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# Spiropyran, chromene and spirooxazine, mélange á trois: Molecular logic systems through selective and reversible deactivation of photochromism mediated by $CO_2$ gas

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ABSTRACT

We report a new expanded molecular logic system based upon combinations of spiropyrans, spirooxazines and chromenes, whereby the photochromism of some molecules can be selectively preserved while reversibly deactivating the photochromism of others. The non-photochromic molecules can be reversibly activated by $CO_2$ gas. It was found that the photochromic effect of spiropyrans, in general, and one spirooxazine (with a hydroxyl group on the naphtho-ring) could be reversibly deactivated by DBU, while a chromene and an unsubstituted spirooxazine remained photochromic in the system under the same conditions. The presence of protic solvent was necessary for the deactivation of some of these photochromic molecules and hence it was used as an additional sensitizer in the system. This afforded the expansion of stimuli for molecular logic operations and allowed combinations of the benign stimuli of UV, visible light, $CO_2$, and $CO_2$ depleted with protic and aprotic solvents. This effect provided the mechanism for molecular logic systems that do not suffer from the usual problems of dilution effects and hence become truly reversible. This is highly significant when designing molecular switches to perform logic operations.



## 1. Introduction

The search for molecules that switch between two or more states in response to multiple or independently addressable inputs or stimuli are of great interest [1–11]. This effect is important to researchers in the field of information technology; where molecules perform logic operations and are used in applications such as memory storage, switches and sensors [12–23]. In this respect, organic photochromes such as spiropyran, spirooxazine and chromene are finding widespread use. These photochromes (as photoswitching systems) are attracting attention because of their technological potentials in the field of photonic devices, where each isomer of the photochromic compound can represent "0" or "1" of a digital binary code [24,25]. The spiro form (SP) has an absorption band in the ultraviolet range 200–370 nm. Irradiation in this range, initiates reversible photoisomerisation and forms the coloured merocyanine form (MC), which has strong visible absorption bands in the range of 370–600 nm. The deep colour of this form is due to the extended conjugated system established between the two parts of the molecule [26–28], which can be protonated by acid to give yellow coloured solutions ($\lambda_{max}$ ~400 nm) [29]. This substantial colour change is due to the unavailability of the oxygen lone pair electrons that contribute to the conjugation. Neutralizing the acidic yellow solution with a base regenerates the red merocyanine form (MC) at the neutralization point [29]. However, when the base is added beyond the neutralization point, a yellow non-photochromic solution can be produced which leads to the loss of reversibility of the system (Fig. 1). Bleached yellow solutions have been reported when a base was directly added to MC forms of some spiropyrans [30]. This is likely to be due to the addition of the nucleophilic base to the reactive indolium fragment in the MC form of the molecule (Fig. 1). The iminium carbon atom adjacent to the positively charged nitrogen in the indolium fragment of the zwitterionic MC species (formerly the spiro-carbon) is highly electrophilic and susceptible to nucleophilic attack. Shiraishi et al. [31] and Tian et al. [32] recently reported the nucleophilic addition of $CN^-$ anion to the iminium carbon of the indolium fragment of the MC form of **SP-NO$_2$** and of fused indoline-benzooxazine fragment, respectively.

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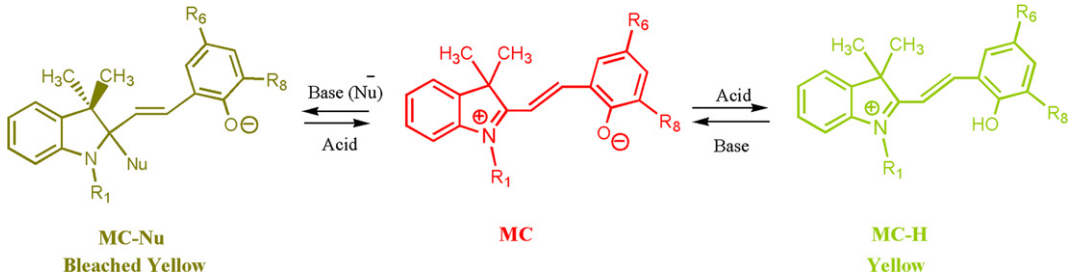



**Fig. 1.** Acid–base reactions of spiropyrans and the nucleophilic addition of a nucleophile ($Nu^-$) at the iminium carbon centre producing a bleached yellow colour solution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In a recent report we have demonstrated a new generic method of reversibly controlling the photochromism of spiropyrans [33]. Amidine (i.e., DBU) added to an alcohol solution of spiropyran molecule caused colour change with addition and removal of $CO_2$ and more importantly, reversibly switched the spiropyran's photochromism on and off. Spiropyran in an alcohol/DBU solution produced a yellow non-photochromic spiropyran–DBU complex. To re-establish the photochromism, $CO_2$ was purged into the solution. The non-photochromic solution can be regenerated by removing the $CO_2$ from solution by using $N_2$ sparging. It was evident that $CO_2$/DBU mixture in methanol is not acidic enough (pH = 6.8) to protonate the phenolate oxygen and thus the MC species was present in solution and did not proceed to the MC–H species (Fig. 2). In fact, upon drop-wise addition of 1 M HCl to the above $CO_2$/DBU methanol solution, the colour changed from purple to bright yellow (pH = 3) with the appearance of a new absorption band at 346 nm (broad) (Fig. 2) (in web version).

A variety of molecule-based logic switches (AND gates, OR gates, etc.) have been reported [21,34–49]. In the vast majority of cases, at least one of the gate inputs requires the physical addition of a chemical species, which often impact the reversibility and applicability of the system due to the induced dilution and fatigue effects. Hence, the development of systems that can switch between many coloured states by using benign triggers which can be easily added and removed multiple times without dilution effects is very significant when designing a completely reversible molecular switch which is intended to perform logic operations. This is especially true when the physical presence of the triggers in the solution does not add complexity to the system or lead to oxidation, which is believed to cause the known photochromic fatigue.

The current report focuses on the use of multiple stimuli (UV light, visible light, $CO_2$ and $N_2$) with individual and multiple dye/DBU systems and discusses the involvement of the solvent as a sensitizer in these systems for designing reversible molecular switches in the field of molecular logic. A combination of one chromene (**CRM**), two spiropyran (**SP-NO$_2$** and **SP-1**) and two spirooxazine (**SOX** and **SOX-OH**) molecules were used (Fig. 3). Systems made of a combination of two and three dyes and the use of up to six different inputs were achieved by modifying the backbone of spirooxazine and spiropyran and using protic (i.e., MeOH) or aprotic solvent (i.e., toluene).

## 2. Materials and methods

Chemicals and reagents of the highest grade commercially available were used without further purification. 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) and methanol were purchased from

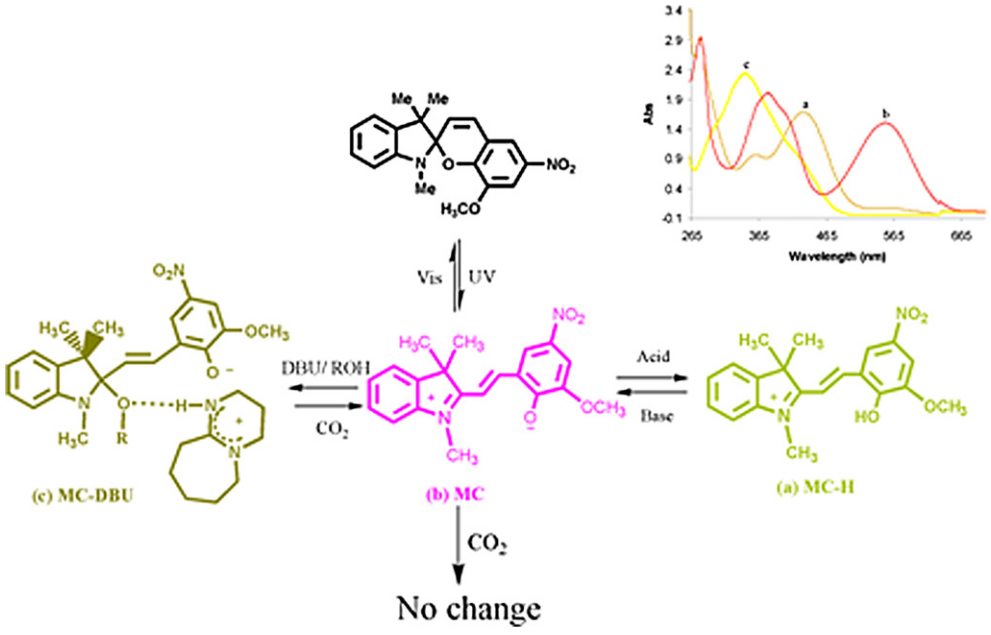



**Fig. 2.** The reactivity of **SP-NO$_2$** in the presence of UV and visible lights and with the addition of DBU and $CO_2$ gas. The inset shows the UV–Vis spectra of the different species (MC, MC–H, MC–BDU complex).

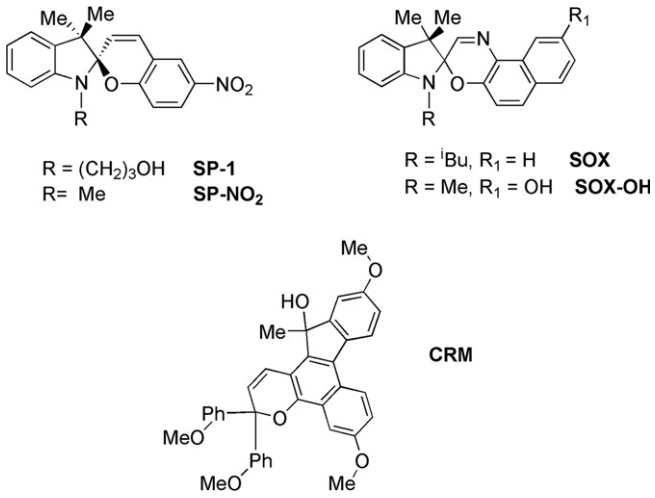



**Fig. 3.** Photochromic compounds used in this study.

Aldrich and used as received without drying. 1′,3′,-dihydro-8-methoxy-1, 3′, 3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (N-methyl spiropyran, **SP-NO$_2$**) and 1,3-dihydro-3, 3-dimethyl-1-(2-methylpropyl)-spiro[2*H*-indole-2,3′-[3*H*]-naphth [2,1-*b*] [1,4]oxazine] (**SOX**) are commercially available and were purchased from Sigma–Aldrich and James Robinson and were used without further purification. $CO_2$ and $N_2$ gases used in this study were purged directly into the solutions through a needle. White light and UV illuminations were conducted using an Abet Technologies 150 W Xe Arc lamp fitted with a water filter and either a 420 nm Schott glass cut-off filter for white light or an Edmund Optics U-340 band pass filter for UV. UV–visible absorption spectra presented in this study were measured, from 200 to 800 nm at a scan rate of 600 nm/s, on a Cary-50 spectrometer fitted with peltier temperature control cell (set at 25 °C). Solutions for UV–visible measurements were made to concentrations of 0.05 mg/mL, unless otherwise specified. All experiments were performed and recorded at room temperature (~25 °C). UV and white light irradiations of solutions were performed for 5 s while shaking the sample in front of the light beam to ensure colour homogeneity. This was carried out directly before UV–Vis measurements and before taking photographic images of the solutions. For photochromic solutions where the colour rapidly bleach after the UV irradiation (e.g., Spirooxazines and chromenes spontaneously bleach within 5 s in toluene after UV irradiation), photographic images were taken directly after the irradiation in the absence of camera's flash light to minimize white light exposure. For photographic images, solutions of dyes were made to concentrations of $\sim 3 \times 10^{-4}$ M for each dye, in case of individual, as well as mixed dye systems. 1,3,3-trimethyl-9′-hydroxy-spiro[indoline-2,3′ (3*H*)-naptho[2,1-*b*] [1,4]oxazine] (**SOX-OH**) was synthesised by condensation of 1,2,3,3-tetramethylindolium iodide and l-nitroso-2,7-dihydroxynapthalene according to literature procedure [50]. The details for the synthesis of **SP-1** and **CRM** were reported elsewhere [33].

## 3. Results and discussion

### 3.1. Spiropyran

**SP-NO$_2$** and **SP-1** have been demonstrated to respond to DBU in alcohol solutions to give yellow non-photochromic solutions, where its photochromism can be regained reversibly in the presence of $CO_2$ gas, see Fig. 4 [33]. **SP-NO$_2$** required the presence of

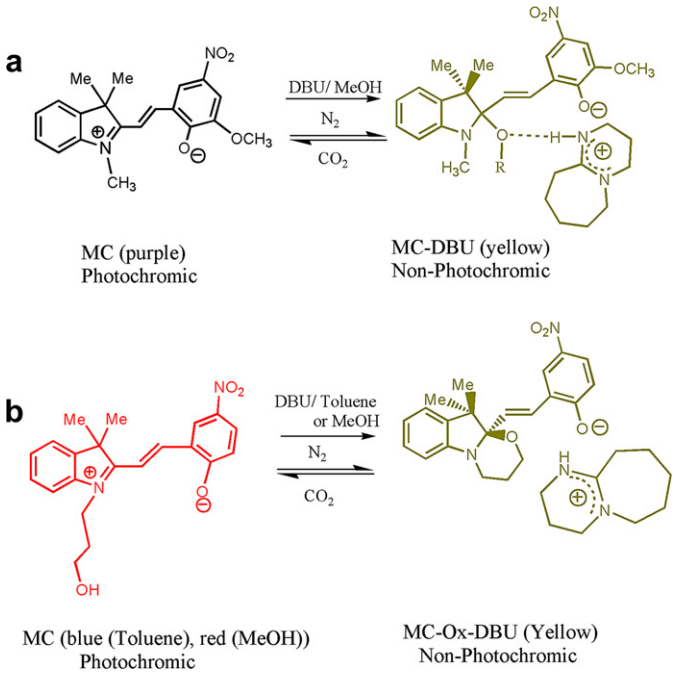



**Fig. 4.** The interaction of DBU with the merocyanine forms of (a) **SP-NO$_2$** in MeOH solution and (b) **SP-1** in toluene or MeOH solutions, showing the colours and the photochromic activity.

alcohol which interacts with the electrophilic iminium carbon centre when DBU is present. However, **SP-1** has an alcohol group already attached to its backbone which interact intramolecularly with the iminium carbon centre in the presence of DBU. Therefore in this case, there is no need to use protic solvent (MeOH) in order to affect DBU responsiveness. In fact, **SP-1** in toluene is slightly blue in colour due to the merocyanine state which becomes yellow and non-photochromic when DBU is added to the solution (Fig. 5) (in web version). It should be noted that the colour of the MC form of **SP-1** is solvent dependent; it is red in MeOH and blue in toluene (a normal solvatochromic effect). In the absence of any light, the MC coloured form of **SP-1** is thermally more stable in MeOH ($K_{eq} = [MC]/[SP] = 0.1$) than it is in toluene [33]. In MeOH the MC form of **SP-1** requires ~5 s of white light irradiation to completely decolourize while it decolourizes spontaneously in toluene (~1 min).

### 3.2. Spirooxazine and chromenes

It was found that **SOX** and **CRM** molecules used in this study are not affected by the DBU stimulus. Both molecules retained their photochromism when DBU was added to their methanol solutions. Upon UV irradiation, both photochromic molecules gave blue colour solutions which decolourized when exposed to visible light (Fig. 6) (in web version). Addition of DBU, $CO_2$ or $N_2$ did not affect the merocyanine coloured forms of both molecules (Fig. 6).

Spirooxazine [51] and chromene [52] molecules are known to take, when illuminated by UV light, quinoidal open forms; while spiropyrans [53] molecule prefers the zwitterionic open form having a positively charged indoline (indolium) fragment and a negatively charged phenolate oxygen. This suggests that DBU interacts with the zwitterionic merocyanine form of **SP-NO$_2$**, while having no effect on the neutral merocyanine forms of the other two dyes.

It was found that by conjugating a hydroxyl group on the naphthol region of a spirooxazine (**SOX-OH**), the molecule becomes

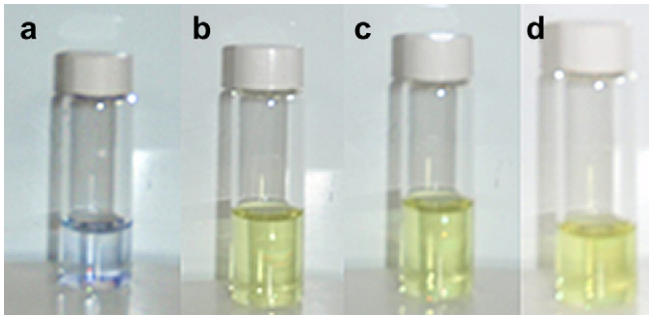



**Fig. 5. SP-1** in toluene with the following in sequence: a) upon dissolving b) addition of DBU c) UV light d) visible light.

sensitive to the addition of DBU to its MeOH solution. In the presence of non-nucleophilic base (DBU), it is suggested that the zwitterionic isomer is more favoured over the quinoidal isomer. It is anticipated that this can occur due to the deprotonation of the hydroxyl group on the naphthol region which destabilizes the quinoidal isomer, favouring the zwitterionic isomer (Fig. 7).

Therefore, **SOX-OH** is reactive towards ROH/DBU in a similar fashion to **SP-NO$_2$** and **SP-1** due to the existence of phenolate oxygen and reactive iminium carbon centre. DBU has no effect on **SOX-OH** when ROH is absent from the solution. In fact, **SOX-OH** in toluene is colourless even when DBU is added (Fig. 8). This solution shows the normal photochromic behaviour (purple when irradiated with UV light and colourless in the presence of visible light or spontaneously decolourizes in the dark in ~5 s). However when MeOH was added to the toluene solution of **SOX-OH**, the colour of solution becomes yellow and the solution loses its photochromic

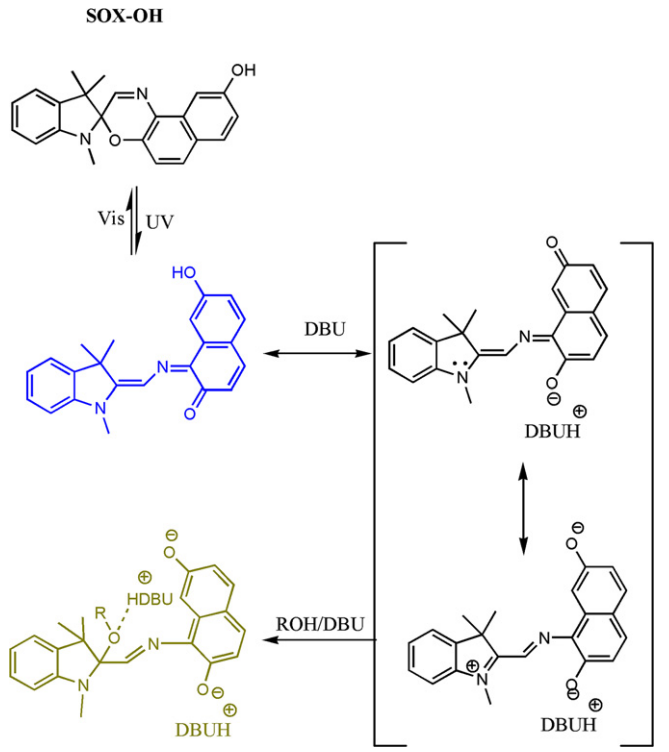



**Fig. 7.** Reactivity of **SOX-OH** with DBU in alcohol solution (ROH). The merocyanine form favours the zwitterionic character over the quinoidal form due to the destabilization of the latter form induced by the presence of a base (DBU). This allows the reactivity of the MC form with DBU/ROH system.

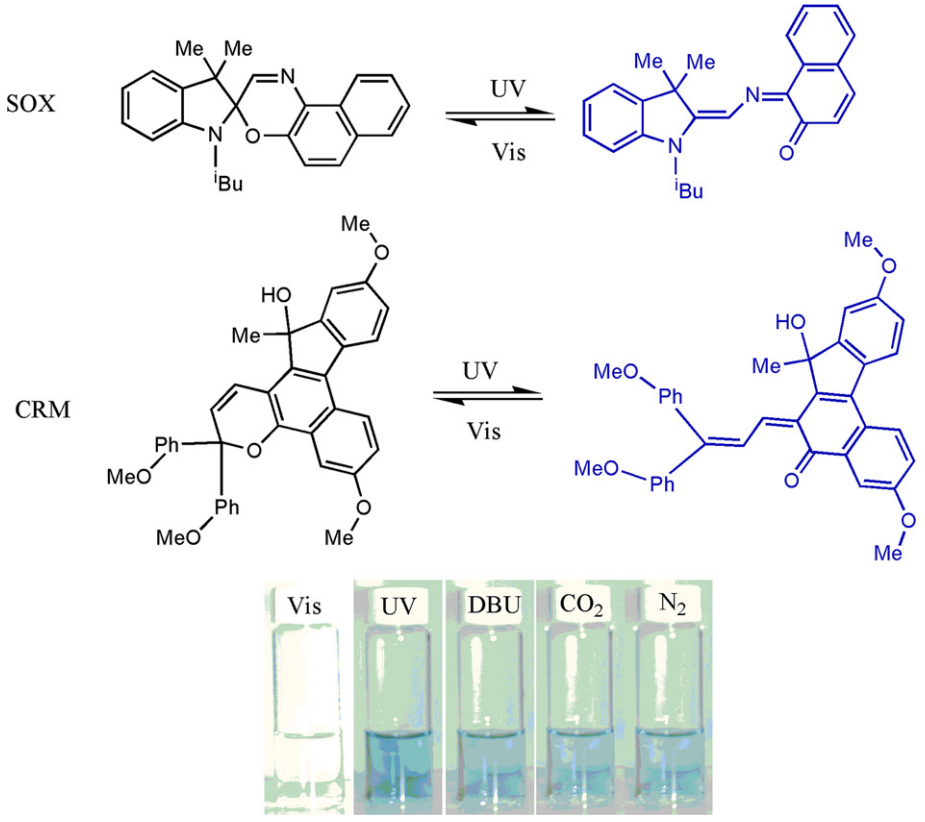



**Fig. 6.** The mercoyanine coloured state of **SOX** and **CRM** showing the absence of zwitterionic characters.

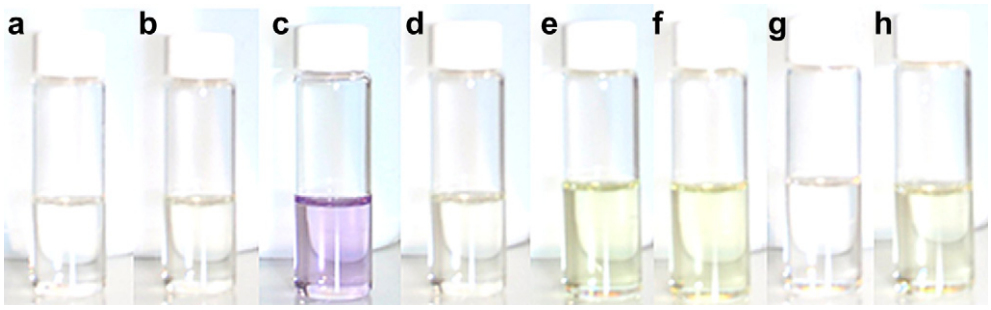



**Fig. 8. SOX-OH** in toluene with the following in sequence: a) upon dissolving (photochromic) b) addition of DBU (photochromic) c) UV light (photochromic) d) visible light (photochromic) e) MeOH (non-photochromic) f) UV light (non-photochromic) g) $CO_2$ purge (photochromic) h) $N_2$ purge (non-photochromic).

activity (remains yellow in the presence of UV light or visible light) until $CO_2$ is introduced which enables the solution to regain its photochromic property (in web version).

### 3.3. Multiple dye systems and logic tables

As shown above, two spiropyran molecules (i.e., **SP-NO$_2$** and **SP-1**) and one spirooxazine (**SOX-OH**) are responsive to DBU in MeOH solution and their photochromism can be deactivated unless $CO_2$ is introduced. On the other hand, **SP-1** was shown to be responsive to DBU in MeOH as well as aprotic solvent (i.e., toluene) due to the presence of the alcohol chain within the molecule. **SOX-OH** is not responsive to DBU in toluene and hence its photochromism stays activated unless MeOH is introduced. The photochromism of **SOX** and **CRM** is always activated; i.e., in the presence or absence of DBU and in MeOH as well as in toluene. As a result, orthogonal activation of mixtures of spirooxazines, spiropyrans and chromene can be achieved to provide multiple colour states by varying the combinations of the stimuli (Fig. 9).

#### 3.3.1. A mixture of *SOX* and *SP-NO$_2$*

One interesting dual dye system is a mixture of **SOX** and **SP-NO$_2$** ($3 \times 10^{-4}$ M of each dye) in MeOH/DBU solution. **SOX** is always photochromic, while the photochromism of **SP-NO$_2$** is deactivated unless $CO_2$ is introduced and can be reversed by purging the $CO_2$ out by using $N_2$ gas sparging. As illustrated in Table 1, the ultraviolet light (in1), visible light (in2), $CO_2$ (in3) and $N_2$ (in4) inputs can be either off or on. Binary digits can be encoded in them applying positive logic conventions (*Off* = *0*, *On* = *1*). The combination of the individual output colours produces a blend of different colours. This is the combination of colourless and yellow to give yellow, blue and yellow to give green, colourless and colourless to give colourless and purple and blue to give deep blue (Table 1). Thus, this chemical system responds to an input string of four binary digits (in1, in2, in3, in4) producing an output string of five binary digits which can be visually recognised (purple, deep blue, yellow, green, and colourless), see Table 2. For example, the input string *0101* indicates that visible light and $N_2$ purge (i.e., $CO_2$ free solution) inputs are on. Under these conditions a yellow output is recorded (output string = *00100*) which corresponds to the combination of the colourless colour of the SP form of **SOX** and the yellow colour of the non-photochromic MC–DBU complex of the **SP-NO$_2$** molecule. Instead, an input string of *1001* indicates that UV and $N_2$ purge are on. Under these conditions, a green output (output string = *00010*) is recorded which is the combination of the blue colour of the MC form of **SOX** and yellow colour of MC–DBU complex of **SP-NO$_2$**. On the other hand, an input string of *1010* indicates that UV and $CO_2$ purge are on. The addition of $CO_2$ in this case activates the photochromism of **SP-NO$_2$** and thus both molecules (**SOX** and **SP-NO$_2$**) become photochromic. Under these conditions, a deep-blue output (output string = *01000*) is recoded which is the combination of the blue colour of MC form of **SOX** and the purple colour of the MC form of **SP-NO$_2$**. The photochromism of **SP-NO$_2$** can be deactivated by removing the $CO_2$ from the system with $N_2$ sparging and hence the whole system can be recyclable. Following similar conditions, five different output strings corresponding to the five possible combinations of input strings can be determined (Table 2). It is interesting to note that each output string in such system is unique since it gives a distinctive visual response. This is important in designing molecular digital multiplexers in the field of molecular electronics which has been the interest of recent studies [54]. An electronic multiplexer can be considered as a multiple-inputs, single-output switch. A multiplexer can combine several input signals into

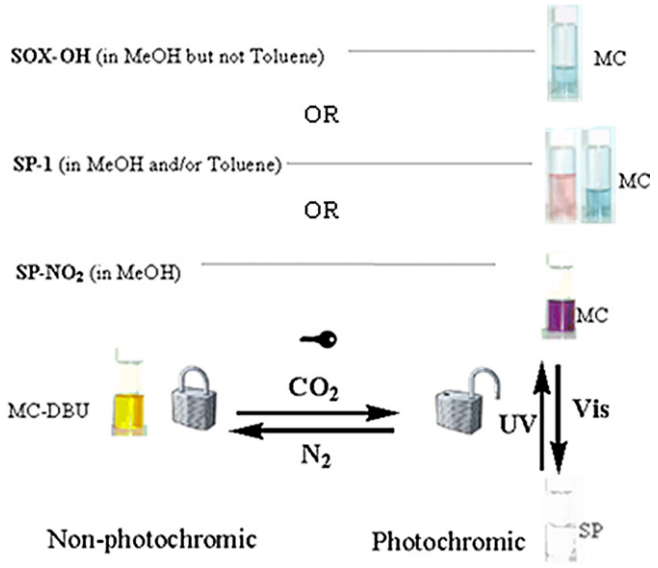



**Fig. 9.** Reversible deactivation of photochromism of **SOX-OH**, **SP-1**, **SP-NO$_2$** in DBU by the absence and presence of $CO_2$. In some of the dyes, the solvent acts as an additional sensitizer for performing logic functions.

**Table 1**
The visual colour responses of **SOX** and **SP-NO$_2$** in MeOH/DBU when using a combination of the relevant stimuli.

| DBU/MeOH | SOX | | SP-NO$_2$ | |
|---|---|---|---|---|
| | Visible | UV | Visible | UV |
| $N_2$ | Photochromic | | Non-Photochromic | |
| | Colourless | Blue | Yellow | Yellow |
| $CO_2$ | Photochromic | | Photochromic | |
| | Colourless | Blue | Colouless | Purple |

**Table 2**
Truth Table for the mixture of **SOX** and **SP-NO$_2$** in DBU/MeOH ($3 \times 10^{-4}$ M of each dye), where a *0* indicates that the corresponding signal is *Off* and a *1* that is *On*.

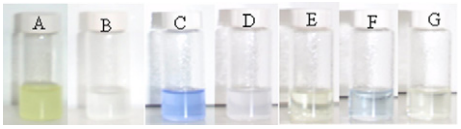
| Input data | | | | Output data | | | | |
|---|---|---|---|---|---|---|---|---|
| in1 UV | in2 Vis | in3 $CO_2$ | in4 $N_2$ |  | | | | |
| *0* | *1* | *0* | *1* | *0* | *0* | *1* | *0* | *0* |
| *0* | *0* | *1*[a] | *0* | *1* | *0* | *0* | *0* | *0* |
| *1* | *0* | *0* | *1* | *0* | *0* | *0* | *1* | *0* |
| *1* | *0* | *1* | *0* | *0* | *1* | *0* | *0* | *0* |
| *0* | *1* | *1* | *0* | *0* | *0* | *0* | *0* | *1* |

[a] Thermal relaxation rate of **SP-NO$_2$** is slow in methanol. This allows a temporary output purple colour, which is the colour of MC form of **SP-NO$_2$** when it regains its photochromism upon addition of $CO_2$ ($in_3$).

a single-output signal for transmission to a receiver, allowing multiple data streams to be transmitted on a single data line [55].

It worth mentioning that molecular switch systems based on thermally stable photochromics are considered to be history-dependent memories and so the following switching effects will also show this behaviour [56]. Spirooxazine are known of their fast thermal relaxation speed (MC to SP form), however spiropyrans are thermally more stable, especially in highly polar solvents such as MeOH. After UV irradiation, the merocyanine forms of **SP-NO$_2$** and **SP-1** relax significantly slower than the mercoyanine forms of **SOX**, **SOX-OH** and **CRM** in methanol solution. This means a "memory" effect can be allowed into the mechanism of these molecular switch systems. In such case, the optical output value becomes defined by the sequence of events and not by the input alone. For example, in the mixture of **SOX** and **SP-NO$_2$** in MeOH (discussed above), when UV light is turned off and in the presence of $CO_2$ (both molecules are photochromically active), MC form of **SOX** relaxes very rapidly to its colourless SP form, while that of **SP-NO$_2$** takes much longer time. This gives a purple colour to the solution which requires, sequentially, a visible light input to switch it to its colourless state. If this "memory" effect is not desired in the molecular switch, then non-polar solvent can be used, such as toluene, which increases the rate of relaxation of MC→SP of spiropyran molecules. This system will be discussed below in Section 3.3.2. In this case a selection of different type of photochromic molecules is required due to the absence of protic solvents that is necessary for the deactivation and activation of particular photochromic molecules. Alternatively to avoid the mismatch in the thermal relaxation of MC forms of spirooxazines and spiropyrans, one can increase the thermal stability of the MC form of a spirooxazine dye by using compounds with strong electron-withdrawing groups incorporated at the naphthoxazine fragment, such as the one reported by Zhu et al. [57].

**Table 3**
A mixture of **SOX-OH** and **SP-1** in toluene/DBU ($3 \times 10^{-4}$ M of each dye). Applying the different stimuli to produce different visual responses.




| Mixture of **SOX-OH** + **SP-1** + DBU in toluene [a] | Stimuli | **SOX-OH** active | **SP-1** active | Response initial colour–final colour |
|---|---|---|---|---|
| Sample | | | | |
| A | – | Yes | No | Yellow |
| B | A + $CO_2$ | Yes | Yes | Yellow to colourless |
| C | B + UV light | Yes | Yes | Colourless to purple-blue |
| D | C + Visible | Yes | Yes | Purple-blue to colourless |
| E | D + $N_2$ (−$CO_2$) | Yes | No | Colourless to yellow |
| F | E + UV light | Yes | No | Yellow to light-green |
| G | F + Visible light | Yes | No | Light-green to yellow |

[a] Water (50 μl) was added to the toluene solvent (5 mL) to allow $CO_2$ solubility in the system.

### 3.3.2. *Mixture of **SOX-OH** and **SP-1***

Another interesting two dye system is a mixture of **SOX-OH** and **SP-1** with DBU. Using an alcohol solvent (e.g., methanol) for this mixture will deactivate the photochromism of both dyes when DBU is added, since both possess an indoline fragment in their open state. However, in toluene the photochromism of **SP-1** is deactivated while **SOX-OH** remains photochromic. Table 3 shows the different colours produced upon applying the different stimuli in a sequence of events. Therefore, one can design a new set of logic functions similar to the one demonstrated above, but where both molecules in the mixture respond relatively quickly to the different inputs applied.

### 3.3.3. *Mixture of **CRM**, **SOX-OH** and **SP-1***

A combination of three dye system can be made of **CRM**, **SOX-OH**, and **SP-1**. In this combination, the photochromism of **SP-1** is always inactive. This is regardless of the solvent used unless $CO_2$ is present, and the photochromism of **SOX-OH** is active unless MeOH is present, while the photochromism of **CRM** is active in any of these scenarios. In other words, a mixture of these three dyes with DBU can be prepared in toluene solution, and therefore the photochromism of the first two dyes are kept active while the photochromism of the third one is controlled reversibly by using $CO_2$ and $N_2$ gases. Then the photochromism of the latter two dyes can be deactivated by introducing MeOH to the toluene solution and hence the first dye stays photochromic while $CO_2$ and $N_2$ control the photochromism of the other two dyes in the system. Similar to the systems described above, the combination of the individual output colours (summarized in Table 4) produces a blend of different colours which are shown in Table 5. This

**Table 4**
The visual colour responses of **CRM**, **SOX-OH** and **SP-1** in toluene/DBU and in methanol/DBU when using a combination of the relevant stimuli.

| DBU | | CRM | | SOX-OH | | SP-1 | |
|---|---|---|---|---|---|---|---|
| | | **Visible** | **UV** | **Visible** | **UV** | **Visible** | **UV** |
| Toluene | $N_2$ | Photochromic Colorless | Blue | Photochromic Colorless | Purple | Non-photochromic Yellow | Yellow |
| | $CO_2$ | Photochromic Colorless | Blue | Photochromic Colorless | Purple[b] | Photochromic Colorless | Blue[b] |
| MeOH | $N_2$ | Photochromic Colorless | Blue | Non-Photochromic Yellow | Yellow | Non-Photochromic Yellow | Yellow |
| | $CO_2$ | Photochromic Colorless | Blue | Photochromic Colorless | Blue[b] | Photochromic Colorless | Red[b] |

[b] The colour of MC forms of **SOX-OH and SP-1** is solvent dependent. For **SOX-OH** it is purple in toluene and blue in MeOH, and for **SP-1** it is blue in toluene and red in Methanol (a normal solvatochromic effect).

**Table 5**
Truth Table for the mixture of **CRM**, **SOX-OH** and **SP-1** ($3 \times 10^{-4}$ M of each dye) with DBU, where a *0* indicates that the corresponding signal is *Off* and a *1* that is *On*.

| Input data | | | | | | Output data | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| in1 UV | in2 Vis | in3 $CO_2$ | in4 $N_2$ | in5 Toluene[a] | in6 MeOH | | | | | | | | |
| *0* | *1* | *0* | *1* | *1* | *0* | *1* | *0* | *0* | *0* | *0* | *0* | *0* | *0* |
| *0* | *0* | *1*[b] | *0* | *1* | *0* | *0* | *0* | *0* | *1* | *0* | *0* | *0* | *0* |
| *0* | *1* | *1* | *0* | *1* | *0* | *0* | *0* | *1* | *0* | *0* | *0* | *0* | *0* |
| *1* | *0* | *0* | *1* | *1* | *0* | *0* | *0* | *0* | *1* | *0* | *0* | *0* | *0* |
| *1* | *0* | *1* | *0* | *1* | *0* | *0* | *0* | *0* | *0* | *0* | *0* | *0* | *1* |
| *0* | *1* | *0* | *1* | *0* | *1* | *0* | *0* | *0* | *0* | *0* | *1* | *0* | *0* |
| *0* | *0* | *1*[c] | *0* | *0* | *1* | *0* | *1* | *0* | *0* | *0* | *0* | *0* | *0* |
| *0* | *1* | *1* | *0* | *0* | *1* | *0* | *0* | *1* | *0* | *0* | *0* | *0* | *0* |
| *1* | *0* | *0* | *1* | *0* | *1* | *0* | *0* | *0* | *0* | *0* | *0* | *1* | *0* |
| *1* | *0* | *1* | *0* | *0* | *1* | *0* | *0* | *0* | *0* | *1* | *0* | *0* | *0* |

[a] Traces of water should be added to toluene in order to allow solubility of $CO_2$ in the system when toluene is used as the solo solvent.
[b] The relaxation rate (MC to SP) of **SP-1** is slower than that of **SOX-OH** or **CRM**. Hence, a temporary output of blue colour is produced, which is the colour of MC form of **SP-1** in toluene, when **SP-1** regains its photochromism upon addition of $CO_2$ (in3) to the mixture. This fades away by thermal isomerisation in 1 min or addition of visible light for 5 s (next set of inputs in the sequence).
[c] A temporary output of pale red colour is produced, which is the colour of MC form of **SP-1** in MeOH/Toluene mixture, when **SP-1** regains its photochromism upon addition of $CO_2$ (in3) in the MeOH/toluene mixture. This fades away by thermal isomerisation (incomplete $K_{eq} = 0.1$ in the dark) or addition of visible light for 5 s (next set of inputs in the sequence).

chemical system responds to an input string of six binary digits (in1, in2, in3, in4, in5 and in6) producing an output string of eight binary digits (pale yellow, pale red, colourless, blue, purple, dark yellow, green, deep blue), see Tables 4 and 5. The explanation detailed in Section 3.3.1 will also apply in this case. It should be noted that this molecular switch system is also completely reversible and recyclable forepart from the solvents when used as inputs (in5 and in6). In order to use the solvents (toluene and methanol) as two additional inputs in this molecular switch system, a sequence of input events should be followed, starting with toluene then introducing MeOH. Once MeOH is added, the reversibility of the system becomes restricted with the last five input strings in Table 5.

## 4. Summary and conclusions

In this work we have demonstrated the expansion of the stimuli available (and their combinations) to perform logic functions with combinations of different photochromic dyes of the type spiropyran, spirooxazine and chromene. It was demonstrated that by the selective use of DBU, different solvents and the presence or absence of $CO_2$, logic tables for molecular logic switches can be produced. Moreover, the use of benign triggers such as visible light, UV, $CO_2$ and $N_2$ enables a more robust molecular logic system that does not suffer dilution effects and hence becomes truly reversible. The use of DBU, that provided access to the $CO_2$ sensitization of spiropyrans and a spirooxazine with hydroxyl group on the naphthol region, was central for this mechanism by allowing the molecules' photochromism to be reversibly deactivated. This opens the way for additional DBU/$CO_2$ control on possibly other photochromic systems such as diarylethene derivatives, which has been recently reported to be photo-inactive in the presence of NaOH as a base [58].

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## References

[1] Nelson A. Nat Mater 2008;7:523.
[2] Stoll RS, Hecht S. Angew Chem Int Ed 2010;49:5054.
[3] Balzani V, Credi A, Raymo F, Stoddart J. Angew Chem Int Ed 2000;39:3348.
[4] Rowan SJ, Cantrill SJ, Cousins GRL, Sanders JKM, Stoddart J. Angew Chem Int Ed 2002;41:898.
[5] Kume S, Murata M, Ozeki T, Nishihara H. J Am Chem Soc 2005;127:490.
[6] Sakamoto R, Murata M, Kume S, Sampei H, Sugimoto M, Nishihara H. Chem Commun 2005;9:1215.
[7] Yagai S, Katatsu T, Kitamura A. Chem Eur J 2005;11:4045.
[8] Champin B, Mobian P, Sauvage JP. Chem Soc Rev 2007;36:358.
[9] Gorodetsky B, Branda N. Adv Funct Mater 2007;17:786.
[10] Roberts MN, Carling CJ, Nagle JK, Branda N, Wolf MO. J Am Chem Soc 2009; 131:16644.
[11] Carling CJ, Boyer JC, Branda N. J Am Chem Soc 2009;131:10838.
[12] Russew MM, Hecht S. Adv Mater 2010;22:3348.
[13] Meng X, Zhu W, Zhang Q, Feng Y, Tan W, Tian H. J Phys Chem B 2008;112: 15636.
[14] Guo Z, Zhu W, Xiong Y, Tian H. Marcomolecules 2009;42:1448.
[15] De Silva AP, Gunaratne HQN, McCoy CP. Nature 1993;364:42.
[16] De Silva AP, Gunaratne HQN, McCoy CP. J Am Chem Soc 1997;119:7891.
[17] Andreasson J, Terazono Y, Eng MP, Moore AL, Moore TA, Gust D. Dyes Pigm; 2010. doi:10.1016/j.dyepig.2010.03.033.
[18] Credi A, Balzani V, Langford SJ. J Am Chem Soc 1997;119:2679.
[19] Pina F, Roque A, Melo MJ, Maestri I, Belladelli L, Balzani V. Chem Eur J 1998;4: 1184.
[20] De Silva AP, Dixon IM, Gunaratne HQN, Gunnlaugsson T, Maxwell PRS, Rice T. J Am Chem Soc 1999;121:1393.
[21] Pina F, Melo MJ, Maestri M, Passaniti P, Balzani V. J Am Chem Soc 2000;122: 4496.
[22] De Silva AP, McClenaghan ND. J Am Chem Soc 2000;122:3965.
[23] De Silva AP, Uchiyama S. Nat Nanotechnol 2007;2:399.
[24] Irie M. Chem Rev 2000;100:1685.
[25] Feringa BL. Molecular switches. Weinheim: Wiley-VCH; 2001.
[26] Crano JC, Guglielmetti R. In: Organic photochromic and thermochromic compounds, vol. 1. New York: Plenum; 1998.
[27] Guglielmetti R. In: Durr H, Bouas-Laurent H, editors. Photochromism: molecules and systems, studies in organic chemistry. Amsterdam: Elsevier; 1990.
[28] Hobley J, Lear M, Fukumura H. Photo-switching spiropyrans related compounds. In: Ramamuthy V, Schanze KS, editors. Photochemistry of organic molecules in isotropic and anisotropic media. Molecular and Supramolecular Photochemistry, vols. 9/10. New York: Marcel Dekker; 2003. p. 353–404,. and references therein.
[29] Raymo F, Giordani S. J Am Chem Soc 2001;123:4651.
[30] Hobley J, Malatesta V, Millini R, Montanari L, Parker W. Phys Chem Chem Phys 1999;1:3259.
[31] Shiraishi Y, Adachi K, Itoh M, Hirai T. Org Lett 2009;11:3482.
[32] Ren J, Zhu W, Tian He. Talanta 2008;75:760.
[33] Darwish TA, Evans RA, James M, Malic N, Triani G, Hanley TL. J Am Chem Soc 2010;132:10748.
[34] Gust D, Moore TA, Moore AL. Chem Commun; 2006:1169. 2006.
[35] Andreasson J, Terazono Y, Albinsson B, Moore TA, Moore AL, Gust D. Angew Chem Int Ed 2005;44:7591.

[36] Straight SD, Liddell PA, Terazono Y, Moore TA, Moore AL, Gust D. Adv Funct Mater 2007;17:777.
[37] Andreasson J, Kodis G, Terazono Y, Liddell PA, Bandyopadhyay S, Mitchell RH, et al. J Am Chem Soc 2004;126:15926.
[38] Andreasson J, Straight SD, Kodis G, Park CD, Hambourger M, Gervaldo M, et al. J Am Chem Soc 2006;128:16259.
[39] Kuciauskas D, Liddell PA, Moore AL, Moore TA, Gust D. J Am Chem Soc 1998; 120:10880.
[40] Langford SJ, Yann T. J Am Chem Soc 2003;125:11198.
[41] Gunnlaugsson T, Mac Donaill DA, Parker D. J Am Chem Soc 2001;123:12866.
[42] De Silva AP, McClenaghan ND. Chem Eur J 2002;8:4935.
[43] Raymo F, Giordani SJ. Am Chem Soc 2002;124:2004.
[44] Saghatelian A, Volcker NH, Guckian KM, Lin VSY, Ghadiri MR. J Am Chem Soc 2003;125:346.
[45] Kompa KL, Levine RD. Proc Natl Acad Sci U S A 2001;98:410.
[46] Guo X, Zhang D, Zhang G, Zhu D. J Phys Chem B 2004;108:11942.
[47] Margulies D, Melman G, Shanzer A. Nat Mater 2005;4:768.
[48] Margulies D, Melman G, Felder CE, Arad-Yellin R, Shanzer A. J Am Chem Soc 2004;126:15400.
[49] Zhou Y, Wu H, Qu L, Zhang D, Zhu D. J Phys Chem B 2006;110:15676.
[50] Kakishita T, Matsumoto K, Kiyotsukuri T, Matsumura K, Hosoda M. J Heterocycl Chem 1992;29:1709.
[51] Berthet J, Delbaere S, Lokshin V, Bochu C, Samat A, Guglielmetti R, et al. Photochem Photobiol Sci 2002;1:333.
[52] Berthet J, Delbaere S, Levi D, Samat A, Guglielmetti R, Vermeersch G. Photochem Photobiol Sci; 2002:665.
[53] Inouye M, Ueno M, Kitao T, Tsuchiya K. J Am Chem Soc 1990;112:8977.
[54] Andreasson J, Straight SD, Bandyopadhyay S, Mitchell RH, Moore TA, Moore AL, et al. Angew Chem Int Ed 2007;46:958.
[55] Andreasson J, Straight SD, Bandyopadhyay S, Mitchell RH, Moore TA, Moore AL, et al. J Phys Chem 2007;111:14274.
[56] He Tian, Qin B, Yao R, Zhao X, Yang S. Adv Mater 2003;15:2104.
[57] Meng X, Zhu WH, Guo Z, Wang J, Tian H. Tetrahedron 2006;62:9840.
[58] Lui H, Chen Y. J Photochem Photobiol A Chem 2010;215:103.