Organic & Biomolecular Chemistry

RSC Publishing

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c3ob41204k

Switchable polarity solvent (SPS) systems: probing solvatoswitching with a spiropyran (SP)–merocyanine (MC) photoswitch†

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Received 11th June 2013,
Accepted 23rd July 2013

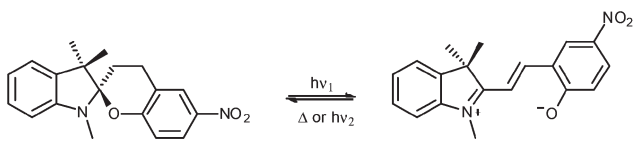
DOI: 10.1039/c3ob41204k

www.rsc.org/obc

The switchable polarity solvent (SPS) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and an alcohol (*e.g.* 1-propanol) reversibly switches to a higher polarity ionic liquid, [DBUH$^+$][RCO$_3^-$], when treated with CO_2. A long-lived species with unique properties was detected in an investigation into the use of SPS to control the lifetime of the merocyanine (MC) form in a spiropyran (SP)–MC molecular photoswitch. Irradiation of SP in 1-propanol (PrOH) in the presence of DBU generates a new species (λ_{max} = 420 nm). This species converts to MC upon bubbling with CO_2, which produces [DBUH$^+$][PrOCOO$^-$]. It is proposed that a mixture of 1,2 and 1,4 alkoxide addition products form as a result of nucleophilic attack on the conjugated diene system of MC, where alkoxide formation arises from equilibration of highly basic DBU and the alcohol. These adducts revert to MC upon application of CO_2 or addition of acid. Determination of the overall equilibrium constant for alkoxide adduct formation involving DBU was afforded through Benesi–Hildebrand analysis.

Introduction

Establishment of two (or more) stable molecular states, interconvertible upon application of mild stimuli without degradation of the material, is a key requirement of practical molecular switching.[1–5] Among our materials science research efforts we have been engaged in the study of spiropyran (SP)–merocyanine (MC) interconversion as a model photoswitch.[6–15] SP–MC photoswitching (Scheme 1) involves absorption of UV light (*ca.* 365 nm) by the ring-closed SP (λ_{sp} = 200–300 nm in solution) with a concomitant C–O bond scission and ring opening to the MC (λ_{MC} = 500–610 nm).[8] SP–MC photoswitch development has been hindered by the ready thermal reversion of the open MC form to the closed SP.



Scheme 1 Spiropyran–merocyanine photoswitch.

Solvent modification,[8] metal ion complexation to MC,[7,10–12] acidification,[14,15] and structural modulation of the SP[16] have all been explored as approaches to control reversion of MC to SP *i.e.* to extend the MC lifetime.

Our objective in the study described herein (and briefly described earlier[17]) was to use switchable solvents[18–20] to control the MC lifetime. The utility of these solvents has been recently reviewed.[21] Switchable polarity solvents (SPS), which were invented in our lab,[18] are solvents that can be made to switch polarity with a mild stimulus such as the introduction or removal of carbon dioxide. Consequently, these solvents have been found useful in reactions such as Heck couplings[22] and the polymerization of styrene in post-polymerization removal of catalyst from polymer[19] and for the extraction of oil from algae.[23] Further applications of these versatile media are wide ranging.[21]

Because we have previously shown that MC lifetime is enhanced in polar solvents,[8] we wondered whether our switchable solvents might allow better control of the MC lifetime. For example, the rate constant for MC→SP thermal reversion drops from 1.22×10^{-1} s^{-1} in less-polar toluene (π^* = 0.54[24]) to 2.85×10^{-3} s^{-1} in more polar dimethylformamide (DMF; π^* = 0.88[24]), *i.e.* $t_{1/2}$ increases from about 6 s in toluene to over 4 min in DMF. The Kamlet–Taft parameter, π^*, is a polarity/polarizability scale from 0 to 1 referenced to cyclohexane and dimethyl sulfoxide, respectively.[25] As an example of a SPS, an equimolar mixture of 1-propanol and DBU has medium

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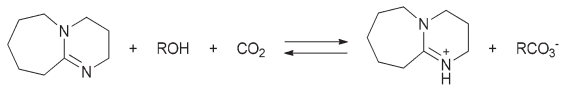
†Electronic supplementary information (ESI) available: Supplementary tables and figures. See DOI: 10.1039/c3ob41204k



Scheme 2 DBU/alcohol switchable polarity solvent.

polarity (π^* = 0.71[20]). Introduction of CO_2 (0.1 MPa; 1 atm) converts the liquid into a more polar liquid: an ionic liquid (π^* = 0.98[20]) having protonated DBU as the cation and propylcarbonate as the anion [$DBUH^+$][$PrCO_3^-$] (Scheme 2).[18]

The system acts as a polarity switch; removal of carbon dioxide *via* nitrogen purging restores the original DBU–PrOH medium with its lower polarity. In terms of π^*, the initial DBU–PrOH medium is found to be slightly less polar than DMF, but after CO_2 treatment the polarity approaches that of water. It was the aim of the current study to utilise this polarity switching to introduce a new level of control over the lifetime of the MC species. Therefore, enhanced merocyanine lifetime could arise from the solvatoswitching from lower to higher polarity media upon introduction of CO_2 to DBU–PrOH and comparable systems.

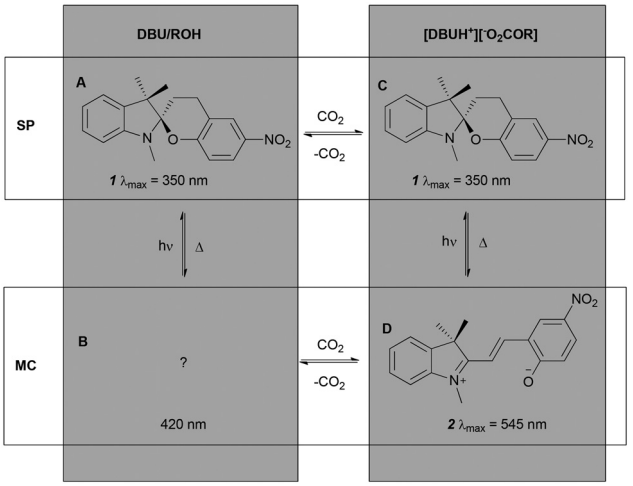
The present study sought to control the lifetime of the MC species, formed by irradiation of 1′,3′,3′,-trimethylspiro[2*H*-1-benzopyran-2,2-indoline] (6-nitroBIPS), with the use of switchable polarity solvents. However, an unexpected and stable product was observed when the photochromic switch was triggered in the switchable solvent,[17] as was also found by Darwish *et al.*[26–28] We now report further the interesting effects of SPS switching on SP–MC interconversion and the nature of the long-lived species formed in DBU–PrOH upon irradiation of the SP.

Results and discussion

Overview of solvatoswitching and photoswitching

Photoswitching in PrOH, without DBU present, is accomplished by irradiation at 365 nm, which causes the maximum absorbance (λ_{max}) of the spectrum to shift from 350 nm for SP **1** to a new position at 545 nm, attributed to MC **2**.

Scheme 3 depicts the four states in which this system exists. The UV-vis spectrum of **1** in a DBU–PrOH mixture (1 : 1 v/v or 0.01 : 1 v/v) was found to have a λ_{max} at 350 nm (A). Solvatoswitching to the [$DBUH^+$][$PrCO_3^-$] system did not affect the UV-vis spectrum of **1** (C). However, irradiation at 365 nm in DBU–PrOH caused a shift to 420 nm (B), as observed by Darwish *et al.*,[26] which did not revert to the 350 nm peak of **1** over the period of monitoring (more than one month). The UV-vis spectrum after the introduction of CO_2 to this system has the same λ_{max} (545 nm) as **2** in PrOH alone, and **2** reverts back to **1** at the same rate as it would in PrOH alone (D). After removing CO_2 from the system by bubbling N_2 with mild heating (60 °C), the irradiated system is observed to absorb primarily at 420 nm (B), with a small peak at 545 nm which decays quickly leaving only the absorbance at 420 nm.



Scheme 3 Schematic illustration of the SP–MC and SPS system interconversions. Processes are described in text.

The overlaid spectra shown in Fig. 1 depict the combination of photoswitching (**1** → **2**) and CO_2 controlled SPS switching displayed in Scheme 3. The initial spectrum in 1-propanol alone is that of SP **1** with its major band at 350 and no significant absorbance in the 450–650 nm region. Irradiation at 365 nm photogenerates MC **2** in PrOH with its dominant band at 545 nm; with addition of DBU the *ca.* 545 nm peak diminishes in intensity almost to baseline (Absorbance < 0.05) along with the appearance of the 420 nm species (B, Scheme 3). Bubbling with CO_2 triggers the solvent switch from DBU–PrOH to [$DBUH^+$][$PrCO_3^-$]. As shown in Fig. 1, the MC **2** spectrum is effectively restored. The presence of DBU in the system indefinitely delays the ring closure of the system back to **1** by the formation of the new species responsible for the 420 nm band.

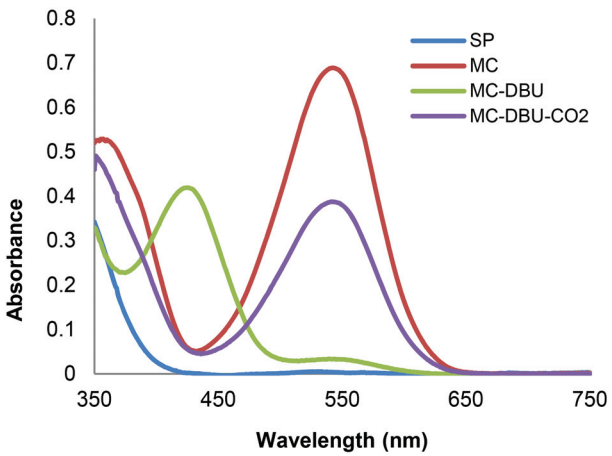


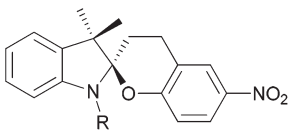
Fig. 1 SP, **1**, in PrOH medium prior to irradiation has no significant absorbance in 450–650 nm region (blue trace). Irradiation at 365 nm photogenerates the MC form (red trace, λ_{max} = 545 nm). Addition of DBU reduces the absorbance of the band for MC to <0.05 and generates the species that absorbs at 420 nm in this DBU–PrOH solvent mixture (green trace). Saturation with carbon dioxide (to switch to the $DBUH^+$ $PrOCOO^-$ medium) results in almost complete restoration of the band for MC, **2** (purple trace).

This meets, therefore, the criterion of enhanced stabilization of one of the bi-stable states needed in molecular switching.

Candidates for the 420 nm species

The crux of the foregoing interpretation based on Scheme 3 and illustrated by the spectra in Fig. 1 rests on the identification of the 420 nm species.

There are a number of candidates for the 420 nm species. In a study of a set of spiropyrans, **3**, in a series of room temperature ionic liquids (RTILs), Wu and coworkers[29] found that dissolution and irradiation of **3** in a family of *N*-alkyl-*N*′-methylimidazolium salts (where the alkyl group was $(CH_2)_3CH_3$ or $(CH_2)_2OH$ and the anions were typically alkylcarboxylates or alkyldicarboxylates) gave a UV-vis spectrum dominated by a 420–450 nm absorbance band with a small 350–360 nm peak for unmodified SP forms, **3**. Further irradiation caused no spectroscopic change. Here the 420–450 nm species was ascribed to the *cis*-form of the relevant MC, **4**, stabilized by electrostatic and hydrogen-bonding interactions with the RTIL including the carboxylate counterions. The 420–450 nm band was not observed upon dissolution of the SP **3** in RTILs having non-nucleophilic anions such as BF_4^-, PF_6^-.



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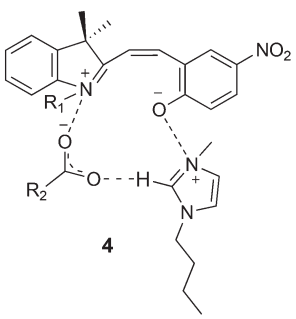
In contrast with these results[29] where the 420–450 nm species is formed upon dissolution of **1** in the carboxylate RTILs, **1** absorbs at 350 nm in $[DBUH^+][PrCO_3^-]$. Instead, the 420 nm species in our study forms upon irradiation of **1** in the low polarity DBU–PrOH medium or upon removing CO_2 from the $[DBUH^+][PrCO_3^-]$ containing **2**. Noting that our system does not reproduce the conditions found by Wu *et al.*, it appears unlikely that a *cis*-**2**: solvent complex comparable to **4** accounts for our observed 420 nm band. Furthermore, spectroscopic evidence in previous related work supports **2** as a more stable *trans* conformer rather than a *cis* form;[10] DFT computational studies also support the *trans* form of MC as the most stable MC conformer in general.[12]



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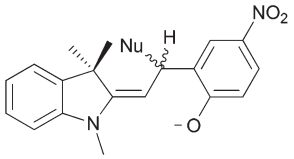
Clearly, DBU plays an essential role in these transformations, not just as a solvent system component.

DBU is well-recognised both as a base[30,31] and a nucleophile.[32] As a nucleophile, DBU could, in principle, attack the conjugated indolium moiety in a 1,2 fashion (across the Me–N^+=C– double bond) or in a 1,4 Michael mode involving the exocyclic double bond of **2**. Hence, the MC is considered an ambident electrophile.[32] On steric grounds alone, the 1,4 addition should be preferred and would give rise to **5** as a possibility for the 420 nm species.

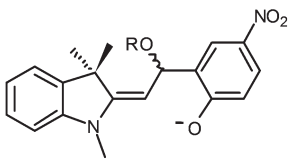


5 Nu=DBU

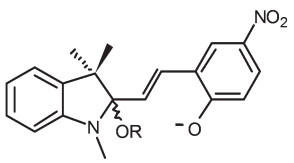
This species would derive resonance stability through delocalisation of the negative charge over the nitrophenoxide ring as well as delocalization of the positive charge inside the DBU group. A large hypsochromic shift from 545 nm of **2** to give the observed 420 nm λ_{max} is concordant with adduct **5**, which has curtailed conjugation compared to MC **2**.

Further support for assignment of structure **5** as the 420 nm species is afforded by the study of Baidya and Mayr into the nucleophilicity of DBU among other bicyclic amidines.[32] DBU was assigned a Mayr nucleophilicity value, *N*, of 15.29, making it a relatively strong nucleophile. More to the point, with a set of seven Michael acceptors DBU added in the 1,4 manner, requisite for the formation of adduct **5**.

Alternative MC adducts could result from DBU acting preferentially as a base rather than as a nucleophile. In this case, alkoxide, RO^-, would be produced by equilibration of DBU and the alcoholic co-solvent. The position of the equilibrium depends on the pK_a of the relevant ROH. In turn, the efficacy of trapping free MC as an adduct (*e.g.* **6a**) *via* nucleophilic addition (1,4) is tied to the concentration of alkoxide present.



6a

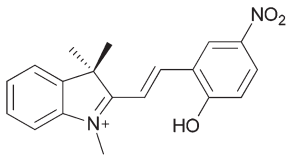


6b

As a nucleophile that is not as sterically hindered as DBU, RO^- could add either 1,4 (to give **6a**) or 1,2 (to give **6b**). These possibilities will be discussed further below.

Acidification of 420 nm species

Addition of trifluoroacetic acid (TFA) to the solution containing the 420 nm species and free MC leads to significant spectroscopic changes (Fig. 2). First, the 420 nm peak declines as the intensity of the 545 nm band of free MC **2** rises. The spectrum is more complex, however, as a result of overlap of bands in the 360–280 nm region.



2-H$^+$

As a control experiment, SP **1** was irradiated with 365 nm light in pure EtOH to give free MC **2**. Upon TFA acidification free **2** was protonated to give **2**-**H**$^+$, *i.e.*, the MC form protonated on the phenoxyl oxygen which has been previously observed.[14]

Comparison of the spectra from the control experiment and those of Fig. 2 show that when TFA is added to the DBU–EtOH system containing the 420 nm species and free **2** results in partial reversion of the 420 nm species to **2** but also protonation of some of the free MC to give **2**-**H**$^+$.[13–15]

Extension to other bases

The behaviour of MC **2** in a number of base–PrOH mixtures provide support for the structural assignment of the propoxide adducts, **6a**/**b**, and rules out an N-centred adduct comparable to the DBU addition product, **5**. Injection of 1,1,3,3-tetramethylguanidine (TMG) into a cuvette containing a 5×10^{-5} M PrOH solution of **1** (0.01 : 1 v/v), which was irradiated for 90 s to form MC **2**, results in almost complete disappearance of the 545 nm band for **2** with immediate formation of the 420 nm species (ESI, Fig. S1†). Over time the small peak for free **2** continues to decline in intensity in favour of the 420 nm peak.

With *N*-*tert*-butyl-*N*′,*N*′-dimethylformamidine (BDF; 0.01 : 1 v/v) the intensity of the 545 nm band for **2** is not suppressed to the same extent as in the TMG–PrOH or DBU–PrOH and the 420 nm peak recorded shortly after mixing is also not as intense (ESI, Fig. S2†).

The fact that both amidines and guanidines result in formation of the 420 nm band suggests a common species, the propoxide addition products **6a**/**b** proposed above. It is apparent that **2** can be intercepted by PrO$^-$ to form **6a**/**b**, effectively locking up **2** and preventing its re-cyclization to **1**.

A useful comparison to the foregoing results with the amidines is provided by the amines pyridine and *N*-ethylbutylamine (ESI, Fig. S3 and S4†). The 420 nm band is not present in the UV-vis spectrum when either *N*-ethylbutylamine or pyridine are added to a solution containing **2** in propanol. If the 420 nm band could be assigned to a N-centred adduct comparable to **5** from DBU and **2**, then one would expect to observe it in the presence of less sterically hindered bases as well. The absence of the 420 nm species here argues against such an amine addition product as the identity for the 420 nm species.

The two sets, the amidines on one hand, and pyridine and *N*-ethylbutylamine on the other, have distinctly different basicity ranges. In acetonitrile, DBU has been reported to have a pK_{aH} value of 23.0 ± 0.1,[30] 24.13,[33] and 23.93[34] while TMG is similarly basic in acetonitrile with a pK_{aH} reported as 23.3.[35] BDF would be expected to have a similar basicity.[36] The other amines are notably weaker bases. For pyridine, the pK_{aH} in acetonitrile is 12.13–12.33.[34,37] Although the corresponding pK_{aH} value for *N*-ethylbutylamine in acetonitrile has not been reported, Coetzee and Padmanabhan[37] have determined the comparable pK_{aH} value for diethylamine (18.75) and di-*n*-butylamine (18.31) and it is reasonable to suggest that *N*-ethylbutylamine would have a pK_{aH} value falling within this range. Thus, the amidines are significantly more basic (pK_a 24–23) than pyridine and *N*-ethylbutylamine (12.3–18.8). While the current

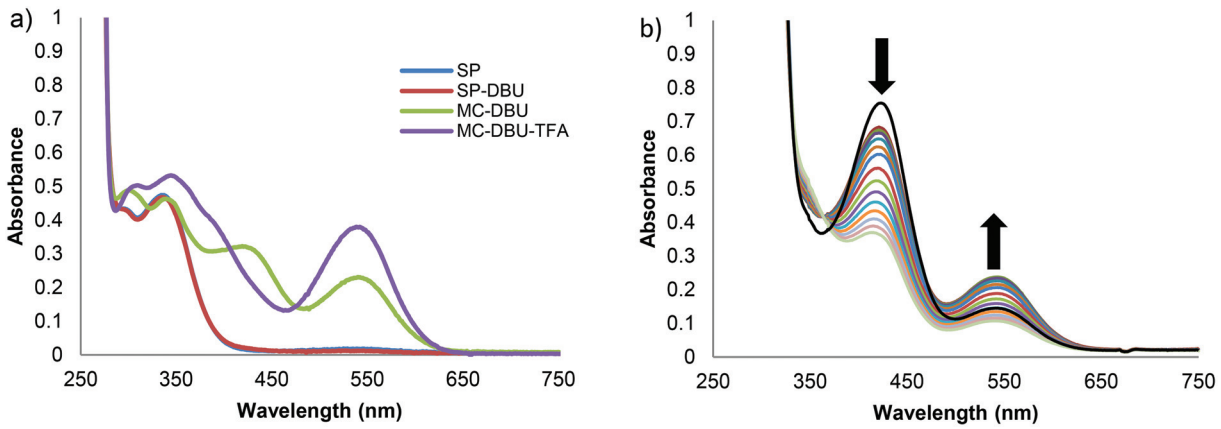


Fig. 2 (a) Control experiment: SP in EtOH prior to irradiation (light blue trace). The spectrum of SP does not change with the introduction of DBU into the system (red trace). Irradiation gives both free MC at 545 nm and the species that absorbs at *ca.* 420 nm (green trace). Addition of trifluoroacetic acid (TFA) results in an increase in intensity (concentration) of MC **2** with concomitant decline (and wavelength shift) for the species at about 420 nm in this medium. The 280–360 nm region reflects a combination of absorbances for free **2** and protonated MC, *i.e.* **2**-**H**$^+$. (b) Overlay spectrum of the change over time of the SP–MC–DBU spectrum after the addition of TFA.

data precludes a definitive demarcation line it is clear that very strong neutral bases are required to yield significant concentrations of propoxide (or alkoxide generally) leading to adduct formation with **2** (or related MC).

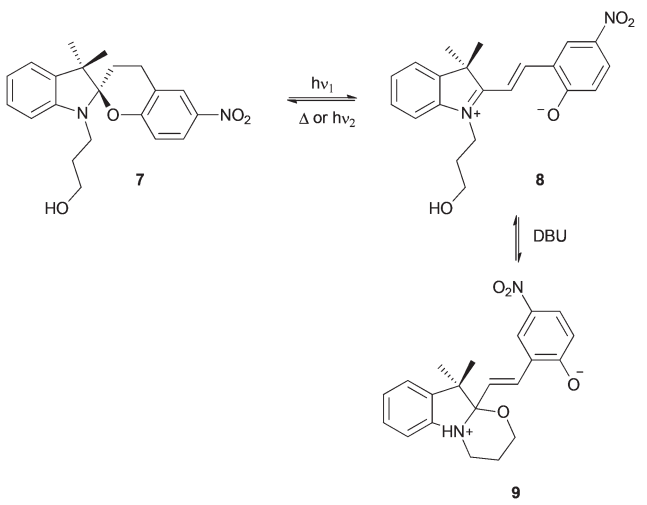
Identification of the 420 nm species

The work by Darwish *et al.* with spiropyrans in DBU–MeOH resulted in a species that absorbed at 432 nm, comparable to the 420 nm species observed in the current work; the 432 nm species formed upon irradiation of a spiropyran related to **1** in DBU–MeOH.[26] ^{1}H NMR spectra of the system (DBU–MeOH-d_4) were complex and could not be assigned definitively. However, in the Darwish work the 432 nm peak was attributed to the methoxide adduct comparable to **6b**, the product of 1,2 addition to the indolium MeN^+=C–bond.

Among the evidence in support of this assignment of the 432 nm species,[26] the Darwish group prepared the SP, **7**, that photoisomerises upon irradiation to the merocyanine **8** (530 nm in MeOH). Addition of equimolar (or greater concentration) DBU gave a 413 nm band comparable to the 432 nm peak observed in the original system by Darwish *et al.* Deprotonation of the OH of the pendant *N*-3-hydroxypropyl group of **8** accompanied by 1,2 addition to the indolium moiety gave the cyclic adduct, **9** (413 nm). As in our system, addition of CO_2 restored the free MC form (530 nm band for compound **8** in methanol) in the case of the system studied by the Darwish group (Scheme 4).[26]

The regiochemistry in formation of the 1,2 adduct **9** from **8** in the presence of DBU–MeOH is controlled by the length of the pendant N-$(CH_2)_n$OH group. In this regard, the 4-position is difficult to access by the relatively short *N*-propyl alkoxide formed from the MC, **8**, and would yield a less stable eight-member ring adduct if formed.

In our system with MC, **2**, in DBU–ROH either 1,2 or 1,4 addition could occur. It is pertinent that Shiraishi and coworkers have reported the use of SP **1** as a sensitive, selective and reversible cyanide receptor in aqueous media.[38] Hence, UV irradiation (334 nm) of **1** generates the merocyanine **2** that is efficiently trapped by CN^- as a 1,2 adduct (421 nm). Calculations support the assignment of the UV-vis spectrum as the 1,2 adduct in this case,[38] as do ^{1}H NMR spectra, determined in acetonitrile-d_3 solvent, that will be considered further below.



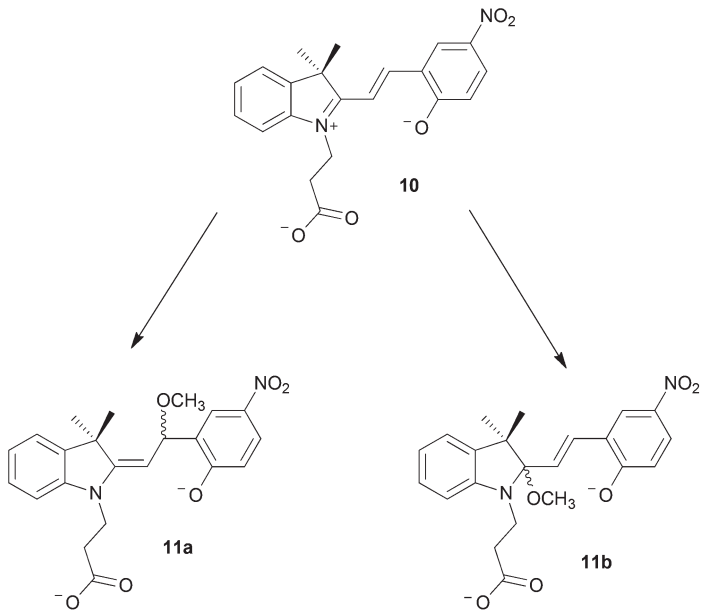
Scheme 4 SP–MC photoswitch modified with an *N*-3-hydroxypropyl group (**7**/**8**). Addition of DBU causes deprotonation of the hydroxy group causing a cyclic adduct to form (**9**).

At this stage there are two competitive candidates for the 420 nm species found in our study, formed upon irradiation of **1** in the presence of DBU–ROH: (a) a DBU adduct—likely on steric grounds to be a 1,4 adduct, **5**, from addition of DBU to the 4-position of the open MC, **2**, or, (b) 1,4- and/or 1,2-alkoxide adduct(s), **6a** and/or **6b**, respectively, formed by the conjugate base of the alcohol component of the relevant DBU–ROH medium. Both could revert to the original open form **2** upon addition of carbon dioxide to the system.

Saturation of the medium with carbon dioxide would both remove DBU from the system by converting it to its conjugate acid, $DBUH^+$, *and* remove alkoxide and ROH through addition of these to carbon dioxide to yield $ROCOO^-$, the other component of the RTIL medium. The decrease in concentration of free DBU from the equilibrium between DBU and **2** and the DBU addition product, **5**, would lead to dissociation of the adduct back to DBU and **2**. Hence saturation of the DBU–ROH system containing **5** with CO_2 should regenerate the spectrum of the MC **2** and this is observed. However, if the adducts are alkoxide addition products, **6a** and/or **6b**, CO_2 saturation would give $DBUH^+$ that could protonate the RO moiety and convert it into a good leaving group, ROH. Alternatively, removal of alkoxide from the system *via* addition to carbon dioxide would again shift the equilibrium back to free MC, **2**. Effectively CO_2 saturation of the DBU–PrOH medium is a mechanism of formation of acid, $DBUH^+$, that causes reversion of the adduct(s) to free MC.

Similarly, the TFA experiments show that the 420 nm peak declines and the 545 nm band of **2** increases in intensity with added acid. Again, protonation of the DBU group of **5**, or of the RO function(s) of **6a**/**b** converts these into good leaving groups and the corresponding complexes would be expected to dissociate to give free MC, as observed. These control experiments do not differentiate between the two possibilities.

In a study of an *N*-ethyl carboxylic acid analog of **1**, irradiation in the presence of excess $NaOCH_3$ gave the deprotonated form of the MC, *i.e.* **10**, and both 1,4 and 1,2 methoxide adducts, **11a**, **b** (Scheme 5).[39] ^{1}H NMR spectra confirmed the structures shown. Simulated spectra (ChemDraw) are in major agreement with the recorded spectra; some peaks of **11a**, **b** are not present as a result of H/D exchange or are buried under similar signals, *e.g.* OCH_3 of **11a**, **b** addition products and the CH_3O^-/CH_3OH of the reagent, present in excess[39] (see ESI, Tables S1 and S2†). Comparison with spectra of the 1,2 cyanide adduct reported by Shiraishi *et al.*[38] and the 1,2 methoxide adduct here are also in reasonable agreement, within the differences imposed by the different nucleophiles.



Scheme 5 *N*-Ethyl carboxylic acid analog of MC (**10**) and the two adducts observed after the addition of NaOMe (**11a/b**).

The results found with the MC **10**, as well as the results reported by the Darwish group,[26–28] argue in favour of the 420 nm species being assigned to an alkoxide adduct or adducts, **6a/b**. More recently, Darwish and coworkers have reported that when a spirooxazine, structurally analogous to **1**, is irradiated to photogenerate the merooxazine in DBU–toluene the merooxazine forms cleanly[27] without the appearance of spectroscopic bands comparable to the 420 nm absorbance of the present work.

Other evidence that argues against formation of a DBU-adduct, **5a**, comes from the report of Muthyala *et al.*[40] who prepared an ionic liquid of the *N*-methylimidazolium type substituted with a 1,5,7-triazabicyclo[4.4.0]decen-5-ene (TBD) moiety, which would be expected to have basicity and nucleophilicity comparable to DBU. When a wide-range of substituted chalcones were added to a solution of this RTIL containing an acidic carbon acid, such as malononitrile, the carbanion generated by equilibration of the TBD component of the RTIL with the active methylene compound added to the chalcones in Michael fashion. No addition of the TBD moiety (similar to the 1,2 and/or 1,4 propoxide adducts, **6a/b**) is reported.[40]

A further issue is whether a single alkoxide adduct is formed or both 1,2 and 1,4 adducts form. The evidence from the study of the merocyanine **10** suggests that both 1,2 and 1,4 adducts could be expected to form in the present DBU–ROH systems.[39] In fact, with the model ambident electrophile methyl vinyl ketone (3-buten-2-one) cyanide addition in the 1,2 manner is known to be kinetically controlled while 1,4 addition is thermodynamically controlled.[41,42] As pointed out by Mayr, Breugst and Ofial,[43] 1,4 additions are essentially additions to a C=C and are, generally, more exergonic than the corresponding 1,2 additions to C=O. Another way to frame this is that 1,4 addition results in an adduct in which the double bond is more highly substituted by groups other than hydrogen; the 1,2 adduct contains a double bond that is not so highly substituted. The 1,4 adduct presumably is the more stable by analogy to common alkene systems. The structural reorganisation inherent in 1,4 addition, however, raises the activation barrier for this mode of reaction and makes the process kinetically disfavoured. Drawing the analogy to the merocyanine systems, then, the cyanide adduct characterised by Shiraishi *et al.*[38] is likely also a kinetic product. With alkoxides and by appeal to the results concerning **10** it seems likely that both adducts are formed in the current case, *i.e.* **6a/b**. The distribution of the two regioisomers could change depending on the steric bulk of the alkoxide nucleophile.

A final point should be made concerning the UV-vis spectrum. The 420 nm band in DBU–PrOH does not change over time (>1 month observation). If the 1,2 adduct gives way to the more stable 1,4 adduct over time then the spectrum of both adducts must be virtually identical, since no change in the spectrum over this time can be detected.

On the basis of this assignment of the 420 nm UV-vis band in our system to a mixture of the two alkoxide addition products, a Benesi–Hildebrand analysis[44] was used, as discussed next.

Benesi–Hildebrand analysis of alkoxide adduct formation from MC, 2

A series of spectra were recorded, starting with pure PrOH solvent and **2** formed by irradiation of **1** (Fig. 3). Successively increasing concentrations of DBU were introduced and each spectrum was determined for the system that now consisted of DBU and **2** in 1-propanol. Ratios of concentrations of DBU : **2** ranged from 5 : 1 to 150 : 1. The sequence of spectra (Fig. 3) display the progressive decline in the 545 nm peak for **2** accompanied by the appearance and step-wise growth in the

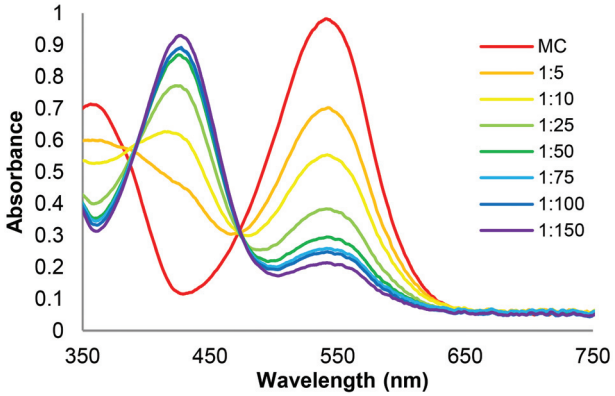


Fig. 3 Series of UV-vis spectra commencing with MC (from irradiation of SP) in pure PrOH (red spectrum), overlaid by spectra with increasing concentration ratios of **2** : DBU (*e.g.* 1 : 5 orange spectrum and 1 : 100 indigo spectrum). Note that as the ratio of DBU increases the peak at 545 nm for free MC declines in intensity as that at 420 nm increases correspondingly. These absorbance and concentration data were used to construct the Benesi–Hildebrand plot (eqn (5) and figure).

band at 420 nm assigned to the 1,2 and 1,4 alkoxide addition products, **6a/b**. From the absorbances for MC **2** at 545 nm and the concentrations of **2** and DBU a Benesi–Hildebrand plot[44] was constructed as per eqn (1):

$$\frac{[\mathrm{MC}]_0}{A_{420}} = \frac{1}{K\varepsilon_{420}} \times \frac{1}{[\mathrm{DBU}]_0} + \frac{1}{\varepsilon_{420}} \quad (1)$$

where A_{420} is the 420 nm absorbance of **2**, K represents the overall equilibrium constant for formation of the adducts **6a/b**, and ε_{420} corresponds to the molar absorptivity of the addition product(s) band at 420 nm.

The resulting Benesi–Hildebrand plot is shown in Fig. 4 and, as can be seen, shows excellent linearity (R^2 = 0.999). The equilibrium constant, K, determined this way has a value of 4.1×10^3 M^{-1} with a molar absorptivity for the alkoxide adducts of 1.8×10^4 M^{-1} cm^{-1}.

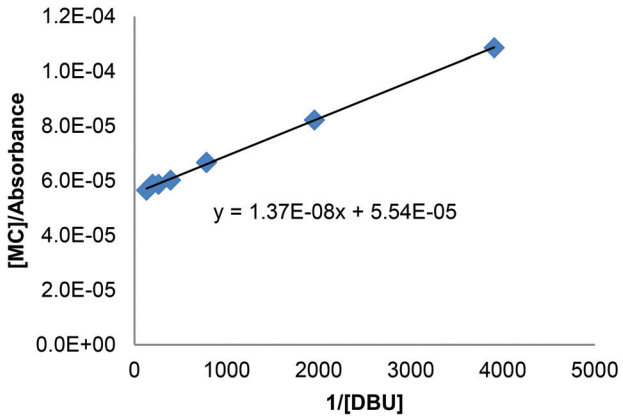


Fig. 4 Benesi–Hildebrand plot constructed using the data shown in figure. The equilibrium constant determined from the plot is $K = 4.1 \times 10^3$ M^{-1} and the molar absorptivity of the peak at 420 nm is 1.8×10^4 M^{-1} cm^{-1}.

Clearly, the equilibrium constant, K, determined here represents formation of the alkoxide addition products, **6a/b** *as a function of DBU concentration*. It is plausible that the constant K arises from two coupled equilibria. The first generates alkoxide (PrO^- in the current case) *via* equilibration of PrOH with DBU:

$$\mathrm{DBU} + \mathrm{PrOH} \overset{K_1}{\rightleftharpoons} \mathrm{DBUH}^+ + \mathrm{PrO}^- \quad (2)$$

In the second equilibrium, PrO^- adds reversibly to MC **2** to give the mixture of 1,2 and 1,4 adducts, **6a/b**:

$$\mathrm{PrO}^- + \mathrm{MC} \overset{K_2}{\rightleftharpoons} \mathbf{6a/b} \quad (3)$$

Therefore, K, the equilibrium constant measured *via* the Benesi–Hildebrand treatment, is an overall equilibrium constant as given in eqn (4):

$$\mathrm{DBU} + \mathrm{PrOH} + \mathrm{MC} \overset{K}{\rightleftharpoons} \mathrm{DBUH}^+ + \mathbf{6a/b} \quad (4)$$

Eqn (4) is equal to the product of K_1 and K_2, *i.e.*, $K = K_1 \times K_2$. Note, as well, that the adducts **6a/b** bear an overall negative charge relative to the starting MC, **2**, and eqn (4) is charge balanced.

Examination of K_1 shows that it may be estimated from the acid dissociation constants, K_a, for 1-propanol (K_a-PrOH) and for the conjugate acid of DBU (K_a-$DBUH^+$):

$$K_1 = \frac{K_a\mathrm{PrOH}}{K_a\mathrm{DBUH}^+} \quad (5)$$

The pK_a for $DBUH^+$ has been measured by Leffek and coworkers,[30] who assigned a value of 23.9 ± 0.1 in acetonitrile solvent. This value is in good agreement with that more recently determined in the same solvent by the Koppel group.[34] The Leffek group, through a correlation between the pK_a values in acetonitrile with those in water for a series of guanidines and amidines, calculated a value for DBU in water: 14.3.[30] If the pK_a value for 1-propanol, anchored to water as the standard state, is taken to be approximately 16, in line with other common low molar mass alcohols,[45] then K_1 could be estimated to be about 10^{-2}, *i.e.*, K_1 = K_a-PrOH/K_a-$DBUH^+$ = $10^{-16}/10^{-14} = 10^{-2}$. It follows that K_2, the equilibrium constant associated with propoxide attack on **2** to give the 1,2 and 1,4 addition products, has an approximate value of 10^5 M^{-1}, *i.e.* $K/K_1 = K_2$. The second addition step in the overall process is very favourable and accounts for the ready formation of the adducts in the DBU–PrOH system upon photogeneration of **2** in this medium.

This is in accord with the experimental results where irradiation of SP **1** gives the 420 nm species as the only band in the DBU–PrOH system. The free MC **2** that was anticipated to be formed was not seen. *Instead,* **2** *is efficiently trapped as the thermodynamically more stable propoxide adducts,* **6a/b**. It has been thus shown that the lifetime of the merocyanine form **2** is extended at will.

Conclusions

The current study probing SPS using the SP–MC molecular photoswitch has highlighted the following conclusions:

1. A long-lived species (420 nm) is formed in lower polarity DBU–PrOH upon irradiation of SP, **1**.

2. The 420 nm species is proposed to comprise a mixture of 1,2 and 1,4 alkoxide adducts formed by reversible addition to the conjugated diene system of MC, **2**.

3. The adducts revert to free MC, **2**, when the SPS switches to higher polarity, $DBUH^+/PrOCOO^-$ upon application of CO_2.

4. UV irradiation (365 nm) of SP, **1**, in the room temperature ionic liquid-like $DBUH^+/PrOCOO^-$ medium gives MC **2** in photoswitching which metamorphoses into the adducts at 420 nm upon discharge of CO_2 by N_2 purging. Thus, MC **2** may be indefinitely locked up in the form of the long-lived adducts and MC lifetime thereby extended at will.

5. Thus, the present work combines two distinct areas of switching: SPS[18,19] and molecular photoswitching with the SP–MC system.[1–16]

Experimental

Materials and instrumentation

DBU (Aldrich 98%) was refluxed over CaH_2, distilled *in vacuo*, bubbled with CO_2 for 1 h, filtered to remove the resulting bicarbonate salt and stored in a solvent bomb under N_2. 1-Propanol (PrOH; Aldrich) was stored over 4 Å molecular sieves. Trifluoroacetic acid (TFA; Aldrich) was used as purchased. Other common solvents and bases were obtained commercially and used without further purification. Supercritical CO_2 (99.999%, <0.5 ppm H_2O) and N_2 (99.998%, <3 ppm H_2O) were used as received from Praxair. DBU–PrOH (1 : 1 v/v) was prepared in a nitrogen atmosphere glove box from the appropriate volumes of the components in a volumetric flask that was then septum-sealed; the medium had a viscosity of 5.5 cP. The spiropyran (**1**, 6-nitroBIPs = 6′-nitro-1,3,3-trimethylspiro(indolino-2,2′benzopyran) was prepared by condensation of 2-methylene-1,3,3-trimethylindoline (Aldrich) with 2-hydroxy-5-nitrobenzaldehyde (Aldrich), according to literature methods;[6,46] after recrystallization from isopropanol (70% yield), spectroscopic and other physical properties were in good agreement with literature.[47] NMR spectra of samples of **1** dissolved in $(CD_3)_2SO$ were recorded using a Bruker-Avance 400 spectrometer (400.0 mHz, ^1H; 100.0 mHz, ^{13}C).

UV-vis spectra (scans and single wavelength) were recorded using a HP 8542 photodiode array spectrophotometer, thermostatted to 25 °C (±0.5 °C). UV-vis irradiation of samples was performed in a Spectroline CX Series ultraviolet fluorescence analysis cabinet, equipped with a Spectroline XX-15N UV lamp (dual 15 W, 365 nm) and the sample was irradiated for 90 s.

Solvent switching UV-vis experiments

General spectrophotometric method. Stock solutions of SP (5×10^{-3} M) were prepared in toluene in 5 mL volumetric flasks. Samples were prepared using 2.5 mL of the desired solvent (*e.g.* 1-propanol) added to the quartz cuvette using a 2.5 mL syringe, followed by addition of 25 μL of the SP stock solution using a 25 μL microsyringe. Samples were irradiated for 90 s at 365 nm. For studying the effects of DBU or another base, 25 μL of the base was added to the cuvette, unless otherwise specified. Spectra were recorded for a period of 3.5 h to obtain kinetic data.

DBU–PrOH (1 : 1), SP. To a quartz cuvette that contained 2.5 mL of DBU–PrOH (1 : 1 v/v), 25.0 μL of a 0.005 M solution of SP, **1**, in toluene (stock solution) was injected (final concentration in the cell: 5.00×10^{-5} M). The spectrum was scanned and recorded (350 or 275 nm to 700 nm).

DBU/PrOH with 1 irradiated to give 2. The above-mentioned cuvette was then placed in the UV-vis/fluorescence cabinet and irradiated at 365 nm for 20 min, at which point it was returned to the spectrophotometer cell compartment and a spectrum of the resulting yellow solution (λ_{max} = 420 nm) was obtained.

DBU–PrOH with 1 → $DBUH^+/PrOCOO^-$. The same cuvette was then bubbled with carbon dioxide (2 bubbles per s) for 1 h *via* a narrow gauge stainless steel needle and the cell was then returned to the spectrophotometer. Bubbling this solution with CO_2 regenerated MC, **2**, as shown by the UV-vis spectrum.

DBU–PrOH with 1 irradiated then treated with TFA. Two experiments were conducted to determine whether TFA would disrupt the MC–DBU system. First, a cuvette was prepared as stated previously of 5×10^{-5} M SP in ethanol and the spectrum was acquired. An equal molar amount of DBU was added and new spectra were acquired both before and after irradiation. An equal molar amount of TFA was then added and the subsequent spectrum acquired.

To show the changes over time, overlay spectra were acquired over a period of 88 min. Two stock solutions were prepared; a stock solution of 0.1 M DBU was prepared in propanol, and one of 0.1 M TFA was prepared in toluene. A cuvette was prepared of 5×10^{-5} M SP in propanol with 25 μL of the DBU stock solution. The sample was irradiated and the spectrum was acquired, after which 25 μL of the TFA stock solution was introduced into the sample and the spectrum was recorded as shown in Fig. 2.

Benesi–Hildebrand experiments

A series of spectra were recorded (separate cuvettes) starting with SP, **1** (5.00×10^{-5} M final concentration) in pure PrOH. Generally, after mixing, the sample was irradiated at 365 nm for 90 s and the spectrum of MC and the 420 nm species (if present) then recorded. Solvent media were prepared by mixing appropriate volumes of SP-containing PrOH and DBU such that the following ratios of **2** (=SP initial) : DBU were obtained: 1 : 5, 1 : 10, 1 : 25, 1 : 50, 1 : 75, 1 : 100 and 1 : 150. Each sample was scanned from 350 to 750 nm. These spectra are compiled sequentially in Fig. 4. Data from Fig. 3 (*i.e.* absorbance for MC, **2**, at 545 nm) were used to construct the Benesi–Hildebrand graph (Fig. 4) according to eqn (1).

Acknowledgements

The authors gratefully acknowledge funding from NSERC (EB, PJ), The Canada Research Chairs Program (PJ), Xerox Research Centre Canada (EB, PJ), Grenfell Campus Vice President's Research Fund (JD), Walter C. Sumner Foundation (AB).

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