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# Photo-/ baso- chromisms and the application of a dual-addressable molecular switch

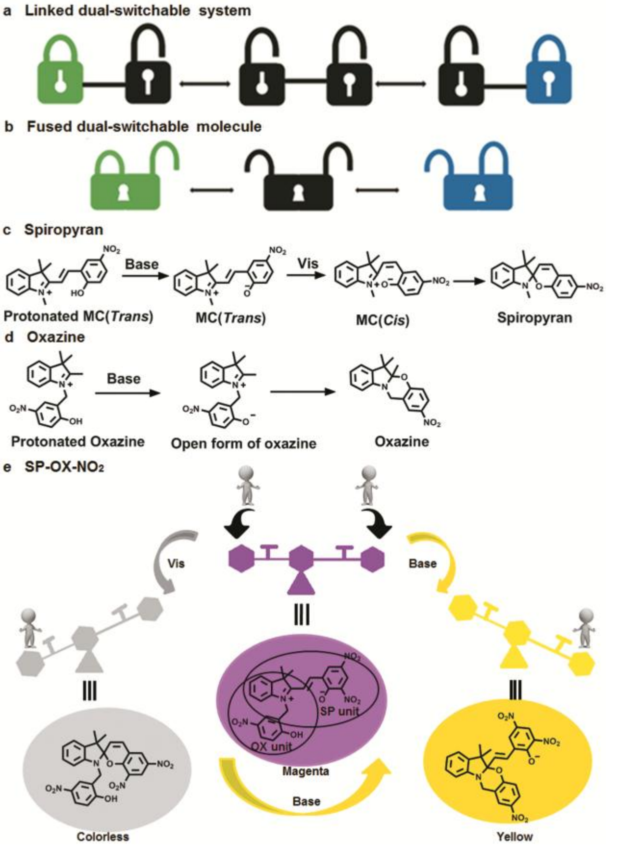
Danyang Liu, Binhong Yu, Xing Su, Xiaojun Wang, Yu-Mo Zhang, Minjie Li* and Sean Xiao-An Zhang*

**Abstract:** Two typical molecular switches of spiropyran (SP) and benzoxazine (OX) were fused by sharing an indole to achieve a new dual-addressable molecular switch (SP-OX-$NO_2$). Through proper molecular modification with $NO_2$, the transformation from merocyanine (MC) to ring-closed SP or ring-closed OX can be controlled separately with visible light or base stimuli in solution, respectively, and these processes are proved by UV-vis, NMR spectra and control experiments. The *cis*-merocyanine (*cis*-MC) form is involved in basochromic process in solution. DFT calculation suggests the bidirectional switching property of the fused SP-OX molecular switch can be controlled separately, when the OX isomer is more stable than the deprotonated SP isomer. Because of the significant color variations in solution, the simple dual-addressable switch has been further applied to construct a multicolor reversible display on paper successfully.

## Introduction

Multi-addressable molecular switches have attracted a lot of attention recently because of their multi-stimuli responsive properties.[1-7] By integration of the typical molecular switches, such as spiropyrans,[8-9] diarylethenes,[10-14] azobenzenes,[15-16] oxazolidines[17-18], etc.[19-20] into one molecule, a series of multi-addressable molecular switches have been achieved, which not only expands the stimuli species, but also enriches the output signals. Despite these efforts, there are still some challenges, e.g., the difficulty in synthesis and the independent control of the different switching units in single molecule.[16] In general, most of the multi-addressable molecular switches are achieved by linking two individual switches with non-covalent[21-27] or covalent[28-32] bonds (Scheme 1a). However, switching motifs with fewer and simpler units are more beneficial from the point of atomic efficiency.[8] Therefore, dual-addressable systems by fusing two switches through a shared central unit are designed.[12,33-35] These molecular systems can also achieve the independent control of each unit (Scheme 1b).[32]

The typical photochromic spiropyrans (SPs) are well known to undergo light-stimulated reversible isomerization between the colored merocyanines (MCs) and the colorless SPs. And the transition requires the changing of the C=C bond from *trans* to *cis* configuration first and reforming the C–O bond subsequently (Scheme 1c).[36-37] In addition, the benzoxazines (OXs) (Scheme 1d) are versatile switches with photo-, pH-, force- and electro-addressabilities.[37-40] In order to give out different outputs, incorporating different color switching units into a single molecule is an effective strategy[1,12]. Based on the above considerations, a dual-addressable molecule (SP-OX-$NO_2$) containing SP and OX (different absorption peaks) was designed and synthesized by sharing an indole group (Scheme 1e). Through proper molecular modification with nitro functional groups, both SP and OX isomers could be achieved separately upon exposure to different stimuli to give out different colors. Besides, the stimulation of base caused the SP isomer of SP-OX-$NO_2$ to undergo a ring-switching (spiral ring to oxazine ring) process to OX isomer.[41-43] Interestingly, a metastable *cis*-MC isomer was involved in the isomerization of MC or SP to OX necessarily. The new molecule SP-OX-$NO_2$ not only preserved the bidirectional switching property under visible light and base stimuli in solution, but also showed high contrast in both visible and fluorescent color. Furthermore, the application of SP-OX-$NO_2$ with photochromic and basochromic properties in multicolor rewritable paper was achieved.



**Scheme 1.** Illustration of the design of the (a) linked dual-switchable system and the (b) fused dual-switchable molecule. (c) Photo-/ baso- chromisms of a typical (c) nitrospiropyran and (d) oxazine. (e) Design and control of the transformation of SP-OX-$NO_2$ among its multiple states.

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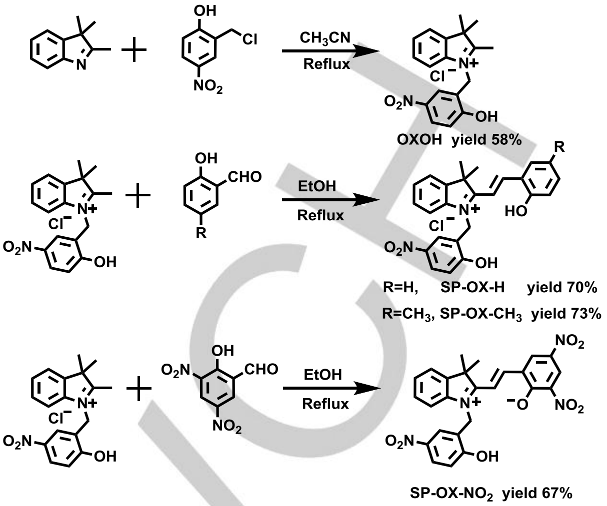
## Results and Discussion

### Investigation of the photochromic and basochromic properties of SP-OX-NO$_2$ in solution

The synthesis of SP-OX-NO$_2$ was shown in Scheme 2. First, the [1,3]oxazine part of the molecular switch was prepared by reaction of 3H-indole with 4-nitro-2-chloromethylphenol.[44] Then ortho-para-dinitrophenol was introduced to the protonated [1,3]oxazine to synthesize SP-OX-NO$_2$. And two control molecules, SP-OX-CH$_3$ and SP-OX-H as shown in Figure 1a were also synthesized.

Because SP-OX-NO$_2$ combined both a light responsive spiropyran and a base responsive oxazine, we investigated the photophysical properties of SP-OX-NO$_2$ to explore whether it had the bidirectional switching property in solution. Firstly, the state of SP-OX-NO$_2$ in solution was studied by NMR and UV-vis spectra. In the $^1$H NMR spectrum of SP-OX-NO$_2$ in DMSO-$d_6$ (Figure 2a), the single peak of dimethyl and methylene on indole and a coupling constant ($J_{10\text{-}11}$ = 15.5 Hz) indicated that the SP-OX-NO$_2$ existed in its ring-open *trans* MC form (Figure 1a). Besides, the DMSO solution of SP-OX-NO$_2$ was magenta with the absorption peak at 539 nm (Figure 1b, 1c), consistent with the control molecule of dinitrospiropyran in its MC form (Figure S5, S26).[45] Additionally, there was only one single peak for OH (chemical shift above 11 ppm) in SP-OX-NO$_2$ (Figure 2a, S23a) while there were two single peaks in SP-OX-CH$_3$ and SP-OX-H (Figure S24, S25) for both phenol groups, which meant one of the two hydroxyls lost a proton in SP-OX-NO$_2$. Because the phenolic hydroxyl on conjugated dinitrophenol was more acidic than that on non-conjugated nitrophenol, the hydroxyl on the conjugated dinitrophenol was inclined to dissociate and became phenolate (Figure 1a). The above results were all in accordance with the proposed structure of SP-OX-NO$_2$ in Figure 1a.

After exploring the initial state of SP-OX-NO$_2$ in solution, we investigated the tautomerization property with the stimuli of visible light and base. A yellow LED lamp (20W), which emitted light with a wide overlap with the absorption of SP-OX-NO$_2$, was chosen as the irradiation source. After irradiation for 5 min, the magenta solution turned colorless and its absorption peak shifted to 327 nm (Figure 1b, 1c). The color fading was caused by the formation of ring-closed SP form of SP-OX-NO$_2$, which was confirmed with NMR spectra. In the $^1$H NMR spectrum of SP-OX-NO$_2$ after irradiation (Figure 2b), the single peaks for dimethyl and methylene split into double and double-double peaks respectively because of the formation of spiral ring. Compared with $^1$H NMR spectrum of *trans* MC form (Figure 2a), the $^1$H NMR spectrum of SP form (Figure 2b) exhibited obviously highfield shifts overall. Hereinto, H10 exhibited the largest shift (about 2.38 ppm) owing to the transition of the electron-withdrawing effect of the nitrogen (imine cation) to the electron-donating effect. In addition, an absorption tail was detected and it could be attributed to the small amount of transformation of *trans* MC from ring-closed SP during the dark spectra measuring condition (Figure 1c, 1e).



**Scheme 2.** Synthetic routes for SP-OX-H, SP-OX-CH$_3$ and SP-OX-NO$_2$.

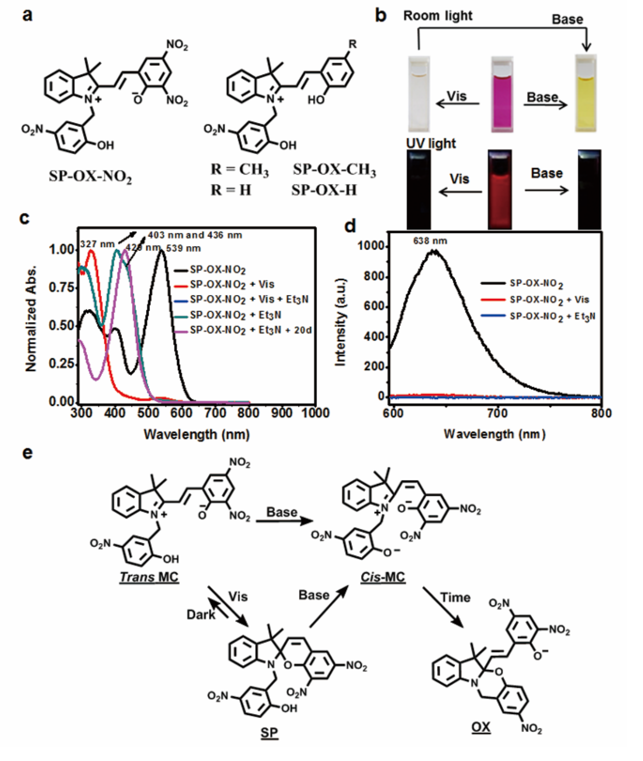


**Figure 1.** (a) The chemical structures of SP-OX-NO$_2$ and the control molecules, SP-OX-CH$_3$ and SP-OX-H. (b) The natural color and fluorescent images of SP-OX-NO$_2$ upon adding different stimuli. (c) The normalized absorption spectra of SP-OX-NO$_2$ upon exposure to different stimuli (blank, yellow light irradiation for 5 minutes, 1 equiv. Et$_3$N after yellow light irradiation, adding 1 equiv. Et$_3$N directly and being kept at room temperature for 20 days after adding 1 equiv. Et$_3$N) (The blue and green curves are overlapped). (d) The emission spectra of SP-OX-NO$_2$ upon exposure to different stimuli. (e) The structure speculation of SP-OX-NO$_2$ upon exposure to different stimuli. Solution: DMSO. Concentration: 50uM. Excitation wavelength: 577nm; slits: 3, 3.

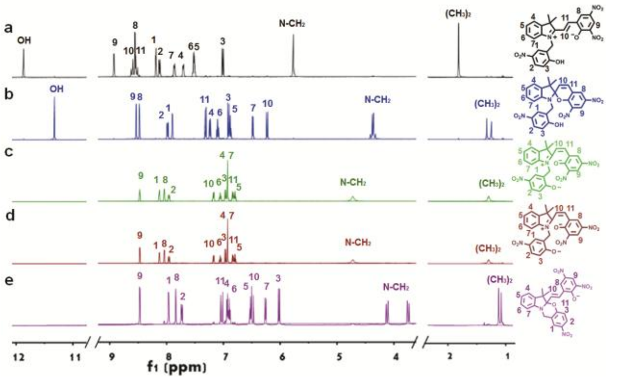


**Figure 2.** $^1$H NMR spectra of (a) *trans* MC form of SP-OX-$NO_2$, (b) SP-OX-$NO_2$ with yellow light irradiation for 5 minutes, (c) SP-OX-$NO_2$ with $K_2CO_3$ after yellow light irradiation, (d) SP-OX-$NO_2$ with $K_2CO_3$ directly and (e) SP-OX-$NO_2$ being kept at room temperature for 20 days after adding $K_2CO_3$ in DMSO-$d_6$ solution.

Following, the colorless solution of ring-closed form of SP-OX-$NO_2$ changed to yellow immediately upon adding 1 equiv. $Et_3N$ with new absorption peaks at 403 nm and 436 nm (Figure 1b, 1c). Referring to the absorption peak at 439 nm of control molecules (SP-OX-$CH_3$, SP-OX-H) (Figure S4) and the absorption peak at 434 nm for nitrophenol (Figure S6a) upon adding base, the new long-wavelength peak (436 nm) might come from the formation of non-conjugated nitrophenoxy anion and the new short-wavelength peak (403 nm) could be assigned to the adjustable structure of ring-closed SP form of SP-OX-$NO_2$. Moreover, in contrast to SP or OX segments of SP-OX-$NO_2$ (Figure S5), the absorption peak at 403 nm and 436 nm might be relevant to both the phenoxy anions after adding base. Therefore, we had a bold speculation that the new isomer of SP-OX-$NO_2$ with absorption peaks at 403 nm and 436 nm could be the *cis* form of merocyanine with two phenolate anions. The structure of this metastable *cis* merocyanine was denoted as *cis*-MC (Figure 1e) and confirmed by NMR measurement (Figure 2c). Specially, the peaks of dimethyl and methylene groups changed from double and double-double to both singlets; the coupling constant of the olefinic protons was 7.5 Hz; the peaks of hydrogen in aromatic region was between the *trans* MC form (Figure 2a) and ring-closed SP of SP-OX-$NO_2$ (Figure 2b), meaning that the indole part and dinitrophenol part of the new molecule did not conjugate each other as well as in the planar *trans* MC structure. All of the above results proved that the twisted *cis*-MC form was produced from SP form of SP-OX-$NO_2$ upon adding base. Compared with $^1$H NMR spectrum of SP isomer, H10 and methylene of *cis*-MC isomer (Figure 2c) exhibited downfield shift due to the electron-withdrawing effect of imine cation, while H11 exhibited a highfield shift owing to the electron-donating effect of oxygen anion on the conjugated structure; the H1, H2 and H3 exhibited nearly no shift thanks to the dual effects of nitrophenolate anion and the imine cation. These results also demonstrated the *cis*-MC isomer with two phenolate anions were generated, which indicated that the spiral ring of SP structure was destroyed and the C-O bond broke upon adding base (Figure 1e). In addition, the absorption spectra (Figure 1c) and $^1$H NMR spectra (Figure 2d) of the SP-OX-$NO_2$ solution with base directly coincided well with the results of SP-OX-$NO_2$ with base after visible light irradiation (Figure 1c, 2c), which indicated the initial *trans* MC form of SP-OX-$NO_2$ could also converted to *cis*-MC upon adding base.

It's reported the *cis-trans* isomerization can be triggered by light as reported in the literature[2, 46-47]. By irradiating the *cis*-MC with blue light (20W, 441nm), the absorption peaks of *cis*-MC isomer decreased and the absorption peak at 539nm increased (Figure S3b), indicating the *cis*-MC could photo-isomerize into *trans* MC, in agreement with the literature report on *cis-trans* isomerization[46]. Because the *trans* MC form of SP-OX-$NO_2$ can convert to ring-closed form of SP quickly with blue light irradiation (Figure S3c), the generated *trans* MC then transformed to ring-closed form of SP. So the photoinduced ***cis*−*trans*** isomerizations indicate the structure *cis*-MC is truly existence after adding base to *trans* MC of SP-OX-$NO_2$.

After keeping the SP-OX-$NO_2$ solution with base for 20 days at room temperature, the spectrum exhibited absorption changes and the absorption peak shifted to 429 nm, which was most likely due to the fact of isomerization from *cis*-MC to OX isomer. This conclusion was further confirmed by $^1$H NMR spectra (Figure 2e, S7). It was worth mentioning that the single peaks of dimethyl and methylene split into double and double-double peaks respectively because of the formation of oxazine ring; the coupling constant of H10 and H11 converted to 16Hz, meaning the C=C bond underwent a *cis-trans* isomerization; the spectrum of OX exhibited obvious highfield shifts comparing with the initial MC form of SP-OX-$NO_2$ (Figure 2a) because the electron-withdrawing effect of the nitrogen (imine cation) transformed to the electron-donating effect. All of these phenomena declared that the *cis*-MC isomer transformed to the OX isomer, accompanying with a *cis-trans* isomerization of C=C bond. Hence, *cis*-MC isomer of SP-OX-$NO_2$ was the key intermediate for the transformation process of SP or *trans* MC to OX after adding base in solution. The transformation of *cis*-MC to OX isomer could be promoted by increasing the temperature but below 40°C, because heating SP-OX-$NO_2$ at higher temperature with base resulted the irreversible cleavage of the oxazine heterocycle (Figure S8). Besides, the UV light (365nm, 20W) can also be beneficial for the transformation of *cis*-MC to OX, which is proved by UV-vis spectra and $^1$H NMR spectra (Figure S9). In brief, with visible light irradiation or base addition, the control molecules (SP-OX-$CH_3$, SP-OX-H) transformed to the ring-closed SP isomer (Figure S10, S11), while SP-OX-$NO_2$ showed bidirectional switching property via structural transformation among the initial *trans* MC, SP, *cis*-MC, and OX isomers (Figure 1e, 2). What's more, the strong red fluorescence of SP-OX-$NO_2$ was quenched by either yellow light or base in solution (Figure 1d, S13).

### DFT calculation to speculate the basochromism mechanism

As we designed, there would be two competitive nucleophilic reactions of the fused SP-OX molecular switches when two phenolate anions of phenols were generated. One the one hand, the conjugated phenol oxygen anion took a nucleophilic reaction to generate deprotonated SP form with a negative charge (SP-N). On the other hand, the nitrophenol attacked the carbon positive on indole to switch to OX. However, only one kind of ring-closed switch existed under the specific occasion and the thermodynamic reaction was inclined to generate the more stable isomer.

In order to investigate which isomer of OX and SP-N is more stable, the DFT calculation was carried out. A comparison between the calculated energies of the *cis*-MC, SP-N and OX isomers revealed that OX was energetically the most favoured conformer (Figure 3b, S15). The DFT calculation showed the reaction of cis-MC to SP-N released 12.27 kcal/mol energy while the reaction of *cis*-MC to OX released 20.93 kcal/mol energy (Figure 3b), so the tautomerization of *cis*-MC to OX was expected thermodynamically. We got the conclusion that when the energy of OX isomer was lower than the deprotonated SP isomer, the final product of the alkalization reaction was OX isomer. And the ring-closed SP was generated from the fused SP-OX molecule with visible light irradition, so the fused SP-OX molecule could behave as SP or OX depending on conditions.

Besides, owing to the strong electron-withdrawing property of nitro, the electron density of oxygen anion in dinitrophenol was lower than that in nitrophenol. Thus, the nucleophilic reaction of imine cation and nitrophenolate anion of *cis*-MC isomer was much easier to take place and then to form OX, which was consistent with the results of the NMR and UV-vis spectra.

For control molecules, SP-OX-$CH_3$, SP-OX-H, the energy difference of OX to SP-N yielded a value of 19.87 kcal/mol, 19.80 kcal/mol respectively (Table 1), indicating that the reaction to generate SP-N released more energy than the reaction to generate OX upon adding base, thus the SP-N was expexted thermodynamically, which also fitted well with the experimental data (Figure S3, S10-S11). According to the above results, the control molecules (SP-OX-$CH_3$, SP-OX-H) could only transform to the ring-closed SP form with the stimuli of either visible light or base, while the *trans* MC form of SP-OX-$NO_2$ could transform to the ring-closed form of SP and OX respectively thanks to the more stable OX isomer.

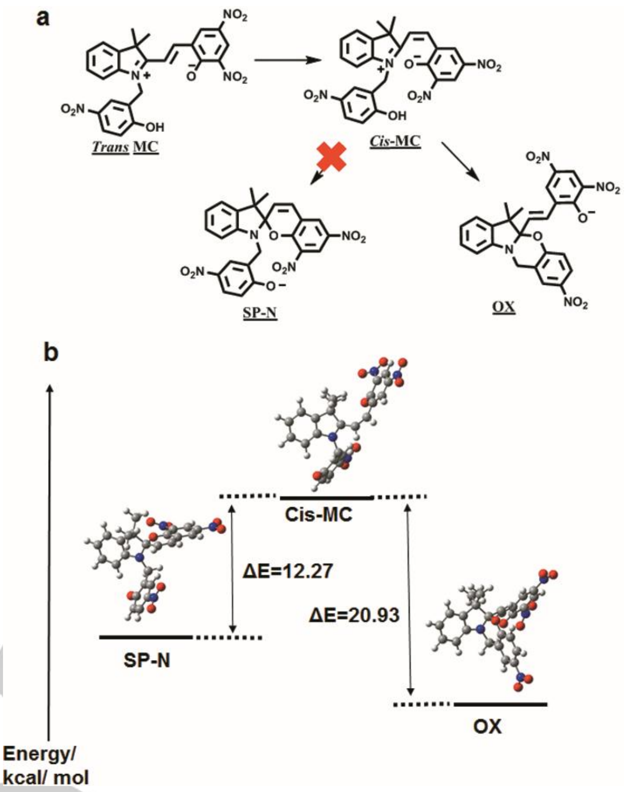


**Figure 3.** (a) The structural transformation of SP-OX-NO2 upon adding base. (b) The optimal structure and comparison of the relative energies (kcal/mol) of the ground states of cis-MC, OX and SP-N isomers based on B3LYP/6-31G(d) level by Gaussian 09.

**Table 1.** The energy differences (kcal/mol) between the different isomers of SP-OX-$NO_2$, SP-OX-$CH_3$ and SP-OX-H.

| Molecules | ΔE(RB3LYP)/ kcal/mol (*Cis*-MC to OX) | ΔE(RB3LYP)/ kcal/mol (*Cis*-MC to SP-N) | ΔE(RB3LYP)/ kcal/mol (OX to SP-N) |
|---|---|---|---|
| SP-OX-$NO_2$ | 20.93 | 12.27 | -8.66 |
| SP-OX-$CH_3$ | ----[a] | ----[a] | 19.87 |
| SP-OX-H | ----[a] | ----[a] | 19.80 |

(a) The cis-MC isomer of SP-OX-$CH_3$ and SP-OX-H is not obtained by B3LYP/6-31G (d, p) calculations.

### Investigation of the multichromic property of SP-OX-$NO_2$ on the solid substrate

The observation of bidirectional switching property and obvious color changes of SP-OX-$NO_2$ in solution encouraged us to further investigate the multi-color switching property on solid matrix. Filter paper was chosen as a substrate, upon which polyethylene glycol (PEG) was loaded to passivate the multi-hydroxyl of paper (Figure 4a).[48-49] To examine the photochromic and basochromic properties of the SP-OX-$NO_2$ based paper, reflective UV–vis spectra were measured with an integrating sphere upon exposure to the visible light or base. Before any stimulation, the magenta paper exhibited a broad reflectance peak at 539 nm, which was assigned to the *trans* MC form of SP-OX-$NO_2$ (Figure 4b). Besides, the SP-OX-$NO_2$ based paper showed highly red fluorescence with a 643 nm emission peak (Figure 4d). With yellow light irradiation, a safe and convenient stimulating method, the paper displayed a light yellow color owing to the presence of the proton accepter PEG (Figure S22). The light yellow paper returned to its initial magenta state reversibly by heating at 80 $^{o}$C within 30 seconds (Figure S21a). These results indicated that the photochromic property of SP-OX-$NO_2$ was retained in solid substrate. Treating the magenta paper with a methanol solution containing 5mM $Et_3N$ resulted in a bright yellow color on the paper. And about 20% of reflectance at 442 nm was observed, meaning that the color was quite obvious in naked eyes (Figure 4c). The yellow paper could be repetitively wrote with base and erased by heating at 80 $^{o}$C (Figure S21b). What's more, the fluorescence of the SP-OX-$NO_2$ could be quenched with the stimuli of either visible light or base (Figure 4d, 4e). Additionally, both the natural-color and fluorescent microscopy images of different states of SP-OX-$NO_2$ revealed that there was no aggregation on the paper substrates before and after treatment with light and base (Figure 4f).

The visible light, base and heat stimuli could be applied independent of each other, which was beneficial for drawing more colorful patterns (Figure S19) and practical usage. In Figure 5, various patterns were drawing on the SP-OX-$NO_2$ based paper by yellow light with photomasks and a base-ink pen.

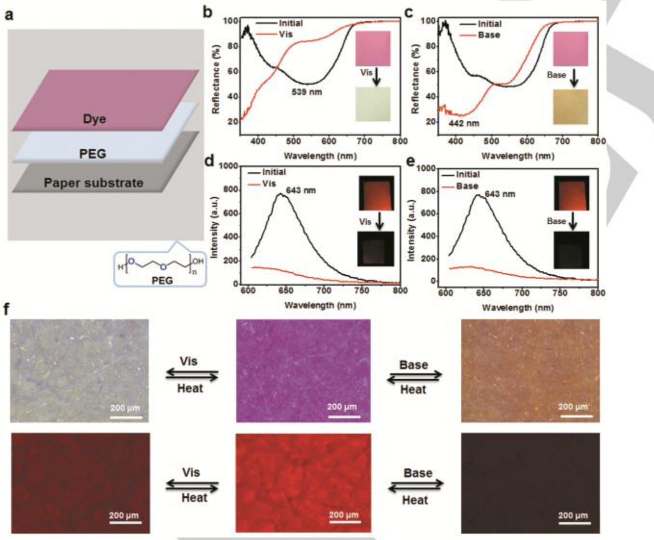


**Figure 4.** (a) Illustration of the three-layer structure of rewritable paper based on the SP-OX-$NO_2$. Reflective UV−Vis spectra of the SP-OX-$NO_2$ based rewritable paper, (b) before and after yellow light irradiation, (c) before and after adding 5mM $Et_3N$. The emission spectra of the SP-OX-$NO_2$ rewritable paper, (d) before and after yellow light irradiation, (e) before and after adding 5mM $Et_3N$. (f) The natural-color and fluorescent microscopy images of the initial state, with the stimuli of vis-light and 5mM $Et_3N$ (scale bar = 200μm).

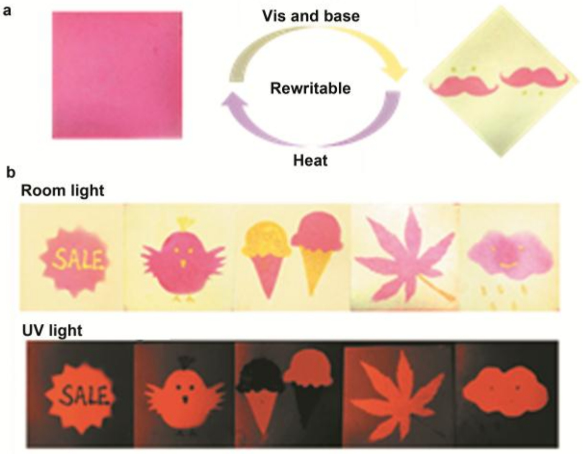


**Figure 5.** (a) Schematic illustration of the rewritable paper based on SP-OX-$NO_2$ upon exposure to visible light and base. (b) The natural-color and fluorescent images of the SP-OX-$NO_2$ based rewritable paper.

The pictures in ambient light or under UV light all gave naked-eye legibility and good resolution (Figure 5b). Placing the drawing paper with yellow painting and purple background upon exposure to sunlight for a week, the background of the paper gradually faded to light yellow, which was agreed with the advocated reduction of light pollution to human's eyes and the characters kept bright as initial color stably (Figure S20). In brief, the paper material based on SP-OX-$NO_2$ displayed multi-color using yellow light, base and heat with stability and reversibility.

## Conclusions

A dual-addressable molecular switch SP-OX-$NO_2$ by fusing the switches of SP and OX through a sharing central indole has been synthesized. The *trans* MC form of SP-OX-$NO_2$ transformed to ring-closed form of SP or OX upon visible light irradiation or base addition in solution respectively. An unexpected formation of *cis*-MC was also observed in untreated or visible light irradiated SP-OX-$NO_2$ solution upon adding base and could be regarded as the intermediate during the OX switching process. The interconversions of the four different states were proved by UV-vis, NMR spectra and DFT calculation. The calculated results also suggested that the fused SP-OX molecular switches showed the bidirectional switching property highly dependent on more stable isomer of OX than SP-N. Moreover, this attractive multistate photo- and basochromic molecule SP-OX-$NO_2$ was used for rewritable paper with high contrast in both visible and fluorescent color, repeatability and good resolution. The strategy adopted in this work simplifies the molecular design for multi-addressable systems, and encourage us to further explore the multi-function in multicolor reversible display, sensing, logic gates and so on.

## Experimental Section

### Materials

DMSO (chromatographic grade), acetonitrile (chromatographic grade), trifluoroacetic acid (TFA) and triethylamine (TEA) were purchased from Aladdin Reagent Company (Shanghai, China), ethanol (EtOH) and dichloromethane ($CH_2Cl_2$) were purchased from Beijing Chemical Works (Beijing, China). 3,5-dinitrosalicylic aldehyde, 5-methylsalicylaldehyde, salicylaldehyde, p-nitrophenol, dinitrophenol, 1,2,3,3-tetramethyl-3H-indol were purchased from Energy Chemical Company (Shanghai, China). PEG 20000 (molecular weight: 17,000-22,000) was purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). Cellulose filter paper (Whatman-Xinhua, grade 91, Hangzhou, China) was used as the paper substrate.

### Instruments

$^1$H NMR spectra were recorded on a 500 MHz BrukerAvance at room temperature. $^{13}$C NMR spectra were recorded on a 126 MHz BrukerAvance. The deuterated solvents of DMSO-$d_6$ were used for $^1$H NMR and $^{13}$C NMR. Tetramethylsilane (TMS, δ = 0.00 ppm) was used as an internal standard for $^1$H NMR. DMSO-$d_6$ (δ = 77.00 ppm) were used as internal standards for $^{13}$C NMR. Absorption spectra were measured on a Shimadzu UV-2550 PC double-beam spectrophotometer. Reflective spectra were tested by integrating sphere on Analitik Jena Specord®210 plus UV-Vis spectrophotometer, using $BaSO_4$ as background, slit was 2 cm. Fluorescence spectra were measured with a RF-5301PC spectrofluorometer. LC-HRMS analysis was performed on an Agilent 1290-micro TOF-Q II mass spectrometer (electrospray ionization (ESI) source). The LED light source and ultraviolet lamp was used for irradiation experiments (yellow light and bule light, 20 W; 365nm, 8W). The Microscale colors of the media were imaged in transmission mode using Leica DM4000 M microscope. The melting point was measured by using a SGW X-4B microscopy melting point apparatus (Shanghai, China).

### General Synthesis and characterizations of SP-OX-$CH_3$, SP-OX-H and SP-OX-$NO_2$

SP-OX-$CH_3$, SP-OX-H and SP-OX-$NO_2$ were synthesized in the same way according to the synthetic routes shown in Scheme S1[44].

**(E)-2-(2-(1-(2-hydroxy-5-nitrobenzyl)-3,3-dimethyl-3H-indol-1-ium-2-yl)vinyl)-4,6-dinitrophenolate:**

1-(2-hydroxy-5-nitrobenzyl)-2,3,3-trimethyl-3H-indol-1-ium chloride (1mmol, 0.35 g) and 2-hydroxy-3,5-dinitrobenzaldehyde (1.2mmol, 0.25 g) were heated and refluxed in 10 ml ethanol solution for 8 h under argon atmosphere. After cooling to ambient temperature, the solvent was filtered to get the precipitate and washed with ethanol for several times to obtain a red-black solid powder (338 mg, 67%). Melt point: 195.3 $^o$C.$^1$H NMR (500 MHz, DMSO-*d₆*), δ= 11.87 (s, 1H), 8.93 (d, *J* = 3.0 Hz, 1H), 8.62 (d, *J* = 15.5 Hz, 1H), 8.56 (d, *J* = 3.0 Hz, 1H), 8.54 (d, *J* = 15.5 Hz, 1H), 8.19 (d, *J* = 2.5 Hz, 1H), 8.14 – 8.11 (dd, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* =8.0 Hz, 1H), 7.52 (t, 2H), 7.02 (d, *J* = 9.0 Hz, 1H), 5.77 (s, 2H), 1.84 (s, 6H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ = 183.84, 169.52, 162.05, 152.92, 143.14, 141.07, 140.98, 139.57, 134.62, 128.89, 128.45, 128.40, 126.21, 126.18, 125.55,124.98,122.97, 120.35, 115.92, 114.77, 110.86, 51.70, 45.82, 26.47. LC-HRMS: m/z calcd. [M+H]$^+$ 505.1359, found 505.1355.

**(E)-2-(2-hydroxy-5-methylstyryl)-1-(2-hydroxy-5-nitrobenzyl)-3,3-dimethyl-3H-indol-1-ium:**

1-(2-hydroxy-5-nitrobenzyl)-2,3,3-trimethyl-3H-indol-1-ium chloride (1mmol, 0.35 g) and 2-hydroxy-5-methylbenzaldehyde (1.2mmol, 0.16 g) were heated and refluxed in 10 ml ethanol solution for 6 h under argon atmosphere. The solvent was evaporated and added with ether to extract precipitate. The product was filtered and washed for several times with ethyl acetate and anhydrous ether to obtain the orange solid product (338 mg, 73%).$^1$H NMR (500 MHz, DMSO-$d_6$), δ= 12.00 (s, 1H), 11. 00 (s, 1H), 8.60 (d, *J* = 16.5 Hz, 1H), 8.49 (s, 1H), 8.14 (dd, 1H), 7.90 (m, *J* = 16.5 Hz, 2H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.57 (m, 2H), 7. 31 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 9.0 1H), 7. 01 (d, *J* = 9.0 Hz, 1H), 5.96 (s, 2H), 2.28 (s, 3H) ,1.80 (s, 6H). LC-HRMS: m/z calcd. [M+H]$^+$ 429.1809, found 429.1804.

**(E)-1-(2-hydroxy-5-nitrobenzyl)-2-(2-hydroxystyryl)-3,3-dimethyl-3H-indol-1-ium:**

1-(2-hydroxy-5-nitrobenzyl)-2,3,3-trimethyl-3H-indol-1-ium chloride (1mmol, 0.35 g) and 2-hydroxybenzaldehyde (1.2mmol, 0.15 g) were heated and refluxed in 10 ml ethanol solution for 6 h under argon atmosphere. The solvent was evaporated and added with ether to extract the precipitate. The product was filtered and washed for several times with ethyl acetate and anhydrous ether to obtain red solid product (314 mg, 70%). $^1$H NMR (500 MHz, DMSO-$d_6$) , δ= 12.05 (s, 1H), 11.24 (s, 1H), 8.64 (d, *J* = 16.0 Hz, 1H), 8.42 (s, 1H), 8.13 (dd, 1H), 7.96 (d, *J* = 16.0 Hz, 1H), 7.90 (d, *J* =7.0 Hz, 1H), 7.82 (d, *J* = 7.0 Hz, 1H), 7.58 (m, 2H), 7.49 (t, H), 7.12 (m, 2H), 6.98(t, 1H), 5.96 (s, 2H), 1.81 (s, 6H). LC-HRMS: m/z calcd. [M+H]$^+$ 415.1652, found 415.1645.

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## Conflicts of interest

The authors declare no conflict of interest.

**Keywords:** multi-addressable molecular switch • spiropyran• benzoxazine • visible light and base• rewritable paper

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Layout 1:

## FULL PAPER

A dual-addressable molecule (SP-OX-$NO_2$) containing SP and OX was designed by sharing indole in a single molecular system. The bidirectional switching property could be controlled with the stimuli of visible light or base in solution, respectively. Further, SP-OX-$NO_2$ was applied in rewritable paper displaying multi-color with different stimuli including vis-light, base and heat.

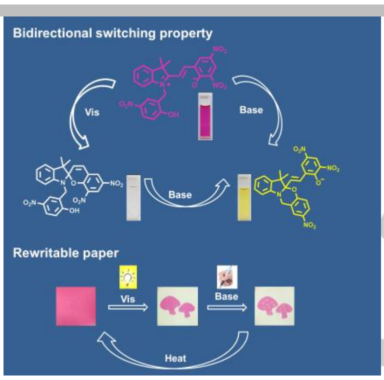

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**Photo-/ baso- chromisms and the application of a dual-addressable molecular switch**

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