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The Generic Enhancement of Photochromic Dye Switching Speeds in a Rigid Polymer Matrix.

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Abstract:

The switching or isomerization speed of photochromic dyes in a rigid polymeric matrix (i.e. an ophthalmic lens) is generally significantly slower than that observed in the mobile environment of a solution. Here we describe that the attachment of flexible, low Tg oligomers such as poly(dimethylsiloxane) to photochromic dyes greatly increases their switching speeds in a rigid polymer matrix. Greatest impact was observed in the thermal fade parameters $T_{1/2}$ and $T_{3/4}$ which were reduced by 40-95% and 60-99% respectively for spirooxazines, chromenes and an azo dye in a host polymer with a glass transition temperature of 120 ºC. The method does not alter the electronic nature of the dyes but simply protects them from the host matrix and provides greater molecular mobility for the switching process The generic nature of the method may find further utility in the anticipated applications of data recording or optical switching.

Photochromic molecules undergo a colour change on irradiation that can be reversed to the initial colour thermally or by subsequent irradiation.[1]. Although photochromic compounds are being extensively investigated for applications such as data recording[2-4], optical switching[3-5]and non-linear device components[6], the major commercial application of photochromic dyes is currently ophthalmic lenses where rapid fading in lenses is highly desired, yet elusive[7]. The reason for the difficulty in obtaining fast fade in a rigid matrix is that the performance of a number of classes for photochromic dyes such as the opthlamically important spirooxazine and chromenes, shows great sensitivity to the viscosity of their medium.[7-10] Lowering the glass transition temperature of the host matrix will improve switching speeds[10,11] but logically, it compromises other physical properties such as hardness. A generic method is required that allows dyes to switch more rapidly in a rigid polymer matrices.

Spirooxazine and chromene photochromic dyes require a ca. 90 º rotation of one half of the molecule when switching between the clear and coloured states (**Fig. 1**)[1,7,9,10]. The switching event can be thought of as a light/heat powered mechanical process and the viscosity of the surrounding medium has a large effect on switching speed because of the size of the fragments that must rotate relative to each other. Azo dyes undergo a wagging motion between trans and cis isomers.[1] Fade speed is normally more strongly affected than coloration speed. Thermal fade speeds are typically many times slower in a rigid polymer matrix suitable for ophthalmic lenses than fade speeds observed for the same dye in solution[10].

The slow switching speed problem is essentially a problem of rotational mobility of the molecule in the host matrix. Our solution was to apply concepts developed in drug and gene delivery, where polymer conjugates are made in order to protect the drug, peptide or oligonucleotide from a harsh biological environment[12-14]. We created covalent photochromic-oligomer conjugates between the dye and a soft, low Tg oligomer such as

poly(dimethylsiloxane) or poly(ethyleneglycol) to protect the dye from a harsh switching environment (i.e. a rigid or high glass transition temperature (Tg) polymer). The dye is de facto encapsulated by the spontaneous coiling of its attached low viscosity oligomer, which insulates the dye or aggregates of dyes from the surrounding high Tg, high viscosity bulk matrix. The dye can be thought of as being permanently lubricated and protected at the molecular level to allow facile photochromic switching. As the dye is covalently bonded to the highly localised favourable switching environment provided by the oligomer, it can never be separated from it. This means that very little oligomer is added to the matrix so minimizing any change to the mechanical properties of the host matrix. Bulk softening agents that would compromise hardness of the matrix are not required.

We synthesised examples of spirooxazines, chromenes and an azo dye (**1**, **3**, **4**, **7**, **9**) and attached oligomers of polyethylene glycol (PEG) or polydimethylsiloxane (PDMS) to create dye-oligomer conjugates.(**Fig. 1**) Corresponding control dyes (**2**, **5**, **6**, **8**, **10**) with only a propylate group were synthesised to allow comparison between electronically matched pairs. Known dyes with hydroxy groups or functional groups that could be readily converted into hydroxy groups from the academic[15, 16] and patent literature[17] were made and reacted directly with a monofunctional acid terminated PDMS or PEG oligomer via the acid chloride.[18] Initially PEG (Mn ca. 750) was used as the oligomer; however, PDMS (Mn ca. 1000) is the oligomer of choice for speed enhancement because of its lower Tg and relative incompatibility with most polymers. The dyes with PDMS or PEG oligomers attached were oils or viscous amorphous gums and not crystalline solids like most spirooxazines, chromenes and azo compounds. This made dissolution into monomers considerably more easy than the conventional form of the dyes that can display poor solubilities requiring extensive stirring.

A standard ophthalmic lens formulation that was not optimised for photochromic performance was used to evaluate the dyes performance in a rigid polymer matrix[19]. The dyes were dissolved in a standard monomer mix of 1:4 polyethyleneglycol(400)dimethacrylate (9G) and 2,2'-bis[4-(methacryloxyethoxy)phenyl] propane (nouryset 110) at a concentration of ca. 1.0 mg dye per 1g of monomer and thermally cured into rigid test lenses (Tg 120 ºC). The lenses were examined on a light table with incident UV irradiation and the visible absorption spectrum was monitored at the λ_{max} of the coloured form of the dye to obtain colouration (UV light on) and thermal fade (UV light off) kinetics. A convenient measure of speed of fade are the $T_{1/2}$ and $T_{3/4}$ values which are the times it takes for the optical density to reduce by ½ and ¾ of the initial optical density of the coloured state[19]. The smaller $T_{1/2}$ and $T_{3/4,}$ the faster the fade. In general, we found spirooxazines, chromenes and theed azo dye show reductions in $T_{1/2}$ of 40-95 % and $T_{3/4}$ of 60-99% in the commercially critical thermal decolouration rates (**Tab. 1**). Detailed studies of the spirooxazine-PDMS conjugate **1** using UV-Vis and NMR spectroscopy were performed. The colouration and fade kinetics of our PDMS conjugate **1** ($T_{1/2}$ 3 s , $T_{3/4}$ 7 s) as compared to the electronically identical un-conjugated **2** ($T_{1/2}$ 12 s , $T_{3/4}$ 110 s) is shown in Fig. 2a. Note the unusual kinetics of the spirooxazine-PDMS conjugate **1**. On colouration, it overshoots and then rapidly returns to a steady state optical density as self-filtering is established. This phenomenon was an indicator of very high switching speeds and was not an artifact due to a shift in the λ_{max} of the coloured merocyanine (the coloured form of a spirooxazine) during irradiation. Only the fastest spirooxazines (**1** & **4)** displayed this behaviour and it is ascribed to highly mobile dye within the lens being able to switch before the build up of merocyanines nearer the UV source effectively blocks further irradiation. Once this self filtering is established, those inner spirooxazines now deprived of UV , will no longer switch and total optical density reduces to the observed steady state value. The un-conjugated

dye **2** shows a typical asymptotic approach to a maximum optical density[10]. When the UV source is switched off (at t = 1000 s) the PDMS conjugate **1** fades at a substantially faster rate than the control dye with 75% and 94% reductions in $T_{1/2}$ and $T_{3/4}$ respectively. If compound **6** with a C17 alkyl chain is used as the control dye then the reduction of $T_{1/2}$ (32 s) and $T_{3/4}$ (441 s) becomes 91% and 98% respectively. Thus, by manipulating the local environment around the dye we can tune the fade speeds (i.e. rotational mobility) over an order of magnitude.

Both colouration and fade behaviour indicate that the dye of **1** is in a highly mobile, near solution-like environment within the rigid matrix. The extent of the solution-like performance provided by PDMS oligomer is clearly evident when the fade performance of **1** (curve **1P**) in a rigid polymer matrix is compared with genuine solution fade performance of **1** and **2 (**curves **1S** and **2S** respectively) and contrasted with the rigid matrix performance of **2** (curve **2P**) (**Fig. 2b**). Application of the biexponential decolouration model to the lens data and monoexponential model to the solution data quantified the solution-like performance of the conjugate **1** in the test lens **(Tab. 2**). The lens decolouration curves were analyzed using the standard biexponential equation.[11, 20, 21]

$$A(t) = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} + A_{th}$$

A(t) is the optical density at the λmax, A_1 and A_2 are contributions to the initial optical density A_0, k_1 and k_2 are the rates of the fast and slow components and A_{th} is colouration when time approaches ∞. The fade of the spirooxazine **1** in the test lens consisted mostly of the fast fade component k_1 as evidenced by the 0.91 for A_1 and low 0.061 for A_2 resulting in a near mono-exponential kinetic expression typical of solution decolourizations.[11, 20, 21] The value of k_1 itself approached that of the solution speed of 0.27 min^{-1}. This is contrasted with the lens kinetics of the control dye **2** that contained a significant contribution of the slow component k_2 with A_1 now only 0.49 , A_2 of 0.19 and the fast fade component k_1 was only 0.037 min^{-1} as

compared to the 0.26 min^{-1} for **1**. When placed in a solution, **1** and **2** displayed expected monoexponential behaviours.

This fast switching behaviour in polymers appears to be completely counter-intuitive as it is not expected that the addition of a ca. 1000 gm/mole oligomer to a spirooxazine would make it switch faster than the electronically identical comparison dye that only has a 29 g/mole (ie CH_2CH_3) substituent. Indeed, bonding photochromic dyes to polymers in low concentrations has been shown to slow the switching process[10, 22]. The key difference is that a low Tg oligomer provides a localized favourable switching environment and provides it where it is needed; near/around the dye. The oligomer must be attached to the dye for the effect to occur; simply having an equimolar quantity of oligomer in the matrix with the dye does not give fade enhancement (**Fig. 2a**).

In addition to confirming the previous reports[23, 24] of preferred isomer (trans-cis-cis) of the coloured form of the spirooxazine (shown in **Figs. 1,4**) NMR spectroscopy provided evidence of intramolecular association between the oligomer chain and spirooxazine in solution with the association being stronger with the dye in the coloured state. This was observed for both PDMS (**Fig. 3**, Supplementary Information B,C) and PEG oligomers (Supplementary Information E). It was surprising to see such interactions as acetone was the solvent for both the **1** and **3** NMR experiments and it might have been expected to compete with the spirooxazine for the oligomer. This would be thought to be especially the case for the PEG oligomer. It is testament to the strong localization effect of tethering the oligomer to the dye and the attractive nature of the merocycanine form that interactions were observed. When these observations are translated to the rigid polymer matrix environment, the dye is likely to be more protected due to the incompatibility of the PDMS with the host matrix. Undesirable gross phase separation of the PDMS-dye conjugates in the lenses was not observed at the

concentrations used but some haze can be observed at higher loadings (ca. >10mg/gm) of dye. PDMS conjugated to a dye was significantly more compatible than pure PDMS which was observed to cause haze at lower concentrations. Thus, the each component of the PDMS-dye conjugate reduced the limitations of the other; the dye compatibilized the PDMS and the PDMS provided a favourable switching environment to the dye.

The use of PEG oligomer (**3**) also gave reductions in fade speed (**Tab. 1**). The reductions were not as great as that observed for the PDMS-spirooxazine conjugates as the PEG does not have the flexibility of PDMS and the matrix has a significant PEG component which may lower availability of the PEG to localise around the dye. The PDMS could be attached to the dye at any conveniently available position as shown by compound **4** to give large reductions in fade times.

The general applicability of the method was examined by attaching PDMS to a chromene (**7**) and azo dye (**9**) which also showed large reductions in fade times (**Fig. 3**). The presence of the PDMS on the chromene produced a more square wave-like colouration-decolouration profile than the saw-tooth profile of the control dye (**8**). (**Fig 3a**) The azo dye which undergoes a wagging motion rather than a internal rotation during isomerization, showed a large change in its colouration-decolouration profile as a result of addition of PDMS with >98% reduction in $T_{1/2}$ compared to the control dye (**10**) (**Fig. 3b**).

An important aspect of this methodology is that it does not alter the electronic nature of the dye to provide the control over the switching speed. The colour of the dye (**Tab. 1**) is unaffected as it is essentially the same dye but with a protective tail. The control is obtained indirectly by controlling the environment immediately around the dye. Initially, it was thought that multiple oligomers would need to be attached to the dyes to achieve the desired goal of fast fade in a rigid matrix. This has proved largely unnecessary with the results obtained using

only a single oligomer. As the electronic nature of the dye is unaffected, this method can not make an inherently slow switching dye switch like compounds **1** and **4**. The oligomer can only provide an environment favourable for switching and protection from the surrounding rigid host matrix. A common feature of the dyes described is that they all possess a thermal decolourization pathway and the low Tg oligomer methodology specifically addresses the problem of slow thermal fading. Colourations of the some PDMS-dye conjugates are obviously faster than the control dyes (**Fig. 3**). It is now of interest if the oligomers can affect or improve the isomerisation speeds of potential data storage and molecular switching compounds (i.e. fulgides and diarylethenes among others) that are purely photo driven reactions[2-4, 8]. Isomerization speed of such compounds in a rigid host matrix may impact on write, erase and switching speeds of those applications.

We have demonstrated generic control over the photochromic process of three classes of photocromic dyes spirooxazines, chromenes and an azo dye through local environment effects without any need for modification to the dye's electronic structure or the host matrix. The use of short PDMS oligomers in particular has resulted in dramatic increases in rotational mobility in a rigid ophthalmic polymer matrix and is of direct and immediate applicability to current photochromic dye technology. The power of this method is that it is essentially a "bolt-on" method and could be expected to permit the functioning and control of non-photochromic molecules whose functions derive from mechanical motions.

Methods.

Syntheses. The photochromic dyes described have all been made by others previously or are commercially available. Our task was to either simply attach an oligomer to an available hydroxy group on the dyes or modify the oligomer or dye to allow them to be coupled. Spirooxazine dyes **1-3,6** were synthesised from 9'-hydroxy-1,3,3-trimethylspiro[indoline2,3'-[3H]naphtha[2,1-b][1,4]oxazine by esterification with poly(dimethylsiloxane) monocarboxyldecoyl chloride (from the carboxylic acid MCR-B11 ABCR GmbH) propanoyl chloride and steroyl chloride respectively[18]. Compound **3** was made as described[18]. It required the modification of mono-hydroxy terminated PEG(750) (Aldrich) with succinic anhydride to provide a carboxylic acid group[13, 18] This was further converted to an acid chloride using thionyl chloride. This was readily reacted with 9'-hydroxy-1,3,3-trimethylspiro[indoline2,3'-[3H]naphtha[2,1-b][1,4]oxazine to give **3**.[18] 5- Hydroxy-1,3,3-trimethylspiro[indoline2,3'-[3H]naphtha[2,1-b][1,4]oxazine made as described by Shagina et al[16] followed esterification with the appropriate acid chloride to give **4** and **5.** The chromene for **7, 8** was made by the general method described by Corns et al [17] except the methyl ester function was changed to a 2-hydroxyethyl ester to allow reaction with the poly(dimethylsiloxane) monocarboxyldecoyl chloride or propanoyl chloride[18]. The 4-phenylazophenol (Aldrich) used to make **9** and **10** was commercially available. The explicit synthesis of **1** is described in supplementary material E.

Experimental conditions

The test lenses were then evaluated on a light table consisting of a Cary 50 UV-Vis spectrophotometer using a 300 W Oriel Xenon lamp. A combination of Schott WG 320 cut-off filter, UV band pass filter (Edmund Scientific U-360) and water bath were placed in front of the Xenon light source giving a resulting light source of 5 mW of UV light (320-400nm). The lamp filters were cooled with water continuously circulating through to a central reservoir. Colouration and decolouration were monitored at the λ_{max} of the coloured form of the

individual photochromic dye at 20 ºC (temperature controlled via a peltier sample accessory). Solution kinetics were examine in toluene ([dye] = 10^{-4} M) at 20 ºC. NMR spectra were obtained on Bruker DMX500 and DMX600 spectrometers with irradiation of sample by 1000 W Oriel lamp via optical fibre (Supplementary Information B)[25]. Test lenses were made from 1:4 weight ratio of 9G (NK ester) and nouryset 110 (Akzo) containing 0.4% weight of AIBN initiator and ca. 1mg of dye per gram of monomer. Lenses cured in a mould 14mm diameter x 2.6 mm thick for 16 hour at 80 ºC.

References.

1. Bouas-Laurent, H. & Durr, H. Organic photochromism. *Pure and Applied Chemistry* **73**, 639-665 (2001).
2. Kawata, S. & Kawata, Y. Three-dimensional optical storage using photochromic materials. *Chem. Rev.* **100**, 1777-1788 (2000).
3. Yokoyama, Y. Fulgides for memories and switches. *Chem. Rev.* **100**, 1717-1739 (2000).
4. Irie, M. Diarylethenes for memories and switches. *Chem. Rev.* **100**, 1685-1716 (2000).
5. Berkovic, G., Krongauz, V. & Weiss, V. Spiropyrans and spirooxazines for memories and switches. *Chem. Rev.* **100**, 1741-1753 (2000).
6. Delaire, J.A. & Nakatani, K. Linear and nonlinear optical properties of photochromic molecules and materials. *Chem. Rev.* **100**, 1817-1845 (2000).
7. Higgins, S. Chasing a rainbow. *Chem. Br.* **June**, 26-29 (2003).
8. Feringa, B.L. (ed.) *Molecular Switches* (Wiley-VCH, Weinheim, 2001).
9. Guglielmetti, R. in *Photochromism - Molecules and Systems, Studies in Organic Chemistry*, Vol. 40. (ed. H. Dürr, Bous-Laurent, H.) 314-455 (Elsevier Science Publishing House, Amsterdam, 1990).
10. Such, G., Evans, R., Yee, L. & Davis, T. Factors Influencing Photochromism of Spiro - compounds within Polymeric Matrices. *J. Macromol. Sci. (R)Part C - Pol. Rev.* **C43**, 547-579 (2003).
11. Krongauz, V.A. in *Photochromism: Molecules and Systems*, Vol. 40, Edn. 1. (ed. H. Dürr, Bous-Laurent, H.) 793-820 (Elsevier Science Publishing House, Amsterdam; 1990).
12. Langer, R. Drug Delivery and Targeting. *Nature* **392**, S 5-10 (1998).
13. Hermanson, G.T. *Bioconjugate Techniques*. 606-618 (Academic Press, San Diego; 1996)
14. Allen, T.M. & Cullis, P.R. Drug Delivery systems: entering the mainstream. *Science* **303**, 1818-1822 (2004).
15. Kakishita, T., Matsumoto, K. & Kiyotsukuri, T. Synthesis and NMR study of 9'-substituted Spiroindolinonapthoxazine Derivatives. *Journal of Heterocyclic Chemistry* **29**, 1709-1715 (1992).
16. Shagina, L., Buchholz, F., Yitzchaik, S. & Krongauz, V. Searching for photochromic liquid crystals. *Liq. Cryst.* **7**, 643-655 (1990).

17. Corns, S.N. et al. Neutral coloring photochromic 2H-naphtho[1,2-b] pyrans and heterocyclic pyrans. *US Patent*, 6,248,264 B241 (2001).
18. Evans, R.A. et al. Photochromic compositions and light transmissible articles. PCT/AU03/01453 (2003).
19. Walters, R.W. & Van Gemert, B. Hydroxylated/carboxylated naphthopyrans. PCT/US01/05881 (2001).
20. Schaudel, B., Guermeur, C., Sanchez, C., Nakatani, K. & Delaire, J.A. Spirooxazine- and spiropyran-doped hybrid organic-inorganic matrixes with very fast photochromic responses. *J. Mater. Chem.* **7**, 61-65 (1997).
21. Hobley, J. et al. Ultrafast Photo-Dynamics of a Reversible Photochromic Spiropyran. *Journal of Physical Chemistry A* **106**, 2265-2270 (2002).
22. Hu, A.T., Wang, W.-H. & Lee, H.-J. Photochromism of spirooxazine doped or bonded in polymer matrixes. *J. Macromol. Sci., Pure Appl. Chem.* **A33**, 803-810 (1996).
23. Nakamura, S., Uchida, K., Murakami, A. & Irie, M. Ab initio MO and proton NMR NOE studies of photochromic spironaphthoxazine. *J. Org. Chem.* **58**, 5543-5545 (1993).
24. Maeda, S., Mitsuhashi, K., Osano, Y.T., Nakamura, S. & Ito, M. The molecular design and applications of spirooxazines. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **246**, 223-230 (1994).
25. Geftakis, S. & Ball, G.E. Direct observation of a transition metal alkane complex, $CpRe(CO)_2$(cyclopentane), using NMR spectroscopy. *J. Am. Chem. Soc.* **120**, 9953-9954 (1998).

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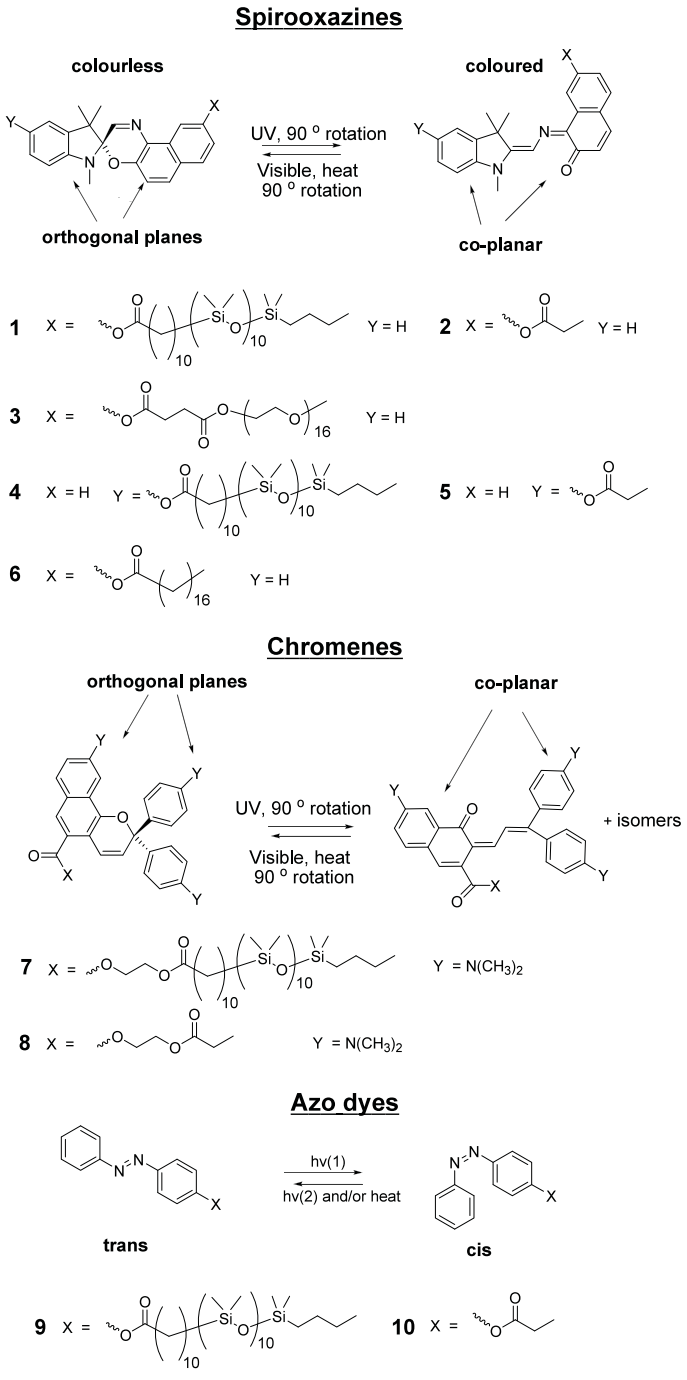


Figure 1. Structural changes of spirooxazines, chromenes and azo compounds during photochromic switching. The spirooxazines and chromene shown are specifically 2,1-b naphthoxazines and 1,2-b naphthopyrans. The number of repeat units of the dimethyl siloxane and ethyleneglycol units are an average value.

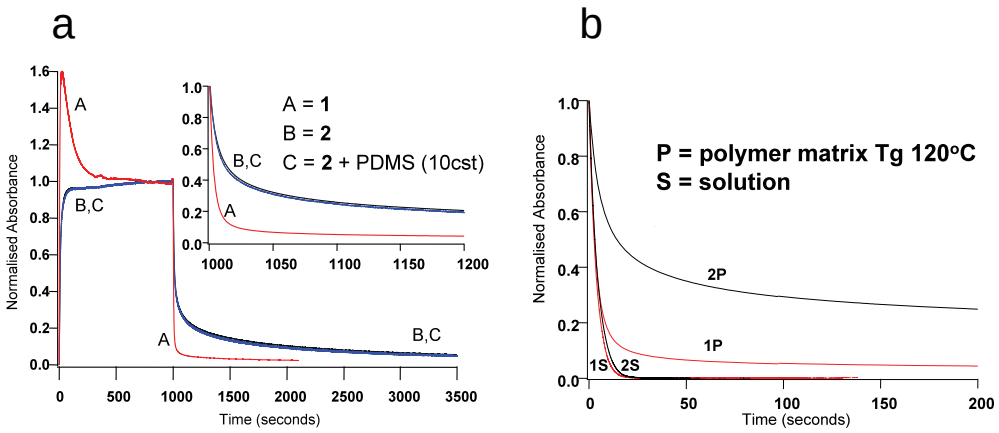


Figure 2. Near solution-like decolourization speed of a spirooxazine in a rigid polymer matrix.

a, The positive effect of conjugating a spirooxazine with a short PDMS chain on colouration and decolouration speeds (curves A vs. B) and the need for covalent bonding between dye and oligomer (curves A vs. C) placed in a rigid polymer matrix (Tg 120 ºC). Absorbance monitored at 605 nm. Irradiation commenced at t = 0 and ceased at t = 1000 seconds. The inset shows the normalised fade kinetics illustrating the large fade speed enhancement. **b,** The solution-like fade performance of **1** (curve **1P**) in a rigid polymer matrix (Tg 120 ºC) as compared to **1** and **2** in toluene solution (curves **1S** and **2S**) and **2** (curve **2P**) in an identical rigid polymer matrix.

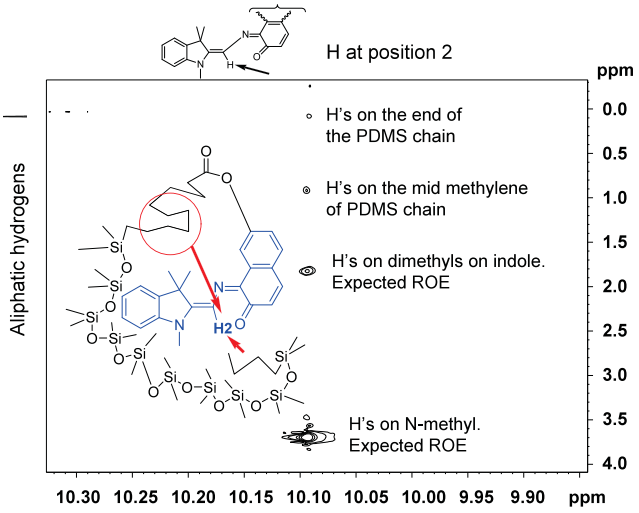


Figure 3. Intramolecular interaction of PDMS oligmer with dye. Rotational Overhausen Effect 2D NMR spectrum showing PDMS oligomer interactions between the coloured form of dye (**1**) by observation of enhancement of central H2 via energy transfer from hydrogens on mid-methylene and terminal butyl groups of the PDMS oligomer.

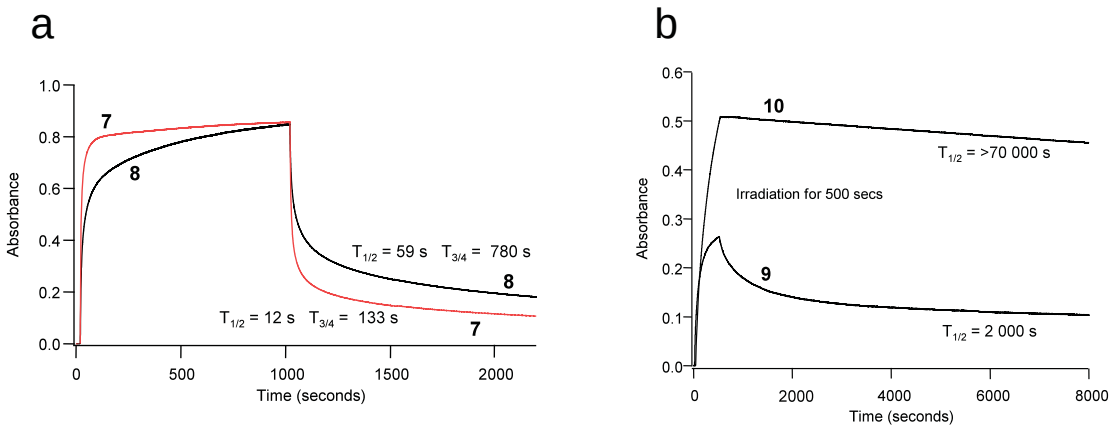


Figure 4. Enhancement of photochromic switching speeds of a chromene and azo dye in a rigid matrix. The chromene and azo dyes were examined in standard test lens formulation (Tg =120 ºC, 1:4 9G:nouryset 110). **a,** The PDMS-chromene conjugate **7** displays both faster colouration and decolouration as compared to the control dye **8** not possessing the PDMS oligomer. Absorbance monitored at 615 nm. Irradiation commenced at t = 0 and ceased at t = 1000 seconds. **b,** The azo dye showed one of the largest observed improvements in switching speed with the $T_{1/2}$ reduced by >98% on the addition of a PDMS oligomer to the dye (**9**)**.** Absorbance monitored at 450 nm. Irradiation commenced at t = 0 and ceased at t = 500 seconds.This sample was measured at 40 ºC in order to obtain fade data in a reasonable period of time and because at 20 ºC the source of the spectrometer excited the dye at a rate comparable to fade rate.

Table 1. Fade speed of photochromic dyes cast into a cured polymer matrix consisting of 4:1 2,2'-bis[4-(methacryloxyethoxy)phenyl]propane and poly(ethylglycol (400) dimethacrylate.

Example Number	Dye (mg)	Monomer (g)	A_o[3]	λ_{max} (nm)	$T_{1/2}$ (seconds)	$T_{3/4}$ (seconds)
1	3.7	1.008	1.63	605	3	7
2[1]	1.6	1.615	1.10	605	12	110
3	7.0	2.015	1.61	607	9	50
2[1]	1.9	1.920	1.10	605	12	110
4	3.9	1.009	1.13	606	3	12
5	1.0	1.021	1.07	608	34	633
6	1.22	1.257	1.67	605	32	441
2[1]	1.6	1.615	1.10	605	12	110
7[2]	2.6	2.646	0.86	615	12	133
8	0.93	3.123	0.83	615	59	780
9	1.92	1.030	0.26	450	2000	n/a
10	1.39	1.339	0.5	450	>70000	n/a
2+ PDMS (10cst)	1.7 dye 2.5 PDMS	1.717	0.7	605	11	100

[1] This value is slightly different to that reported in the patent PCT/AU03/01453 ("CE2" $T_{1/2}$ 14s, $T_{3/4}$ 191 s). We remade this sample a number of times and feel the faster fade time is the appropriate result for comparisons. [2] This value is different to that reported in the patent PCT/AU03/01453 ("Ex. 17" $T_{1/2}$ 7.5 s, $T_{3/4}$ 94 s). The above example is at a molar concentration closer to the control dye (unavailable at the time of filing) and should be used in preference to the faster fade times for that dye. [3] The photophysical measurements are of the test lenses. A_o is the absorbance of the coloured or switched form of the dye immediately prior the cessation of irradiation.

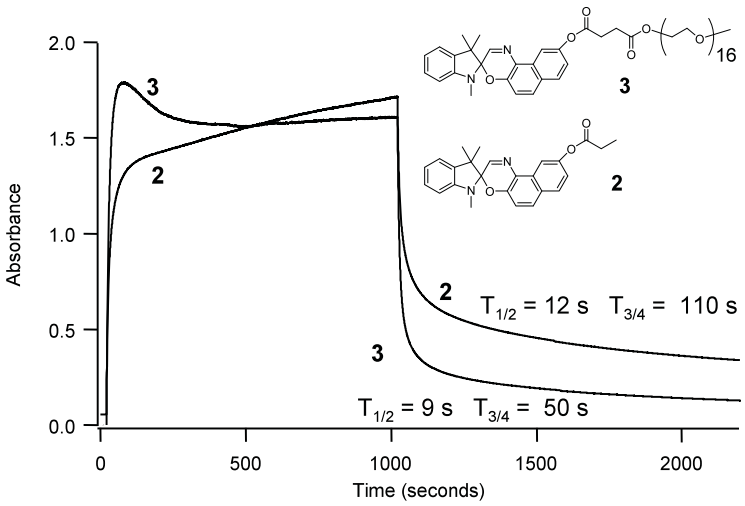
Table 2. Decolouration kinetic parameters for 1 and 2 in lens and solution.

Sample[1]	k_1 (min^{-1})	k_2 (min^{-1})	A_1	A_2	A_{th}
1 lens	0.26	0.0074	0.91	0.061	0.030
1 solution[2]	0.27	-	1.00	-	-
2 lens	0.037	0.00077	0.49	0.19	0.07
2 solution[2]	0.23	-	1.00	-	-

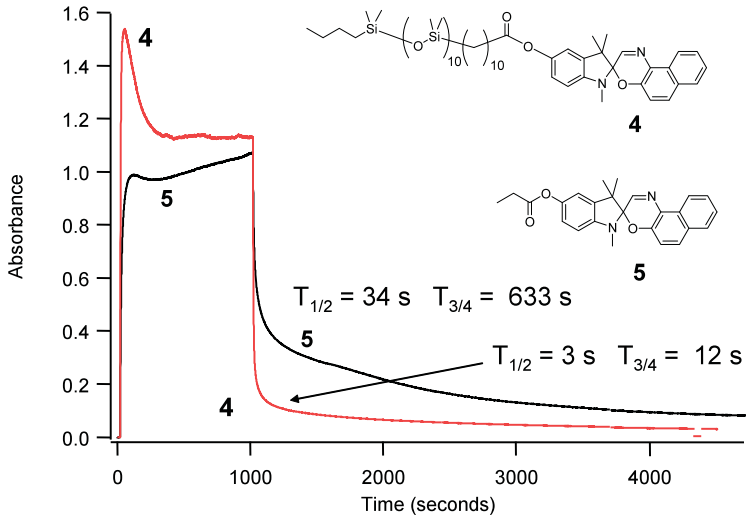
[1.] Fade of merocyanine form of spirooxazine monitored at 605 nm. [2.] Toluene solution at 20 ºC . [dye] = 10^{-4}M

Supplementary Material

Figure A. Spirooxazine photochromic performance.



a, Coloration and fade speeds obtained with PEG oligomer. **3** and **2** in standard polymer (Tg =120 ºC, 1:4 9G:nouryset 110).



b, Coloration and fade speeds dye- PDMS oligomer conjugate with a different point of attachment on the spirooxazine. **4** and **5** in standard polymer (Tg =120 ºC, 1:4 9G:nouryset 110).

Supplementary Material (B)

NMR spectroscopic observation of dye-oligomer associations. Experimental.

Spectra were recorded on Bruker DMX 500 and DMX 600 spectrometers fitted with ^{1}H-^{31}P-BB TBI-Z and ^{1}H-^{13}C-^{15}N TXI XYZ probes respectively. Temperature control was maintained using a standard Bruker variable temperature unit employing a liquid nitrogen evaporator to achieve the temperatures of 193 and 233K. Standard gradient DQF-COSY, HSQC and HMBC experiments were acquired for resonance assignment purposes. ROESY type two-dimensional experiments were used to elucidate through space interactions. The mixing time in the ROESY experiments was maintained at 200ms at 193K and 250ms at 233K. For quantitative work involving extraction of internuclear distances, a compensated ROESY experiment was employed as described previously (Griesinger, C. & Ernst, R. R. *J. Mag. Res. (1969-1992)* **75**, 261-71 (1987)).

UV Irradiation using a Mercury ARC Lamp

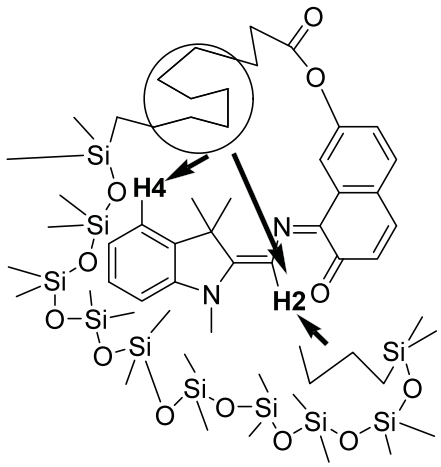
The irradiation setup has been described previously (Geftakis, S. &Ball. G. E. Direct Observation of a Transition Metal Alkane Complex, $CpRe(CO)_2$(cyclopentane), Using NMR Spectroscopy. *J. Am. Chem. Soc.*, **120**, 9953-9954 (1998)). Irradiation was achieved using a 100W Oriel research arc lamp, coupled via condenser to an optical fibre. Focus and mirror were optimised and 200 – 250mW of power at 455nm was obtained at the sample end of the optical fibre, a 7m long, 1500micron core, non-solarizing UV transmitting fibre (Ceramoptec P/N SMA1P/UV1500/1600N-NS/7.0M)

Experimental Setup

In a typical experiment, **3**, (10mg) (for example) was dissolved in d_6-acetone (0.47g) to create a 21.9 mM solution at room temperature. The free oligomer samples (where spirooxazine and oligomer were separate), the mass of both **2** and oligomer **1** and **3** reflected the molar ratios present in the attached oligomer samples. Samples were frozen in liquid nitrogen within their septa sealed NMR tubes and placed under a vacuum, the sample was isolated and allowed to thaw in an effort to remove entrained oxygen within the sample which could interfere by causing oxidation whilst under UV irradiation. Nitrogen was then pumped into the head space above the solution prior to NMR analysis. The fibre optic was placed through the septa and approximately 1mm above the surface of the solution. The NMR probe containing sample was then cooled to 193K for **3**. A higher temperature of 233K was required for **1** to prevent precipitation. Spectra were collected before, during and after photoirradiation of the sample.

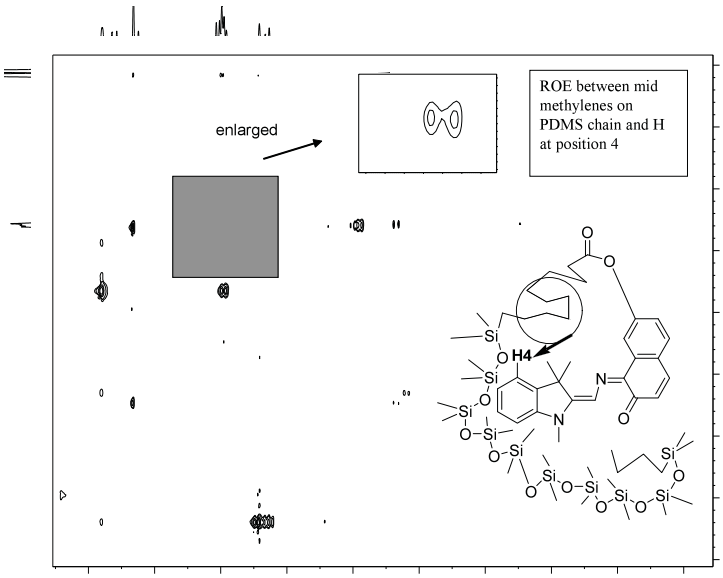
Supplementary Material (C)

NMR spectroscopic observation of dye-oligomer associations.
Compound **1**. Spirooxazine and PDMs interactions in solution.



1

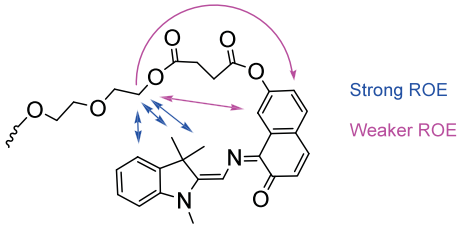
a, Summary of PDMS oligomer interactions with **1** merocyanine form of the spirooxazine.



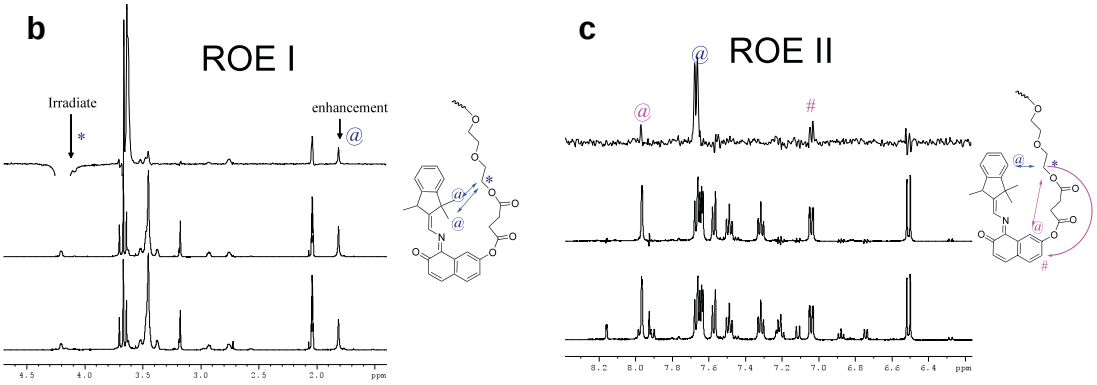
b, ROESY 2D NMR experiment. Interaction of PDMS oligomer with indole H4 of coloured form of spirooxazine (**1**).

Supplementary Material (D)

NMR spectroscopic observation of dye-oligomer associations.
Compound **3**. Spirooxazine and PEG interactions in solution.



a, Summary of PEG chain interactions with **3** merocyanine form.



b, PEG chain interactions with gem dimethyl groups of **3** merocyanine form. Top spectrum is the ROESY experiment. Middle spectrum is a synthesised spectrum with clear form of spirooxazine subtracted. Bottom spectrum original spectrum of both clear (spirooxazine) and coloured (merocyanine) form of **3**.

c, PEG chain interactions with aromatic hydrogens on indole and naphthyl parts of **3** merocyanine form. Top spectrum is the ROESY experiment. Middle spectrum is a synthesised spectrum with clear form of spirooxazine subtracted. Bottom spectrum original spectrum of both clear (spirooxazine) and coloured (merocyanine) form of **3**.

The first PEG unit interaction with the opposite side of the spirooxazine is readily identifiable because of its asymmetrical chemical environment. Due chemical similarity of all the other PEG units in the oligomer, it is not possible to unambiguously identify other PEG interactions with the spirooxazine. The polar nature both of the PEG oligomer and the coloured from of the spirooxazine make it likely the rest of the PEG oligomer will be localised around the dye.

Supplementary Material (E)

Synthesis of 9'-(PDMS(855)-undecoyl)-1,3,3-trimethylspiro[indoline-2,3'-[3h]naphtha[2,1-b][1,4] oxazine] **1.**

9'-Hydroxy-1,3,3-trimethylspiro[indoline-2,3'-[3H]naphtha[2,1-b][1,4]oxazine] (1g, 2.9 mmoles) and triethylamine (0.9 mL, 655 mg, 6.5 mmoles) were added together in dichloromethane (20 mL) and then poly(dimethylsiloxane) monocarboxydecoyl chloride terminated (3.0 g, 2.8 mmol) in dichloromethane was added dropwise to the solution at room temperature under argon protection. The reaction was monitored by tlc (DCM or ether:hexane 1:1) and was completed after a few hours. The reaction was worked up by washing with water, brine (plus a little of very dilute HCl to break the emulsion), dried (MgSO4) before evaporation to a dark liquid. The oil was chromatographed on silica with ether:hexane (1:3) to give 2.1 g (52%) of pale brown green oil as the desired product. A second slower fraction (200 mg) was obtained that was spectroscopically similar to the product except it had a vinyl (terminal) group and had much less DMS content. ^{1}H NMR (acetone-d6)(Shown below) δ = 0.09 (d, J = 1.8 Hz, Si-Me), 0.10 (d, J = 1.83 Hz, Si-Me), 0.12 (d, J = 1.8 Hz, Si-Me), 0.13 (s, Si-Me), 0.6 (mult., 4H, alkyl), 0.90 (mult., 4H, alkyl), 1.3-1.4 (mult, 22H, 9,10-H, alkyl, CH2-CH3), 1.50 (mult, 2H, 'c'-H), 1.80 (pent., J = 7.3 Hz), 2H, 'b'-H), 2.68 (t, J = 7.3 Hz, 2H, 'a'-H), 2.77 (s, 3H, 8-H), 6.65 (d, J = 7.8 Hz, 7-H), 6.87 (t, J = 7.3 Hz, 5-H), 7.03 (d, J = 8.5 Hz, 5'-H), 7.14 (d, J = 7.3 Hz, 4-H), 7.19 (apparent t, 2H, 6 & 8'-H), 7.80 (d, J = 9.3Hz, 6'-H), 7.82 (s, 2'H), 7.86 (d, J = 8.6Hz, 7'-H), 8.23 (d, J = 2.3 Hz, 10'-H) ppm. MS (FAB), M+ 1368 (100%) (corresponds to 11 DMS units in oligomer), 1145.9 (90%)(corresponds to 8 DMS units in oligomer), 1591.4 (85%)(corresponds to 14 DMS units in oligomer, 923.6 (corresponds to 5 DMS units in oligomer), 1813.5 (corresponds to 17 DMS units in oligomer). Peaks for all other oligomer lengths between 4-19 DMS units were also observed in a small bell curve distribution centred around 12 DMS units (12 MDS 40% of M+ with other peaks being smaller).