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Photochromic Spirooxazines Functionalized with Oligomers: Investigation of Core−Oligomer Interactions and Photomerocyanine Isomer Interconversion Using NMR Spectroscopy and DFT

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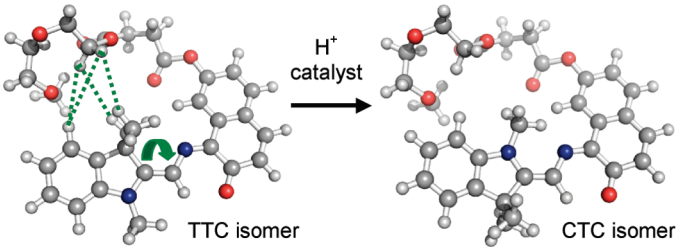

Photochromic spirooxazines functionalized with poly(ethylene glycol) (PEG) and poly(dimethylsiloxane) (PDMS) oligomers were monitored using NMR spectroscopy at temperatures between 193 and 233 K before and after in situ exposure to UV irradiation. NOESY and ROESY experiments reveal the TTC (trans−s-trans−cis) isomer to be the dominant merocyanine isomer formed on photolysis, with some CTC (cis−s-trans−cis) isomer also present. Significant ROE cross peaks were observed between the "bulk" of the oligomeric units and protons across the entire photochromic core of the molecule, the intensity of these cross peaks suggesting that the interaction of the oligomer side chain and core of the molecule is significantly enhanced by the permanent attachment, especially with the PDMS side chain. The 2D NMR spectra indicate that there is exchange between the TTC and CTC isomers even at 193 K. This isomerization of the parent spirooxazine compounds, lacking the oligomeric side chains, was found to be acid-catalyzed, and DFT calculations support the strong possibility that it is the protonated merocyanine form that undergoes the facile isomerization process. Interconversion of the different merocyanine isomers is suggested to be fast on the NMR time scale under many experimental conditions, precluding the observation of different isomers using NMR spectroscopy at room temperature.

Introduction

The ability of certain molecules to change color in response to an external stimulus has wide and increasing application in materials. Photochromic compounds, for example, which change color in response to light as a stimulus, have great utility in areas such as optoelectronic applications, optical data storage, self-assembly, and optical lenses, the latter application being of massive commercial importance already.[1−7]

A key property of any photochromic material is how rapidly the material can respond to the light stimulus or lack thereof, i.e., its switching speed. In optic lens ("sunglasses")

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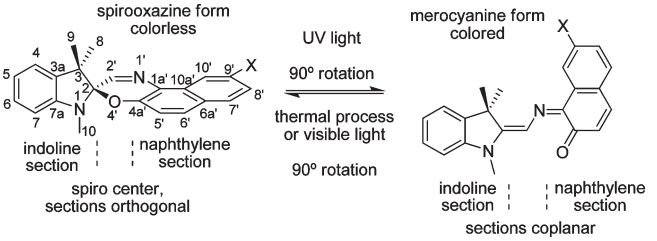
SCHEME 1. Spirooxazine (Left) to Merocyanine (Right) Interconversion

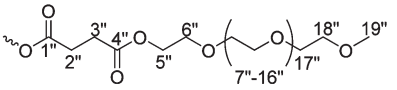
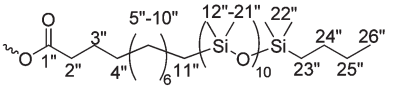
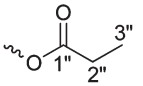


applications, for example, it is desirable for the photochromic molecule to switch rapidly to the highly colored form in the presence of bright sunlight and switch rapidly to the transparent form in dimmer lighting, the switch to the transparent form most often being a thermal process. This process is illustrated above for the spirooxazine system, an important class of photochromic molecules (Scheme 1).[4,7]

The forward reaction is driven by UV light absorption, whereas a thermal reaction or visible light will initiate the reverse reaction; the spirooxazine form is thermodynamically preferred over the merocyanine form. The spirooxazine molecule has a spiro center with two orthogonal planes, while the merocyanine form exists in a single plane. The indoline and naphthylene sections rotate through 90° with respect to each other during the interconversion process. The numbering scheme employed is shown for the spirooxazine form; it is retained in the merocyanine form.

Encasing unmodified photochromic molecules in rigid, solid polymer matrices greatly retards the switching rates of the photochromic species in comparison to those obtained in solution, limiting their performance and utility.[8] We have developed a strategy for overcoming this slowing of switching speeds in important classes of photochromic molecules such as naphthopyrans and spirooxazines.[5,9−11] This is achieved by attaching one or more oligomeric side chains, such as a short, controlled length of poly(dimethylsiloxane) (PDMS) or poly(ethylene glycol) (PEG), to the photochromic molecule. These side chains provide a relatively mobile region of low viscosity that is in the vicinity of the photochromic molecules, even when this molecule is embedded in the solid state in an otherwise rigid matrix. In turn, this promotes faster switching of the photochromic moiety, since the locally mobile environment, much like a solution, is less hindering of the intramolecular rotations and wholesale changes of shape that are required and are the source of the photochromic behavior. Previously, we reported that in comparison with the nonfunctionalized molecules reductions of up to 99% in the switching speeds of the thermal reversion of various dyes to their colorless forms in the absence of light was achieved by attachment of a single oligomeric unit to various photochromic dyes.[12] For example, the oligomerically modified merocyanine containing

TABLE 1. Side Chains, Identifiers, and Corresponding Numbering Scheme of Carbons in the Side Chains Employed in This Study[a]

X Label, (number)	$T_{1/2}$ (s)	$T_{3/4}$ (s)
H SOX, (1)	-	-
 SOX-PEG, (2)	-	-
 SOX-PDMS, (3)	3	7
 SOX-Prop, (4)	12	110

[a]Also shown are selected fade times ($T_{1/2}$ and $T_{3/4}$) of the photochromic dyes cast into a cured polymer matrix consisting of 4:1 2,2′-bis[4-(methacryloxyethoxy)phenyl]propane and poly(ethylene glycol (400)) dimethacrylate.[12]

a PDMS side chain (**3m**) decolorized (reverted to the spirooxazine form) in 75−94% less time (based on $T_{1/2}$ and $T_{3/4}$) than the electronically similar merocyanine (**4m**), which lacked the attached side chain when the spirooxazines were cast into a polymer matrix (Table 1). (The suffix s after the numeric identifier indicates the spirooxazine form, and the suffix m indicates the merocyanine.)

Our previous study also included preliminary NMR data that outlined evidence for the close proximity between the side chain and the spirooxazine core in molecules such as **1**; further analysis is included here. Spirooxazines absorb UV light, which results in the cleavage of the spiro C−O bond in the oxazine ring, leading to the planar photomerocyanine forms (Scheme 1) of which there are 8 possible isomers and 2 dominant isomers as determined by NMR, the most prominent of which is shown in Scheme 1.[13,14]

The use of NMR to characterize spirooxazines and their photoproducts is well established[13,15−17] with numerous examples that investigate several facets including the coexistence of four transoid photomerocyanines,[18] photoelectrocyclized structures of spirooxazine derivatives,[19] through to the polyphotochromic behavior of biphotochromic compounds,[20] for example. However NMR studies investigating oligomerically functionalized spirooxazines, wherein the oligomers are essential in allowing "liquid-like" switching speeds when covalently attached to spirooxazines impregnated into solid polymer

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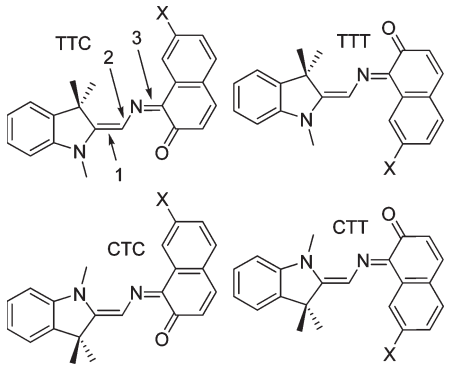
CHART 1



matrices, and consequential interactions have not been reported.[12] The original aim of this study was to investigate (i) the locality of the oligomers relative to the spirooxazine in solution and whether any observed interactions require the covalent attachment between oligomer and spirooxazine, and (ii) whether the side chain had any electronic effect on the photochromic core of the molecule or the distribution of merocyanine isomers observed. Therefore two oligomers, poly(ethylene glycol) (PEG) and poly(dimethylsiloxane) (PDMS) both covalently attached to a spirooxazine host and free in solution were investigated. NOE and ROE type through space interactions between the oligomer side chain and the spirooxazine host were measured. In situ UV radiation within the NMR probe was used to generate the merocyanine forms, permitting the examination of interactions between the oligomers and the merocyanine core in the open form as well. Full NMR assignment of all spirooxazine and oligomer combinations was achieved along with use of ROESY NMR spectral analysis to determine how the oligomers were interacting with spirooxazines both in attached and nonattached forms.

Previous studies have established that the merocyanine form of the dyes may exist as four possible stereoisomers as shown in Chart 1.

The labels refer to either cis (C) or (s-)trans (T) stereochemistry for the three bonds labeled 1, 2, and 3, respectively in the TTC isomer. Isomers in which bond number 2 is s-trans are thermodynamically preferred. The dominant isomer is usually the TTC (trans−s-trans−cis) form.

During the course of this study, exchange between different isomers of the photomerocyanine forms was observed to occur even at relatively low temperatures (~193 K) in the NMR experiments. The rates of isomeric exchange were found to be faster than would be predicted on the basis of existing calculations in the literature.[21] This led to an investigation of the possible mechanism for the interconversion of the two isomers. The observation that the process is acid-catalyzed suggests that it is the transiently protonated form of the merocyanine that undergoes the isomeric interconversion, and this needs to be accounted for in related studies.

Results and Discussion

In this investigation, four main groups of NMR experiments were conducted (Table 2). Two oligomeric identities were investigated, a moderately polar carbon-based form represented by PEG and a silicon-based oligomer represented by PDMS with an alkyl spacer group. Both covalently attached and free oligomer configurations with photochromic were investigated.

TABLE 2. Experimental Conditions of NMR Analysis of Combinations of Oligomers (PEG, PDMS), Attached or Mixed with Spirooxazine Molecules (SOX)

description[a]	temperature (K)	solvent
SOX-PEG (**2**)	193	d_6-acetone
SOX-Prop (**4**) and PEG	193	d_6-acetone
SOX-PDMS (**3**)	233	d_6-acetone
SOX-Prop (**4**) and PDMS	233	d_6-acetone

[a]"-" denotes covalent attachment between compounds. SOX-Prop is a spirooxazine with a proprionyl group at the point of attachment for the SOX-PEG and SOX-PDMS compounds.

TABLE 3. ^{1}H and ^{13}C Chemical Shifts of SOX-PEG (193 K) and SOX-PDMS (233 K) in d_6-Acetone in Spirooxazine Form

	SOX-PEG		SOX-PDMS	
position (multiplicity H only)	δ_H[a] (ppm)	δ_C[b] (ppm)	δ_H (ppm)	δ_C (ppm)
2 (-)		98.8		98.8
3 (-)		51.9		51.9
3a (-)		135.7		136.0
4 (d)	7.225	121.8	7.18	121.8
5 (dd)	6.88	120.1	6.87	120.0
6 (dd)	7.218	128.1	7.19	128.2
7 (d)	6.75	107.6	6.70	107.5
7a (-)		147.7		147.9
8 (s)[c]	1.28	24.6	1.31	25.6
9 (s)[c]	1.25	19.6	1.28	20.1
10 (s)	2.72	29.13	2.73	29.1
1a′ (-)		122.5		122.8
2′ (s)	7.93	152.4	7.86	151.6
4a′ (-)		144.6		144.8
5′ (d)	7.11	116.8	7.07	116.9
6′ (d)	7.91	130.4	7.86	130.6
6a′ (-)		127.3		127.5
7′ (d)	7.98	129.9	7.92	130.0
8′ (d)	7.23	120.0	7.20	120.0
9′ (-)		149.8		150.2
10′ (s)	8.16	113.0	8.16	113.0
10a′ (-)		131.3		131.8

[a]^{1}H NMR shifts Relative to acetone at 2.04 ppm. [b]^{13}C NMR shifts calibrated relative to hypothetical TMS.[23] d_6-Acetone has a shift of 29.43 ppm at 193 K under the conditions employed. [c]Methyl group 8 is closest to 2′, while 9 is pointing away from 2′.

NMR Assignments. The NMR assignments for the parent molecules (i.e., spirooxazine (SOX) without oligomer attached) have been reported in both spirooxazine[22] and merocyanine form.[13] Therefore the assignments for the SOX-PEG and SOX-PDMS molecules alone will be presented here in Tables 3 and 4. Oligomer assignments were also performed (Tables 5 and 6). The numbering scheme employed is shown in Scheme 1.

In transforming from the orthogonal spirooxazine configuration to the planar merocyanine form, the *gem* methyl groups convert from two distinct NMR resonances into a single resonance, since they are rendered equivalent in the planar form.

The spectra of the merocyanine forms are complicated by the fact that it was not possible to convert all of the spirooxazine form of the compound into the merocyanine

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TABLE 4. ^{1}H and ^{13}C Chemical Shifts of SOX-PEG (193 K) and SOX-PDMS (228 K) in d_6-Acetone in Merocyanine Form[a]

	SOX-PEG (**2m**) TTC		SOX-PEG (**2m**) CTC	SOX-PDMS (**3m**) TTC		SOX-PDMS (**3m**) CTC
position (multiplicity H only)	δ_H (ppm)	δ_C (ppm)	δ_H (ppm)	δ_H (ppm)	δ_C (ppm)	δ_H (ppm)
2 (-)		175.37			175.0	
3 (-)		49.68			49.5	
3a (-)		142.03			142.0	
4 (d)	7.67	122.5	7.69	7.59	122.4	
5 (dd)	7.32	124.93		7.27	124.7	
6 (dd)	7.49	128.45		7.45	128.5	
7 (d)	7.57	111.08	7.53	7.49	111.0	
7a (-)		143.41			143.6	
8 (s)	1.81	27.35	1.52	1.82	27.6	1.53
9 (s)	1.81	27.35	1.52	1.82	27.6	1.53
10 (s)	3.70	30.77	4.25	3.70	30.7	4.24
1a′ (-)		132.1			132.9	
2′ (s)	10.11	121.5	10.04	10.09	121.0	10.00
4a′ (-)		179.4			179.8	
5′ (d)	6.51	128.9		6.49	129.1	
6′ (d)	7.65	137.6		7.61	137.8	
6a′ (-)		125.9			126.4	
7′ (d)	7.64	129.9		7.60	130.1	
8′ (d)	7.04	118.8		7.03	118.9	
9′ (-)		150.9			151.3	
10′ (s)	7.97	115.3	7.80	7.96	115.8	7.79
10a′ (-)		138.1			138.4	

[a]Where no chemical shifts are given for the CTC isomers, it is assumed that the chemical shifts are almost identical to those observed for the corresponding TTC isomers, as no off diagonal exchange peaks were observed in the ROESY/NOESY spectra.

TABLE 5. ^{1}H and ^{13}C Chemical Shifts of the Oligomer Attachments of SOX-PEG (193 K) in d_6-Acetone

	SOX-PEG (**2s**) spirooxazine form		SOX-PEG (**2m**) merocyanine form TTC	
position	δ_H (ppm)	δ_C (ppm)	δ_H (ppm)	δ_C (ppm)
1″		171.9/172.6		171.7/172.6
2″	2.97	28.3	2.93	28.5
3″	2.76	28.1	2.76	28.3
4″		171.9/172.6		171.7/172.6
5″	4.16	64.2	4.21	64.2
6″	3.62	68.3	3.63	68.4
7″	3.53	69.8−70.4	3.52	69.8−70.4
8″−16″	3.44−3.49	69.8−70.4	3.44−3.49	69.8−70.4
17″	3.44	69.8−70.4	3.44	69.8−70.4
18″	3.38	71.5	3.38	71.6
19″	3.18	57.9	3.18	57.9

TABLE 6. ^{1}H and ^{13}C Chemical Shifts of the Oligomer Attachments of SOX-PDMS (233 K) in d_6-Acetone

	SOX-PDMS (**3s**) spirooxazine form		SOX-PDMS (**3m**) merocyanine form TTC	
position	δ_H (ppm)	δ_C (ppm)	δ_H (ppm)	δ_C (ppm)
1″		172.1		171.9
2″	2.68	33.7	2.64	33.8
3″	1.70	25.1	1.71	25.1
4″	1.40	29.3	1.43	29.0
5″−10″, 24″, 25″	1.2−1.4	23.1−34.0	1.2−1.4	23.1−34.0
11″[a]	0.53	ca. 17.9	0.52	ca. 17.9
12″−22″	0.02−0.13	−0.4−1.2	0.02−0.13	−0.4−1.2
23″[a]	0.53	ca. 17.9	0.52	ca. 17.9
26″	0.85	13.7	0.85	13.7

[a]11″ and 23″ are highly overlapped.

form. After prolonged photolysis, typically 30% of the spirooxazine form remained and hence cross peaks from the spirooxazine form were also present in the mixture, occasionally overlapping resonances from the merocyanine form. An analysis of the ROESY spectra was performed.

Isomeric Configurations of the Merocyanine Form. Several parties have investigated the isomeric conformation of the photomerocyanine form in the absence of attached side chains.[13,14,24] It is understood that of the 8 possible stereoisomers, only the 4 isomers that are transoid with respect to the C2′−N linkage are possible because of the steric restrictions of the cisoid isomers (Chart 1).[25] Lacking is a study of the *effect* that an oligomeric attachment to the naphthylene portion of the spirooxazine has on the isomeric configuration. Isomeric configurations were determined for the attached oligomeric compounds. Having compared the results obtained from NOESY and ROESY experiments, it was found at the lower temperatures with these relatively bulky molecules, the ROESY spectra gave higher intensity signals than the NOESY with relatively less t_1 noise associated with the experiments. NOEs at 193 K were negative (same sign as the diagonal) in the case of SOX-PEG, so exchange and NOE peaks were the same sign in the NOESY spectra but readily differentiated in the ROESY spectra.

Isomers of SOX-PEG. After photolysis of SOX-PEG to generate the merocyanine form, the TTC (trans−s-trans−cis) isomer was observed to be the dominant species. The keys for identification of the TTC isomer (Chart 1) as the major product were observation of strong ROEs between H-8,9 and H-10′ as well as a strong ROE from H-10 and H-2′. This is further supported by the lack of an observable ROE between 10 and 10′, which would be expected for the two less likely isomers of CTC and TTT. The prevalence of the TTC isomer suggests oligomeric attachment does not play a significant role in stereoisomer population.

Under UV irradiation, 70% conversion toward the photolyzed merocyanine form was determined from the relative integrals of the merocyanine and spirooxazine NMR peaks.

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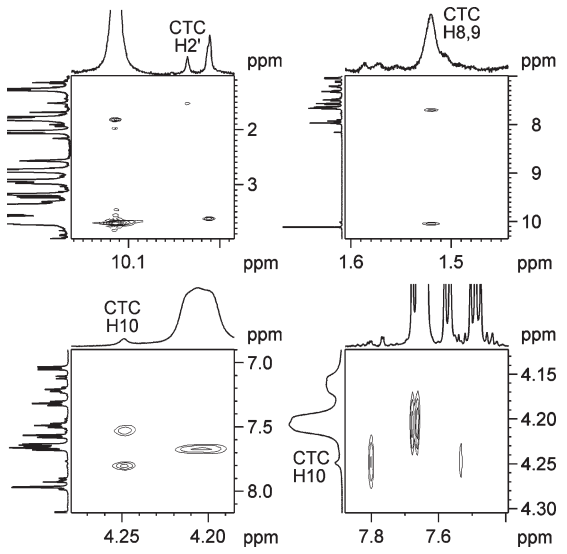


FIGURE 1. Selected expansions of 200 ms ROESY spectrum of SOX-PEG (**3**) after photolysis at 193 K. Low intensity peaks used to identify the CTC isomer of **3m** are highlighted.

Previous work carried out by Nakamura et al.[14] reported the predominant isomeric form for a standard spirooxazine configuration is the TTC form. Their ab initio calculations indicated the second most likely stereoisomer based on relative energies would be the CTC isomer. The region of the spectrum containing the signals from the H2′ proton in the open form is relatively clear and shows evidence for low concentrations of three other similar species (< 3% each compared to the TTC isomer). The CTC isomer was identified as one of these minor species, having an H2′ chemical shift at δ 10.04 with an intensity 42 ± 7 times lower than the TTC isomer, implying the TTC isomer is favored by 6.0 ± 0.3 kJ mol^{-1} over the CTC isomer. The CTC isomer is identified by an ROE between 2′ and methyls 8 and 9 at δ 1.52 and an ROE between a peak identified as 10 at δ 4.25 and a resonance assigned as 10′ at δ 7.80 (Figure 1).

Hydrogens 4 and 7 were also identified in the CTC isomer due to the presence of ROEs from 8, 9, and 10, respectively. The low quantity of this isomer and overlap with resonances of the more concentrated TTC isomer prevented complete assignment of all resonances, but it is highly likely all unassigned protons have very similar/overlapped chemical shifts with the corresponding hydrogen in the TTC isomer. Assignment of several of the protons in the CTC isomer (H2′, 8, 9, 10, 10′) was aided by the presence of exchange cross peaks between these protons and the corresponding proton from the TTC isomers that were definitively assigned. From integration of the 200 ms NOESY/EXSY spectrum at 193 K, the exchange rate is calculated to be 0.012 ± 0.002 s^{-1} for TTC to CTC and 0.49 ± 0.10 s^{-1} for the reverse CTC to TTC process (consistent with the equilibrium TTC:CTC ratio). This corresponds to a free energy of activation barrier, $\Delta G^{\ddagger}_{193K}$ of 53.7 ± 0.3 kJ mol^{-1} for the TTC to CTC process. The activation barriers are calculated using the Eyring equation with the usual assumption that the transmission coefficient κ is equal to unity, i.e., $\Delta G^{\ddagger} = RT(23.759 - \ln(k/T))$, where R is the gas constant. The other two peaks in the H2′ region at δ 10.011 and 10.014 are likely due to the photoproducts of similar impurities present in the starting spirooxazine and not the TTT or CTT isomers; these isomers would be expected to show large NOE/ROE to H10′ which was not observed and the chemical shifts of these protons are consistent with being close to the carbonyl moiety as is observed in the TTC and CTC isomers.

Isomers of SOX-PDMS. Analysis of ROESY data indicates that the predominant isomeric configuration is the same as determined in the SOX-PEG analysis where the stereoisomer TTC is clearly observed. This is confirmed primarily by the strong ROEs between H-10′ with the *gem* methyls H-8,9 and H-2′ with 10. There is clear evidence of a second open form isomer, in slow exchange with the main isomer at 228 K. For example, methyl groups 8 and 9 at δ 1.82 show a clear exchange peak in the ROESY spectra with a species at δ 1.53. Similar exchange cross peaks can be seen for methyl 10 and protons 2′ and 10′. The pattern of chemical shifts observed for the minor isomer is essentially identical to that seen in the case of SOX-PEG merocyanine, indicating the minor species is the CTC isomer. The CTC isomer has 38 ± 5 times lower intensity than the main isomer. In typical samples, the CTC isomer converts back to the main TTC isomer at an estimated rate of 26 ± 8 s^{-1} at 228 K based on increased line widths compared with the main isomer. This gives estimates that the second isomer is ca. 6.9 ± 0.3 kJ mol^{-1} higher in energy than the major isomer and that the free energy of activation for the process of interconversion of the two isomers, $\Delta G^{\ddagger}_{228K}$ for TTC → CTC, is 56.0 ± 0.7 kJ mol^{-1}.

Isomers and Isomerization of a Model Spirooxazine. Previous investigations have calculated the relative energies and the energy barrier to interconversion of *neutral* TTC and CTC merocyanine molecules.[14,21] Of most direct relevance, Horri and co-workers[21] calculated that the TTC isomer was more stable than the CTC isomer by 6.6 kJ mol^{-1} in the gas phase and 6.6 kJ mol^{-1} in acetone and that the activation barrier for the TTC → CTC process is 127.2 kJ mol^{-1} in the gas phase and 98.9 kJ mol^{-1} in acetone at the B3LYP/6-31G(d,p) level of theory. While the difference in energy of the observed isomers correlates very well with the experimentally observed values (6.0 and 6.9 kJ mol^{-1} for PEG- and SOX-PDMS, respectively), the calculated barrier is significantly higher than the barriers observed experimentally for the TTC → CTC process (53.7 and 56.0 kJ mol^{-1} for PEG- and SOX-PDMS, respectively),

To further investigate the nature of the discrepancy between the experimental and calculated barrier to the rotation about the C=C bond that results in the interconversion of the TTC and CTC isomers, the quantum chemical calculations were first investigated in greater depth. In the interests of computational manageability, the side chains were omitted and isomers of the base SOX merocyanine compounds (**1m**, X = H) were studied.

Similar calculations to those of Horri[21] were performed with higher levels of theory (Table S1, Supporting Information), specifically B3LYP/6-311+G(2d,p)//B3LYP/6-311G(d,p) (method 2) and MP2/6-311+G(2d,p)// B3LYP/6-311G(d,p) (method 3). It was calculated that the TTC isomer is lower in energy by 6.0 kJ mol^{-1} (method 2) in the gas phase compared to the CTC isomer and the activation barrier for the TTC → CTC process is 111.0 kJ mol^{-1} (method 2) in the gas phase. In acetone polarization continuum model (PCM) solvent, the activation barrier for the TTC → CTC process is calculated to be 71.6 or 67.3 kJ mol^{-1}

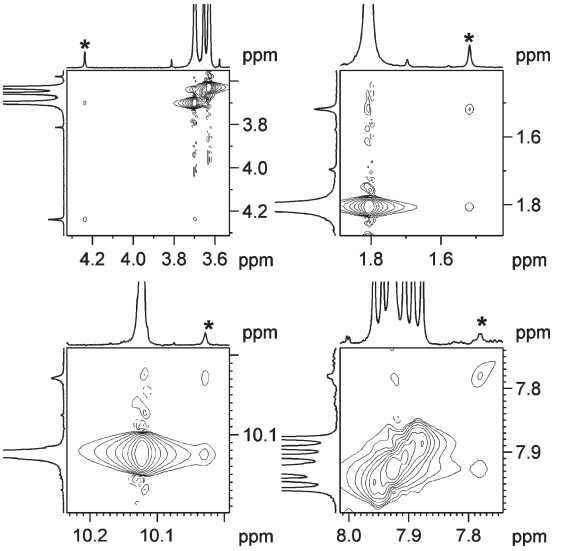


FIGURE 2. Expansion of 100 ms NOESY spectrum of SOX-Prop (**4**) after photolysis at 198 K showing exchange peaks between the TTC isomer (off scale) and corresponding peaks in the CTC isomer of **4m**.

using method 2 and method 3, respectively. Employment of an even larger basis set did not reduce the TTC to CTC barrier further, this barrier being calculated to be 72.2 kJ mol^{-1} at the B3LYP/6-311+G(3df,2dp)//B3LYP/6-311G(d,p) level in acetone solvent. While the inclusion of vibrational corrections, larger basis sets, and polar solvents lower the calculated energy barrier for the TTC → CTC process, the calculated energy barrier is still too high to be consistent with the rate of the observed exchange process. The expected rate for the TTC → CTC process based on the calculated energy barrier of 71.6 kJ mol^{-1} would be 1.7×10^{-7} s^{-1} at 193 K and $\sim 4 \times 10^{-4}$ s^{-1} at 233 K, rates that would not be observable in the NMR experiments employed at these two temperatures.

These calculations raise two possibilities. The first is that the computational methods employed are significantly overestimating the barrier to interconversion of TTC to CTC forms (72 kJ mol^{-1} calculated vs 53.7 to 56.0 kJ mol^{-1} observed) and that more complex methods (e.g., multireference methods, treatment of the complete rather than model molecules, explicit solvent molecules, etc.) may provide closer agreement. The second possibility is that a different path is being followed and the possibility that the TTC to CTC interconversion is catalyzed is explored below.

The possibility of trace amounts acid being a catalyst were examined experimentally. Further NMR experiments on model compounds without a long oligomeric attachment at C2′′, specifically, **4m** that has X = proprionyl (Table 1), were conducted. A control experiment was performed in which the sample was prepared in d_6-acetone (freshly opened) and then photolyzed at 198 K in the spectrometer. A similar mixture of primarily the TTC isomer and 52 ± 8 times smaller amount of the CTC isomer was identified in the NMR spectra. From the 2D NOESY/EXSY (exchange) spectrum, the rate for the TTC → CTC process was found to be 0.11 s^{-1} at 198 K (Figure 2).

Repeating the experiment on a sample identical to the control to which traces of acid (1 μL, 0.01 M aqueous HCl) had been added resulted in clear line broadening for all of the peaks due to the merocyanine forms produced after photolysis (Figure 3).

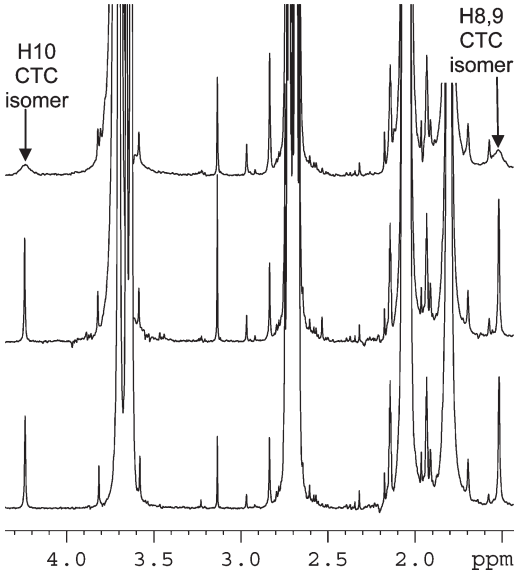
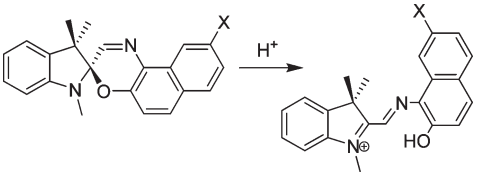


FIGURE 3. ^{1}H NMR spectra of SOX-Prop (**4**) with various additives after photolysis at 198 K. Samples contain a mixture of the merocyanine form (**4m**) and spirooxazine form (**4s**) of SOX-Prop at 198 K. Bottom: no additive. Middle: 1 μL of 0.01 M NaOH added. Top: 1 μL of 0.01 M HCl added. Peaks due to the CTC isomer are visibly broadened in the top spectrum. The off-scale peaks are from the more abundant TTC isomer of **4m**, nonphotolyzed spiro form (**4s**), and solvent (acetone). Lower intensity sharp peaks that do not broaden on addition of acid either are due to impurities or are ^{13}C satellites of the abundant species.

SCHEME 2. Acidochromism of Spirooxazine



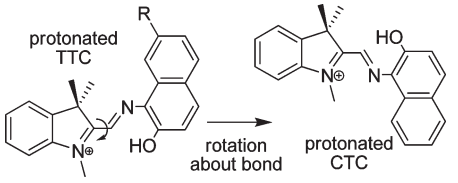
The CTC isomer converts back to the main TTC isomer at an estimated rate of 108 ± 12 s^{-1} at 198 K based on increased line widths compared with the main isomer, implying the TTC → CTC rate is 2.1 ± 0.3 s^{-1}, around 20 times faster than before the acid was added. A third sample, identical to the first except with the addition of 1 μL of 0.01 M aqueous NaOH, produced merocyanine forms with sharp peaks postphotolysis and an exchange rate extracted from the EXSY spectrum for the TTC → CTC process of 0.086 s^{-1}, slightly reduced from the value observed in the unadulterated control sample. Clearly then, the process can be catalyzed by acid.

The acid-catalysis process was also investigated by computational methods. The protonated form of merocyanine is well described because of the documented acidochromism observed in this class of compounds, addition of acid to the closed spirooxazine form leading directly to the protonated merocyanine form (Scheme 2)[26]

Protonation of the neutral merocyanine form results in protonation at the oxygen in the merocyanine structure, and a pK_a value of 4.00 ± 0.05 for the protonated merocyanine

(26) Kol'tsova, L. S.; Zaichenko, N. L.; Shiyonok, A. I.; Marevtsev, V. S. *Russ. Chem. Bull., Int. Ed.* **2001**, *50*, 1214.

SCHEME 3. TTC to CTC Isomerization in Protonated Merocyanine



form has been measured.[27] Calculations at the (method 2) level of theory confirmed this, protonation at oxygen being 28 and 112 kJ mol^{-1} lower in energy than protonation at the imine (N1′) and indole (N1) nitrogens, respectively.[28]

After protonation at oxygen, calculations now suggest that the TTC isomer is now lower in energy by 2.2 or 4.1 kJ mol^{-1} and the activation barrier for isomerization from TTC → CTC is 37or 30.6 kJ mol^{-1} (methods 2 and 3, respectively). Inclusion of acetone solvent has little effect, the activation barrier for TTC → CTC calculated to be 32.6 kJ mol^{-1} (method 2) or 26.4 kJ mol^{-1} (method 3).

Protonation in essence removes the resonance form in which there is a formal double bond between C2 and C2′, lowering the bond order between these two atoms and making rotation around this bond feasible even at low temperatures (Scheme 3).

The low energy barrier of 32.6 kJ mol^{-1} for a protonated isomer would correspond to a rate of 10350 s^{-1} at 198 K. Hence only a small fraction of the sample needs to be in the protonated form to explain the observed interconversion rate (2.1 s^{-1}) of the two isomers. Given the pK_a value of 4.00 measured previously[27] and the concentration of acid present (ca. 1.67×10^{-5} M[29]), a sufficient concentration of the protonated form would be expected under these conditions that could account for the observed rate. The moderate basicity of the neutral merocyanine form, revealed by this pK_a value, indicates that small, pH-dependent equilibrium amounts of the protonated form will be present and capable of causing exchange between the isomers even at neutral or higher pH. Rigorous removal of acidic protons, including water, would therefore be required to observe different merocyanine isomers using NMR at higher temperatures, and the likelihood that spectra observed would be of weighted averages of different isomers in fast exchange should be borne in mind.

Oligomeric Interactions to Host Spirooxazine. The initial aim of the NMR investigations was to elucidate spatial interactions between the oligomer side chain and photochromic core of the molecule in both spirooxazine and merocyanine forms of the molecule. Because of the instability of the photogenerated merocyanine form, NMR experiments on these compounds were performed at temperatures between 193 and 233 K to allow sufficient lifetime for their characterization. Observation and quantification of NOE interactions were expected to form the basis of outlining the interaction of the photochromic core and the oligomeric attachment. In general, rotating frame based experiments (ROESY) were

(27) Rys, P.; Weber, R.; Wu, Q. *Can. J. Chem.* **1993**, *71*, 1828.

(28) The CTC isomer is the lowest energy isomer in the case of protonation of the indoline nitrogen.

(29) One milliliter of 0.01 M HCl in ~600 mL of acetone. The concentration of acid assumes the d_6-acetone was neither acidic or basic initially and was not buffered and so is approximate.

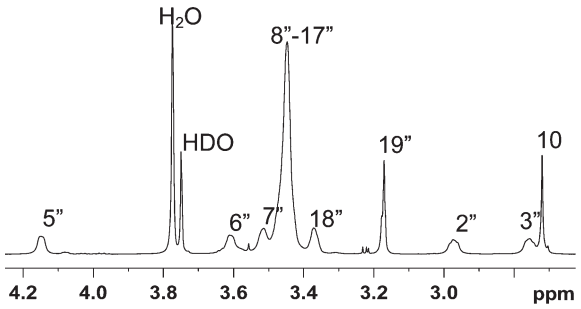


FIGURE 4. Region of ^{1}H spectrum containing resonances from PEG side chain of SOX-PEG (**2s**) in acetone at 193 K.

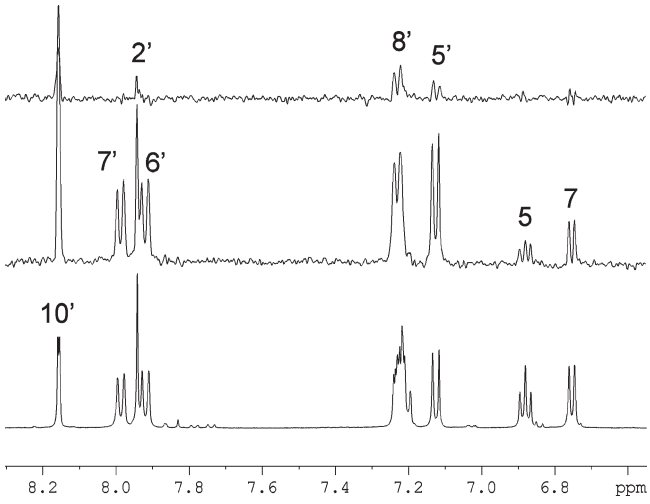


FIGURE 5. Aromatic region of 500 MHz ^{1}H spectrum of SOX-PEG (**2s**) in acetone at 193 K (bottom) with traces from 200 ms ROESY through the diagonal peaks of the PEG side chain, 8″−16″ (middle) and 5″ (top).

favored over laboratory frame NOE experiments (NOESY) to avoid problems that could have occurred as a result of operating under conditions where NOEs would be close to zero intensity at intermediate correlation times. These conditions of near zero laboratory frame NOE were likely to occur in some of the temperature ranges below room temperature that were required to stabilize the photogenerated merocyanine forms of the compound, since NOEs were observed to be positive at room temperature and negative at 193 K. Problems with differentiating spin diffusion cross peaks were also greatly attenuated by employing ROESY experiments.

NMR Evidence for Interaction between the Spirooxazine and Attached PEG Oligomer. In comparing analyses performed on SOX-PEG versus SOX-PDMS, the PEG oligomer interaction with spirooxazine host provided the most conclusively clear NMR spectra (Figure 4). The PEG oligomer and the diester linker have greater (in quantity) variation in chemical shifts in the ^{1}H NMR spectrum for the different CH_2 groups along the PEG side chain that are further along the oligomeric chain from the point of attachment to the merocyanine structure.

In the SOX-PEG (spirooxazine) form, the central portion (8″−16″) of the PEG side chain shows ROEs to the majority of the peaks in the aromatic region of the entire spirooxazine form (Figure 5, middle trace). The ROEs are larger to the protons in the naphthylene side of the molecule and largest to

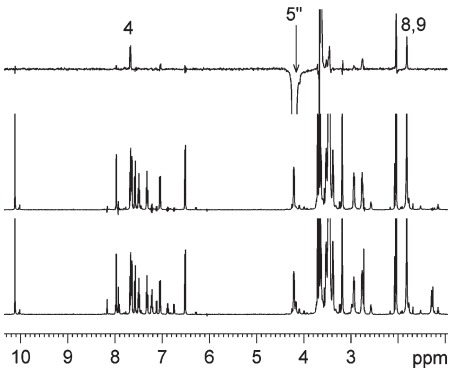


FIGURE 6. ROE slice of SOX-PEG (**2m**). Top: slice through proton 5″ of the PEG chain; observable are the through space interactions to *gem* methyl groups 8 and 9, along with H in position 4 of the indoline side of the SOX. Middle: photolysis product only, having mathematically subtracted all spirooxazine peaks. Bottom: actual mixture of both spirooxazine and merocyanine forms.

the two protons on the aromatic ring adjacent to the substitution site, namely, those at 8′ and 10′. This indicates that the PEG side chain spends slightly more time, on average, closer to the naphthylene side of the molecule in this case. Importantly, because of the $1/r^6$ dependence on internuclear distance of cross peak intensities, a decrease by a factor of 4 in terms of intensity translates to an increase in internuclear separation by a factor of only 1.26. The first methylene group in the PEG side chain after the linker, 5″, shows a more selective pattern of ROEs. The largest are to the protons adjacent to the attachment point 8′ and 10′, and there is a suggestion of a small ROE to 5′.

In the SOX-PEG (merocyanine) form, inspection of Figure 6 shows that specific ROEs that are much more intense than expected are observed between protons 5″ and 4 and also between protons 5″ and 8,9, indicative of a significant preference for conformations that brings these parts of the molecule into close proximity.

Comparing the ROE cross peak intensity from 5″ to 4 with that from the methyl groups 8 and 9 to 4 (fixed distance) it can be calculated that the NOE from 5″ to 4 is equivalent to the 5″ protons being fixed at a distance of 4.5 Å away from H4. This is based on assuming an average distance of 3.51 Å from the six methyl hydrogens of 8 and 9 to H4, obtained from the DFT model and using the usual $1/r^6$ relationship to obtain the relative distances from H4. This is not meant to be taken as a meaningful distance per se. The PEG side chain is undoubtedly highly flexible, causing very large fluctuations of specific side chain−core internuclear distances such as H4−H5″. This unexpectedly large ROE does indicate that there must be a relatively strong conformational preference for locating H5″ around 3.5−5 Å away from H4 for a significant proportion of the time. Rudimentary conformational searches using molecular dynamics simulations support this hypothesis. Given the relatively large separation these two moieties could have (> 10 Å), this is a notable interaction.

The possibility that the ROE peaks observed in the spectra are due to intermolecular contacts between two or more associated molecules was investigated. Most notably, ROEs/NOEs between the oligomeric side chain and the spirooxazine core of the molecules did not decrease when a sample

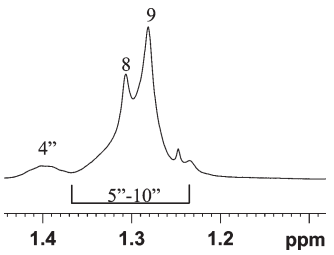


FIGURE 7. ^{1}H spectrum of closed SOX-PDMS (**3s**) at 233 K in d_6-acetone showing region of spectrum containing resonances from alkyl portion of the side chain (4″−10″) and overlapped CH_3 groups.

dilution of a factor of 3.5 to 5 was employed, consistent with the ROEs being intramolecular.

Propyl SOX and PEG Mixture. In comparison with the covalently attached PEG, only very weak, nonspecific ROEs from the resonances in the center of the PEG chain to most of the aromatic protons of the spirooxazine were observed. The ROEs are a factor of approximately 5−10 times less intense than those observed when the PEG chain is covalently attached in both spirooxazine and merocyanine forms, indicative of less interaction between the two moieties.

NMR Evidence for Interaction between the Spirooxazine and Attached PDMS Oligomer. Analysis of spectra in the spirooxazine form is significantly hampered in the case of PDMS side chains due to overlap of resonances (Figure 7). There is generally less separation of chemical shifts in the alkyl portion of the side chain remote from the aromatic core due to fewer functional groups along the side chain. The alkyl region is also overlapped with resonances from methyl groups 8 and 9. Any specific interaction, such as that found between the side chain and H4 seen in the merocyanine form with a PEG side chain is therefore masked by a large ROEs from 8,9 to 4 in the 2D spectra.

The ROESY spectra show weak ROEs from the siloxane methyl groups to all aromatics with little selectivity, indicative of general but nonspecific interactions between the siloxane chain and the aromatic core. Diluting the sample by a factor of 5 did not appear to change the pattern of ROEs significantly, although some of the smaller ROEs from the siloxane methyl groups to the aromatic protons lacked sufficient signal-to-noise to be observed after dilution.

Analogous to the case of the merocyanine form with a PEG side chain, an unexpectedly large ROE from the alkyl protons of the PDMS side chain (5″ to 10″) to the aromatic proton H4 is observed, along with a similar sized ROE between the alkyl chain and methyls 8,9. The later resonances (8,9) are not overlapped in the open form. Because of the increased overlap in the NMR spectra in the side chain of the PDMS form, these ROEs could not be attributed to a specific CH_2 group in the alkyl chain, e.g., H6″. Using the same method applied in the case of the merocyanine−PEG compound, comparing the ROE cross peak intensity from the alkyl protons to 4 with that from the methyl groups 8 and 9 to 4 it is calculated that the NOE from the alkyl chain to 4 is equivalent to 6 protons at distance of 5.1 Å or 2 protons at a distance of 4.2 Å. Again, these numbers are not to be interpreted as true distances, but they provide a pointer to a specific interaction between the alkyl portion of the side chain with the H4, 8,9 region of the molecule and a significantly populated conformation that

gives rise to this. As with the spirooxazine form, ROEs from the siloxane methyl groups to all aromatics are observed with little selectivity and dilution did not change the pattern of ROEs significantly.

Propyl SOX and PDMS Mixture. In contrast to the SOX-Prop and PEG mixture, no ROEs from free oligosiloxane to the photochromic molecule were visible in either spirooxazine or merocyanine forms. It appears that covalent attachment of the PDMS is essential for significant interaction of these two moieties to occur.

Conclusions

The domination of stereoisomer TTC and secondary CTC is independent of a covalently attached PEG or PDMS oligomer side chain to the naphthylene portion of the spirooxazine host. The rate of interconversion of the TTC and CTC isomers is more rapid than is predicted by computational methods, and one likely explanation is that it is the protonated, positively charged varieties of these species that facilitate the more rapid interconversion of the TTC and CTC isomer. At higher temperatures or in the presence of trace acid, NMR spectra of these systems are likely to reflect the presence of a weighted average of TTC and CTC isomers in rapid exchange rather than the separate species.

ROESY NMR coupled with a UV light source has provided a means of confirming the specific interactions between an attached oligomer side chain and a spirooxazine host. This interaction is at least 5 times greater in intensity compared to a similar system but with the oligomer side chain unattached and independent of the spirooxazine molecule. This is encouraging evidence for the influence an attached oligomeric chain has over the spirooxazine host and how a specific nanoenvironment could conceivably form in molecules of this nature. When the dye−polymer conjugate is confined within a rigid matrix rather than a solution, then one would expect increased localization of the oligmer, particular a PDMS oligomer, around or close to the dye. This rationalizes the large switching speed increase of PDMS-spirooxazines in rigid polymer matrices in comparison to the spirooxazine alone.

Experimental Section

Poly(ethylene glycol) functionalized spirooxazine, 99% (SOX-PEG) (**2s**); poly(dimethylsiloxane) functionalized spirooxazine, 99% (SOX-PDMS) (**3s**); and proprionyl spirooxazine, 99% (SOX-Prop) (**4s**) were synthesized as described previously.[12] Poly(ethylene glycol) 99%, M_w ca. 250 (PEG) and poly(dimethylsiloxane) 5.0 cSt, 99% (PDMS) were obtained commercially and used as supplied. Perdeuterated acetone (d_6-acetone) was used as supplied.

NMR spectra were recorded on 500 and 600 MHz spectrometers fitted with ^{1}H-^{31}P-BB triple resonance broadband inverse Z gradient and ^{1}H-^{13}C-^{15}N triple resonance inverse XYZ gradient probes, respectively. Temperature control was maintained using a standard variable temperature unit employing a liquid nitrogen evaporator to achieve the temperatures of 193−233 K. ^{1}H and ^{13}C peak assignments for SOX-PEG and SOX-PDMS were completed by performing ^{1}H, ^{13}C, and standard gradient DQF-COSY, HMBC, and HSQC experiments for each molecule.

ROESY and NOESY type two-dimensional experiments were used to elucidate through space interactions. The mixing time in the ROESY experiments was maintained at 200 ms at 193 K (500 MHz) and 250 ms at 228−233 K (600 MHz). For semiquantitative work involving extraction of internuclear distances, a compensated ROESY experiment was employed.[30]

UV irradiation was performed using a mercury arc lamp, and the setup has been previously described.[31] In brief, irradiation was achieved using a 100 W mercury arc lamp, coupled via condenser to an optical fiber. Focus and mirror were optimized, and 200−240 mW of power around 455 nm was measured at the sample end of a 7 m, 1500 μm core, nonsolarizing UV transmitting fiber (Ceramoptec P/N SMA1P/UV1500/1600N-NS/7.0M). It was assumed that the output at lower wavelengths (< 400 nm) was roughly proportional to the output of the lamp at 455 nm.

NMR solutions of spirooxazine compounds in d_6-acetone were typically prepared with a concentration of 22 ± 1 mM at ambient temperature. The samples of SOX-PEG and SOX-PDMS were also reinvestigated later after dilution by a factor of 3.5 to 5 to permit examination of any changes in NOE/ROE relative intensities. Samples were frozen in liquid nitrogen within septa-sealed NMR tubes and placed under a vacuum, and the sample was isolated and allowed to thaw in an effort to remove entrained oxygen within the sample that could interfere by causing oxidation while under UV irradiation. Nitrogen was then pumped into the headspace above the solution prior to NMR analysis. This deoxygenation procedure was performed in duplicate. The fiber optic was placed through the septa, and the tip was located approximately 2 mm above the surface of the solution. The NMR probe containing sample was then cooled to the appropriate temperature. Spectra were collected before, during, and after photoirradiation of the sample.

While the 600 MHz instrument was preferred for these studies, a lower operating limit of 223 K for the probe on the 600 MHz instrument precluded its use at temperatures below this. SOX-PDMS was studied at a higher temperature (228−233 K) to prevent precipitation of the compound, which occurred at temperatures below this.

Quantum Chemical Calculations. Calculations were performed using the Gaussian03 (rev. E) software package[32] running on quad/dual core linux workstations. Geometries were optimized at the B3LYP/6-311G(d,p) level (method 1) in vacuum and also in acetone solvent using the default polarization continuum model implemented in Gaussian03. Single point energies were then calculated employing these geometries using B3LYP/6-311+G(2d,p) or MP2/6-311+G(2d,p). All minimum energy structures were calculated without any symmetry constraints and were confirmed to be minima by calculating their normal vibrations within the harmonic approximation and observing that there were no imaginary frequencies. Transition structures were calculated using the Synchronous Transit-Guided

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Quasi-Newton method (opt = qst3 keyword), and calculation of the vibrational frequencies confirmed them to contain just one imaginary frequency corresponding to motion along the reaction coordinate for isomerization. Energies quoted include correction for zero-point vibrational energy. The B3LYP and MP2 energies are corrected using the zero point energies from the B3LYP/6-311G(d,p) calculations. The calculations employed the standard optimization and SCF convergence criteria and the default grid implemented in the Gaussian03 software. Energies and coordinates of the calculated structures are given in Supporting Information.

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Supporting Information Available: Full ^{1}H NMR spectra of SOX-Prop (**4**) with various additives before and after photolysis at 198 K. Selected 2D NMR spectra with expansions and further experimental details. Results of DFT and MP2 calculations. This material is available free of charge via the Internet at http://pubs.acs.org.