Three-state photochromic switching in a silyl bridged diarylethene dimer†

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The synthesis and photochemical characterization of bi-component molecular switches based on covalently tethered dithienylethene photochromes is described. Both photochromic units undergo complete switching between the fully cyclised and fully non-cyclised states despite a significant level of electronic communication between the individual units and their proximity.

The photochromic properties of diarylethenes continue to receive considerable attention,[1] in particular those based on heterocyclic aryl rings, due to their efficient switching between a coloured (closed) and non-coloured (open) molecular state with high fatigue resistance and excellent thermal stability over multiple cycles.[2] These properties make them excellent candidates for application in optical memory,[3] photoswitching,[4] molecular electronics[5] and display devices.[6] Recently efforts have been directed towards the construction of multicomponent molecular systems for multi-mode switching based on the diarylethene photochromic unit by connecting two or more switches covalently. These multi-functional systems offer the possibility of increasing the number of photochromic states available from two {*i.e.*, open (o) and closed (c)} to three {*i.e.*, o–o; c–o; c–c} or more, allowing for the possibility of achieving higher logic operations than possible with a two state system (Fig. 1). Ultimately multicolour materials or multifrequency optical memories might be developed. However, to achieve operations of a higher order of logic, the systems should behave in a supramolecular manner. That is, both photochromic units must show a significant level of intercomponent interaction *i.e.* that the first ring closing event is 'felt' by the remaining open photochrome, while still retaining the photochemical reactivity of the individual units.

Several bi- and tri-component organic photochromic based systems have been reported, which employ a bridging single bond,[7] phenyl,[8] phenylene,[9] ethynylene,[10] or diyne[11] as well as a combination thereof.[12] The photochemical behaviour of these multicomponent systems has proven to be sensitive to the nature of the bridging unit. In the case of dithienylethene based photochromic switches, substitution of the thienyl rings with conjugated units (*e.g.*, phenyl, thienyl and pyridine rings, alkenes and alkynes)[13] can result in stabilisation of the LUMO of the dithienylethene photochromic unit in the closed state. This stabilisation has the effect of reducing the quantum efficiency of the ring opening reaction[14] and, in multicomponent systems, can
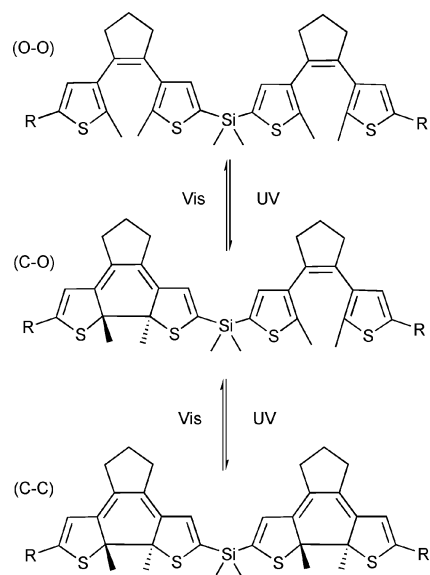

Fig. 1 Photochromic reactions of diarylethene dimer.

lead to more efficient energy transfer from an open component to a closed component, inhibiting and even preventing full ring closure of the multicomponent system.[15]

Indeed, in the majority of multicomponent dithienylethene systems reported to date only one of the diarylethene units can convert to the closed-ring form upon irradiation with ultraviolet light. When the c–o form of the dimer is irradiated with UV light, intramolecular energy transfer from the open dithienylethene unit to the closed unit prevents the formation of the c–c state.

A number of diarylethene dimers have been prepared which can, upon UV irradiation, convert to the c–c closed state, using phenyl[13] or fluorene[16] based spacer units to separate the photochromic units. The absence of communication between the photochromic units in these systems is either complete and the c–o intermediate state cannot be accessed independently of the c–c state or the first ring closing step results in a significant perturbation of the electronic structure of the second chromophoric unit.[8,13]

In this report we focus on examining the communication between two proximately connected diarylethene units, which are bridged *via* a single silicon atom {*e.g.*, **2H(o–o)**, Fig. 2}. Of special interest is how close the two photochromic units can be brought together to allow for intercomponent communication without a loss of the photochromic properties of each component. A key aspect of through bond communication between photochromic units is the overlap integral of the orbitals of the bridging unit with the two photochromic units. If this overlap can be reduced (as in the case of a dimethylsilyl bridge) then through bond interaction can

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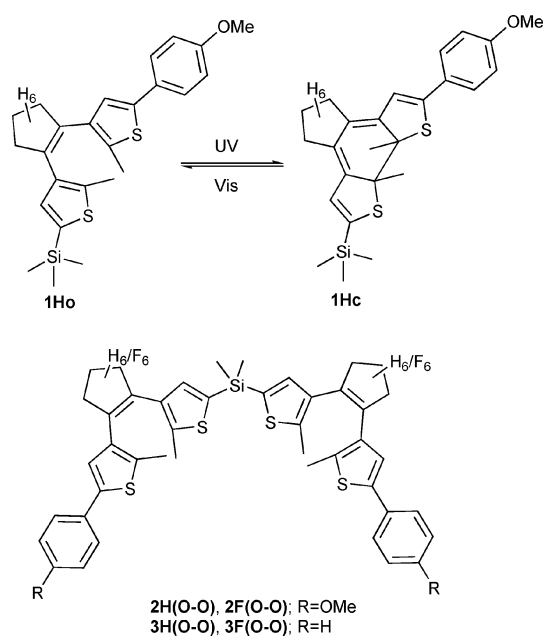This journal is © The Royal Society of Chemistry 2007

Fig. 2 Monomeric (**1**) and dimeric (**2**) and (**3**) photochromic switches.

be minimised resulting in through space interactions dominating any communication between the components observed.

The diarylethene dimer **2H(o–o)** was prepared as outlined in Scheme 1. Starting with the dichloro compound **5Ho**, **6Ho** was prepared by a Suzuki coupling reaction of the boronic ester[17] of **5Ho** with 4-iodoanisole. Lithiation of **6Ho** with *t*-BuLi and subsequent silylation[18] by dichlorodimethylsilane yielded compound **2H(o–o)**. **1Ho**, **2F(o–o)**, **3H(o–o)** and **3F(o–o)** were prepared by a similar route (see electronic supplementary information†).

Photolysis of the monomeric switch **1Ho** at 312 nm resulted in formation of the ring closed forms of the compounds with a photostationary state (PSS, by HPLC) of 37 : 63 (**1Ho** : **1Hc**, see ESI†).

Photolysis of **2H(o–o)** at 312 nm in hexane converts the colourless solution to a coloured solution, with the appearance of new absorption bands in the visible region (Table 1, Fig. 3). The
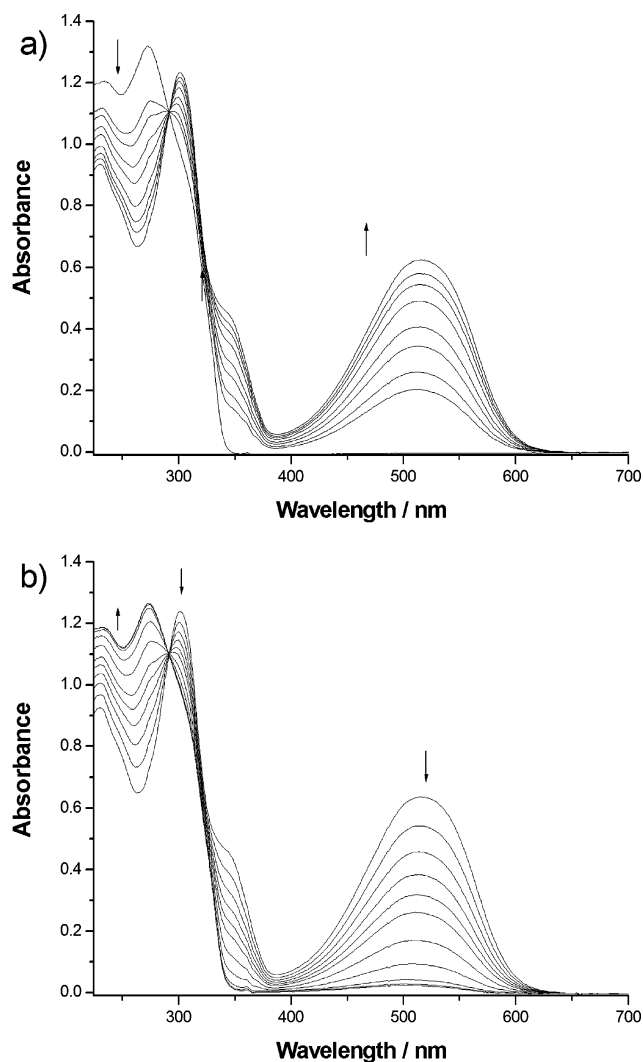

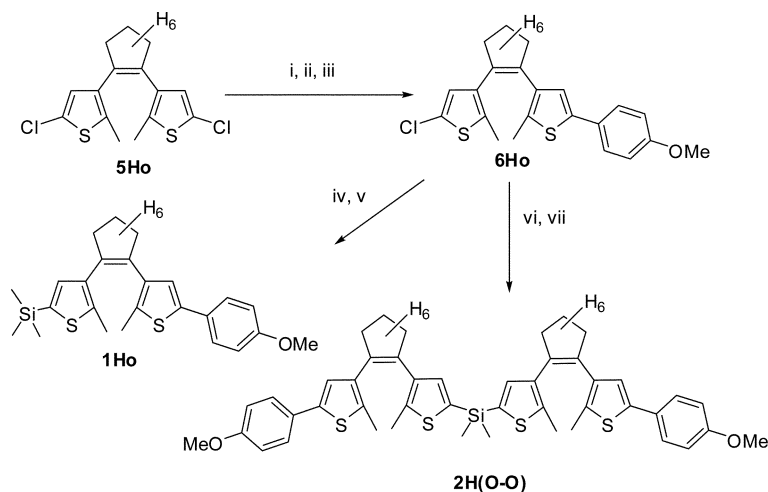Fig. 3 a) UV–vis spectral changes of **2H(o–o)** upon irradiation with 312 nm light. b) Photochromic bleaching of **2H(c–c)** (isolated by thin layer chromatography) upon irradiation at >455 nm.

Scheme 1 Syntheses of monomeric and dimeric dithienylethene based switches. (i) *n*-BuLi/THF, (ii) B(OBu)₃, (iii) 4-iodoanisole/Pd(PPh₃)₄/Na₂CO₃/THF, (iv) *t*-BuLi/THF, (v) Me₃SiCl, (vi) *t*-BuLi/THF, (vii) Me₂SiCl₂.

	(O) λ_{max} (ε)	(C) λ_{max} (ε)	PSS$_{312\,nm}$
1H	275 (24.5)	296 (25.5), 500 (10.43)	37 : 63[b]
2H	274 (50.0)	300, 506 (21.8)	7 : 37 : 56[c]
2F	256 (45.0), 294 (50.7)	340 (37.7), 578 (26.5)	1 : 99[d]
3H	233 (44.0), 270 (45.0)	345 (15.6), 518 (21.9)	8 : 36 : 56[c]
3F	256 (53.0), 282 (48.0)	369 (13.0), 568 (21.0)	1 : 99[d]

[a] λ in nm, ε in mM^{-1} cm^{-1}. In heptane solution. [b] Ratio by HPLC of **1Ho** : **1Hc**. [c] Ratio by HPLC of o–o : c–o : c–c isomers. [d] Ratio by HPLC of o–o : (c–o + c–c) isomers. (O) = open form; (C) = closed form.

absorption bands are typical of the formation of the closed-ring forms, **2H(c–o)** and **2H(c–c)**. Irradiation with >455 nm light leads to a complete reformation to the colourless **2H(o–o)** state. A single isosbestic point at 292 nm was maintained during both ring closing and opening. The photostationary state (PSS) was determined by HPLC to be a mixture of all three forms in the ratio of 7 : 37 : 56 {**2H(o–o)** : **2H(c–o)** : **2H(c–c)**}.‡ Similar results were obtained for **2F**, **3H** and **3F**, however, as chromatographic separation of all three isomers was achieved only for **2H**, the remainder of the discussion will focus on this compound. The lower PSS of **2Ho** compared with **2Fo** is as expected by comparison with related symmetrically substituted systems (Table 1).[19]

2H(c–o) and **2H(c–c)** were generated photochemically and isolated by preparative thin-layer chromatography (see ESI for isolation and characterisation†). Fig. 4 shows the ^{1}H NMR spectra in the range of 3.6 to 8.0 ppm of the three isomers. For **2H(c–o)**, the heterocyclic proton absorptions of **2H(o–o)** at 6.84 and 6.96 ppm are replaced by a new set of four singlets at 6.04, 6.25, 6.87, and 7.03 ppm (Fig. 4b), two of which appear close to the absorptions of **2H(o–o)**. The absorptions at 6.04 and 6.25 ppm are shifted significantly upfield as expected for the ring-closed state.[20] The asymmetric nature of this product confirms that the singly-closed ring isomer **2H(c–o)** has formed. Moreover, Fig. 4c shows only two heterocyclic proton signals at 6.17 and 6.25 ppm confirming that both diarylethene units are in the closed state *i.e.*, **2H(c–c)**.

In contrast to the ^{1}H NMR spectra of the three isomers of **2H**, the UV–vis spectrum of the singly closed form **2H(c–o)** is identical to a 1 : 1 mixture of the fully open {**2H(o–o)**} and closed {**2H(c–c)**} forms. The visible absorption spectra (*i.e.* >400 nm) of both **2H(c–o)** and **2H(c–c)** are identical except with respect to the molar absorptivity (ε 11.0 and 21.8 mM^{-1} cm^{-1} at λ_{max} 506 nm, respectively). Hence, although it is clear from ^{1}H NMR spectroscopy that the two dithienylethene photochromic units show considerable through space steric interaction (as evidenced by the difference in the chemical shift of the thienyl protons of the open and closed units in the three isomers), UV–vis spectroscopy shows that the extent of electronic communication between the units is, at most, minimal.

The PSS of **2H** indicates that the efficiency of photochemical ring closing to the c–o state is good (>93%), and it is higher than observed for the monomeric model compound **1Ho**. However,
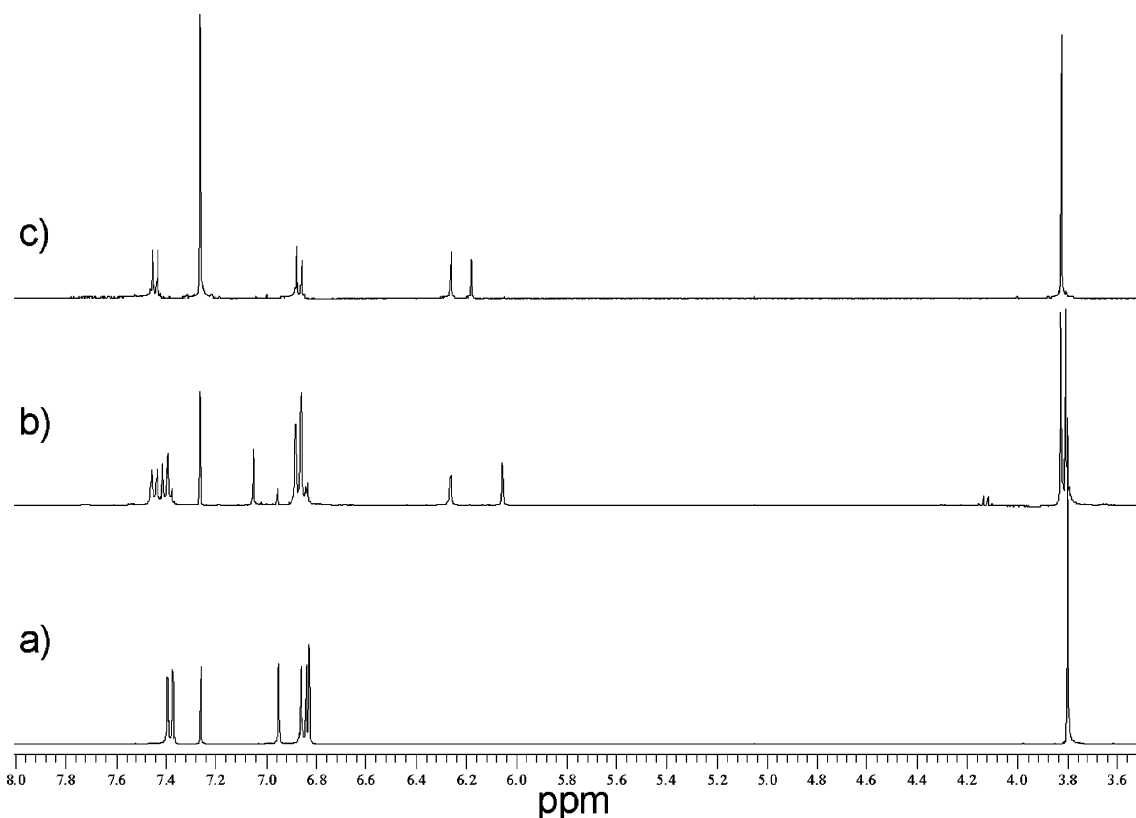
Fig. 4 ^{1}H NMR (400 MHz) spectra of a) **2H(o–o)**, b) **2H(c–o)** and c) **2H(c–c)** in CDCl$_3$.

the efficiency of the second ring closing step is considerably reduced, presumably due to through space quenching of the excited state of the open photochromic unit by the closed unit, reducing the quantum yield of the photochemical ring closing reaction and hence the equilibrium point reached with the reverse photochemical ring opening reaction.

Although photochemical ring closure is an essentially temperature independent process above 80 K, the reverse process, that of ring opening, is a thermally activated process and typically below 130 K ring opening of dithienylethenes is not observed even under prolonged visible irradiation.[14a,21] In order to confirm that the low photostationary state between the c–o and c–c forms at 298 K (Table 1) is due to impedance of the second photochemical ring closing step, photochemical ring closure of the o–o form was carried out under conditions designed to avoid photochemical ring opening. Hence the photochemical ring closure of both **2H(o–o)** and **2H(c–o)** was followed by visible spectroscopy at 120 K. For both, complete conversion to **2H(c–c)** was observed, and although the ring closure is monoexponential for **2H(c–o)**, it is distinctly biexponential for **2H(o–o)** ring closure, with the initial ring closing step (o–o to c–o) being three times faster than the second step (c–o to c–c, Fig. 5). In addition to this, the photostationary state reached at 120 K was >98% in favour of **2H(c–c)**. Thus the lower PSS achieved at room temperature (Table 1) provides strong evidence that although the two photochromic units do not show through bond interaction, *i.e.* delocalisation, they nevertheless show modest through space electronic communication.
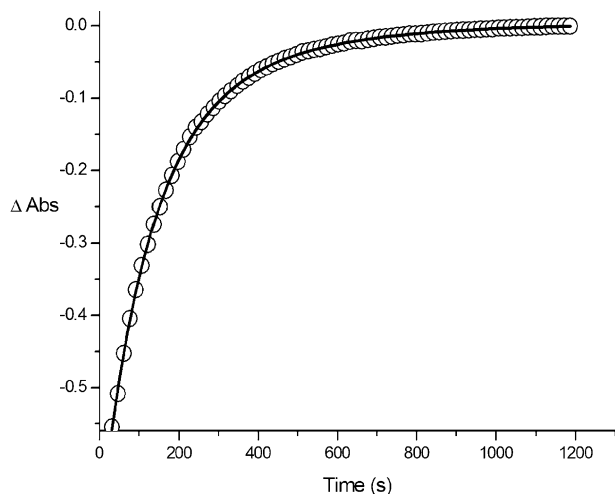

Fig. 5 Formation of **2H(c–c)** from **2H(o–o)** at 120 K (λ_{exc} 312 nm) in isomethylpentane monitored at 510 nm (data: circles, bi-exponential growth; fit: solid line).

In summary, we have demonstrated that multicomponent dithienylethene based switches in which the components are connected *via* a very short Me_2Si spacer unit can undergo ring closing and opening between three distinct photochromic states even with a small but significant electronic communication between the photochromic units present. By introducing asymmetry in the bicomponent system, this approach may allow for the development of functional systems for incorporation into molecular logic devices. Furthermore the present system demonstrates that spatial proximity between components can be achieved independently of

electronic communication. It is apparent that the silicon atom spacer[22] precludes effective through bond interaction presumably due to poor orbital overlap with those of the dithienylethene components.

Acknowledgements

Notes and references

‡ Although the fully open form of all compounds could be separated by HPLC from the partial and fully closed forms, with the exception of **2H**, separation of the single and the doubly closed forms was not achieved.

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