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Full Color Light Responsive Diarylethene Inks for Reusable Paper

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“Digitalization” represents one approach to shift society’s dependence on paper-based communication. However, thus far, this tactic has not had a significant impact on global paper consumption, which has risen over the past few decades. The escalating demand of paper making and consumption has resulted in an intensified negative effect on the environment. Because of this, the development of rewritable paper or erasable ink appears to be an ideal approach to alleviate the increasing demand for paper. In the investigation described herein, novel light-stimulated (UV–vis), reversible color switching, photochromic diarylethene (DE) derivatives are designed, which serve as cyan, magenta, and yellow colored ink materials for full color ink-jet printing. The structures of the DE derivatives are unique in that they contain hydrophilic ethylene glycol chains that enable them to be compatible with aqueous based, ink-jet printing systems. The results of these studies demonstrate that the new DE derivatives can be used in a printing system based on the “write–erase–write” concept that utilizes the same paper multiple times. The approach appears to be ideal for reducing the negative environmental consequences of paper production and consumption.

1. Introduction

Paralleling advances made in technology, electronic-based communication and digitalization have grown significantly to a point where they are an integral part of the lives of most human beings. In spite of these advances, society still relies on paper as the key material used to communicate and record information. Paper has played an extremely important role in recording history and enabling the cultural development of society. The creation of electronic based communication methods that substitute for paper has not been as rapid as was expected, which is evidenced by threefold increase in the global consumption of paper over the past few decades.[1,2]

According to findings made in recent surveys, most documents containing information recorded on paper are disposed after a one-time use. This trend is creating serious and growing environmental problems associated with deforestation, solid waste, and chemical pollution in air, water, and on land.[3,4] As a result, much attention has been given to the development of rewritable paper that can be used multiple times. If successful, the new technology would help bring about a balance between the socioeconomic advancement of society and environmental protection. In this context, several types of rewritable papers and erasable inks have been described recently. One elegant approach to this problem utilizes a rewritable composite paper, containing a photocatalyzed, color switchable redox dye. In this system, ink-free replication of a text/pattern created by using a preprinted photomask is possible.[5] In another remarkable effort, a hydrochromic dye embedded paper was designed for water-jet printing where water serves as the trigger for color switching.[6] By taking advantage of their tunable refractive index property, photonic crystals have been utilized to fabricate rewritable paper. In this system, a well-ordered photonic coating is embedded on substrate for pattern-on-demand printing using water,[7] hygroscopic salts,[8] and silicon fluid[9] as inks. Furthermore, a wide range of photoresponsive color switchable functionalized azobenzenes,[10,11] flugides,[12,13] bisthienylethenes,[14] spironapthooxazine,[15] and spiropyrans[16] have been explored in potential rewritable paper applications. In similar approaches, phenomenon involving reversible halochromism of oxazine derivatives[17] and thermochromism of leuco dyes[18,19] has been employed to develop rewritable paper systems.

In the investigation described below, we devised and tested a new strategy for the design of light-responsive ink for rewritable paper, which is based on the photochromic switching properties of diarylethenes (DEs). DEs are known to undergo light-stimulated (UV–vis) reversible photochemical cyclization and cycloreversion reactions, which are accompanied by color switching from colored closed to colorless open ring forms.

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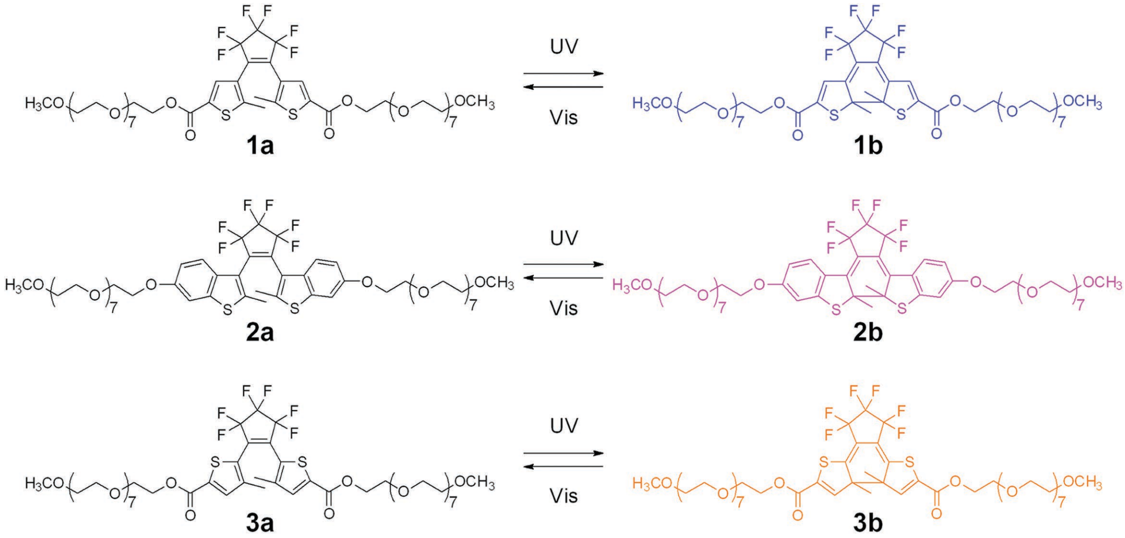

Figure 1. Structures of the hydrophilic DEs. Light-stimulated (UV–vis) reversible isomerization, colorless-ring open form **1a–3a** & colored-ring closed form **1b–3b**.

Among various types of photochromic molecules, DEs are the most promising class in terms of their thermal stability and fatigue resistance, as well as their ability to participate in repeatable color switching cycles.[20–32] Specially, photochromic performance of nonionic water soluble DEs inspired us to design erasable ink system.[33,34] The results of the study show that well designed hydrophilic DE derivatives (**Figure 1**) can be readily synthesized and that they can be employed in erasable inks for rewritable paper that can be used in multiple "print–erase–print" cycles.

2. Results and Discussion

2.1. Design of Hydrophilic DEs

Based on knowledge about the photochromism of DEs combined with our objective to develop erasable full color inks for ink-jet printing, we designed hydrophilic photochromic substances for use as cyan, magenta, and yellow primary colors in inks. The core structures of the DEs were selected based on existing knowledge about the substances that undergo light-stimulated color switching (Figure S1, Supporting Information). The results of a literature survey indicated that the colors of the ring-closed isomers of these substances could be readily manipulated by simply changing the position of sulfur atom in the thiophene ring.[35] Accordingly, the photochromic DEs **1a**, **2a**, and **3a** (Figure 1) were designed to produce cyan, magenta, and yellow colors, respectively, upon UV irradiation. The required hydrophilicity of the molecules used in the inks was installed by incorporating covalently linked, polar ethylene glycol chains of proper length to the DE cores. The ethylene glycol moieties not only make the molecules suitable for use as ink material but it also offer advantages over ionic salts and sulfonic acid group in terms of long term stability, nontoxicity, and environmental friendliness.

2.2. Synthesis of DE Derivatives

The initial goal of this effort was to develop the light-responsive, cyan colored dye **1a** as an ink to replace traditional, high color intensity black ink. The strategy utilized for the synthesis of **1a**, depicted in **Figure 2**, begins with 4-bromo-5-methylthiophene-2-carbaldehyde (**4**). This substance was prepared in high yield by formylation of 2,5-dibromo-3-methylthiophene using *n*-butyllithium and dimethylformamide (DMF). The aldehyde group in **4** was protected as its diethyl acetal derivative by reaction with triethyl orthoformate to generate **5**,[36–38] which was then lithiated by using *n*-butyllithium. The organolithium intermediate was then reacted with octafluorocyclopentene followed by acid hydrolysis using trifluoroacetic acid to form photochromic diformyl substituted DE **6**.[39,40] Jones oxidation of **6** produced the corresponding dicarboxylic acid derivative **7**,[41] which upon treatment with oxalyl chloride and a catalytic amount of DMF gave the acid chloride intermediate, which was directly used for coupling with octaethylene glycol monomethyl ether to generate the target DE **1a** (Supporting Information).

Next, we extended our synthetic strategy to prepare the respective magenta and yellow colored DEs **2a** and **3a** as light-responsive inks for full color ink-jet printing. For magenta, thianaphthene derivative **2a** was synthesized starting from 3-methoxythiophenol by employing multistep synthetic route[42–44] (Supporting Information). In case of yellow (**3a**), synthetic strategy similar to **1a** was employed (for scheme and experimental details, see the Supporting Information). The structures of synthetic **1a**, **2a**, and **3a** were confirmed by using IR, ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectra (HRMS) spectral methods (Figures S2–S10, Supporting Information).

2.3. Photochromic Properties

Photochromic properties of DEs **1a**–**3a**, all of which are highly soluble in water, were examined. These substances in aqueous

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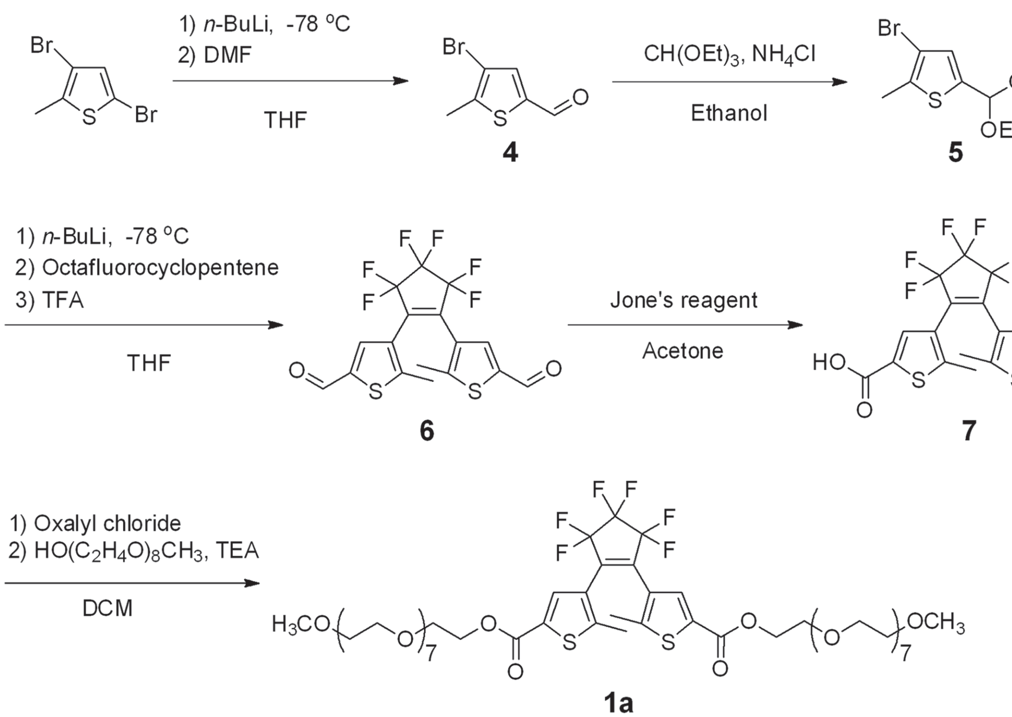

1a

Figure 2. Synthetic route for the preparation of DE **1a**.

solutions were observed to undergo light stimulated, reversible isomerization accompanied by significant color-switching. Inspection of the absorption spectra and images displayed in **Figure** 3a–c shows that the open-ring isomers **1a**, **2a**, and **3a** have absorption maxima at 256 (ε: 34 × 10^3 M^{-1} cm^{-1}), 269 (ε: 18.6 × 10^3 M^{-1} cm^{-1}), and 333 (ε: 12.6 × 10^3 M^{-1} cm^{-1}) nm, respectively. Upon UV light irradiation, colorless solutions of **1a**, **2a**, and **3a** transform to respective cyan, magenta, and yellow colored solutions, as a consequence of formation of the respective closed-ring isomers **1b**, **2b**, and **3b**. Absorption maxima of the closed-ring isomers **1b**, **2b**, and **3b** are 592 (ε: 8.2 × 10^3 M^{-1} cm^{-1}), 533 (ε: 10.4 × 10^3 M^{-1} cm^{-1}), and 441 (ε: 4.6 × 10^3 M^{-1} cm^{-1}) nm, respectively. Visible light irradiation of the colored solutions containing the ring-closed isomers regenerates the original colorless solutions that have identical absorption spectra to that of **1a**, **2a**, and **3a**.

The quantum yields for cyclization and cycloreversion reaction, and conversion ratio were measured in water at room temperature by reference method.[45,46] Conversion ratios (C. R.) from the open- to the closed-ring form, upon irradiation with UV light, are 90%, 14%, and 18% for **1a**, **2a**, and **3a**, respectively. The quantum yield of the cyclization reaction of **1a** (Φ: 0.65) was determined to be much higher than its cycloreversion process (Φ: 0.025). While the quantum yields for cyclization reaction of **2a** (Φ: 0.088) and **3a** (Φ: 0.45) were lower than cycloreversion process (Φ: 0.11, 0.64). Quantum yield, absorption maxima, and their coefficients for the open- and closed-ring isomers were also calculated in ethyl acetate (**Table 1**). The solvent effect of **1a**–**3a** for cyclization process has been studied in series of aprotic solvents and protic solvents in Figure S11 (Supporting Information).

We also investigated the photofatigue properties of **1a**–**3a** in water at room temperature.[47,48] Figure S12 (Supporting Information) illustrates the irradiation time dependent absorbance changes of **1a**–**3a** at the absorption maximum of their closed-ring isomers by applying UV light (254 nm) for 6 h in dark. The absorption maxima for **1b** and **2b** significantly declined over the time and decayed about 50% after 90 and 230 min of irradiation time, respectively, indicating by-product formation from the closed-ring isomer. In contrast, compound **3b** does not show any significant decay for 6 h of irradiation. Upon alternating irradiation with UV (254 nm) and visible light (>450 nm), photocyclization and cycloreversion cycle of **3a** could be repeated for ten times without noticeable change in absorption maxima. Significant loss of photochromic material was observed for **1a** and **2a** after a few switching cycles (Figure S13, Supporting Information).

2.4. Ink Formulation

To achieve optimal printing performance, the nonionic surfactant Brij 78 was utilized in the ink formulation. The inks, individually containing DEs **1a**–**3a**, were prepared using the following generic formulation: 1 g (10 wt%) of DE, 0.5 g (5 wt%) of Brij 78, and 8.5 mL (85 wt%) of deionized water. The solutions were sonicated for 30 min to ensure that they are homogeneous, and then irradiated with a hand-held laboratory UV lamp (254 nm, 1 mW cm^{-2}) for 30 min. The colorless solution containing **1a**, **2a**, and **3a** were observed to change to cyan (**I1**), magenta (**I2**), and yellow (**I3**), respectively (Figure 3g). Absorption maxima for ink solutions **I1**–**I3** were compared with the commercial ink (HP 703 tricolor) solutions (Figure S14, Supporting Information).

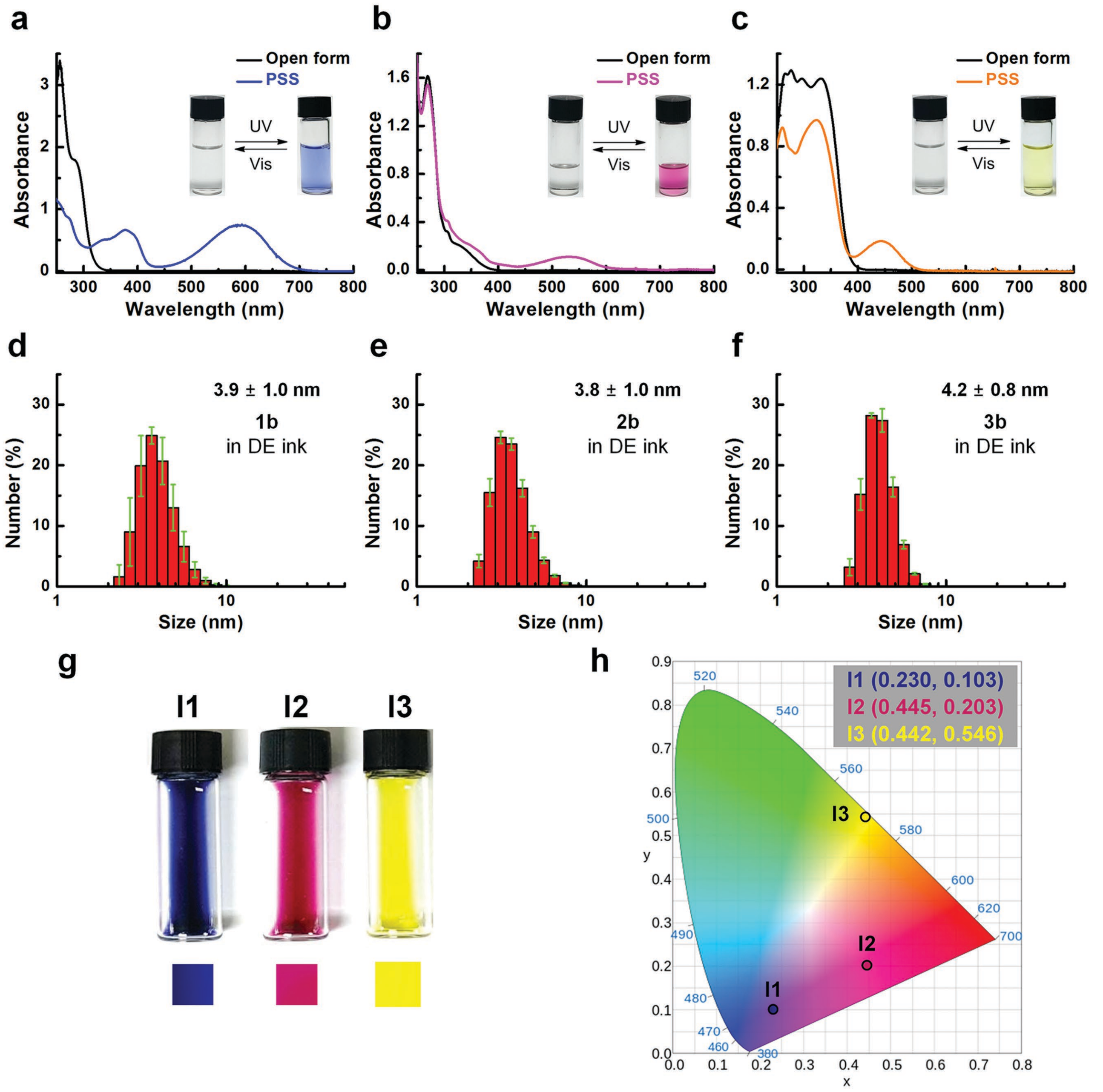

Figure 3. a–c) UV–vis spectra of aqueous solutions of compounds **1**–**3** (1×10^{-4} mol L^{-1}) in open form (solid black line) and at photostationary states (PSS), (solid colored line) formed by irradiation with UV light (254 nm for compounds **1**, **2** and 365 nm for compound **3**). The inset in each figure shows color change of the photochromic solution. d–f) Particle size distributions of DE inks **I1**–**I3** obtained by using DLS. g) Photographs of UV-irradiated DE inks **I1**–**I3** and their extracted color samples below. h) CIE coordinates of DE inks **I1**–**I3**.

2.5. Particle Size Distribution

Amphiphilic substances display self-assembly properties in aqueous environments. Consequently, dynamic light scattering (DLS) analysis was carried out to determine particle size distributions of ink solutions **I1**–**I3**. The results show the existence of self-assembled nanospheres with respective average spherical diameters of 3.9 nm ± 1.0, 3.8 nm ± 1.0, and 4.2 nm ± 0.8 (Figure 3d–f). DLS measurements on **1a**–**3a** (open-ring form) in pure water and **1a**–**3a** (open-ring form) in DE ink solutions also show existence of self-assembled nanospheres with average spherical diameters <5 nm (Figure S15 and Table S1, Supporting Information).

2.6. Viscosity Measurements

The viscosities of the ink solutions **I1**–**I3** were measured at room temperature and were found to be in the range acceptable for ink-jet printing with 2.4, 3.0, and 2.7 cP, respectively.

Table 1. Photochromic properties of DE derivatives **1**–**3**.

Compound	Solvent	λ_{max} [nm]/ε [10^3 M^{-1} cm^{-1}]		$\Phi^{c)}$		C. R.$^{d)}$ [%]
		Open-ring isomer$^{a)}$	Closed-ring isomer$^{b)}$	Cyclization $\Phi_{o\text{-}c}$	Cycloreversion $\Phi_{c\text{-}o}$	
1	Water	256/34	592/8.2	0.65	0.025	90
	Ethyl acetate	257/34.4	593/10.4	0.41	0.24	84
2	Water	269/18.6	533/10.4	0.088	0.11	14
	Ethyl acetate	268/23	534/12.7	0.59	0.25	99
3	Water	333/12.6	441/4.6	0.45	0.64	18
	Ethyl acetate	331/15	443/6.8	0.53	0.40	37

$^{a)}\lambda_{max}$ (absorption maximum) and ε (absorption coefficient) of open-ring isomers; $^{b)}\lambda_{max}$ (absorption maximum) and ε (absorption coefficient) of closed-ring isomers; $^{c)}$Quantum yields of cyclization reaction ($\Phi_{o\text{-}c}$) and cycloreversion reaction ($\Phi_{c\text{-}o}$); $^{d)}$Photoconversion ratio from the open- to the closed-ring isomers at photostationary state.

These values are in good agreement compared to respective commercial inks. Measurements of **1a**–**3a** (open-ring form) in DE ink solutions did not show any significant difference in the viscosity (Table S2, Supporting Information).

2.7. Commission Internationale de l'Éclairage (CIE)

Colors of formulated inks are depicted in CIE color space. The scanned images (PNG format) of ink were normalized in Adobe Photoshop (despeckle, dust and scratches, median filters) to minimize artifacts introduced by scanner hardware noise to determined CIE coordinates.[49,50] CIE coordinates of cyan (**I1**), magenta (**I2**), and yellow (**I3**) at (x,y) = (0.230,0.103), (0.445,0.203), and (0.442,0.546), respectively (Figure 3h).

2.8. Ink-Jet Printing

The excellent dispersion properties of the DE derivatives in water are compatible with those required for ink-jet printing. In order to demonstrate the quality of print obtained by using the inks, text was printed on conventional A4 size paper using the light-responsive cyan (**I1**) ink. For this purpose, a commercial black ink cartridge was filled with **I1** ink and ink-jet printing was carried out using a common office printer (HP Deskjet Ink Advantage K209) (**Figure 4**a). In order to obtain information about the printing resolution, the quality of **I1** ink-printed images on a paper substrate were compared to those generated using conventional black ink (Figure 4b,c). Inspection of the images demonstrates that the resolution and color intensity of the light-responsive ink-printed image are ideal for general reading purposes, and the legibility of the prints can last at least 3 h under ambient condition.

Importantly, the printed text, formed by using ink **I1**, is completely erased by using visible light irradiation (35 W Xe lamp) (Figure 4a). To demonstrate that the erasable light-responsive ink formulations are applicable to rewriteable paper, repeated "print–erase" cycles were carried out with cyan (**I1**) ink (**Figure 5**a). Visible light from a 35 W Xe lamp at a 1 cm distance above the printed image was used for erasing the text and patterns created using ink **I1**. The image was observed to completely disappear upon irradiation with the Xe lamp for 30 s. Each "print–erase" cycle was found to take place without reduction in the quality of the paper. The nature of the "print–erase" cycle was also probed by using absorption spectroscopy (Figure 5b). Visible light irradiation of the printed-paper results in the nearly complete disappearance of absorption in the 500–700 nm region. In Figure 5c are shown absorbance changes at 592 nm during ten consecutive "print–erase" cycles. The legibilities of printed text and images were found to last for more than several months under dark conditions (Figure S16, Supporting Information). Importantly, printed images on paper, stored under dark conditions for several months, are also readily erased by using visible light irradiation. Finally, similar results were observed for text and images printed with magenta (**I2**) ink (Figure S17, Supporting Information).

Next, we explored techniques to obtain full color images. Owing to the low color intensity of the yellow ink (**I3**), direct ink-jet printing of a full color image with cyan (**I1**), magenta (**I2**), and yellow (**I3**) inks using a commercial tricolor cartridge does not lead to high quality full color images. Consequently, the optimal composition of the ink was created by adding appropriate amounts of yellow (**I3**) ink to both cyan (**I1**) and magenta (**I2**) inks. The optimum molar ratios were found to be **I1**:**I3** = 3:7 for the new cyan **MI1** and **I2**:**I3** = 7:3 for the new magenta **MI2** inks. **Figure 6** displays a full color image printed using these ink combinations. As expected, the full color image can be erased by using visible light irradiation and a new erasable full color image can be printed on the same paper.

3. Conclusion

The photochromic performances of **1a**–**3a** in aqueous solutions were found to be excellent, with generating the corresponding three primary colors, cyan, magenta, and yellow, upon UV irradiation. Brij 78 was found to be an effective stabilizer of ink formulation. The average particle size of 3.7–4.2 nm was observed for DE inks (**I1**–**I3**), caused by the presence of ethylene glycol pendant, made the inks compatible with typical ink cartridge nozzles (no clogging of the nozzle vicinity of the ink-jet head), reduced image unevenness and blurring, and

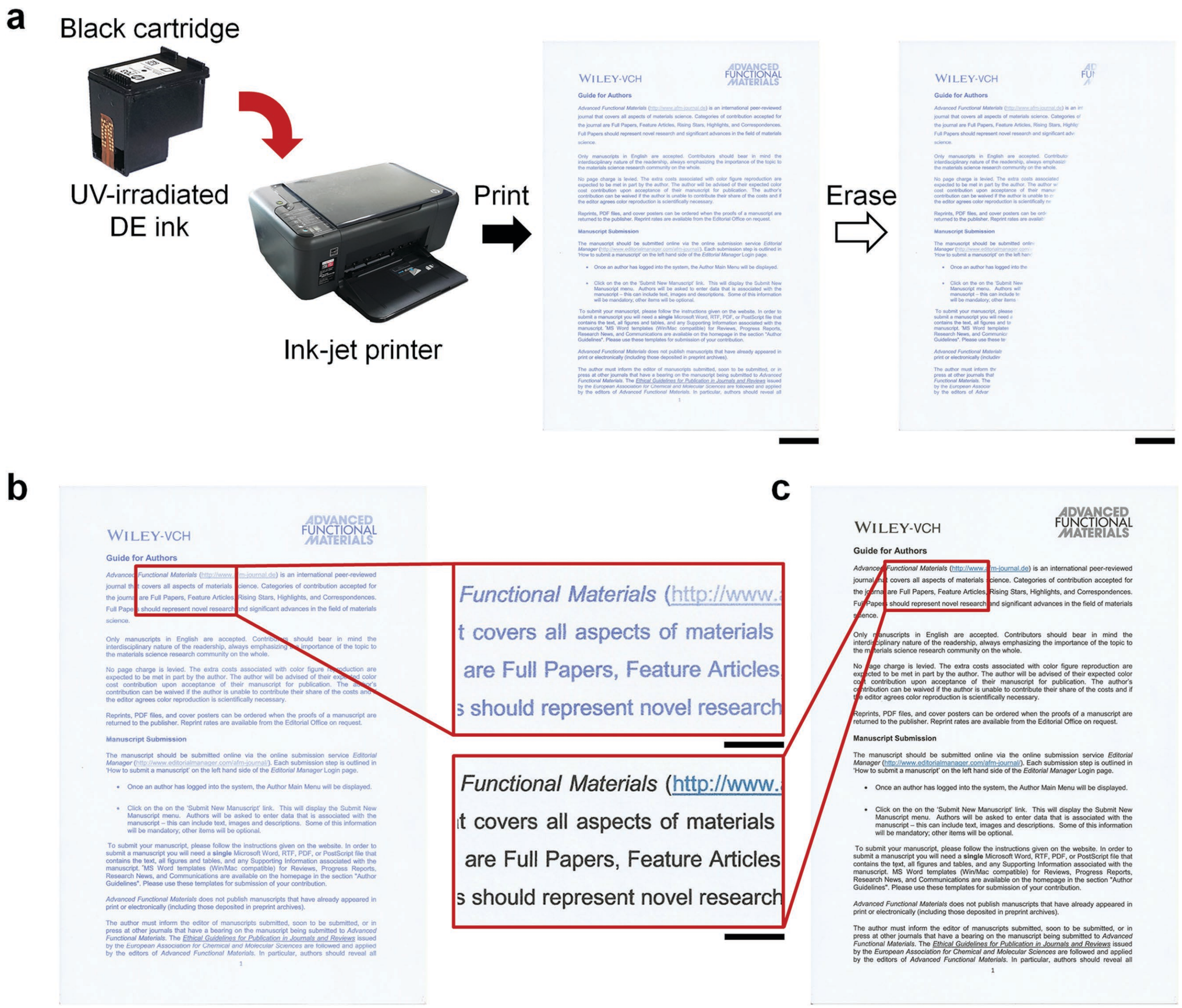

Figure 4. a) Scanned images of cyan-color prints obtained using an ink-jet printer with a black cartridge filled with **I1** (200 μL). Image and text were half-erased by using visible light. Scale bars, 3 cm. b,c) The resolution of printed text using the light-responsive cyan ink (b) is compared to the text printed with a commercial inkjet printer (c). Scale bars, 1 cm.

contributed to higher optical densities of the printed images. Viscosity values were also in acceptable range of aqueous-based inks, for high quality ink-jet printing. Printed text, arising from using cyan (**I1**) and magenta (**I2**) inks, was found to have a good resolution and patterns created from the inks have sharp edges. Printing of satisfactory images was possible even after prolonged storage (>one month) of the light-responsive inks loaded in a cartridge.

We observed for the first time that these primary colored inks can be used to produce full-color images on conventional paper. The printed full-color text/pattern can be erased by irradiation with visible light without affecting the quality of the paper. Also, "print–erase" cycles can be carried multiple times with no deterioration of the quality of the images. We believe that the substances explored in this effort will be useful in developing aqueous-based ink for ink-jet printing. This approach is ideally suited to rewriting paper multiple times without any resource-intensive processing. An additional meritorious feature of the new ink is that, even when the printed image is stored in the dark for several months, it can be readily removed by irradiation with visible light.

It should be noted that the limitation associated with low color intensities of images printed using the yellow colored ink needs to be overcome in order to avoid the need for multiple printing events. It also should be emphasized that printing with cyan ink alone gives a high quality, readily erasable image that is good for general reading purposes (Figure S18 and Movie S1, Supporting Information). Further advancements in structural modifications of diarylethene derivatives and optimization of printing condition are under progress. The proof of concept arising from the results of the current study should open a new avenue to the development of erasable full color inks that are compatible with common office inkjet printers.

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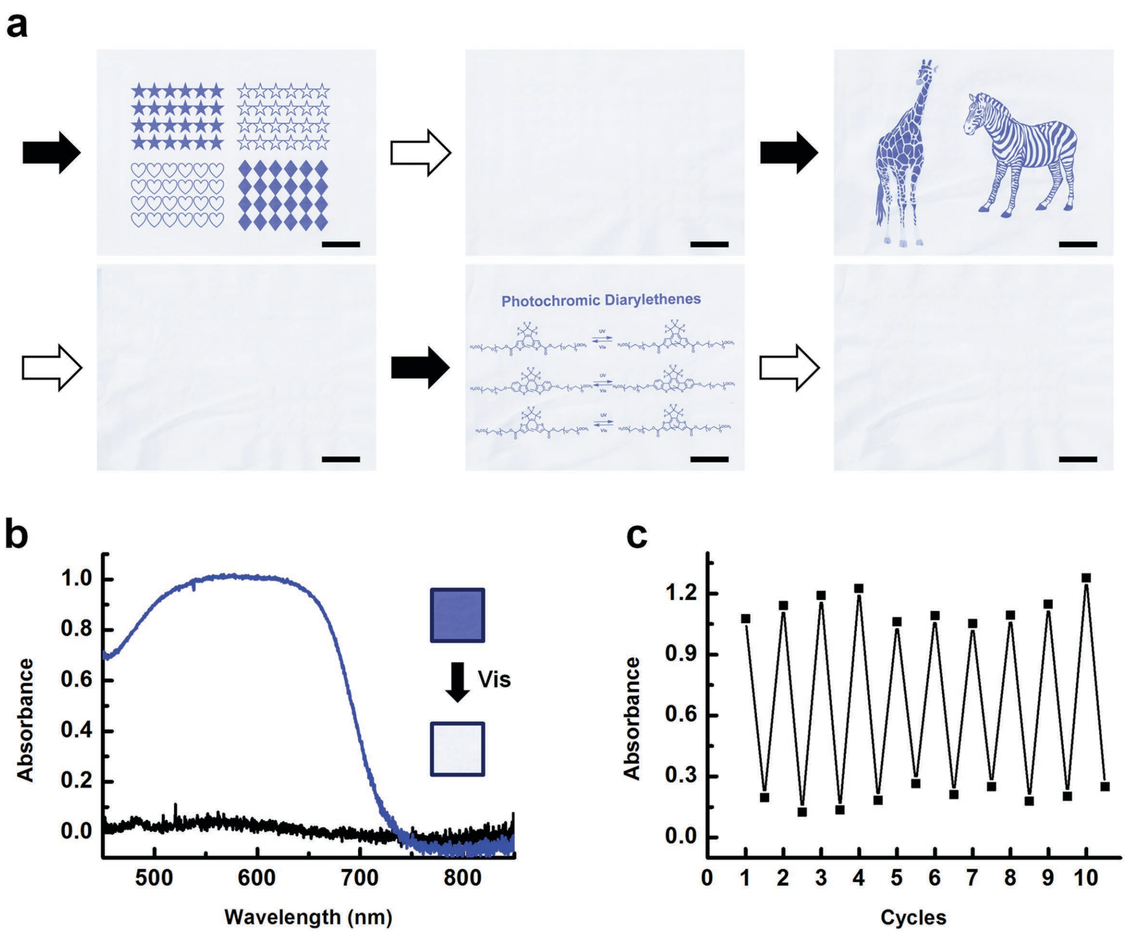

Figure 5. a) Scanned cyan-color images after repeated print–erase cycles on the same paper using ink-jet printer with black cartridge filled with cyan (**I1**) ink. Scale bars, 3 cm. b) Visible absorption spectra of a cyan-color print before (blue line) and after (black line) visible light irradiation. The size of the print is 4 cm by 4 cm. c) A plot of absorbance of a printed image measured during ten consecutive print–erase cycles. Printed images are erased by using visible light irradiation and printed again on ink-jet printer.

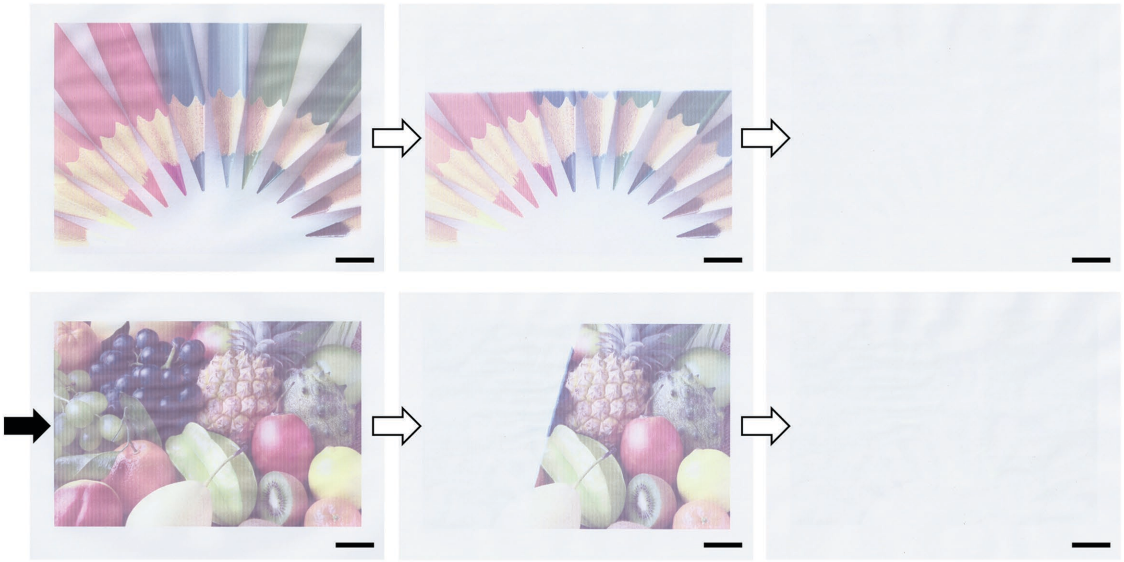

Figure 6. Scanned full-color images after repeated print–erase cycles on the same single paper using ink-jet printer with tricolor cartridge filled with DE inks cyan (**MI1**), magenta (**MI2**), and yellow (**I3**). To obtain full-color image identical to that of one printed using commercial HP ink-jet ink, each image was printed five times. Scale bars, 2 cm.

4. Experimental Section

Materials and Instruments: All chemicals were purchased from Sigma-Aldrich, Korea and Tokyo Chemical Industry, Korea, were of highest commercial quality, and were used without further purification. All reactions were carried out under a nitrogen atmosphere using dry solvents under anhydrous conditions, unless otherwise noted. ^{1}H NMR spectra were recorded on a Varian Unitylnova (300 MHz) spectrometer. Proton chemical shifts were reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.0 ppm) or with the solvent reference relative to TMS ($CDCl_3$, δ 7.26 ppm). Splitting patterns were indicated as s, singlet; d, doublet; t, triplet; m, multiplet. ^{13}C NMR spectra were recorded on a Varian VNMRS (600 MHz) spectrometer with proton decoupling. Carbon chemical shifts were reported in ppm (δ) relative to TMS with the $CDCl_3$ (δ 77.0 ppm) as the internal standard. HRMS were recorded on a Jeol JMS-700 LTQ-Orbitrap-Ms (ESI+). IR spectra were recorded on a Thermal Nicolet Nexus 670 spectrometer. Thin-layer chromatography was performed on Merck silica gel plates (60 F254; Merck) using UV light as the visualizing agent and basic aqueous potassium permanganate as the developing agent. Merck silica gel (60–120 mesh size) was used for column chromatography. Nomenclature used for all compounds was assigned with help of ChemBio Draw Ultra 12.0 software. UV–vis absorption spectra were measured on a single beam Agilent 8453 spectrophotometer. All optical measurements were performed using a quartz cell. DLS data were collected using a MalvernZEN3600. Reflectance spectra were recorded on an USB2000 miniature fiber-optic spectrometer (ocean optics). Viscosity was measured with a RheoSense microVISC viscometer. 35 W Osram Xe arc lamp was used as visible light source.

Ink Formulation and Ink-Jet Printing: Ink was formulated in the manner described in the text above and a 254 nm UV-light source was used for irradiation. The HP Deskjet Ink Advantage K209 a-z printer was used for printing on regular A4 size paper with 80 g m^{-2}. The commercial cartridges (black and tricolor, HP 703) were used after washing with methanol, sonication (2 h), and drying by N_2 blowing. Ink solutions were loaded into cartridges (200 µL) and printed using default standard settings. 35 W Xe lamp was used as the visible light source to erase printed text and images. For "print–erase" cycles, printed text or images were erased for 1 min. All printed and corresponding erased paper were scanned using a HP Deskjet Ink Advantage K209 a-z printer with 600 dpi (300 dpi was selected for print–erase cycle).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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