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Stabilization of an Organic Photochromic Material by Incorporation in an Organogel

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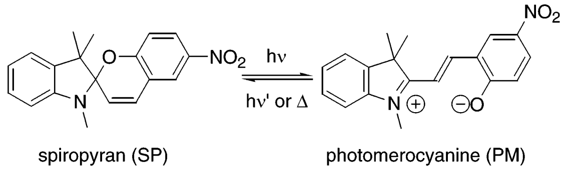
A series of 1′-substituted 6-nitro-3′,3′-dimethylspiro(2*H*-1-benzopyran-2,2′-indoline) compounds (**3**−**8**) of different functionality were synthesized, and the rate of thermal decay was measured in polar and nonpolar solvents and in two organogels. A significant retardation of the decay rate was observed for spiropyrans substituted with a succinyl ester functionality in a gel derived from 4-*tert*-butyl-1-phenylcyclohexanol (BACO1). The gel network has been shown to consist of a three-dimensional network of bimolecular associations of the BACO1 molecules, and it is hypothesized that a unique mode of interaction exists between the succinyl group of the spiropyran and the gelling agent. The lifetime of the colored photomerocyanine was increased by over 300-fold in the organogel versus solution with a succinyl ester functionality present. Structurally similar spiropyrans without the succinyl ester functionality showed relatively little change in the lifetime of the photomerocyanine.

Introduction

The application of organic photochromic materials such as spiropyrans for switching devices is restricted by both the short lifetime of the colored photomerocyanine (PM) species, which reverts thermally to the closed colorless spiropyran, and by the oxygen-mediated degradation of the molecules[1] (Scheme 1). The stabilization of the PM state of spiropyrans and related compounds such as spirooxazines and spironaphthoxazines has mainly focused on incorporating these photochromic systems into rigid matrixes such as polymers[2] and sol−gels,[3] thereby restricting the mobility of the PM and the diffusion of oxygen. By incorporating photochromic spironaphthoxazines in a polymer, a commercially useful application of variable-transmission ophthalmic lenses has been realized.[1c,d] The photochromic molecules can be either covalently linked to the polymer backbone or incorporated as a dopants into the bulk polymer.

In our studies, we incorporated the PM as dopants in optically clear organogels. Organogels are thermally reversible viscoelastic rigid solutions of organic solvents immobilized by the addition of low concentrations of low molecular mass organic gelator molecules.[4] These gelator molecules are able to self-associate to form long two- and three-dimensional networks, entrapping solvent molecules within their void space. The molecules interact through hydrogen-bonding, $\pi-\pi$ stacking, and dipolar and van der Waals interactions. It is difficult to predict a priori which molecular structures will contribute toward a good gelator molecule, and often the gelling ability of very closely related molecules is affected by slight isomeric modifications. As such, there is a large and growing class of seemingly unrelated molecules with the ability to gel a variety of organic solvents ranging from nonpolar alkanes to alcohols to aromatic solvents.[5]

Scheme 1. Spiropyran Photochromism



Due to the optical transparency of the organogels, and the good processability to form the organogels in different shapes, this project was undertaken to study the possible interactions between the organogel medium and the photogenerated photochromic component as a potential system to build a switching device.

Results

Five spiropyrans having different functionality were synthesized according to Scheme 2, and the decay rates

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(1) (a) Bertelson, R. C. In *Techniques of Chemistry*; Brown, G. H., Ed.; John Wiley and Sons: New York, 1971; Vol. III, Chapter III. (b) Guglielmetti, R. In *Studies in Organic Chemistry. Photochromism: Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; Chapter 8. (c) Crano, C. J.; Guglielmetti, R. J., Eds. *Topics in Applied Chemistry: Organic Photochromic and Thermochromic Compounds*; Kluwer Academic: New York, 1999; Vol. 1 and Vol. 2. (d) Van Gemert, B. *Mol. Cryst. Liq. Cryst., Sect. A* **2000**, *344*, 57−62. (e) Becker, R. S.; Lenoble C.*J. Phys. Chem.* **1986**, *90*, 62−65.

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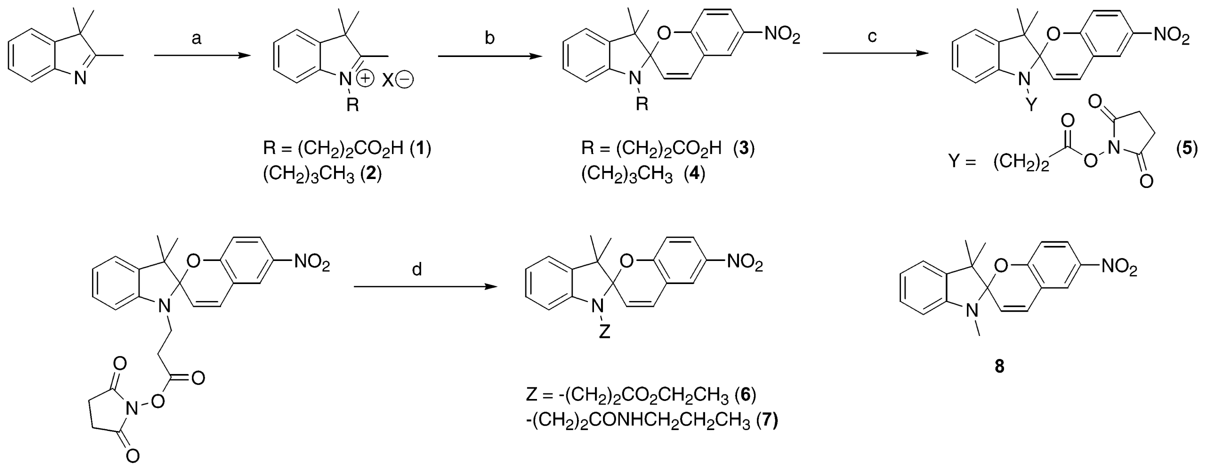
Scheme 2. Preparation of Substituted Spiropyrans[a]



[a] (a) RX, 60 °C, (b) 2-hydroxy-5-nitrobenzaldehyde, (c) *N*-hydroxysuccinimide, DCC, DMAP, (d) CH_3CH_2OH, Δ for **6**; 1-propylamine, Δ for **7**.

Table 1. Half-Lives of Spiropyran Decay in Various Solvents[a]

	$t_{1/2}$ (s)		
compd	methanol	toluene	mineral oil
5	1281 ± 3	6.7 ± 0.1	25.7 ± 0.8
6	1539 ± 10	10.3 ± 0.2	36.6 ± 1.4
7	1850 ± 4	19.0 ± 0.5	54.9 ± 0.8
8	5010 ± 20	10.3 ± 0.2	22.5 ± 0.4
4	4511 ± 9	29.7 ± 0.6	51.7 ± 0.5

[a] Samples were run with a 1.4×10^{-4} M solution of SP, and the recorded values are an average of three runs.

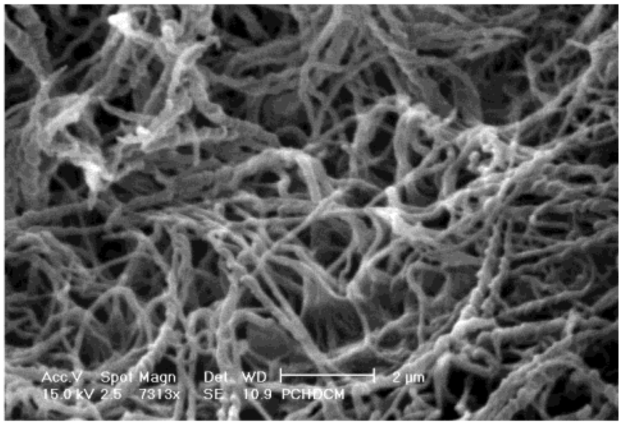
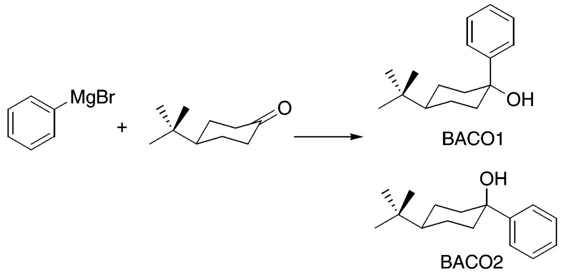


Figure 1. Electron micrograph (SEM) images of BACO1 xerogel. The bar represents a 2-μm length.

Scheme 3. Preparation of BACO1 Gelling Agent



for these and the commercially available 6-nitro-1′,3′,3′-trimethylspiro(2*H*-1-benzopyran-2,2′-indoline) (**8**) were measured in polar and nonpolar solvents and in two organogels, *trans*-4-*tert*-butyl-1-phenylcyclohexanol (BACO1), which was synthesized, and 1,3:2,4-D-dibenzylidenesorbitol (DBS), which is available commercially. The nitro-substituted spiropyrans were studied because they are the most common spiropyrans used, and therefore, the results in this organogel medium may be compared to other systems. Typically, measurements were collected by photoexciting the colorless spiropyran to the PM and taking an absorbance reading of the λ_{max} of the PM as it decays every 15−30 s over a 1−8 h period for the gelled samples and over shorter times for samples in solution.

For spiropyrans in methanol solutions, a monoexponential first-order decay model provided the best fits (Table 1). The decay rates in a polar solvent are relatively slow, due to the stabilization of the polar PM through hydrogen bonding with the solvent. Decay rates in toluene, a nonpolar, non-hydrogen-bonding solvent, and mineral oil were also best fitted to the monoexponential first-order decay model. The half-life of the PMs were several orders of magnitude lower than in methanol.[6] The stabilization of the PM can also be noted by the λ_{max} in different solvents. As the λ_{max} decreases, the PM is stabilized and hence has a longer lifetime (λ_{max}: methanol, 542 nm; mineral oil, 579 nm; toluene, 590 nm).

The gelling agent BACO1 has previously been prepared and characterized[7] and was synthesized as outlined in Scheme 3. Only BACO1 gels organic solvents, so the cis isomer (BACO2) was carefully separated. A scanning electron micrograph (SEM) image of BACO1 in Figure 1 reveals typical organogel features, the image resembling an entangled fibrous three-dimensional network.

Spiropyrans in gels were prepared according to the procedure described in the Experimental Section. For DBS/toluene gel samples, the decay is very rapid, with no appreciable stabilization of the PM in the gel and

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Table 2. Half-Life Data for Organogel Systems[a]

	DBS/tol	BACO1/MO[d]	
compd	$t_{1/2}$ (s)	$t_{1/2}$-1 (s)[b]	$t_{1/2}$-2 (s)[c]
5	9.9 ± 0.1	543 ± 2	5000 ± 200
6	11.5 ± 0.7	58 ± 2	NA[e]
7	34.3 ± 0.2	204 ± 2	NA
8	7.9 ± 0.1	59.3 ± 4.9	NA
4	12.1 ± 0.1	98.8 ± 0.5	NA

[a] All values represent an average of three independent measurements. [b] Corresponds to the half-life of the first exponential term. [c] Corresponds to the half-life of the second exponential term. [d] MO stands for mineral oil. [e] NA means not available—these compounds did not have a $t_{1/2}$-2 value.

Table 3. Enhancement Factor of PM Lifetime in Organogels Versus Solution[a]

	ratio gel/solution	
compd	DBS in toluene	BACO1 in mineral oil
5	1.5	195
6	1.1	1.6
7	1.8	3.7
8	0.77	2.6
4	0.41	1.9

[a] Experiments were run with a 1.4×10^{-4} M concentration of SP in 1% gelling agent.

even some examples of a more rapid decay in the gel sample versus solution, as seen in Tables 2 and 3. The enhancement factor listed in Table 3 refers to the ratio of PM lifetimes in the organogel relative to the solution studies.

Solutions of the spiropyrans (1.4×10^{-4} M) in 1% BACO1 in mineral oil were prepared and decay rates determined as described in the Experimental Section. Mineral oil has been shown to produce the best organogels with BACO1 with good optical transparency and a wide gelling temperature range.[7] The succinyl ester-substituted spiropyran (**5**) fit a sum of two first-order decays, whereas a single first-order decay was a better fit for the alkyl-substituted spiropyrans (**4** and **8**), ethoxypropionate (**6**), and *N*-propylpropionamide (**7**). Thus, the succinyl ester-substituted spiropyrans decay under two different modes, suggesting unique environments for the entrapped spiropyrans in the organogel network. Additionally, there is a significant increase of the PM half-life for the succinyl-containing SP in the BACO1 gel as compared to any other environment.

Thus there appears to be some type of interaction between the succinyl ester-substituted PM species and the gelling agent. Possibilities for this stabilizing interaction could be (i) an intra- or intermolecular electrostatic interaction between the succinyl group and the PM, (ii) an electrostatic interaction between the succinyl group and the gelling agent, or (iii) spatial constraints on the PM preventing its closing to the colorless SP. The spatial constraint is unlikely, since other spiropyrans of similar size (e.g., **6** or **7**) do not show a similar stabilization. The fact that there is a large difference in the half-lives of the differently functionalized SPs indicates an interaction between the SPs and the gelling agent. This interaction is further highlighted due to the importance of the succinyl appendage; when it is present, the enhancement of the PM in BACO1 is dramatic compared to any other appendage.

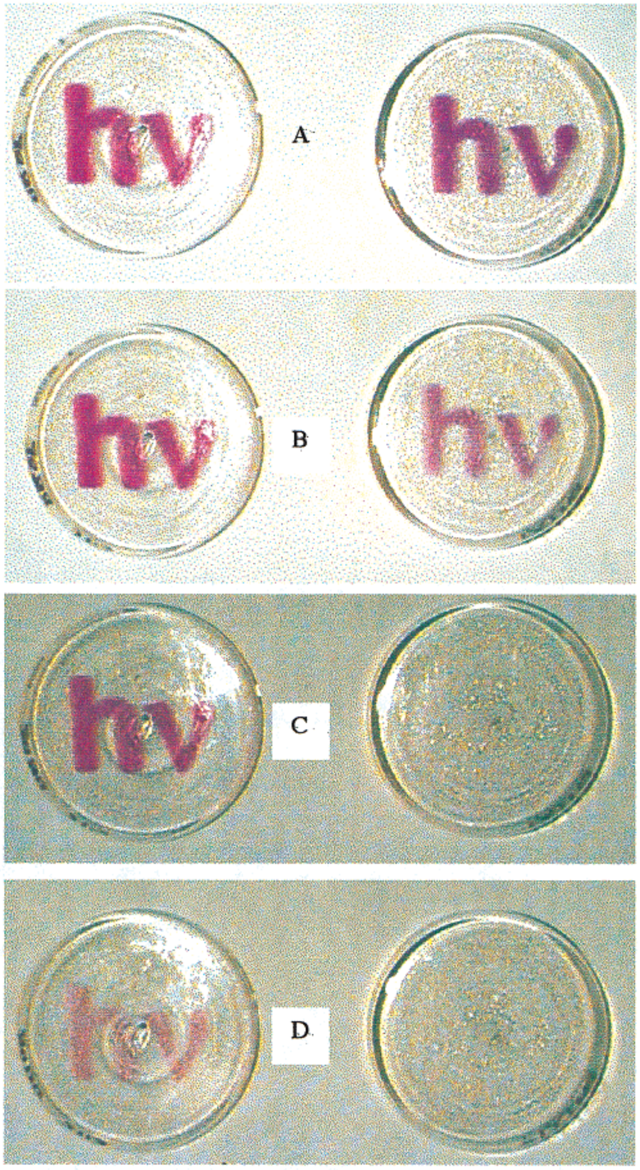

Figure 2. Photochromism of **4** and **5** in 1% BACO1/mineral oil gel in Petri dishes. Spiropyran **5** is on the left and **4** is on the right for all pictures over time at 2.8×10^{-4} M for both spiropyrans: (A) at time 0, when UV light is turned off, (B) after 3 min in the dark, (C) after 25 min in the dark, and (D) after 66 h in the dark. Mask of $h\nu$ was made and only the area colored red was exposed to UV light.

To obtain visual data on the long-term differences in coloration persistence, the loss of coloration of the succinyl propionate-substituted spiropyran (**5**) and butyl-substituted spiropyran (**4**) was compared over several days by forming a colored image in a Petri dish containing the 1% BACO1/mineral oil with a 2.8×10^{-4} M solution of either **4** or **5**. The two samples were photoexcited with a UV light source using a mask to generate an image and monitoring the fading of the color over several days (Figure 2). The colored PM in these samples maintains the same original spatial location, even after several days, which implies that a relatively strong type of interaction binds the PM species to the gelling agent, preventing the long-range thermal motion of the PM. To obtain a more accurate value for the half-life of the succinyl ester-substituted SP in BACO1 and to identify the factor(s) responsible

Table 4. Effect of Concentration of 5 in 1% BACO1/Mineral Oil Gel

SP concn (M)	$t_{1/2}$-1 (s)	$t_{1/2}$-2 (s)[a]	% of $t_{1/2}$-2[b]	ratio $t_{1/2}$-2/sol
3.72×10^{-5}	391 ± 6	6110 ± 70	31.8	238
7.15×10^{-5}	313 ± 2	6010 ± 60	14.1	234
2.14×10^{-4}	575 ± 2	8880 ± 100	12.0	346
2.86×10^{-4}	496 ± 1	8500 ± 50	10.3	331

[a] Error recorded represents fit to one experimental run—the value was consistent to within 3% for each experimental run. [b] % $t_{1/2}$-2 represents percentage of long-lived exponential term relative to short-lived exponential term for biexponential decays.

Table 5. Effect of BACO1 Concentration on Decay of PM of 5[a]

% BACO1	$t_{1/2}$-1 (s)	$t_{1/2}$-2 (s)	ratio $t_{1/2}$-2/sol
0.5	178 ± 3	2290 ± 16	89
1.0	334 ± 2	5000 ± 200	195
1.5	655 ± 7	6140 ± 70	239
2.0	828 ± 8	8250 ± 100	321

[a] All experiments were 1.4×10^{-4} M **5** in mineral oil.

for the stabilization of these molecules in this particular gelling agent, several experiments were carried out using **5**.

First, to test the effect of the gel structure, and not merely the added alcoholic gelling agent, a solution of **5** (1.4×10^{-4} M) in mineral oil with 1 wt % BACO2 was prepared. Unlike the BACO1 isomer, the cis BACO2 does not display gelling properties. When this mixture was photolyzed to generate the PM, a monoexponential decay was observed with a $t_{1/2}$ of 529 s^{-1}. This half-life is nearly identical to the fast decay observed in the BACO1 gel, but is an order of magnitude faster than the slow decay. This experiment indicates the gel structure is important for the long-lived colored PM structure.

The fatigue of the photochromic spiropyran was studied by rephotolyzing a gelled sample of **5** after the thermal annealing of the PM. Upon the third cycle of PM generation, the half-life of decay was nearly identical to the initial studies (the third cycle was 4900 ± 100 s^{-1}), although there was a noticeable decrease (~20% after three cycles) of the absorbance maximum upon repetitive photolysis.

Decay rate dependence on spiropyran concentration has been reported in polymeric systems,[8] and to study if similar effects were present in BACO1, decay rates were determined for gel samples prepared at 1.0% BACO1 concentration with varying amounts of **5**, as seen in Table 4. The gels with higher SP concentration did have longer half-lives, but more importantly, the ratio of the long-lived state versus the short-lived species changed. As mentioned previously, the succinyl-substituted SP was modeled with a biexponential decay term. Of these two decay terms, one is appreciable longer (the long-lived term is labeled $t_{1/2}$-2 in all the tables). This kinetic analysis indicates that for photochromic groups with a succinyl attachment, two different environments are present when the PM decays. As the concentration of SP in the 1% BACO1/mineral oil gel increases, the percentage of the PM in this long-lived environment decreases, thus indicating that only a certain number of microenvironment states are available. Any excess SP above this threshold limit decays by the relatively fast route. These data are inconsistent with an aggregation model. If aggregation was responsible for the increased lifetime of the PM with a succinyl ester appendage, then the amount of aggregation should increase with increasing concentration.

Another factor is the concentration of the gelling agent used to form the organogel. An increase in gelling agent aggregation was reported with increasing gelling agent concentration in dodecanol/BACO1 gel system.[7b] A 1.4×10^{-4} M solution of (**5**) in 0.5, 1.0, 1.5, and 2.0 wt/vol % BACO1/mineral oil gel systems was prepared, and the decay rates were measured. Gels at 0.5% BACO1 had to be cooled in the refrigerator at 4 °C or at room temperature overnight for gel formation, and samples with 2.0% gelling agent tended to form crystalline areas upon cooling; therefore, these two concentrations establish the limits for usable optically clear gels. As seen in Table 5, there is an increase of over 360% in the half-life between gels prepared at 0.5% and 2.0% BACO1 concentration. This further suggests that a certain number of potential microenvironment states exist that offer a long-lived PM and the number of these sites increases with increasing gel concentration.

Since in a 1.4×10^{-4} M spiropyran solution in a 1.0% BACO1/mineral oil gel there is about a 200:1 mole excess of the gelling agent with respect to the spiropyran, the possibility of a direct reaction between these two molecules was considered to account for this long-lived species present only with SPs with succinyl appendages. A transesterification reaction was attempted with **5** and BACO1 in THF at 50 °C. These conditions are similar to the gel-preparation conditions, except the choice of solvent and the time the sample was heated. The solution was heated for 24 h, instead of removing the sample from the heat after addition of the photochromic compound when the gel is formed, and even with this extended heating, only the starting materials were recovered with no 1′-BACO1 propionate 6-nitrospiropyran isolated. This is to be expected, considering the tertiary alcohol on the gelling agent.

Discussion

For the SP tested with a succinyl appendage (**5**), the enhancement ratio of the photogenerated PM with 1.4×10^{-4} M SP in 1% BACO1 organogel was 195 relative to free solution. Also this ratio was shown to increase to >300 by adjusting either the SP or BACO1 concentration. On the other hand, of the four SPs tested without a succinyl appendage (**4**, **6**−**8**), the same enhancement ratio was only 1.6−3.7. These results indicate that the stabilization of the succinyl esters is a result of interaction of the succinyl group of the SPs with the fibers of BACO1 molecules that make up the gel network. An SEM image of a xerogel of BACO1 (Figure 1) shows that the gelling agent forms long fibrous strands ~100 nm in thickness. These strands form a three-dimensional mesh with void spaces varying from 100 to 800 nm. In the gel state, without solvent removal, the widths of the fibers have been determined to be 76−80 Å,[7] and the void spaces would be expected to be even larger than in the xerogel state. The dimen-

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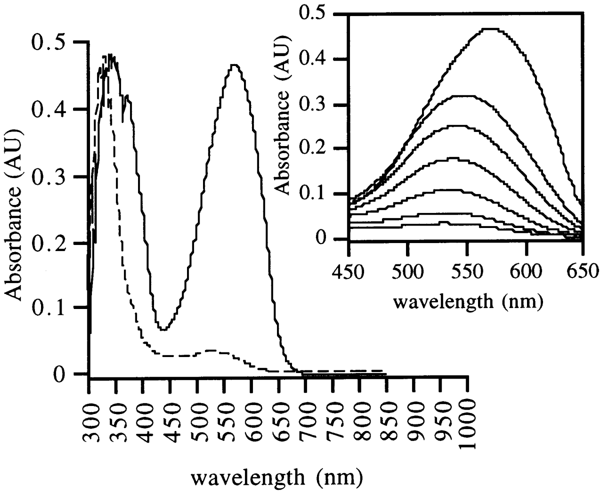

Figure 3. UV−vis spectra for **5** in 1% BACO1/mineral oil gel at ambient temperature. The solid line is when UV excitation is turned off with a maximum absorbance of 571 nm, and the dashed line is sample in dark for 3 h. The inset is photomerocyanine absorption over time. The largest absorbance corresponds to maximum absorption with λ_{max} of 571 nm. Each successive peak (with λ_{max}) corresponds to decay in dark for 4 min (549 nm), 6 min (543 nm), 14 min (538 nm), 32 min (537 nm), 106 min (535 nm), and 214 min (532 nm).

sions of the spiropyrans are much smaller (12 × 13 Å) with respect to the void spaces, and that relatively no stabilization was observed for the similarly sized **6** and **7** suggests that physical constraint of the ring-closure of the PM by the strands of the gelling agent is an unlikely cause to the stabilization.

One type of interaction that would account for the observed data is an intercalation of the succinyl groups of the spiropyran between the phenyl groups of a specific type of bimolecular association of the BACO1 gel aggregates that incorporates phenyl $\pi-\pi$ stacking. This intercalation most likely occurs during cooling of the hot gel/spiropyran mixture. Once the succinyl group is intercalated, formation of the PM leads to molecules with restricted mobility, allowing for a stabilizing interaction with the adjacent fibrous gel network. It is possible that this intermolecular interaction is with BACO1 molecules of neighboring strands, but more likely it is with BACO1 molecules of the strand onto which the PM is tethered, perhaps through wrapping of the gelator strands around the PM. In addition, it is interesting to note that the image in Figure 2 maintains clarity over time in the dark, thus indicating that the PM does not migrate once generated, as would be expected for a nonviscous solution.

The decay spectra of the PM of **5** in the BACO1 organogel shows a shift of ~41 nm to the blue, from 571 nm at the highest absorption to 530 nm when the PM has virtually decayed (Figure 3). This large change in absorption profile of the PM over time suggests that the PM exists in different environments, with the higher absorbing species corresponding to the free, unassociated PM within the void spaces of the gelling agent (the state that decays relatively fast), while the lower wavelength absorbing species corresponds to the constrained molecule that interacts directly with the gel strands, thus causing a blue shift of the PM. This interaction would thus cause the increased lifetime of the colored PM only when the succinyl ester group is attached.

Interestingly, intercalation of molecules into phenyl stacks has been observed in a different gel system based on the anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate plus phenol.[9] Gel formation is proposed to occur as a result of phenol molecules aggregating via $\pi-\pi$ stacking to form the backbone of the gel structure, with hydrogen-bonded AOT molecules absorbed onto the external surface. Dopant molecules such as other substituted phenols, benzoic acid, aniline, benzyl alcohol, and even cholesterol were shown to be able to interact with the gel system by intercalating into the gel stacks

The long half-lives of succinyl-substituted spiropyrans in BACO1/mineral oil gel solutions relative to other spiropyrans of similar dimensions and electronics and also to another organogel suggest a unique interactions between these spiropyrans and the way the BACO1/mineral oil gel system forms. On the basis of observations of phenyl $\pi-\pi$ stacking in other gel systems and intercalation of dopant molecules within these stacks, we have proposed an intercalation of the succinyl appendage of the spiropyrans within a phenyl−phenyl stacking of the gelator molecules. To enhance the effect observed, we are studying the importance of spatial orientation of the spiropyran relative to the organogel fiber by varying the tether length of the succinyl ester. In addition, the application of this organogel system for recording images with spatial resolution is being investigated.

Experimental Section

All chemicals, including 1′-methyl-6-nitro-3′,3′-dimethylspiro-(2*H*-1-benzopyran-2,2′-indoline) (**8**), were obtained from Aldrich and were used without further purification. 1,3:2,4-D-Dibenzylidenesorbitol (DBS) was kindly provided by Milliken Chemical, Spartanburg SC. Thin-layer chromatography was performed on Selecto Scientific F-254 precoated plates. Flash column was performed using silica gel 60 (230−400 mesh) from EM Scientific.

^{1}H and ^{13}C nuclear magnetic resonance spectra were acquired using a JEOL Eclipse 270 MHz spectrometer and referenced to a tetramethylsilane standard. Infrared spectra were obtained on a Nicolet Avatar 360 FT-IR ESP spectrophotometer in KBr mulls or neat. UV−vis spectra were acquired using a Hewlett-Packard 8453 single-beam diode-array spectrophotometer. Variations in the background during the acquisition of the decays were corrected using a three-point drop line or a single reference background correction. All acquisitions were obtained at ambient temperatures with a normal variance of ±2 °C. An Oriel Instruments (model 66032) mercury-arc lamp with a 500-W lamp, a water-cooled infrared filter, and 10-nm-bandwidth line-filters was used to photoexcite the spiropyrans. The SEM sample was prepared by forming a xerogel from a solution in dichloromethane and was coated with 20 nm of gold using an Anatech Ltd. Hummer VII sputter coating system. Images were acquired on a Philips XL-30 scanning electron microscope. Melting points were determined on a Laboratory Devices Mel-Temp II.

Gel Preparation. Gels were prepared by heating a mixture of the gelling agent and the organic solvent on a sand bath until a clear, homogeneous solution forms at 130−150 °C. This was then allowed to cool to below 100 °C and a solution of the

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spiropyran in methanol was added, typically at less than 50 μL volumes to facilitate evaporation of the methanol. An aliquot was then quickly transferred to disposable 1-cm UV−vis cuvettes using a pipet, and the solution was allowed to gel at ambient temperatures. Gels were also prepared by dissolving the spiropyran in methylene chloride before transferring to test the effect, if any, of the alcohol solvent on the decay kinetics. The PM decay was statistically equivalent, regardless if methanol or methylene chloride was used. Gelation for DBS/toluene samples occurs almost immediately after removal of the sample from the sand bath, so a preheated, short tipped pipet was used to minimize gel formation in the pipet.

Kinetic Analysis. Solutions of the spiropyrans in various solvents of concentration ranging from 2×10^{-4} to 2×10^{-5} M were prepared from stock solutions. Using a 365-nm emission-line filter from a 500-W mercury-arc lamp, the samples were irradiated until the newly formed PM peak reached maximum absorbance. The thermal decay was then measured over several hours in the dark. The decay curves were fitted to either mono- or biexponential decay models by varying the values for the preexponential term, k, and C using GraphPad Prism version 3.02 for Windows (see eqs 1 and 2). Equation 1 or 2 was chosen on the basis of the values for R^2 and 95% confidence intervals.

$$A = Be^{-kt} + C \tag{1}$$

$$A = B_1e^{-k_1t} + B_2e^{-k_2t} + C \tag{2}$$

Synthesis. Synthesis of BACO1[7] and compounds **4**,[10] **5**,[11] **6**,[12] and **7**[13] has been reported previously.

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