Journal Name

ARTICLE

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Deceleration of thermal ring closure in a glass-forming mexylaminotriazine-substituted merocyanine (MC) linked to intramolecular hydrogen bonding

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The design and synthesis of a glass-forming nitrobenzospiropyran (SP) functionalized with a mexylaminotriazine group is reported herein. The title compound was synthesized in 63% overall yield by the carbamoylation of a 2-hydroxyethyl SP precursor and an amino-functionalized glass-forming triazine precursor. As a photoswitch, the colourless SP-glass undergoes ring opening upon irradiation at 365 nm to the coloured merocyanine form, MC-glass. The negative solvatochromism (i.e., hypsochromic shift increasing with solvent polarity) and kinetics of thermal ring closure of MC-glass were studied spectrometrically in four solvents: toluene, tetrahydrofuran, N,N-dimethylformamide and 1-propanol. Results were compared to those for previously studied related merocyanines of 6-nitroBIPs. The observed thermal reversion rate from MC-glass to SP-glass in non-polar solvents was surprisingly slow, and is believed to be a result of intramolecular hydrogen bonding. Kinetics in solvents that can accept hydrogen bonds and analysis of activation parameters (E_a, A, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$) highlights the role of intramolecular hydrogen bonding for this MC-glass. Thus, the large negative $\Delta S^{\ddagger}$ (-32.1 $J \cdot mol^{-1} \cdot K^{-1}$) found for the MC-glass reversion in toluene suggests a tighter transition state that reflects the strength of hydrogen bonding in the MC-glass that inhibits the *trans-cis* isomerization that is the rate-determining step in ring closure.

Journal Name

ARTICLE

Introduction

The photochromic behaviour of spiropyrans (SP) has been known since the pioneering work of Fischer and Hirshberg in 1952;[1] the suggestion that spiropyrans might be exploited in the development of a "photochemical erasable memory" may also be attributed to Hirshberg.[2] Since then considerable effort has gone into the investigation of these molecular photoswitches, including their incorporation into quasi-liquid crystals, the investigation of their non-linear optical properties,[3] and their use in real-time holography.[4] Applications ranging from sensors[5,6] and filters, to control of protein activity by covalently bonded spiropyran[7,8] and in three-dimensional optical memory,[9] have been discovered. The impetus to study these photoswitching systems remains high.

Upon irradiation in the 200-400 nm region the colourless spiropyran (SP, e.g. 6'-nitro-1,3,3-trimethylspirobenzopyran, 6-nitroBIPS, **1**) form of the SP-MC photoswitch undergoes C-O bond scission, ring opening and rearrangement to the coloured trans-merocyanine (MC, e.g. **1a**) form (λ_{max} = 500-610 nm; Scheme 1). The MC forms are described as the hybrid of the quinoidal and zwitterionic resonance forms in Scheme 1.

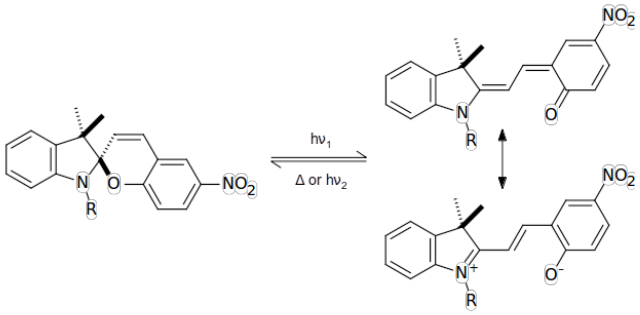
The photogeneration of MC from SP has been shown by Goerner,[10] for a set of 6'-nitro-substituted spiro[2H-1-benzopyran-2,2'-indolines], to proceed via a short-lived merocyanine-like triplet state that leads to *cis*- and *trans*-merocyanines. Equilibration between *cis* and *trans* forms follows, favouring the *trans*-MC.

Although reversion of the MC back to SP can be photostimulated by irradiation at a wavelength in the visible region, thermal reversion occurs rapidly at normal temperatures; the rate of cyclization back to SP is significantly reduced in polar solvents.[10-12] Thus, SP-MC photoswitch development has been hampered by the ready thermal reversion of the open MC form to the closed SP.

Attempts to enhance the MC lifetime and achieve suitable bistability in SP-MC systems have included acidification[13,14] and the use of metal ions to "trap" the MC (or its precursor cis-isomer).[15-19]

Solvent properties other than polarity,[20-22] such as viscosity[23] have also been probed and the use of more exotic media, including room temperature ionic liquids (RTIL),[24] or solvent polarity switching,[25] have been examined. Structural modification of the SP moiety has also been explored by a number of groups (e.g., Scheme 1, **3-3a** and **4-4a**).[10,11,15] These modifications have led to modest extensions of lifetime of the merocyanine form, not all easily controllable.

Scheme 1.



SP		MC
1	$-CH_3$	1a
2	$-(CH_2)_2CO_2H$	2a
3	$-(CH_2)_3SO_3^-\ ^+HNEt_3$	3a
4	$-(CH_2)_2CO_2$-cholesteryl	4a

To bridge the foregoing solution phase results and move towards practical solid-state devices, it was shown that bonding SP **2** in a covalent fashion to commercially available cross-linked polystyrene (PS) resin (Wang resin);[26,27] leads to a significant enhancement of the lifetime of the open-form(24-fold compared to **1a**, where PS-**2a** was monitored in a toluene suspension).[28] Further enhancements of MC lifetime was found for PS-**2a** when thermal reversion was monitored in solid state films.[29] The progression in extension of MC lifetime from solution to swollen polymer matrix to film was attributed to the increasing constriction of the micro-environment surrounding the MC.[28,29] Comparable improvement in MC stability has been reported for SP

Journal Name

ARTICLE

attached to the periphery of nanocrystals, incorporated into hydrophobic cavities of polymer nanoparticles,[30,31] or deposition on a gold surface (Au[111]) at low temperatures.[32] Clearly, there is ongoing interest in the problem of enhancing and controlling SP-MC bistability.

Amorphous polydisperse polymers lack crystallites or microcrystalline regions and form glassy solids below their glass transition temperatures (T_g). Their low-molecular-weight analogues, termed molecular glasses or amorphous molecular materials,[33-38] are monodisperse and are generally found to be easier to purify, characterize and process. The study of molecular glasses, in their own right, offers insights into the still poorly-understood molecular mechanism of glass transition.[33,34] While the glassy state is often more difficult to access as compared to polymers, molecular glasses have been successfully used for nano-lithography[35] and, relevant to SP-MC photoswitching, opto-electronic devices.[36,37] One practical major advantage of a photochromic-labelled molecular glass over a polymer doped with the photoswitch is that molecular glasses form films in which there would be no chromophoric dilution, as one would obtain in doped polymer systems.[38]

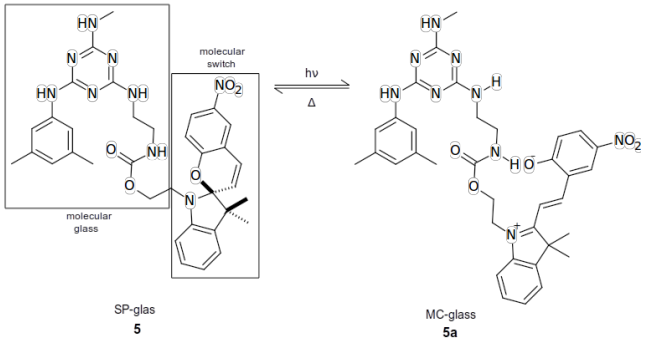
We have developed a number of libraries of molecular glasses based mexylaminotriazine core.[39,40] Mexylaminotriazines are relatively rigid and symmetrical and self-assemble through hydrogen-bonding.[41,42] The aggregates formed through hydrogen-bonding pack poorly, as required for glass formation,[41] although structural factors beyond disruption of hydrogen-bonding play a role in glass transition.[42]

It has been shown recently that mexylaminotriazine units functionalized with reactive groups can be used as building blocks to which chromophores can be covalently bonded, resulting in adducts that possess both the glass-forming ability of the mexylaminotriazine moiety and the optical and/or electronic properties of the chromophore. These adducts can be synthesized with simple, efficient and high-yielding procedures. This was demonstrated recently with a series of azobenzene derivatives.[43,44]

Though the glass-forming adducts do not undergo a significant perturbation of their optical properties, because the mexylaminotriazine units are linked through an alkyl spacer and are not conjugated with the chromophores, their photomechanical behavior can be nonetheless perturbed by the presence of intramolecular non-covalent interactions, principally hydrogen bonding. While this is difficult to observe with azobenzenes because the *cis* and *trans* isomers possess close absorption maxima, the SP-MC system constitutes a more desirable model to study in solution because of the radically different absorption bands of the two isomeric forms. Coincidentally, the presence of intramolecular hydrogen bonding shows the promise of stabilizing the open MC form, which would be desirable for practical applications. As the SP-MC equilibrium is slower in the solid state, studying the phenomenon in solution would allow a direct comparison with other strategies previously used to stabilize MC chromophores by modulating their molecular structures.

The present work aims to synthesize a SP derivative with a mexylaminotriazine unit that is capable of readily forming stable glasses, and study the influence of the triazine group, and the accompanying capacity for hydrogen bonding, (Scheme 2, **5**) on the spectroscopic features of the open MC, **5a**, and the thermal cyclization of **5a** back to **5** in solution in a range of solvents. For simplicity, in Scheme 2 the MC-glass, **5a**, is represented only as the zwitterionic resonance form (cf. Scheme 1, **1a**-**4a**).

Scheme 2.



In our previous studies of photochromic spectroscopic behaviour and in the thermal reversion process in solution, SP **1** showed congruent solvatochromic and solvatokinetic behaviour, namely, hypsochromic spectroscopic shift of the MC **1a** band along with a decreasing rate constant for thermal ring closure as a function of the increasing polarity of the solvent. For **2a**-**4a**, the solvatochromic behaviour was in accord with that found for **1a**.[11] However, in relatively non-

Journal Name

ARTICLE

polar solvents (toluene, diethyl ether, 1,4-dioxane and THF) the rate constants for reversion to the closed spiropyran form for **2a**-**4a** remained approximately unchanged and only showed a solvatokinetic dependence for the more polar set of solvents (acetone, DMF, ethanol), converging to a value of ca. 6.5 x 10^{-4} s^{-1} in EtOH. This result was attributed to a combination of factors. First, that in the non-polar set of solvents the barrier to rearrangement of the trans form of the MC to the cis form of the MC (necessary to ring closure), which is the rate-determining barrier in the reversion, would be lowered by the increased contribution of the quinoidal resonance form to the hybrid. Therefore, rate constants for reversion in non-polar solvents would be faster than reversion in the polar media. Second, the rearrangement could be hindered by the presence of indolino substituents that could interact either by electrostatic repulsion (**2a**, **3a**) with the aryloxyl moiety or through steric hindrance (**4a**). In polar solvents, the hybrid contains a higher weighting from the zwitterionic form in which the central C-C bond that must rotate to permit rearrangement to the *cis* form has a higher bond order and this raises the barrier to rearrangement, slowing reversion. The solvatochromic trend in which the magnitude of the rate constants decline with increasing solvent polarity now comes to the fore.[11] The current study tests these proposals by attaching the hydrogen-bonding mexylaminotriazinyl group, a molecular glass (Scheme 2, **5**-**5a**), to the indolino N of the SP through a 2-hydroxyethyl linker.

Experimental Section

General

2-Methylamino-4-mexylamino-6-(2-aminoethylamino)-1,3,5-triazine (**7**) was purchased from Solaris Chem, Inc., 1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran (**6**) was purchased from TCI America, N,N'-Carbonyldiimidazole (CDI) was purchased from Oakwood Chemicals, and all solvents for synthesis were purchased from Caledon Labs. Solvents for spectrophotometric studies were purchased from commercial sources and were spectrophotometric or HPLC grade. All reagents were used without further purification. Reactions were performed under ambient atmosphere unless otherwise specified. Glass transition temperatures were determined with a TA Instruments 2010 Differential Scanning Calorimeter calibrated with indium at a heating rate of 5 °C/min from 30 to 200 °C. Values were reported as the half-height of the heat capacity change averaged over two heating runs after an initial heating and cooling cycle. FTIR spectra were acquired with thin films cast from CH_2Cl_2 on KBr windows using a Perkin-Elmer Spectrum 65 spectrometer. ^1H NMR spectra were acquired on a 400 MHz Bruker AV400 spectrometer at 363 K, while ^{13}C NMR spectra were recorded on a 300 MHz Varian Oxford spectrometer at 298 K. UV-vis spectra (wavelength scanning and single wavelength monitoring) were recorded using a HP 8542 photodiode array spectrophotometer; the desired temperature of the cell was controlled by a thermostat (T ± 0.5 ºC). For photogeneration of the merocyanine form of **5**, (MC **5a**), a SpectroLine CX ultraviolet irradiation cabinet, equipped with dual 15 W long wavelength (365 nm) tubes, was employed.

Synthesis of SP-glass 5

A solution of 1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran (**6**) (0.897 g, 2.55 mmol) in dry THF (10 mL) was slowly added to a suspension of N,N'-carbonyldiimidazole (1.03 g, 6.36 mmol) in dry THF (5 mL) in a dry round-bottomed flask equipped with a magnetic stirrer at ambient temperature, then the mixture was stirred for 18 h under nitrogen atmosphere. CH_2Cl_2 and H_2O were added, then the layers were separated, and the organic layer was washed two more times with H_2O. The organic extract was recovered, dried over Na_2SO_4, filtered, and the solvent was evaporated. The crude residue was redissolved in THF (20 mL), then 2-methylamino-4-mexylamino-6-(2-aminoethylamino)-1,3,5-triazine (**7**) (0.879 g, 3.06 mmol) was added and the mixture was refluxed for 18 h. The solvent was evaporated, then CH_2Cl_2 and 1M aqueous HCl were added, and both layers were separated. The aqueous layer was extracted three times with CH_2Cl_2, then the organic extracts were combined and washed successively with H_2O and 1M aqueous NaOH. The organic layer was then dried over Na_2SO_4, filtered, and the volatiles were thoroughly evaporated under reduced pressure to yield 1.074 g of pure glass **5** (1.61 mmol, 63%). T_g 88 °C; FTIR (CH_2Cl_2/KBr) 3401, 3287, 3055, 2959, 2923, 2869, 2854, 1709, 1650, 1609, 1566,

Journal Name

ARTICLE

1519, 1481, 1456, 1442, 1399, 1384, 1360, 1337, 1300, 1271, 1188, 1172, 1143, 1125, 1091, 1026, 954, 905, 839, 810, 777, 743, 688 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.29 (br s, 1H), 8.12 (d, ^4J = 2.8 Hz, 1H), 7.98 (dd, ^3J = 9.1 Hz, ^4J = 2.8 Hz, 1H), 7.40 (s, 2H), 7.12 (m, 2H), 6.83 (m, 3H), 6.69 (d, ^3J = 9.1 Hz, 1H), 6.56 (s, 1H), 6.38 (br s, 1H), 6.31 (br s, 1H), 6.00 (d, ^3J = 10.6 Hz, 1H), 4.14 (m, 1H), 4.10 (m, 1H), 3.39 (m, 4H), 3.21 (m, 2H), 2.83 (d, ^3J = 4.5 Hz, 3H), 2.23 (s, 6H), 1.23 (s, 3H), 1.12 (s, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.4, 164.3, 159.5, 156.6, 146.9, 141.0, 137.4, 135.9, 128.4, 128.1, 126.1, 123.2, 122.4, 122.1, 119.7, 119.2, 117.6, 115.8, 106.9, 61.7, 52.8, 42.9, 39.4, 27.7, 26.0, 21.7, 19.9 ppm; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{35}H_{40}N_9O_5$: 666.3147, found: 666.3175.

Spectrophotometric experiments

A stock solution (4.0 mM) of SP **5** was prepared by dissolution of a weighed quantity of SP **5** in toluene in a 5.0 mL septum-sealed volumetric flask under inert atmosphere. For solvatochromic or kinetic experiments 25.0 µL of the stock solution was transferred, via 25.0 µL microsyringe, directly into the 1.0 cm pathlength quartz cuvette that contained 2.5 mL of the relevant solvent. The experimental solution (4×10^{-5} M) was irradiated 90 s in the SpectroLine cabinet; this served to achieve a photostationary state concentration of MC **5a**, in all solvents. For solvatochromic studies, spectra were immediately scanned in the spectrophotometer and recorded (at 25 ºC). As found previously for related merocyanines,[11] absorption intensities of compound **5a** conformed to Beer's Law at the concentration studied.

For kinetic runs, an initial blank UV-vis spectrum was recorded of solvent alone. The SP **5** stock solution was injected, as outlined above, and the quartz cell irradiated in the SpectroLine cabinet (see above) for 90 s to give compound **5a**. The cuvette was transferred to the spectrophotometer and monitored at constant wavelength (λ_{max} for the solvent being studied) and the decrease in intensity of **5a** was followed at constant time intervals; intervals were chosen so that 10 or more data points were acquired per half-life. The decay of MC **5a** absorbance was followed for 10 half lives for at least one run. Replicates were monitored for no less than three half lives. Data were plotted according to equation (1) to yield the thermal reversion rate constants reported (See Results and Discussion). Rate constant values are precise to within ± 5% based upon replicate runs.

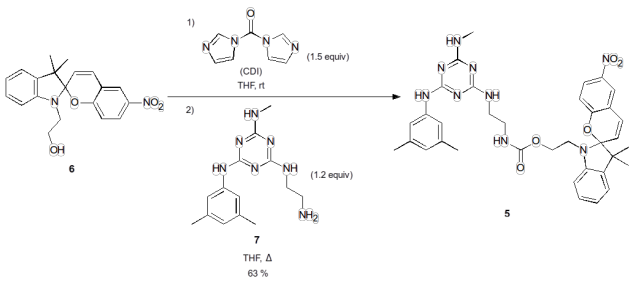
Arrhenius plots were constructed using rate constants determined as outlined at temperatures that varied with the solvents. For toluene, the rate constants were determined at 10, 25, 30, 40 and 50 ºC. For THF the temperatures monitored were 0, 10,25,30,40 and 50 ºC. Temperatures of -15, 0, 10, 25, 30, 40 and 50 ºC were used to determine rate constants for the Arrhenius plot in DMF. For 1-propanol, rate constants were measured at 20, 25, 40 and 50 ºC. The parameters extracted from the resulting Arrhenius plots are given in Table 3, including derived values, $\Delta H^{\ddagger}$ etc.

Results and Discussion

Synthesis of SP-glass 5

Spiropyran glass **5** was synthesized from 2-hydroxyethyl-substituted spiropyran derivative **6** and amino-functionalized glass **7** with N,N'-carbonyldiimidazole (CDI) in a procedure similar to that used for Disperse Red 1 and other azobenzene derivatives.[43,44] Spiropyran **6** was first reacted with CDI in dry THF at ambient temperature to yield the corresponding imidazolylcarbamate, which was then heated with glass **7** to give compound **5** (Scheme 3). The yield of the reaction sequence was 63%, which is significantly lower than the yields from similar azobenzene glass synthesis.

Scheme 3. Synthesis of SP-glass **5**.



The lower yield can be rationalized by the fact that compound **5** is slightly soluble in dilute aqueous HCl, which is

Journal Name

ARTICLE

used for removing unreacted starting materials, leading to losses during purification. Nonetheless, this procedure yields compound **5** in high purity without the need for chromatography, which leads to even higher product loss because of significant amounts of compound **5** remaining adsorbed on silica given its highly polar nature. As expected, compound **5** readily forms glassy phases with a T_g of 88 ºC, and did not show any crystallization upon prolonged standing. Crystallization upon heating above T_g could not be observed because compound **5** starts decomposing above 125 ºC. Interestingly, compound **5** underwent a color change to bright blue when heated over its glass transition temperature. A DSC scan of compound 5 is shown in Figure 1.

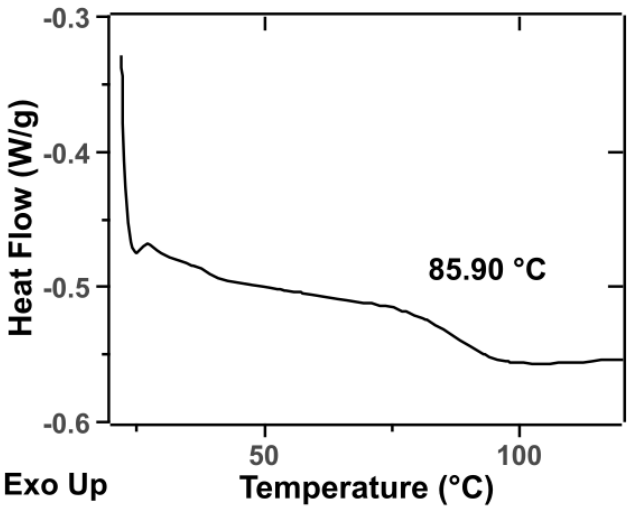


Figure 1. Differential Scanning Calorimetry (DSC) scan of SP-glass **5**, measured at a heating rate of 5 ºC/min.

UV-Visible characteristics of merocyanine 5a

Irradiation (365 nm) of a 0.04 mM solution of SP derivative **5** for a period of 90 s served to photogenerate the merocyanine form, **5a**, in a selection of solvents. Figure 2 shows typical UV-vis scans of both SP **5** and MC **5a** in DMF at 25 ºC, where the wavelength of maximum absorbance, λ_{max}, can be seen at 560 nm. (UV-vis spectra of **5a** in the other solvents used in the study are shown in Figures S1-S3, Supplementary Information). The solvents chosen for study range from the relatively non-polar toluene, to the polar THF and DMF, and the protic 1-propanol (1-PrOH). The λ_{max} values for MC **5a** in the four solvents used in this study are listed in Table 1, along with the solvent parameters, including the Reichardt solvent polarity (ET),[21] and Kamlet-Taft-Abraham hydrogen bonding (α,β) constants.[45-47]

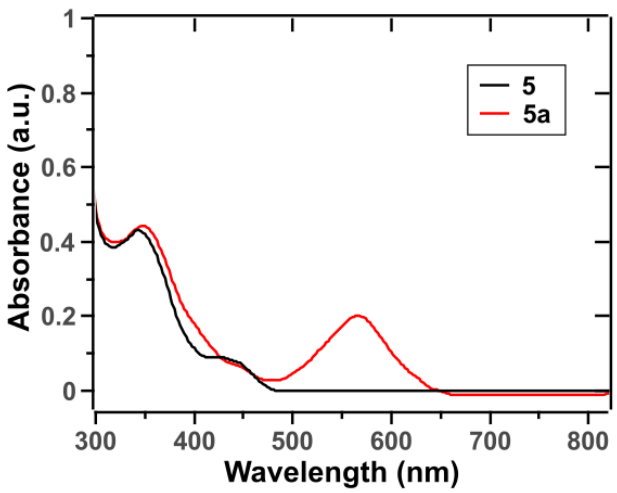


Figure 2. UV-vis spectrum of compound **5** in both its spiropyran (**5**) and merocyanine (**5a**) forms in DMF solution (4 x 10^{-5} M); the spectrum of **5a** was recorded after 90s irradiation.

Table 1. UV-Vis spectroscopic characteristics of merocyanine derivatives **1a** and **5a** in selected solvents at 25 ºC.

Solvent	α, kcal/ mol[a]	β, kcal/ mol[b]	$E_T(30)$, kcal/ mol[c]	λ_{max} 5a, nm	λ_{max} 1a, nm[d]
Toluene	0.00	0.11	33.9	585	600
Dioxane	0.00	0.77	36.0	-	590
THF	0.00	0.55	37.4	568	584
DMF	0.00	0.69	43.8	560	568
1-PrOH	0.84	0.90	50.7	550	545
EtOH	0.86	0.75	51.9	-	540

[a] Kamlet-Taft-Abraham hydrogen-bond donor (acidity) parameter.[45]

Journal Name

ARTICLE

[b] Kamlet-Taft-Abraham hydrogen-bond acceptor (basicity) parameter for the solvent.[45]

[c] Reichardt solvent polarity scale.[21]

[d] Ref. 11, Ref. 25 for 1-PrOH.

As can be seen from Table 1, λ_{max} values for MC **5a** shift from 585 to 550 nm by increasing solvent polarity from toluene to 1-propanol. This trend has been noted previously.[10-12,48] It is interesting to compare the change in λ_{max} (i.e. $\Delta\lambda_{max}$) for toluene and DMF; $\Delta\lambda_{max}$ = 25 nm (that is, 585 to 560 nm) for MC **5a**, compared to $\Delta\lambda_{max}$ = 32 nm for the standard **1a**. In comparison, for analogues **2a**, **3a** and **4a**, $\Delta\lambda_{max}$ is 40, 30 and 38 nm, respectively. Clearly, the trend in solvatochromism for compound **5a**, including the magnitude of the hypsochromic shift as a function of increasing solvent polarity, is within the typical range established for MCs **1a**-**4a**,[11] regardless of the nature of the indolino nitrogen substituent.

The inverse relationship between λ_{max} and solvent polarity, as measured by the $E_T(30)$ parameter,[48] has been termed negative solvatochromism, and is commonly attributed to a ground state (GS) that is more dipolar than the corresponding electronic excited state (ES), i.e. dipole moment GS (μ_{GS}) > dipole moment ES (μ_{ES}).

To effect a change in the electronic (UV-vis) spectrum of an MC any substituent on the chromogen must interact electronically (via resonance etc.) with the chromogen. Note that the triazine glass moiety is as insulated from the MC system **5a** as it is for the other comparative systems, **2a**-**4a**; all are insulated from the indolino nitrogen by at least an ethylene ($-CH_2CH_2-$) tether. This insulator prevents any significant change in the HOMO of the molecules by additional conjugation that would affect the HOMO-LUMO gap that gives rise to the observed λ_{max}. This HOMO-LUMO gap, therefore, would not be expected to change with solvent polarity in a fashion contrary to that of the other MCs studied previously.[10-12,48]

Thermal ring closure kinetics of MC-glass 5a

Rates of ring closure were determined spectrometrically by following the decrease in the intensity of the relevant **5a** λ_{max} peak with respect to time (25 °C). Rate constants for the thermal reversion (k_{5a}) were obtained from the standard integrated first-order rate equation (equation 1):

$$\ln(A_t - A_{inf}) = -k_{5a}\, t + \ln (A_0 - A_{inf}) \qquad (1)$$

where A_0, A_t and A_{inf} refer to MC absorbances at initial time, time = t and time after ten or more half-lives, respectively. The reversion process was monitored for no less than three half-lives to give plots of $\ln(A_t - A_{inf})$ as a function of time that displayed good linearity ($r^2 \geq 0.99$). The rate constants, k_{5a}, calculated from the slopes of the plots have errors of ± 5%, based on replicate runs and these rate constants, k_{5a}, are listed in Table 2. Table 2 also includes ring closure constants for parent compound **1a**, and for cholesteryl ester derivative **4a**.

Table 2. Rate constants for the ring closure of MC **5a** to SP isomer **5** compared to analogues **1a** and **4a** at 25 °C in various solvents.

Solvent	k_{5a}, s^{-1}	k_{1a}, s^{-1} [a]	k_{4a}, s^{-1} [a]
Toluene	9.75×10^{-3}	1.22×10^{-1}	4.75×10^{-2}
THF	2.96×10^{-2}	2.68×10^{-2}	5.25×10^{-2}
DMF	3.36×10^{-2}	2.85×10^{-3}	5.45×10^{-3}
1-PrOH	2.47×10^{-3}	-	-
EtOH	-	6.9×10^{-4}	6.6×10^{-4}

[a] Ref. 11.

It is immediately apparent from examination of Table 2 that MC **5a** does not follow the same solvatokinetic trend as analogue **1a**, i.e. decreasing rate constant with increasing solvent polarity for ring closure back to SP **1**.[11,48] In fact, we have previously reported that for **1a** the rate constants for reversion correlate linearly with the solvent polarity $E_T(30)$ scale.[48] However, the effect of solvent on the ring closure kinetics of compound **5a** does not parallel that of cholesteryl ester **4a**, the previously studied merocyanine that bears a bulky indolino substituent; k_{4a} is approximately constant in toluene and THF with a value close to 5×10^{-2} s^{-1} but ring closure slows in the more polar DMF by a factor of about one order of magnitude ($k_{4a} = 5.45 \times 10^{-3}$ s^{-1}). The rate closure constant of MC **5a** to closed form **5** in toluene (9.75×10^{-3} s^{-1}) is smaller than that of analogue **4a**. Compared to **4a**, MC **5a** reverts faster in THF ($k_{5a} = 2.96 \times 10^{-2}$ s^{-1}), remains approximately constant in DMF ($k_{5a} = 3.36 \times 10^{-2}$ s^{-1}), and only

Journal Name

ARTICLE

reverts appreciably more slowly in polar, protic 1-PrOH (Table 2). Clearly, the behaviour observed for compound **5a** is not due to the bulk of the mexylaminotriazine unit. An overview of the solvent-associated behaviour of **5a** as compared to parent chromophore **1a** is illustrated by Figure 3, where comparative plots of ring closure rate constants are plotted against the $E_T(30)$ polarity parameter.

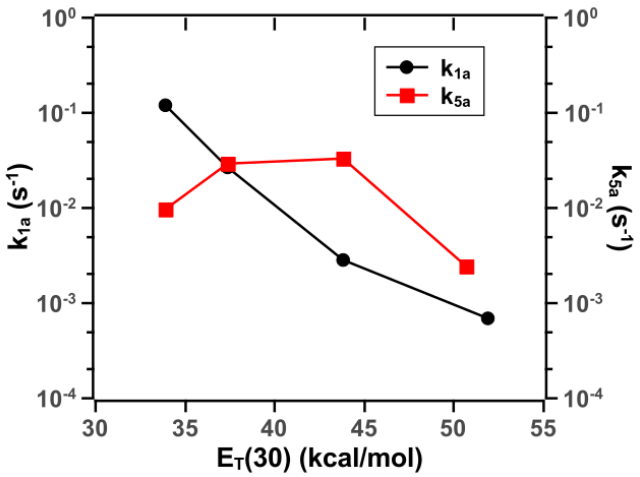
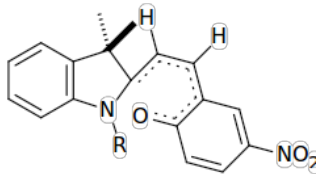


Figure 3. Logarithmic plots of ring closure rate constants for merocyanines **1a** and **5a**, k_{1a} and k_{5a}, as a function of $E_T(30)$. The y axes are plotted on a logarithmic scale.

We have previously argued[11] that whether the final step in the ring closure of a merocyanine to the spiropyran form occurs via an intramolecular electrocyclic process (TS*)[49,50] or is approximated by an anion-cation recombination reaction,[51-53] the rate-determining step in MC ring closure is not this final step but an earlier isomerization of the *trans* form of the MC to the *cis* form that places the aryloxyl oxygen in close proximity to the carbon atom that will become the spiro centre.[11]



TS*

The process of trans-cis MC rearrangement involves rotations about each of the C-C bonds linking the nitrophenoxyl moiety with the benzopyranyl group in any given MC, but most critically the central C-C bond.[11] In non-polar solvents, the quinoidal canonical form contributes more to the hybrid than does the zwitterionic form.[54] In the quinoidal form, the central C-C bond has a bond order of 1, whereas in the zwitterionic form the bond order is 2. Therefore, in non-polar solvents, the *trans-cis* MC rearrangement should require less energy, in that less is required to rotate about the central C-C bond that is closer in description to a single bond than a double bond. The same rearrangement should require more energy in polar solvents, where central bond order rises in the hybrid. Generally, this is true. However, for MC **5a**, the reversion rate constant in polar 1-PrOH (2.47×10^{-3} s^{-1}) is lower than in non-polar toluene (9.75×10^{-3} s^{-1}), though both are within the same order of magnitude. This suggests that as in our previous study,[11] in relatively low polarity solvents the rearrangement barrier is lowered by a higher weighting from the quinoidal resonance form to the overall hybrid and that in high polarity solvents the zwitterionic form dominates the description of the hybrid.

That k_{5a} is significantly lower in toluene than the corresponding ring closure constant for compound **4a**, k_{4a}, could arise from two factors. First, the steric bulk of the mexylaminotriazine attached to the indolino N of **5a** is similar to that of the cholesteryl ester of **4a**. In both **5a** and **4a**, the steric bulk of the N-indolino substituent hinders rotation about the bonds linking the aryloxyl group and the benzopyranyl group of the respective MCs, thereby raising the barrier to *trans-cis* isomerism. The reversion rate constant for **5a** in THF is still lower than that for **4a**, but with a narrower difference than in toluene. The toluene result can not be explained solely by steric bulk, and is believed to be caused by a second factor: hydrogen bonding.

Intramolecular H-bonding between any of the various H-bond donor sites in the mexylaminotriazine moiety to the quinoidal C-O function could act to stabilize the MC form, as shown in Figure 4a. Such hydrogen bonding is not possible with the cholesteryl moiety of compound **4a**.

Thus, rather than a significant difference in steric bulk associated with the mexylaminotriazinyl group as compared to the cholesteryl group, it is intramolecular hydrogen bonding in compound **5a** that further raises the rate-

Journal Name

ARTICLE

determining rearrangement barrier by stabilizing the *trans* MC in non-polar solvents.

In THF and DMF, the rate constants for the ring closure of **5a** remain almost constant (Table 2, Figure 3) although the properties of the solvent differ significantly from those of toluene (Table 1). Here a compensatory effect may operate. THF is more polar than toluene but less so than DMF. If the quinoidal form is dominant in the bonding description for **5a** in THF, as the results with **4a** suggest, then the rearrangement depends as in toluene on the steric bulk of the N-indolino substituent, which remains constant, and on intramolecular hydrogen bonding. However, THF is a much better H-bond acceptor solvent than toluene (β values are 0.55 for THF and only 0.11 for toluene), which results in THF competing with the MC moiety for hydrogen bonds (Figure 4b), leading to an increase in reversion rate relative to toluene.

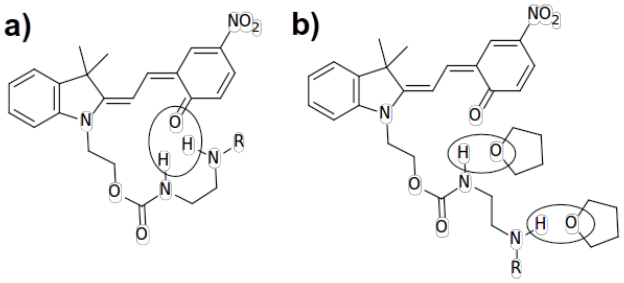


Figure 4. Proposed hydrogen bonding in MC **5a**. a) Hydrogen bonding stabilization between two H-bond donor sites on the mexylaminotrazine moiety with the aryloxyl portion of MC **5a**. b) THF competes with the MC aryloxy group for hydrogen bonding with the N-H groups. Hydrogen bonding interactions are highlighted in the ovals.

For DMF, such intramolecular hydrogen bonds would also be disrupted (β = 0.69 for DMF). However, in this case, as in the case of **4a**, the solvent is polar enough that the hybrid is now weighted in favour of the zwitterionic form and both steric and H-bonding factors are mitigated by the increase in the activation barrier for *trans-cis* isomerisation caused by the increased central C-C bond order in the hybrid.

In proceeding from DMF to 1-PrOH, the reversion rate constant declines in the normal solvatokinetic manner previously described.[10,47] Any intramolecular hydrogen bonding in 1-propanol would certainly be overwhelmed by stronger interactions with the solvent, since 1-PrOH is both a good H-bond donor (α = 0.84) and acceptor (β = 0.90) solvent.

Temperature dependence of ring closure kinetics

Measurement of k_{5a} values in the various solvents studied over temperatures ranging from -15 to 50 ºC led to Arrhenius plots of ln k as a function of 1/T (Figures S4-S7). From the slopes, the Arrhenius activation energies, E_a, were determined; the pre-exponential factor, A, was calculated from the ln A intercepts. The corresponding Eyring enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$) and Gibbs free energy ($\Delta G^{\ddagger}$) of activation were calculated from the Arrhenius parameters by standard methods.[11,56] These activation parameters are given in Table 3.

Table 3. Activation parameters for the cyclization of MC **5a** as a function of solvent..

Solvent	E_a, kJ/mol[a]	A, s^{-1} [a]	$\Delta H^{\ddagger}$, kJ/mol[b]	$\Delta s^{\ddagger}$, J mol^{-1} K^{-1} [c]	$\Delta G^{\ddagger}$, kJ/mol[d]
Toluene	77.6	$6.9x10^{11}$	75.1	-32.1	84.6
THF	92.7	$2.3x10^{14}$	90.2	28.3	81.8
DMF	100.6	$1.2x10^{15}$	98.1	56.0	81.4
1-PrOH	96.1	$9.8x10^{13}$	93.6	19.1	87.9

[a] Determined from slope and intercept, respectively, of linear Arrhenius plots, r^2 = 0.994-0.999

[b] Calculated from $\Delta H^{\ddagger} = E_a - RT$.

[c] Calculated from the equation given by Bunnett.[56]

[d] Calculated from $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\,\Delta S^{\ddagger}$.

Examination of Table 3 shows that while the ring closure in toluene occurs with a relatively low Arrhenius activation energy (77.6 kJ/mol) and corresponding low enthalpy of activation (75.1 kJ/mol), the Arrhenius pre-exponential factor is also low and this translates into a significantly unfavourable entropy of activation ($\Delta S^{\ddagger}$ = -32.1 J•mol^{-1} • K^{-1}). Based on the trends in the rate constants, we have argued (see above) that while the reversion of **5a** in toluene should be favoured by the enhanced contribution of the quinoidal resonance form to the hybrid both the steric bulk of the pendant mexyaminotriazinyl moiety and the presence of

Journal Name

ARTICLE

intramolecular hydrogen bonding would mitigate against this, with the most important factor in this case being hydrogen bonding. The unfavourable entropy of activation in this case supports this hypothesis.

In THF and DMF, the interplay of sterics with the reduced importance of hydrogen bonding combined with the progressively increasing weighting of the zwitterionic form to the hybrid leads to similar rate constants for the ring closure of the MC form in both solvents. Here, these energetic factors combine to give very similar Gibbs free energies of activation ($\Delta G^{\ddagger}$ (THF) = 81.8 kJ/mol; $\Delta G^{\ddagger}$(DMF) = 81.4 kJ/mol).

Reversion in 1-PrOH occurs with the lowest rate constant of the set. However, this result cannot be attributed to a much larger Arrhenius activation energy; it is close to that for ring closure in DMF. Similarly, the enthalpy of activation is close to the values measured in THF or DMF. Here again, the larger Gibbs free energy of activation ($\Delta G^{\ddagger}$ = 87.9 kJ/mol) results from a relatively small entropy of activation term. The transition state for reversion is "tighter" than that in the corresponding THF or DMF cases. This is presumably a manifestation of the major contribution to the hybrid of the zwitterionic form in this polar solvent, which raises the barrier to the rate-determining *trans-cis* isomerisation.

Conclusions

In the present work, a novel spiropyran-labelled molecular glass, SP-glass, **5**, was synthesized in one step and in 63 % yield from a 2-hydroxyethyl-subsituted SP derivative and a mexylaminotriazine functionalized with an amino group in the presence of CDI. The compound could be conveniently purified with a simple procedure. As with other previously reported mexylaminotriazine glasses bearing chromophores, compound **5** readily formed stable glassy phases and did not show any crystallization upon heating or standing. Compound **5**, as with other SP derivatives, undergoes reversible ring opening to MC **5a**.

By comparison to the ring closure of previously reported merocyanines of 6-nitroBIPs, MC **5a** does not show standard solvatokinetic behaviour. MC **5a** reverts more slowly to its SP form (**5**) in non-polar solvents such as toluene, which is caused by intramolecular hydrogen bonding, whereas in polar solvents, the rate of ring closure decreases with solvent polarity, presumably a consequence of the increasing weighting of the zwitterionic canonical form to the hybrid which increases the barrier for *trans-cis* isomerism (the rate-determining step in ring closure). The presence of hydrogen bonding groups on the remote mexylaminotriazine group can thus perturb the photochemical properties of the chromophore under certain conditions, though in the current case the outcome is desirable.

Future studies will focus on photochemical studies of SP **5** in the solid state, and development of an SP-labelled molecular glass in which intramolecular hydrogen bonding is restricted.

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