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A Multi-Addressable Dyad with Switchable CMY Colors for Full-Color Rewritable Papers

Tianyou Qin,[a] Jiaqi Han,[b] Yue Geng,[b] Le Ju,[b] Lan Sheng,*[b] and Sean Xiao-An Zhang*[a]

Abstract: Reversible multicolor displays on solid media using single molecule pigments have been a long-awaited goal. Herein, a new and simple molecular dyad, which can undergo switchable CMY color changes both in solution and solid substrate upon exposure to light, water/acid, and nucleophiles, is designed and synthesized. The stimuli used in this work can be applied independent of each other, which is beneficial for color changes without mutual interference. As a comparison, the mixtures of the two molecular switching motifs forming the basis of the dyad were also studied. The dyad greatly outperforms the corresponding mixed system with respect to reversible color-switching on the paper substrate. Its potential for full-color rewritable paper with excellent reversibility has been demonstrated. Legible multicolor prints, that is, high color contrast and resolution, good dispersion, excellent reversibility, were achieved using common water-jet and light-based printers. This work provides a very promising approach for further development of full-color switchable molecules, materials and displays.

Introduction

Main Text Paragraph. Although electronic media is widely used in daily life, paper, with its long history, still plays an extremely important role in information transmission and knowledge inheritance. Society still enjoys to read, write and paint with paper. Most paper is usually disposed of just after one-time reading, however, paper production and recovery processes are associated with significant environmental problems including deforestation, solid waste disposal issues and chemical pollution.[1] For these reasons, rewritable ink[2] and rewritable paper[3], which can allow a single piece of paper to be reused multiple times, are now attracting much attention from the perspective of sustainable development. To date, numerous examples[2-22] have been reported in this field which make use of both organic and inorganic materials. Among these works, interconversion between colorless and one or two different colors on a sheet of paper have been demonstrated by employing various external stimuli, such as electricity,[2] heat,[3,4] light,[6-12] water,[16-18] and metal ions.[22] Nevertheless, in many cases, the communication of complex messages and images needs to be presented in full color in order to satisfy the demands of the readers. In this context, the development of full-color rewritable papers is especially relevant.

Multi-addressable molecular switches are attractive as candidates that could endow materials with multichromic display capabilities. These molecules are capable of reversibly changing their colors by stimuli-promoted isomerization reactions. One strategy to achieve a full-color display with these types of molecules is to mix together three independent molecular switches, each of which is capable of displaying either cyan (C), magenta (M) or yellow (Y), respectively.[6,9,23,24] This strategy is a simple way to achieve multicolor capabilities in both solution and solid media. Another complementary strategy is to incorporate three or more molecular color switching motifs into a single molecule. Such a single molecule would possess several potential advantages over the above mentioned mixed system, namely, avoidance of phase separation which is necessary for producing high resolution images, exhibiting consistent color balances across large areas, and so on. Even despite these merits, there are only a few single molecule systems[25-29] capable of multichromic display that have been successfully implemented. One among these is a full-color display that relied on a fused dithienylethene trimer demonstrated by Professor Irie and co-authors[26]. Nevertheless, these reported systems only exhibited multicolor switching in solution, and rarely demonstrated its color switching in a solid substrate. Probable technological obstacles include: 1) the challenge to design and synthesize switchable molecules capable of displaying multiple colors, especially the three primary colors, under different stimuli; 2) complications caused by the surrounding microenvironment present in the solid state, wherein the molecules may operate differently than they do in solution; 3) most reported multicolor display systems are based on full-photo mode molecules[25,26,28], which might cross-interfere with each other when imaging on a solid substrate.

Based on these considerations, integrating switchable molecular units capable of responding orthogonally to different stimuli into a single molecule might be a more effective method to realize multicolor displays on solid media. Relative to other stimuli, light and water in this role can be delivered to precise locations, are obviously nontoxic, environmentally friendly, and integrate well with current laser-jet and ink-jet printing technologies. Light and water stimuli can be applied totally independent of each other without mutual interference. Taking into account these characteristics, water- and light-responsive switching units seemed like a good choice from a design point of view. Moreover, from the perspective of atom economy and reducing the potential for deleterious influences among a

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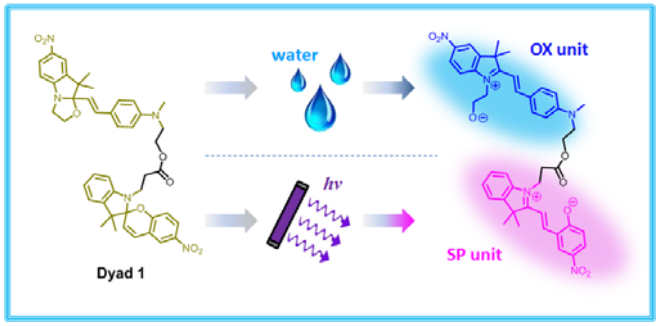

Figure 1. Illustration of the structural design for dyad **1** and the color-changing isomerizations for each subunit.

plurality of structural units, incorporating fewer and simpler switching motifs into one system is more beneficial. Therefore, in this work, we designed and synthesized a simple new dyad **1** with dual-switching capabilities that allowed it to undergo changes in color using water and/or light stimuli (**Figure 1**). Reversible full-color displays, i.e., magenta, blue, and yellow colors, making use of the dyad by employing different stimuli were investigated in solution as well as in solid substrates. As a comparison, simple mixtures of the two molecular switching motifs forming the basis of the dyad were also studied. The application of the dyad in multicolor rewritable paper was developed.

Results and Discussion

1. Investigation of the multi-stimuli chromic properties of dyad 1 and the mixed system in solution

Spiropyrans (**SP**s) are unique photochromic switches, which are known to undergo light-stimulated reversible isomerization between their colorless (ring-closed) and colored (ring-open) forms, and are easy to synthesize. Hence, **SP**s have been widely used in light responsive materials.[30] Oxazolidines (**OX**s) have been reported as a new class of photochromic and halochromic molecular switches, which have been mostly investigated in the context of enhanced nonlinear optical materials.[31] Recently, our group has demonstrated that **OX**s could also be reversibly switched by introduction and removal of water both in solution and solid substrates, resulting in obvious color changes. This feature has been employed for the construction of "water-jet" rewritable paper, making use of standard printer-ink cartridges filled with water.[16] Even though **OX**s and **SP**s are both photochromic molecules, according to the literature, the photochromic ability of **OX**s always depends on their specific molecular structures and the particular ambient conditions, while the photochromism of the **SP** unit is more independent of structure and the surrounding microenvironment. In an attempt to obtain a single molecule capable of hydrochromism- and photochromism-multicolor displays, herein we have designed and synthesized dyad **1,** which consists of an **OX** unit for blue color and an **SP** unit for magenta color display (**Figure 1**). Dyad **1** was prepared by condensation of the hydroxy group of **OX** with the carboxyl group of **SP** making use of (1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide as a condensation reagent (details of the synthesis are in the supporting information). The six-atom non-conjugated bridge between the two units is necessary to ensure each switching unit's ability to act independently.

As a control, mixtures of **OX** and **SP** (**OX+SP**), compounds which constitute the core switching units of dyad **1** were also studied. The photochromic and hydrochromic properties for both dyad **1** and the **OX+SP** mixture in ethanol solutions were investigated first (**Figure 2**). Without external stimuli, the solutions of **1** and **OX+SP** are both initially colorless (**Figure 2a** and **2d**, **black lines**). Upon UV irradiation, the colorless solutions of **1** and **OX+SP** transform to magenta. These colorations are accompanied by the appearance of absorption bands centered at 552 and 537 nm for dyad **1** and **OX+SP**, respectively (**Figure 2a** and **2d**, **magenta lines**). Both colored solutions could be returned back to their colorless states upon visible light irradiation (**Figure 2a** and **2d**, **gray lines**). These color and spectral changes arise from the **SP** unit, a hypothesis which was verified by the respective UV tests of **OX** and **SP** (**Figure S1**). In comparison to the mixed system, there is a 15 nm red shift for the absorption band of dyad **1**. This subtle shift likely arises from the non-conjugated N-substitution of the **SP** subunit necessary for synthesizing dyad **1** (**Figure S2**). Surprisingly, addition of excess NaOH to the solution of dyad **1** after UV irradiation caused the magenta solution to change to a yellow color, an observation which is correlated to a decrease in the absorption band centered at 552 nm and appearance of a new band at 416 nm (**Figure 2a**, **yellow line**). Additionally, the

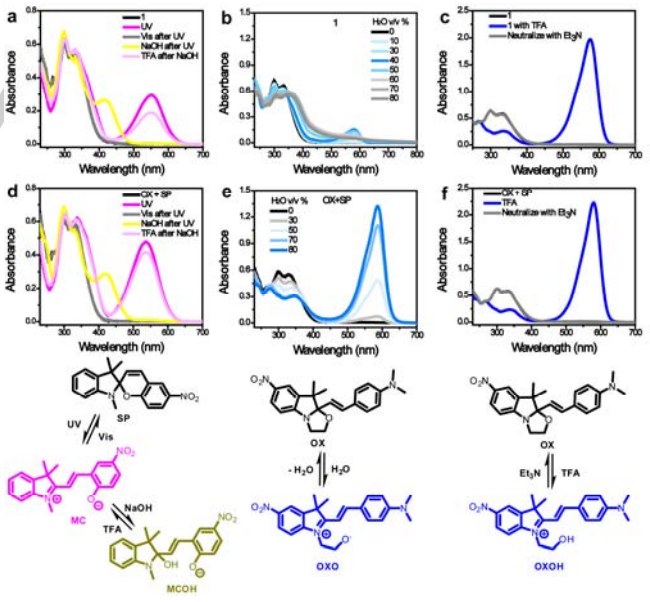

Figure 2. Absorption spectra for **1** and the mixed **OX+SP** system in ethanol, respectively, with a, d) after UV- (254nm) / visible-light irradiation, adding excess NaOH after UV exposure, and adding TFA after NaOH, b, e) different water contents (%), and c, f) acid/base. The concentration was 2 × 10^{-5} M for each molecule. The structural changes shown below for **SP** and **OX** are responsible for the different color-switching behavior under external stimuli.

yellow color can return almost completely back to the original magenta color by adding an appropriate amount of trifluoroacetic acid (TFA) (**Figure 2a**, **light magenta line**). A similar phenomenon was also observed in the mixed system (**Figure 2d**, **yellow and light magenta lines**). The generation of yellow color may be the result of formation of **MCOH** via nucleophilic addition[32] of a hydroxide to the electrophilic imine of the open-ring form of the **SP** switch (**Figure S3**). The corresponding structural changes in **SP** that result in the magenta and yellow colors are shown below **Figure 2d**.

Next, the hydrochromic properties for dyad **1** and **OX**+**SP** were each tested. Increasing the content of water in the ethanol, solution resulted in little color changes for the case of dyad **1**, and only a weak absorption peak was observed in the visible region (**Figure 2b**). In contrast, the mixed system of **OX**+**SP** showed a bright blue color when increasing the water content (**Figure 2e**). Noticeably, during the experiment, the solution containing dyad **1** becomes gradually more turbid with increasing water content (**Figure S4**). This observation indicates that the hydrochromism of dyad **1** might be inhibited by its poor solubility resulting from its larger molecular structure. Taking into account that **OX** is also known for its halochromism, and in order to confirm the **OX** subunit still works as a switch, the halochromism of dyad **1** was investigated. Addition of TFA to a solution of **1** did lead to a blue color change from an initially colorless solution, as well as the appearance of a new absorption band centered at 575 nm (**Figure 2c**, **blue line**). A similar phenomenon was observed for the **OX**+**SP** system (**Figure 2f**, **blue line**). This color change is attributed to the acid-induced ring-opening of the **OX** unit, because **SP** does not have absorption in that region under the same acidic conditions (**Figure S5**). In addition, the blue solutions and their corresponding spectra can completely be returned to their colorless states by adding triethylamine (Et_3N) (**Figure 2c** and **2f**, **gray lines**). These results suggest that the **OX** switching unit on dyad **1** is still functional, even if its hydrochromism is lost in solution likely as a result of its poor solubility. The structural changes of the **OX** subunits that result in the blue-colored solutions upon addition of water or acid are shown below in **Figure 2e** and **2f**, respectively.

The dyad **1** is capable of undergoing reversible photochromic and halochromic switching behavior in solution using mutually compatible stimuli bringing about magenta and blue colors, respectively. An additional reversible yellow color change was also obtained by means of a nucleophilic attack employing NaOH and recovered with TFA. Thus, three primary colors — magenta, yellow and blue — for the dyad **1** can be obtained. Structural transformations for the dyad **1** during these processes, which were further confirmed by NMR and mass spectroscopy (**Figure S6, S7**), and the corresponding color changes observed in its solutions are shown in **Figure 3**. The mixed **SP+OX** system, on the other hand, has the advantage over dyad **1** in that it is still capable of demonstrating hydrochromic behavior in solution.

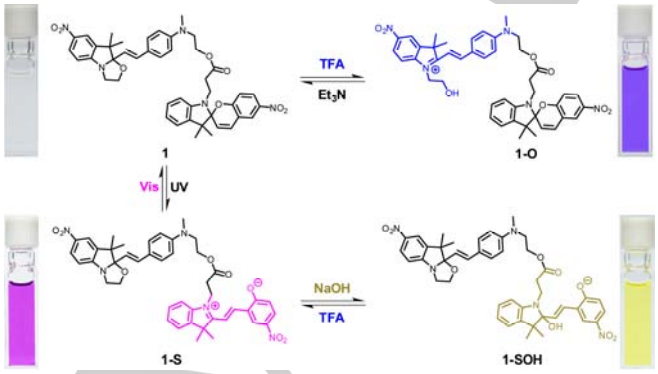

Figure 3. The structural transformations for dyad **1** and corresponding color changes.

2. Investigation of the multi-stimuli chromic properties of dyad 1 and the mixed system on the solid substrate

Encouraged by its switching behavior in solution, the multi-stimuli addressable color switching properties of dyad **1** were investigated next in a solid matrix. Drawing on the experience of our previous work,[16] a stimuli-responsive paper composed of a three-layer structure was designed (**Figure 4a**). Filter paper was chosen as the substrate upon which dyad **1** was loaded. First the filter paper was covered with a layer of polyethylene glycol (PEG, Mn: 20000), a polymer which passivates the hydroxy groups of the paper and stabilizes the initial colorless state. PEG was also introduced into the next imaging layer containing dyad **1** in order to prevent its aggregation. We next examined whether **1** retains the switching properties observed in solution. The experiments were monitored by UV-vis reflective spectroscopy with integral ball. Prior to any external stimuli, the paper appears white, and almost no absorption in the visible region of the spectrum is observed (**Figure 4b**, **black line**). Upon UV irradiation, the paper takes on a magenta color which is accompanied by the appearance of a new reflective peak centered at 556 nm (**magenta line**). The magenta colored paper could be returned to its initial white state by using visible light irradiation and heat (**gray line**). These color changes result from structural changes of the **SP** subunit (**Figure S8**). The results of these irradiation experiments indicate that the photochromism of **1** is retained in this paper-based matrix. The halochromism of **1** in the paper matrix was also tested. Volatile acetic acid (CH_3CO_2H), acting as a weaker and safer acid than TFA, was used in this experiment. Treating the paper with an aqueous solution containing 0.01% CH_3CO_2H resulted in the blank paper taking on a blue color, and a reflective band was observed in the visible region around 594 nm (**Figure 4c**, **blue line**). Based on the understanding of the mechanism in solution, these changes in color and spectral features are a result of the ring-opening transformation of the **OX** subunit. Unexpectedly, heat treatment of the blue paper formed from addition of aqueous acetic acid was unable to revert it completely to its initial colorless state. However, the fact that such a small amount of aqueous acidic solution could trigger the color change seemed to hint that the microenvironment surrounding the dye is playing a crucial role in the ring-opening reaction of the **OX** unit. In addition, the hypothesized influence of poor solubility on the hydrochromic

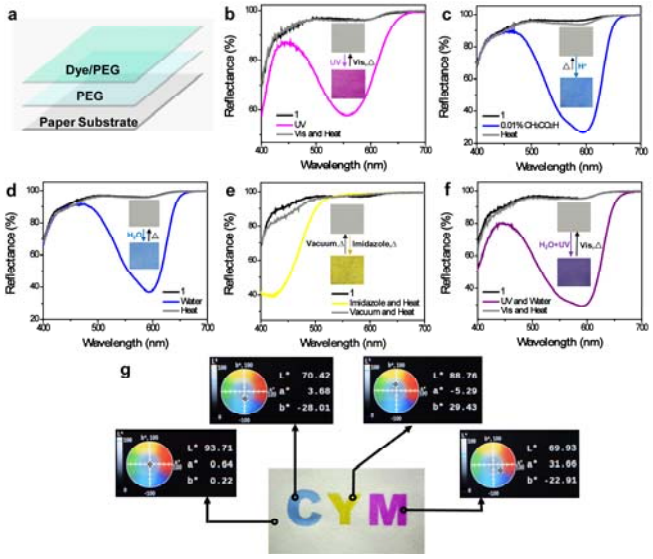

Figure 4. a) Schematic illustrations of the three-layer structural design for the rewritable paper based on **1**. Reflective UV−Vis spectra of the **1**-based paper, b) before (black trace) and after UV irradiation (254 nm, magenta trace), c) before (black trace) and after (blue trace) addition of 0.01% CH_3CO_2H, d) before (black trace) and after (blue trace) addition of water, e) before (black trace) and after (yellow trace) adding imidazole and heating, and f) before (black trace) and after (purple trace) treating with both water and UV light. G) Photograph of the rewritable paper stimulated with water (blue C), imidazole-heat (yellow Y), UV light (magenta M), and the corresponding CIE Lab coordinates.

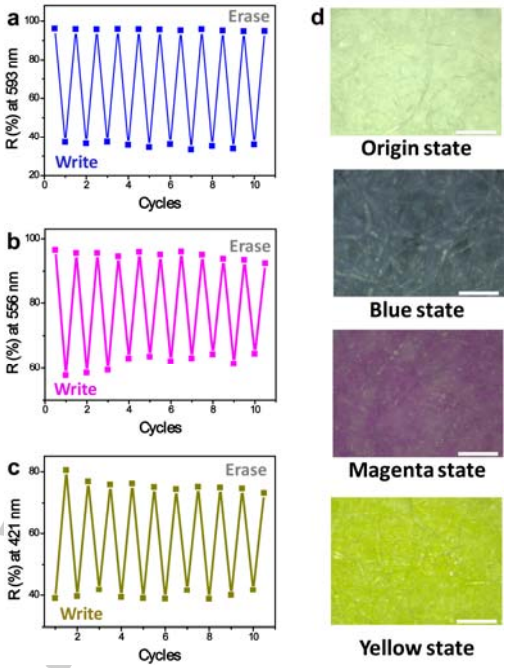

Figure 5. The plot of the reflectance of the rewritable paper loaded with **1** versus the number of write/erase cycles as the rewritable paper was repetitively exposed to a) water spraying (write) and water removal (erase) by means of wetting/heating at 70 °C, b) UV (write) and Vis-heat (erase) irradiation, and c) spraying with an imidazole solution and heating at 70 °C (write), and imidazole removal by heating at 100 °C under vacuum (erase). d) Images of the initial state, after addition of water (blue state), after UV irradiation (magenta state), and after treating with imidazole and heat (yellow state) of the paper as imaged under a microscope. Scale bar: 200 μm.

switching behavior of **1** in solution may not be relevant in the solid paper matrix. These considerations inspired us to investigate the hydrochromism of **1** once again. Upon introduction of water, the paper displayed a blue color accompanied by the observation of a reflective band centered at 593 nm **(Figure 4d**, **blue line**), observations which are the consequences of the change in structure of the **OX** unit to its ring-open form (**Figure S9**). Different from the acid-induced coloration, we found that the colored paper stimulated by water can be completely returned to its initial blank state by removal of the water using heat (**Figure 4d**, **gray line**). These experiments demonstrate that water is a much better stimulus than acetic acid, endowing the paper-based matrix containing **1** with both write and erase capabilities.

Even though the yellow color of **1** can be achieved by addition of NaOH, complete recovery of the initial colorless state both in solution and the paper matrix is very difficult (**Figure S10**). These switching processes were stimulated by introduction of strong alkali solutions (i.e. NaOH) and corrosive acid (i.e. TFA), conditions of which are not ideal for everyday consumer applications. Inspired by the fact that the imidazolyl group of histidine residues functions as an important catalyst in biological processes because of its nucleophilic charac-ter,[33,34] we tried imidazole as the nucleophile instead of hydroxide. Upon the introduction of imidazole, the yellow color is still observed. Furthermore, with the help of heat, development of the yellow color does not require pretreatment of the paper substrate with UV irradiation. Upon introduction of an ethanolic solution of imidazole to the white paper accompa-nied by heating at 70 °C, the yellow color appeared, and a new reflective peak centered at 421 nm was observed (**Figure 4e**, **yellow line**). Different from the yellow color observed when only the **SP** unit is combined with NaOH, the yellow color of **1** in the paper-based matrix that results from the introduction of imidazole arises from nucleophilic additions at both the **OX** and **SP** subunits of **1** (**Figure S11**). In addition, the color could be erased by heating the paper to 100 °C under vacuum and leaving almost no trace (**Figure 4e**, **gray line**). This reversible color change is due to thermal decomposition of the imidazole adducts.[35] In addition, when water and UV acted simultaneously on the paper matrix incorporating **1**, a purple color was obtained (**Figure 4f**). This purple color is a mixture of magenta and blue that results from the ring-opening isomerizations of both the **OX** and **SP** units, respectively. It is worth mentioning that the similar paper matrices prepared from the mixed **OX**+**SP** system with the same concentraiton were unable to revert back to their initial states, no matter what stimuli tested (**Figure S12**, **last column**). Even though decreasing concentration of **OX** or **SP** or both of them could improve its reversibility to a certain extent, the developed colors (i.e. reflectance) upon stimulation were decreased as well (**Figure S12, S13**). This result indicates that the switching performances of the single molecule **1** outperform its corresponding mixed system on solid media. This better

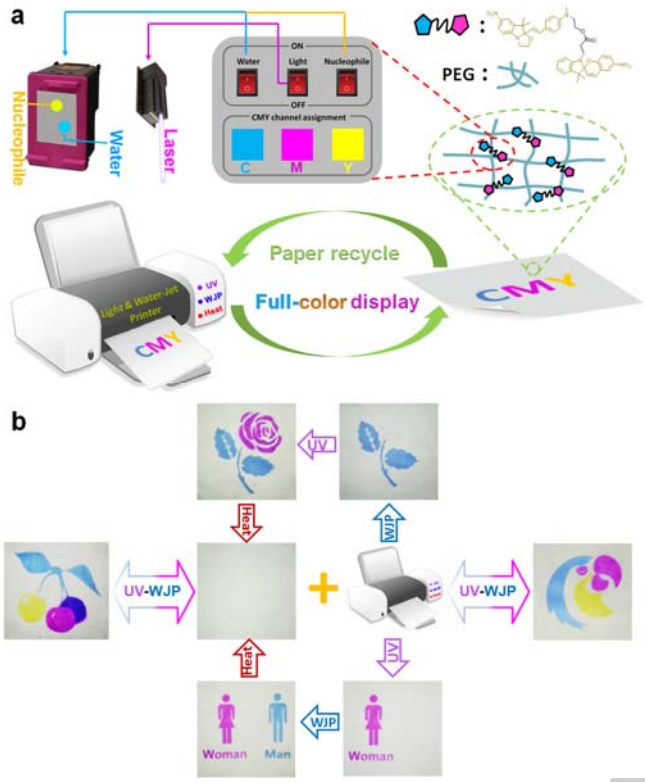

Figure 6. a) Schematic illustration of full-color printing. b) Examples of muliticolor images displayed on the rewritable paper by water-jet printing with pure water for the blue color, a combination of an ethanol solution of imidazole with UV irradiation for the yellow color, and UV irradiation only for the magenta color.

performance might be hinged upon the fact that the structure of **1** helps to prevent undesirable interactions between its two subunits via their covalent linkage, behavior of which can still take place in the case of the **OX**+**SP** physical mixture.

The dyad **1** recovers its hydrochromic property and is capable of displaying a reversible change to yellow in the paper-based substrate. Therefore, this paper is capable of displaying three primary colors each in a reversible fashion using three different stimuli. As shown in **Figure 4g**, a blue letter "C" written by water-jet printing, a magenta letter "M" written by UV irradiation, and a yellow letter "Y" hand-written with an imidazole solution and heat were all obtained on one paper. The detailed information of the colors is described by the CIE Lab coordinates.

3. Application in full-color display rewritable paper and its performance

To further confirm the reversibility of the paper with respect to reversion of the three primary colors of blue, magenta and yellow, their corresponding reflectances at 593 nm, 556 nm, and 421 nm were measured after water-spraying/heating, UV-light irradiation/visible-light irradiation and heating, and imidazole introduction and heating/heating at 100 °C under vacuum, respectively (**Figure 5a-5c**). After 10 write-erase cycles, the paper still works well for each color. Microscopy images reveal that aggregation was not observed on the paper substrates before and after treatment with water, UV light, and imidazole-heat for developing the blue, magenta and yellow colors, respectively (**Figure 5d**). These results support the notion that formation of non-switchable aggregates of **1** are effectively prevented with the aid of PEG in the imaging layer, and that the single molecule system can avoid phase separations unlike the corresponding mixed **OX**+**SP** system resulting in better dispersion of the switchable dye molecules.

In brief, dyad **1** containing just two switch subunits could act as a three-switch molecule and display three-primary colors using water, light and nucleophile. Combining these stimuli with standard printing technologies (i.e., water-jet printing and light printing), **1**-based paper is easy to achieve full-color display printing and reuse (**Figure 6a)**. In order to demonstrate the practical application of this multicolor rewritable paper, we printed colorful patterns containing blue, magenta, yellow and purple. As shown in **Figure 6b**, we could print the blue and magenta patterns with water and UV irradiation, respectively, in a step-by-step fashion. For multicolor display, magenta was printed with UV irradiation; blue and yellow were generated by water-jet printing using water and imidazole inks, respectively. The heat brought on the paper during the deposition of the imidazole ink is sufficient for producing the yellow color. The purple color can be displayed when UV and water act on the same place. All of the patterns written could be erased.

Conclusions

In summary, we have designed and synthesized a new and simple dual-switch molecule **1** consisting of hydrochromic oxazolidine and photochromic spiropyran units, and studied its color switching properties both in solution and a paper-based substrate. Three primary colors of CMY, as well as a composite purple color, for **1** can be written with excellent reversibility by selective exposure from a suite of different stimuli including water/acid, light, nucleophiles and heat. A mixed system composed of the separate spiropyran and oxazolidine subunits (i.e., **SP+OX**) was also investigated for a side-by-side comparison. Even though the mixed system seems to have better performance in terms of hydrochromic switching than the new single molecule **1** at least in solution, the latter greatly outperforms the former with respect to reversible color-switching on the paper substrate. The hydrochromism of **1** that failed to be observed in solution was successfully recovered when loaded, with good dispersion, onto the paper substrate using the assistance of a solid solvent (i.e., PEG). An unexpected reversible display of a yellow color for **1**-based paper was also achieved by making use of imidazole as a nucleophile with simultaneous heating, instead of the more commonly employed strong alkali (i.e., NaOH) and corrosive acid (i.e., TFA) conditions. The potential application of **1** for developing full-color rewritable paper with good reversibility and uniformity has been demonstrated. The stimuli and methods employed in the both the construction as well as writing and erasing of the paper are clean, economic and compatible with current ink-jet and laser-jet

printing technologies. In addition, based on its ability to write and erase information using a variety of different stimuli, dyad **1** should also have potential uses in logic gates and multi-information storage. The strategy utilized herein demonstrates a promising approach for designing new multi-addressable molecular switches as well as extending their applications to full-color rewritable papers that use environmentally friendly ink-free printing technologies.

Acknowledgements

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Conflict of interest

The authors declare no competing interest.

Keywords: rewritable paper • photochromism • hydrochromism • multicolor • water-jet printing

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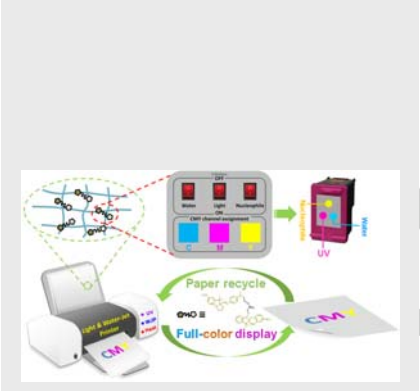

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