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# $CO_2$ Triggering and Controlling Orthogonally Multiresponsive Photochromic Systems

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***Abstract:*** We report a new generic method of reversibly controlling the photochromism of spiropyrans. It was found that the photochromic effect of spiropyrans can be reversibly switched on and off by addition and removal of carbon dioxide ($CO_2$) to spiropyran in alcohol solutions containing an amidine (i.e., DBU) that acts as a $CO_2$ sensitizer. Spiropyrans are not photochromic in the presence of DBU but photochromic when $CO_2$ is subsequently added to the solution. The $CO_2$ is readily removed by inert gas bubbling, thus allowing facile activation and deactivation of the photochromic effect. Carbon dioxide, without the presence of the sensitizing amidine, had no effect on photochromism of the spiropyrans. Other photochromic dyes classes such as spirooxazines and chromenes are not affected by this $CO_2$/DBU stimulus. As a result, orthogonal activation of mixtures of spirooxazines and spiropyrans was achieved to provide four color states (clear, yellow, green, and blue) by varying the combinations of the stimuli of UV, visible light, $CO_2$, and $CO_2$ depleted. This finding now permits the many applications using spiropyrans to be $CO_2$ responsive.

## Introduction

Chemical processes from the natural world have inspired scientists to continue synthesis of new controllable stimuli-responsive molecules to mimic the complexity of biological systems.[1,2] Such systems would ideally include multiple stimuli and responses which are independently addressable. Potential applications are not limited to biomimicry, but stimuli response can also be of use in information technology where molecules perform logic operations.[3] In this respect, organic photochromes such as spiropyran, spirooxazine, and naphthopyrans (chromenes) are receiving increasing attention due to the remote nature of the light stimulus.[4] Photochromic spiropyran units respond to light and undergo a reversible isomerization between colorless spiro and colored mero (merocyanine) forms.[5,6] The reversible behavior of these materials has led to their evaluation in numerous applications including modulation of stem cell attachment,[7] self-assembly,[8] modulation of the fluorescence of organic and inorganic nanoparticles,[9,10] micro- and macroscopic ordering,[11] photoswitching of DNA-binding,[12] recognition and quantification of amino acids,[13] molecular logic devices,[14] electro-optical devices,[15] molecular and supramolecular logic

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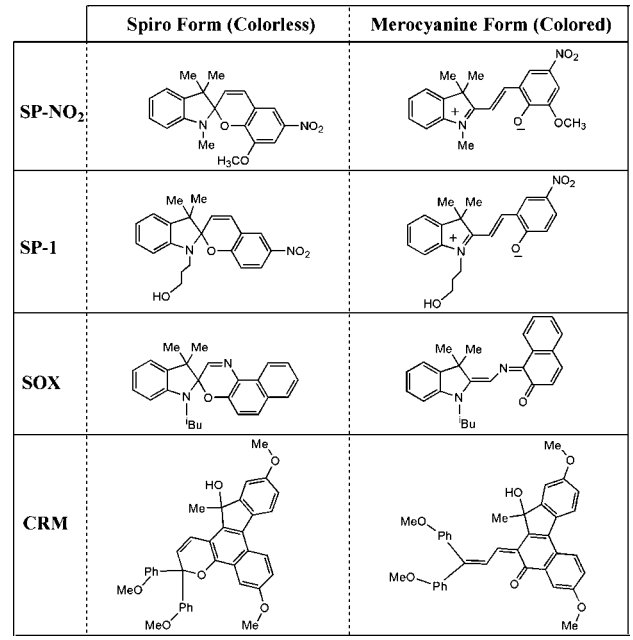
switches,[16] multifunctional artificial receptors, and photoswitchable biomaterials.[17]

Conventionally, photochromic compounds have been used as optical dyes, and as such the majority of work has focused on this application.[18] More recent studies have shown that these molecules are very sensitive to their immediate chemical environment. In a previous report it was demonstrated that the isomerization speed of photochromic dyes in rigid polymeric matrices was enhanced by the attachment of short-chain oligomers to the dye.[19] In this current study, a system was developed where photochromism can be reversibly deactivated, and benign stimuli, such as $CO_2$, can be used together with UV or visible light. The system can be used to effect selectively the structural switching of spiropyran systems when present in multicomponent photochromic solutions. Introducing new dimensions to selectively trigger spiropyran photochromic molecules allows the design of multicomponent stimuli response materials that can respond to multiple inputs and produce multiple outputs. This essentially means the development of logic gate molecular systems with extended logic circuits and truth tables which have been attracting considerable interest lately.[20]

This study reports on a reversible multistimuli response system that combines both photochromism and the switchable properties of a cyclic amidine (1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)), in the presence and absence of $CO_2$ to control the optical responses of spiropyran systems. It was demonstrated that DBU, a non-nucleophilic base, added to an alcohol solution of a photochromic spiropyran dye causes the deactivation of photochromism and activation of $CO_2$ responsiveness. The use of $CO_2$ and $N_2$ (to remove $CO_2$ from solution) as switching triggers maintains the concentration of species in solution and allows for continued, reversible switching. The generic applicability of this method is demonstrated by the use of both a commercially available *N*-methyl spiropyran (**SP-NO$_2$**) and a purposely synthesized spiropyran with a propanol group at the indoline nitrogen (**SP-1**) (Chart 1). The latter molecule allowed the use of NMR spectroscopy to probe the different colored species produced by the different stimuli used.

***Chart 1.*** Photochromic Compounds Used in This Study Showing the Spiro and Merocyanine Forms of Each Dye




## Materials and Methods

**General Materials and Methods.** All solvents used were purified by literature methods.[21] Chemicals and reagents of the highest grade commercially available were used without further purification. DBU and methanol were purchased from 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 inside either the NMR tube or the UV−vis cuvette before recording the spectra.

**Synthesis of SP-1 and CRM.** Details of the experimental procedures for the synthesis of compounds **SP-1** and **CRM** are described in the Supporting Information (SI).

**Instruments.** $^1$H NMR (400 MHz) and $^{13}$C NMR (100.6 MHz) spectra were recorded on a Bruker 400 MHz instrument at ∼25 °C. In $^1$H NMR spectra, chemical shifts (ppm) were referenced to residual solvent protons (3.31 ppm in MeOH-$d_4$). In $^{13}$C NMR spectra, chemical shifts (ppm) were referenced to the carbon signal of the deuterated solvent (49.0 ppm in MeOH-$d_4$). Solutions for NMR measurements were made to concentrations of 16.7 mg/mL. UV−visible absorption spectra were measured, from 200−800 nm at a scan rate of 600 nm s$^{-1}$, on a Cary-50 spectrometer fitted with a peltier temperature control cell. Solutions for UV−visible measurements were made to concentrations of 0.05 mg/mL, unless

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***Table 1.*** Composition of Solutions of *N*-Methyl Spiropyran (**SP-$NO_2$**), *N*-Propanol Spiropyran (**SP-1**) and Spirooxazine (**SOX**)

| *Solution* | *Contents + Stimuli* | *Photo active* | *Response* | $\lambda_{max}$ *(nm)* |
|---|---|---|---|---|
| **S-1** | **SP-$NO_2$ in methanol** | **Yes** | **Colorless** [a] | 269 |
| S-2 | **S-1** + UV | Yes | Purple [b] | 550 |
| S-3 | **S-2** + DBU | No | Yellow [c] | 432 |
| S-4 | **S-3** + $CO_2$ | Yes | Purple [b] | 550 |
| S-5 | **S-4** + $N_2$ | No | Yellow [c] | 432 |
| **S-6** | **SP-1 in methanol** | **Yes** | **Colorless** [a] | 267 |
| S-7 | **S-6** + UV | Yes | Red [b] | 530 |
| S-8 | **S-7** + DBU | No | Yellow [c] | 413 |
| S-9 | **S-8** + $CO_2$ | Yes | Red [b] | 530 |
| S-10 | **S-9** + $N_2$ | No | Yellow [c] | 413 |
| **S-11** | **SOX in methanol**[d] | **Yes** | **Colorless** | 270 |
| S-12 | **S-11** + UV | Yes | Blue [b] | 615 |
| S-13 | **S-12** + DBU | Yes | Blue [b] | 615 |
| S-14 | **S-13** + $CO_2$ | Yes | Blue [b] | 615 |
| S-15 | **S-14** + $N_2$ | Yes | Blue [b] | 615 |

[a] Slightly colored due to the existence of small amount of the photomerocyanine form at equilibrium which decolorizes under direct visible light.[22] [b] The solution decolorizes when exposed to visible light. [c] The solution does not change color when exposed to either UV or visible light. [d] CRM showed the same results as SOX; i.e., blue color in the presence of UV, DBU, $CO_2$, and $N_2$ (see Supporting Information for photos: Figure SI1).

otherwise specified. White light and UV illuminations were conducted using an Abet Technologies arc lamp fitted with a water filter and either a 420 nm Schott glass cutoff filter for white light or an Edmund Optics U-340 band-pass filter for UV. Samples were temperature equilibrated to 25 °C and then illuminated for 5 min prior to measurement.

## Results and Discussion

Table 1 describes the solutions of photochromic molecules investigated in this study, along with the stimuli used to trigger switching. This table also indicates whether the solutions are in a photoactive state, as well as their color and $\lambda_{max}$ after switching.

**SP-$NO_2$** and **SP-1** in methanol (S-1 and S-6) exhibited similar behavior when DBU, UV light, visible light, $CO_2$ and $N_2$ were introduced to each system, and the results are summarized in Table 1. The UV−vis absorption spectroscopy of **SP-$NO_2$** system is described in the Supporting Information, Figure SI2, while that of **SP-1** is described below. This essentially demonstrates the reversible loss of photochromism of both spiropyran molecules with DBU, unless $CO_2$ is present. In contrast, the spirooxazine (**SOX**) and the chromene (**CRM**) dyes, shown in Chart 1, retained their photochromism when DBU was added to the methanol solutions. Upon UV irradiation, both photochromic molecules gave blue-color solutions which decolorized when exposed to visible light. Addition of DBU, $CO_2$, or $N_2$ did not affect the merocyanine colored forms of both molecules. The results for the **SOX** dye are summarized in Table 1; while those results for the **CRM** dye are shown in the SI, Figure SI1. The noteworthy difference among these pyran compounds is that, when illuminated by UV light, the spirooxazine[23] and chromene[24] molecules take quinoidal open forms, while the spiropyran[25] molecule prefers the zwitterionic open form, having a positively charged indoline (indolium) fragment and a negatively charged phenolate oxygen (Chart 1). 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.

The acid−base susceptibility and color-indicating properties of spiropyrans have been reported before, where change in color is reversible upon acidification, neutralization, and basification.[20a] The addition of acid causes spiropyrans to open, and protonation takes place at the phenolate oxygen (pH = 3) leading to a yellow solution (**MC-H**) due to the loss of charge delocalization between the indoline and benzopyran halves of

(22) Unlike **SP-1**, the decolorization of **SP-$NO_2$** in methanol under visible light is very slow. In this case, toluene was added to methanol to reduce the polarity of the solution for the ease of taking photos of the colourless solutions when exposed to visible light.

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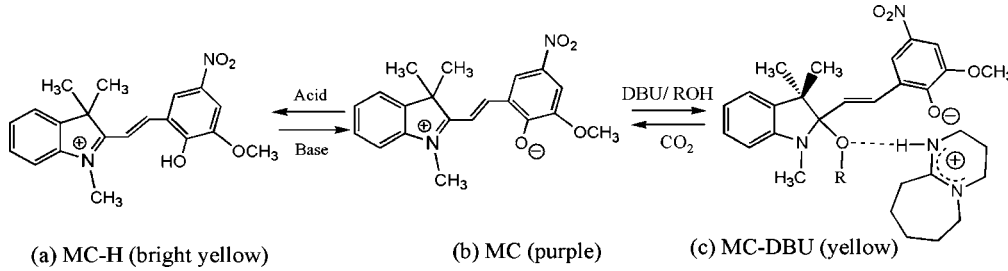
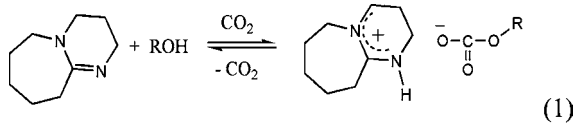



***Figure 1.*** Acid−base reversible reactions of **SP-NO$_2$** and with DBU complexation.

the molecule (Figure 1a). These species remain photochromic and decolorize in visible light.[20a] Neutralizing the acidic yellow solution with a base regenerates the red merocyanine form (MC) at the neutralization point (Figure 1b); however, this is not the same chemistry as reported here in this study. The addition of $CO_2$ to **SP-NO$_2$** in methanol (pH = 5.4) in the absence of DBU did not show any change in color (i.e., remained purple), suggesting that $CO_2$ is not acidic enough to protonate the phenolate oxygen of the MC form of **SP-NO$_2$**. The yellow nonphotochromic solution (S-3) was produced when DBU, a non-nucleophilic base, was added to **SP-NO$_2$** in alcohol solution (pH = 13) (Figure 1c). We propose that this occurs through the interaction of the deprotonated solvent (methanol) with the highly electrophilic indolium fragment of the open MC form of **SP-NO$_2$**. The conjugate acid of DBU (i.e., DBUH$^+$) then acts as a weak ligand and electrostatically interacts with the negatively charged phenolate oxygen on the benzopyran fragment of the molecule, trapping the delocalization of the electrons between the two parts of the molecule. Bleached yellow solutions have been reported when a base was directly added to MC forms of some spiropyrans, however these species remained unidentified due to the complexity of the associated NMR spectra.[26] 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.

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.[27] recently reported the nucloephilic addition of $CN^-$ anion to the iminium carbon of the indolium fragment of the MC form of **SP-NO$_2$**. Intermolecular and intramolecular nucleophilic addition is common for indolium molecules in general.[28]

Recently, it has been demonstrated that the exposure of amidines mixed with water[29] or alcohol[30] to gaseous $CO_2$, results in exothermic reactions that produce bicarbonate or alkylcarbonate salts (eq 1). NMR spectroscopy and conductivity measurements[29] of the reaction between DBU and $CO_2$ detected rapid formation of bicarbonate salt of DBU (i.e., [DBUH$^+$][HCO$_3^-$]) when wet DBU (not dried) is exposed to $CO_2$.




(1)

When $CO_2$ is added to solution S-3 (**SP-NO$_2$** + DBU in methanol) to give S-4, it reacts with the DBU↔DBUH$^+$ equilibrium, acting as a weak ligand with the phenolate oxygen, to give the bicarbonate adduct [DBUH$^+$][HCO$_3^-$] (pH = 6.8).[31] The consumption of DBU/DBUH$^+$ by the added $CO_2$ liberates the negative charge on the phenolate oxygen from its interaction with the countercation DBUH$^+$ and allows the re-establishment of the zwitterionic form of the photochromic molecule. 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 is present in solution and does not proceed to the MC-H species. In fact, upon dropwise addition of 1 M HCl to the above $CO_2$/DBU methanol solution, the color changed from purple to bright yellow (pH = 3) with the appearance of a new absorption band at 346 nm (broad) (see SI: Figure SI3c). This is different to the absorption band attributed to the yellow solution S-3 that results from the addition of DBU to solution S-2 ($\lambda_{abs}$ = 432 nm) (see SI: Figures SI2 and SI3a).

In an attempt to obtain a clearer picture of the molecular interactions in these solutions, NMR spectroscopy was used. However, the $^1$H and $^{13}$C NMR spectra of **SP-NO$_2$** with DBU in MeOH-$d_4$ were too complicated to make clear assignments. The complexity of these NMR spectra was likely to be due to solvent exchange and the production of isomeric species. Therefore, a new photochromic spiropyran molecule was synthesized with a propanol linker attached to the indoline nitrogen, N-propoanol spiropyran (**SP-1**), in an attempt to affect intramolecular interactions. This was anticipated to generate less isomeric and more stable species that would be easier to characterize by NMR spectroscopy. A solution of **SP-1** in methanol (S-6)[33] demonstrated typical photochromic behavior (Scheme 1). When irradiated with UV light (S-7), it exhibited an intense red color with an absorbance centered at 530 nm, indicating the formation of the **MC** form (Figure 2). When left in the dark following exposure to UV, this absorption band decreased in intensity (see SI: Figures SI4 and SI5) with the

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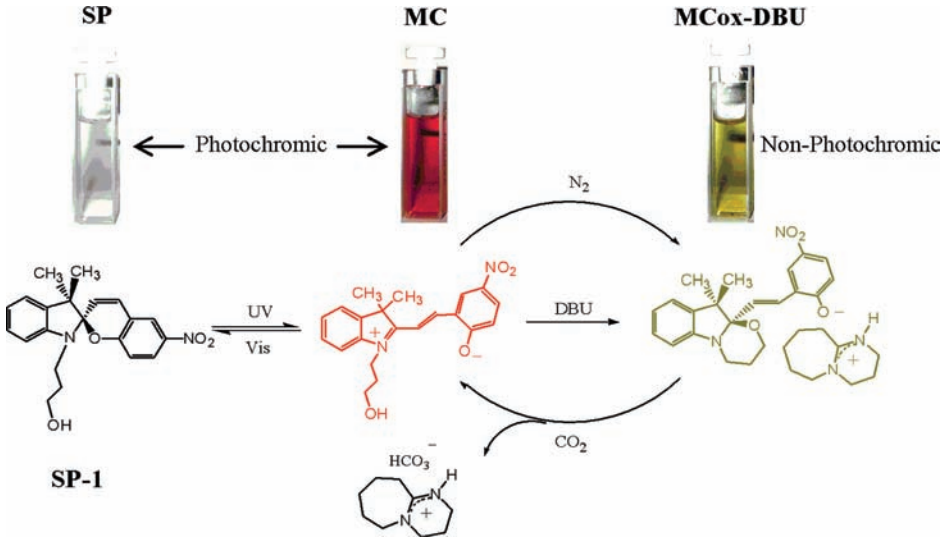
(33) Ethanol and isopropanol were also used as alcohol solvents, and similar effects were observed.

***Scheme 1.*** Photochromic and $CO_2$ Switching between **SP** and **MC** Forms of **SP-1**, and the DBU Complex **MCox-DBU**




simultaneous growth of an absorbance at 267 nm associated with the **SP** form. It is noted that the absorption band at 530 nm does not disappear entirely and reaches an equilibrium intensity indicating some of the **SP-1** remains in the open **MC** form. The absorption spectrum of **SP-1** in methanol at 530 nm increases linearly with the concentration of the dye (see SI: Figure SI6). From this correlation and the equilibrium constant ($K_1 = 0.1 \pm 0.03$), determined by $^1$H NMR spectroscopy (see SI: NMR Spectroscopy Results), the molar extinction coefficient of **MC** can be estimated to be $18 \pm 6 \times 10^3$ $M^{-1}$ $cm^{-1}$. The time dependence of the absorbance at 530 nm (see SI: Figure SI7) indicates that the rate constant ($k_1$) for the thermal interconversion of **SP** form into **MC** form and the rate constant ($k_{-1}$) for the opposite process are $(1.5 \pm 0.5) \times 10^{-5}$ $s^{-1}$ and $(1.5 \pm 0.5) \times 10^{-4}$ $s^{-1}$, respectively, at 298 K.[34]

When at least an equimolar amount of DBU was added to the red **MC** solution, it produced a yellow nonphotochromic solution of **MCox-DBU** (S-8).[35] Correspondingly in the UV−vis spectrum (Figure 2, S-8), the total disappearance of the absorbance at 530 nm and the appearance of an absorption band at 413 nm were observed. The latter grew with time in the dark at the expense of the **SP** absorbance at 267 nm (see SI: Figure SI8). Ultimately, neither visible nor ultraviolet light made any changes to the color of the resulting yellow solution.[36] Modeling the increase in intensity of the 413 nm band (**MCox-DBU**) with time gave a rate constant $k_{obs} = 1 \times 10^{-5}$ $s^{-1}$ (see SI: Figure SI9). This is the same order of magnitude as $k_1$, the rate constant for the thermal interconversion of **SP** to **MC.** This suggests that DBU interacts with the **MC** rapidly and the observed rate constant of this reaction depends on the slow thermal interconversion of the **SP** to **MC**. The latter is consumed by the added DBU and thus shifts the **SP** ↔ **MC** equilibrium to the right, leading ultimately to the consumption of the **SP** species and the formation of the **MCox-DBU** (Scheme 1). In fact, the disappearance of the 530 nm band corresponding to **MC** upon the addition of DBU happens instantaneously and could not be followed either by UV−vis or by NMR (shown below). Additionally, when DBU was added to **SP-1** in methanol, the pale-yellow color of the solution did not increase in intensity as long as the solution was kept under direct white light. The yellow color only increased in intensity when the solution was kept in the dark where the interconversion of **SP** to **MC** can occur, and an equilibrium was

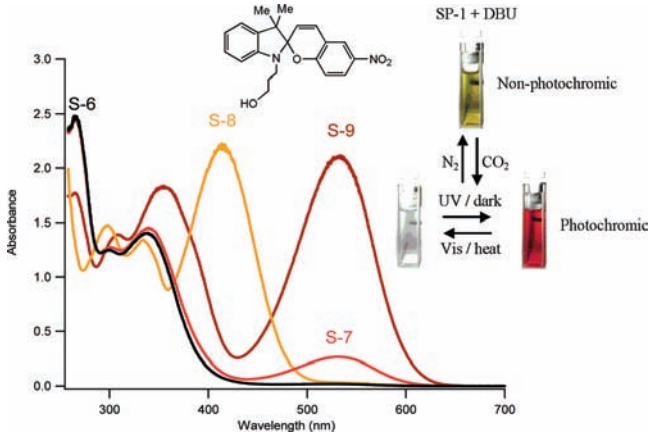



***Figure 2.*** UV−vis spectra for **SP-1** with the curves corresponding to the different solutions. S-6: black (**SP** form); S-7: red (a mixture of ∼18% **MC** form and ∼82% **SP** form, calculated using $\varepsilon_{MC}$); S-8: yellow (**MCox-DBU**) with DBU after three days in the dark; S-9: brown curve (**MCox-DBU** + $CO_2$) upon addition of $CO_2$ (resulting in ∼86% of **MC** form: the amount of MC form immediately starts to diminish with time and continues until it reaches equilibrium state (see SI: Figure SI10)). The inset shows the different colors under the different stimuli.

(34) Molar extinction coefficient ($\varepsilon_{530}$) and rate constants ($k_1$ and $k_{-1}$) for the thermal equilibrium of **SP** ↔ **MC** were calculated according to the method described in detail by Raymo *et. al* in ref 20b.

(35) A competing effect is anticipated to exist between the solvent hydroxyl group (MeOH) and the propanol linker on the **SP-1**; however, intramolecular interaction is believed to be thermodynamically more favored which produces exclusively **MCox-DBU**. Molar extinction coefficient of **MCox-DBU** was estimated to be $(26.1 \pm 1) \times 10^3$ $M^{-1}$ $cm^{-1}$ (see SI, Figure SI25).

(36) When **SP-1** was dissolved in toluene to which a small amount of DBU was added, the toluene solution turned quickly yellow in color with the loss of photochromism (see SI: Figure SI24). This suggests the involvement of the propanol linker in the photochromic deactivation through its intramolecular cyclization at the iminium carbon center in the open merocyanine form. To reproduce the photochromic activity of this solution, $CO_2$ was bubbled in the toluene solution; however, the solubility of $CO_2$ in toluene was not sufficient unless wet toluene was used (i.e., 50 $\mu$L of $H_2O$ in 3 mL of toluene) or some methanol is added. This showed $CO_2$ responsiveness similar to that in the systems described above.

reached after 3 days (as indicated by UV−vis and NMR). When the same solution was irradiated by UV light for 10 min following the addition of DBU, the yellow color increased in intensity and reached equilibrium rapidly. Therefore, production of **MCox-DBU** only occurs when **MC** is present in solution.

When the yellow solution of **MCox-DBU** was briefly purged (for a few seconds) with $CO_2$ (producing S-9), the solution turned red again, reforming the **MC** species. The UV−vis spectrum (Figure 2, S-9) shows the immediate disappearance of the 413 nm absorption band and the instantaneous reappearance of the 530 nm band associated with **MC** and the 267 nm band associated with **SP** due to the re-establishment of the **SP** ↔ **MC** equilibrium. Probing the subsequent evolution of these signature absorption bands with time (see SI: Figure SI10) indicates an initial increase in the amount of **MC**, before a decrease in the quantity of **MC** and an increase in **SP** over time until an equilibrium state was reached. Solution S-9 regained its photochromism and could be switched between colorless **SP** and red **MC** forms as long as the solution was kept under an atmosphere of $CO_2$. When solution S-9 was purged for approximately one minute with $N_2$ to remove $CO_2$ from the solution,[37] the band at 530 nm disappeared along with the return of the yellow color and the reappearance of the absorption band at the 413 nm band, corresponding to nonphotochromic **MCox-DBU**.

$^1$H NMR spectroscopy was also used to probe the same progression of photochromic and molecular switching of **SP-1** under the action of DBU and $CO_2/N_2$ (Figure 3). This enabled the determination of the detailed molecular structures at each stage and showed the reproducibility of the species when the different stimuli were used. Figure 3a is the spectrum associated with solution S-6 in MeOH-$d_4$ (equilibrated for one day in the dark) showing mainly peaks attributed to **SP** with a small amount of **MC** (indicated by "*" ~10% by $^1$H NMR, which corresponds to equilibrium constant $K_1 = 0.1 \pm 0.03$), which is enough to give a pale-red color to the solution due to the very high molar absorption coefficient of this form of the molecule. The structure of the **SP** form was completely characterized by $^1$H and $^{13}$C NMR (see SI: Figures SI11−SI13 and Table S1). Upon addition of an equimolar amount of DBU (S-8), the $^1$H NMR spectrum showed the complete disappearance of the signals attributed to **MC** and the formation of a new set of signals associated with the new **MCox-DBU** species. As observed in the UV−vis data, when solution S-8 was kept in the dark at room temperature over a period of three days, residual $^1$H NMR signals from the **SP** form gradually disappeared, leaving a spectrum composed almost entirely of **MCox-DBU** (Figure 3b). $^1$H and $^{13}$C, 1D and 2D NMR spectral analyses confirmed the structures of the existing species *in situ*. The spiro structures of **SP** and **MCox-DBU** and the planar structure of **MC** species can be simply followed by probing the $^1$H NMR of the geminal methyl groups on the indoline ring (Figure 3). These two methyl groups are nonequivalent in the spiro structures, thus giving two different pairs of resonances, i.e. 1.26 and 1.16 ppm for **SP**, and 1.35 and 0.98 ppm for **MCox-DBU**. While these methyl groups become equivalent in the planar structure of **MC**, they therefore produce only one resonance at 1.82 ppm (for more characterization see notes in SI: NMR Spectroscopy Results, Figures SI14−SI23 and Table S2). Key structural information relating to **MCox-DBU** (Scheme

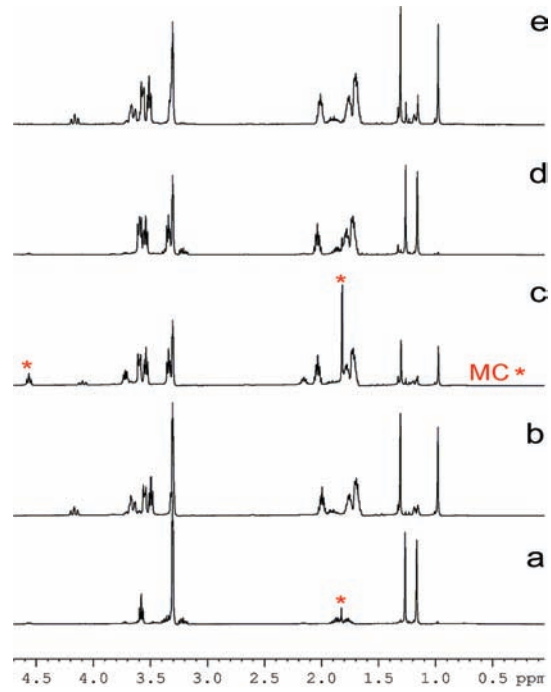



***Figure 3.*** Partial $^1$H NMR spectra (400 MHz, MeOH-$d_4$, 298 K) of the **SP**, **MC**, and **MCox-DBU** forms of **SP-1** under gas and photochromic switching conditions. (a) **SP-1** in MeOH-$d_4$ equilibrated in the dark for one day, showing **SP** signals and a small amount of **MC** ("*"); (b) after addition of DBU and equilibration in the dark for 3 days, showing **MCox-DBU**; (c) after addition of $CO_2$, showing the disappearance of signals of **MCox-DBU** and the appearance of **MC** and **SP** signals; (d) the same solution after 355 min in the dark showing mostly **SP**; (e) after purging with $N_2$ showing the re-emergence of **MCox-DBU** signals. For full spectra, see SI Figure SI16.

1) determined by NMR spectroscopy were (a) the propanol linker in **MC** form that had cyclized at the former spiro carbon in the indoline fragment to form a six-membered 1,3-oxazine ring and an open pyran fragment; (b) the *trans* configuration of the bridging carbon−carbon double bond; (c) the neutral charge on the indoline nitrogen which is otherwise positively charged in **MC** form; and (d) the negatively charged phenolate oxygen. Examination of the $^1$H NMR signals associated with DBU showed an evolution over a three-day period during the formation of **MCox-DBU**. The presence of positively charged amidinium species was concluded from the observed H/D isotope exchange between the deuterated solvent (MeOD) and the allylic amidinium protons (see SI: NMR Characterization of Complexed DBU and Table SI3), which became labile due to the positively charged nitrogen atoms. The presence of a positively charged amidinium cation and a negatively charged phenolate oxygen anion suggests the presence of electrostatic interaction between these two charged species. Similar ion-pairing interactions have been previously proposed for the merocyanine forms of spiropyrans when binding polar and charged molecules, such as amino acids,[13] ionic liquids,[38] and metal ions.[39]

Solution S-8 containing **MCox-DBU** was purged with $CO_2$ in the NMR tube before being sealed, producing solution S-9.

(37) Heat (40−60 °C) can be used to speed up the depletion of $CO_2$ from the solution.

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***Table 2.*** Optical Responses of a Dual Dye System of **SP-NO$_2$** and **SOX** with DBU in Methanol Using the Different Stimuli Combinations and Showing the Reversibility of the System

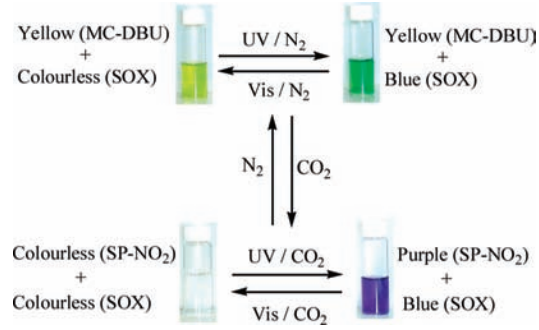
| **N-1 = SPNO$_2$+SOX+DBU (in MeOH)** | Stimuli | **SOX** photo-active (Color) ($\lambda_{max}$ (nm)) | **SP-NO$_2$** photo-active (Color) ($\lambda_{max}$ (nm)) | Response (Final Color) |
|---|---|---|---|---|
| N-1 | $N_2$-Vis | Yes (Colorless) (< 300) | No (Yellow) (440) | Yellow |
| N-2 | N-1 + $N_2$-UV | Yes (Blue) (610) | No (Yellow) (440) | Green |
| N-3 | N-2 + $CO_2$ | Yes (Colorless) (<300) | Yes (Purple) (560) | Purple |
| N-4 | N-3 + $CO_2$-Vis | Yes (Colorless) (<300) | Yes (Colorless) [a] (<300) | Colorless |
| N-5 | N-4 + $CO_2$-UV | Yes (Blue) (610) | Yes (Purple) (560) | Deep Blue |
| N-6 | N-5 + $N_2$-Vis | Yes (Colorless) (<300) | No (Yellow) (440) | Yellow |
| N-7 | N-6 + $N_2$-UV | Yes (Blue) (610) | No (Yellow) (440) | Green |

[a] See ref 22.

The $^1$H NMR signals of the **MCox-DBU** species decreased rapidly and the ratio of compounds **MCox-DBU: SP: MC** were observed to evolve from 196:10:1 to 72:22:123 within the first two minutes after the addition of $CO_2$ and then continued to change to reach equilibrium after ~6 h with a ratio of 10:184:16.[40] The corresponding signals of the **MC** and **SP** forms re-emerged due to the **SP** ↔ **MC** equilibrium (Figure 3c,d). The rate of disappearance of **MC** to give **SP** (going from c to d in Figure 3) was followed by $^1$H NMR (see SI Figure SI19) and showed a first-order rate constant ($k_{obs}$) of $2 \times 10^{-4}$ s$^{-1}$, which was the same as that observed using UV−vis in the absence of DBU and $CO_2$. This indicates that the presence of DBU and $CO_2$ in solution has essentially no effect on the photochromic switchability of **SP** and **MC**. $^{13}$C NMR signals from solutions of **SP-1** in methanol were also used to probe the evolution of molecular species and complexation under the above conditions (see SI: Figures SI17 and SI18). Addition of $CO_2$ to the yellow solution S-8 (**SP-1** and DBU in methanol), giving S-9, led to the appearance of a new $^{13}$C resonance at 161.4 ppm which was attributed to the bicarbonate carbon in [DBUH$^+$][HCO$_3^-$] (see SI Figure SI18) which has been reported by Jessop et al.[29] Purging of solution S-9 with $N_2$ removed the $CO_2$ from solution (producing S-10) and restored the $^1$H NMR signals of the nonphotochromic **MCox-DBU** species (Figure 4e).[37] This was accompanied by the disappearance of the carbonate $^{13}$C signal at 161.4 ppm (see SI Figure SI18). Hence, the photochromic switching of **SP-1** (and **SP-NO$_2$**) can be turned on or off by the presence or absence of $CO_2$, respectively.

The insensitivity of the photomerocyanine forms of **CRM** and **SOX** to the addition of DBU makes them good candidates to use in a mixture with spiropyrans for the design of multicomponent dye systems. In these systems, distinct dye components can be triggered separately using the different stimuli (i.e., UV light, visible light, $CO_2$, and $N_2$) to produce a combination of optical responses. For example, in a mixture of **SP-NO$_2$** and **SOX** (or **CRM**) in methanol with a small amount of DBU (N-1, Table 2), the photochromism of **SOX** (or **CRM**) is retained where it can switch colors in the presence of UV and visible lights, while the photochromism of **SP-NO$_2$** is switched off and can be reversibly switched on by the addition and removal of $CO_2$ gas. This means the system becomes responsive to a combination of the different optical and gaseous triggers. The results of exposure of the mixed solution (N-1) to combinations of stimuli are tabulated in Table 2 and Scheme 2.

***Scheme 2.*** Mixture of 1:1 **SPNO$_2$** and **SOX** in Methanol with DBU Exposed to a Combination of Lights and Gases Showing the Optical Responses




The orthogonal dimensions of the stimuli reported in this study can allow the design of a three (or more)-dye system. For example, in a mixture of **SOX**, **SP-NO$_2$**, and **SP-1** in methanol solution with DBU, the photochromic activity of the later two dyes can be controlled by $CO_2$ while the first dye remains photochromic. From such multistate molecular switch systems, combinational logic circuit can be designed similar to those reported else where,[20a,41] yet with many more possible combinations.

## Conclusion

We have demonstrated that DBU can reversibly switch off the spiropyran's photochromism unless $CO_2$ is present. By reversibly switching the basicity of DBU using $CO_2$ or nitrogen gases, one can control the different responses of spiropyran

(40) From this ratio, the equilbrium constant between **SP** and **MC** species ($K_{eq}$ = [MC]/[SP]) is calculated to be 0.08, which is comparable to $K_1 = 0.1 \pm 0.03$ calculated for the same equilbrium reaction in the absence of any DBU and $CO_2$. This shows that the presence of DBU and $CO_2$ has no effect on the equilibrium ratio of the two species and that the initial equilibrium system can be restored by addition of $CO_2$ to DBU.

molecules and switch the photochromism on and off. Multiresponsive photochromic systems have been demonstrated by using **SP-$NO_2$** and **SOX** in methanol solution, where the photochromic response of **SP-$NO_2$** can be controlled by the addition and removal of $CO_2$ gas from the systems. Importantly, this work demonstrates that the addition of DBU can possibly be applied to any spiropyran system and opens the way for additional $CO_2$ control into systems such as those described in the introduction, and more generally to any photochromic system with an active indolium fragment. Photochromic oxazines and bichromophoric photochromes (which have been reported recently by Raymo et al.[42]) would possibly be good candidates for such application due to the presence of indolium cation in their open states. Carbon dioxide is an excellent stimulus for photochromic systems as it is easily added and removed; it does not contribute to contamination or dilution effects. Furthermore, $CO_2$ is a mild reagent and is present in low concentrations in numerous biological systems. The increasing use of spiropyrans cited in this work makes the discovery of molecular switching by amidine/$CO_2$ addition of great importance. Its general use and applicability suggest additional possible applications in bioresponsive materials based on $CO_2$ gradients found in biological environments.

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**Supporting Information Available:** Details on the synthesis of **SP-1** and **CRM**, UV−vis spectroscopy, $^{1}H$ and $^{13}C$ (1D and 2D) NMR spectroscopy characterizations (including spectra) of the different species, and photographs of solutions. This material is available free of charge via the Internet at http://pubs.acs.org

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