	$\Phi_{a\rightarrow b}\ \varepsilon_a{}^d$	Conversion	$\Phi_{b\rightarrow a}$
1	0.12	3000	0.62	0.31
2	0.23	800	0.60	0.30
3[c]	0.35	1000	0.43	0.35

[a] Photochromic reactions were performed in cyclohexane solution. [b] For all the compounds, the conversion of cycloreversion were 1. [c] Taken from ref. 6. [d] This product characterises the efficiency of the colouration photoreaction.

Table 2 Transition temperatures (°C) as determined by DSC[a]

Compound	Transition temperature/°C
1a	Cr 140.1 (96.1 N) Iso
1PS	Cr 122.2 (62.1 N) Iso

[a] () denotes a monotropic transition; Cr: crystalline; N: nematic; Iso: isotropic liquid.

System **1a** melts at 140.1 °C and on cooling from the isotropic liquid exhibits a nematic phase at 96.1 °C (monotropic LC behaviour, not thermodynamically stable). Irradiation with UV light alters these properties significantly. For **1PS**, the reduction in flexibility due to ring closure of the system reduces the stability of the nematic phase by 34 °C to 62.1 °C while the melting point is less altered and decreases by 17.9 °C to 122.2 °C.

In conclusion, we have demonstrated that the introduction of cyanobiphenyl groups in 2,2′-positions *via* alkyl spacers in a diarylethene derivative enhances the rate of photoswitching without altering the other photochromic properties *via* a Förster type process. This also affords a new alternative in the design of photochromic liquid crystals based on diarylethene derivatives.

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