Dyes and Pigments 106 (2014) 71–73

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Short communication

Saving paper with switchable ink

Jaume Garcia-Amorós, Subramani Swaminathan, Françisco M. Raymo*

Laboratory for Molecular Photonics, Department of Chemistry, University of Miami, 1301 Memorial Drive, Coral Gables, FL 33146-0431, USA

ARTICLE INFO

Article history:
Received 16 January 2014
Received in revised form
19 February 2014
Accepted 21 February 2014
Available online 11 March 2014

Keywords:
Carbazole
Halochromism
Molecular switch
Switchable ink
Oxazine
Heterocycle

ABSTRACT

An oxazine auxochrome and a carbazole chromophore can be integrated within the same covalent skeleton to generate a halochromic molecular switch. Upon addition of acid, the oxazine ring opens to bring the carbazole fragment in conjugation with a 3*H*-indolium cation. This structural transformation shifts the main absorption of the carbazole chromophore from the ultraviolet to the visible region and, as a result, is accompanied by the appearance of an intense red color. This species can be formulated into an ink to print colored patterns on conventional paper. Upon treatment with base, however, the oxazine ring closes to restore the initial colorless state and erase the printed pattern. In fact, the very same sheet of paper can be recycled for multiple printing and erasing steps. Thus, this structural design for switchable inks can evolve into viable operating principles to enable innovative printing technologies and reduce drastically paper consumption.

The average consumption of paper worldwide currently approaches 400 million tons per year [1]. This overwhelming figure poses serious environmental concerns and is, for the most part, a consequence of printing and writing. In spite of the on-going digital revolution and the constant presence of electronic gadgets in our daily routines, we seem to be still relying very much on books, magazines, newspapers, photocopies and any possible iteration of printed documents on a regular basis. A viable strategy to alleviate the pressing demand for paper, and its raw sources, is the development of rewritable inks. The identification of pigments that could easily be removed, or at least decolored, from the surface of conventional paper would offer the opportunity to recycle sheets multiple times and reduce consumption drastically. In this context, the development of switchable organic dyes [2] would be particularly valuable. Indeed, the level of sophistication reached by modern organic synthesis, together with the need to avoid toxic heavy metals, is definitely encouraging the formulation of all-organic inks [3–5]. The further design of operating principles to erase the color of their constituent components with appropriate stimulations, after printing, would also ensure the rewritable character essential for recycling. In fact, a few remarkable examples of rewritable inks, based on switchable organic dyes, have been reported in the literature already [6–12].

In the wake of our work on halochromic compounds [13], we envisaged the possibility of developing switchable inks based on the opening and closing of oxazine rings under the influence of acid and base respectively. Specifically, we designed a molecular switch (**1** in Fig. 1) incorporating an oxazine auxochrome and a carbazole chromophore within its covalent skeleton and prepared this compound in a single synthetic step (Fig. S1). Upon addition of acid, the oxazine ring of **1** opens to form **2** and bring the carbazole appendage in conjugation with a 3*H*-indolium cation. This structural transformation is accompanied by significant changes in the visible region of the absorption spectrum (Fig. S6) and the appearance of an intense red color (Fig. 1). The process can be fully reversed with the addition of base to restore the original and colorless state.

The pronounced changes in color associated with the reversible interconversion of **1** and **2** suggest that these halochromic transformations can indeed be exploited to develop switchable inks. Specifically, a solution of the colored form can be used to print a given pattern on conventional paper. Treatment with base can then switch the colored form to the colorless one and erase the printed information. As a result, the very same sheet of paper can subsequently be recycled for further printing. In order to test these operating principles, **1** (300 μg) was dissolved in a mixture of acetonitrile (250 μL) and ethanol (250 μL) and then switched to **2** with the addition of TFA (10 μL). The resulting red solution was

* Corresponding author.
E-mail address: fraymo@miami.edu (F.M. Raymo).

http://dx.doi.org/10.1016/j.dyepig.2014.02.019
0143-7208/

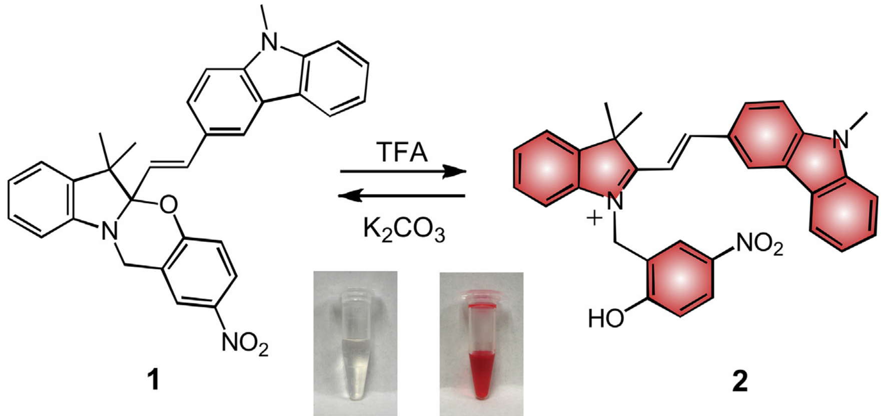

Fig. 1. Reversible interconversion of **1** and **2** under the influence of acid and base and photos of the corresponding MeCN solutions.

applied with a capillary tube within a defined region of a pattern pre-printed on a conventional sheet of paper. The corresponding photo (***a*** in Fig. 2) clearly reveals the red color of the applied ink. Furthermore, the colored area remains virtually unchanged for several months after storage of the printed sheet under ambient illumination at room temperature [14]. However, the color can be erased by immersing the sheet of paper in a diluted aqueous solution of potassium carbonate (15 mM) for 15 min. Consistently, a photo (***b*** in Fig. 2), taken after oven drying at 80 °C for 5 min, shows the complete decoloration of the printed area. At this point, the colored solution of **2** can be applied again in the very same region to restore color (***c*** in Fig. 2) and then the sheet of paper can be treated with base to erase it once again (***d*** in Fig. 2). In fact, coloration and decoloration steps can be reiterated several times without damaging the printed paper. Thus, such a switchable ink offers the opportunity to recycle the very same sheet for multiple printing and erasing steps and, in principle, would permit to save a significant amount of paper. For example, the use of a single sheet for just four times translates already into a 75% reduction in paper consumption. Furthermore, an additional advantage of this switchable ink is the possibility to recover printed information. After treatment with base to erase color (***b*** and ***d*** in Fig. 2), the deleted pattern can be fully restored by immersing the sheet of paper in an aqueous TFA solution (Fig. S7).

Our results demonstrate that halochromic transformations can be the basis for the development of switchable inks. Indeed, they offer the opportunity to reiterate printing and erasing steps on conventional paper and, hence, to recycle the very same sheet multiple times. Thus, these findings can lead to the realization on an entire family of rewritable inks and, possibly, enable valuable printing technologies for the drastic reduction of paper consumption.

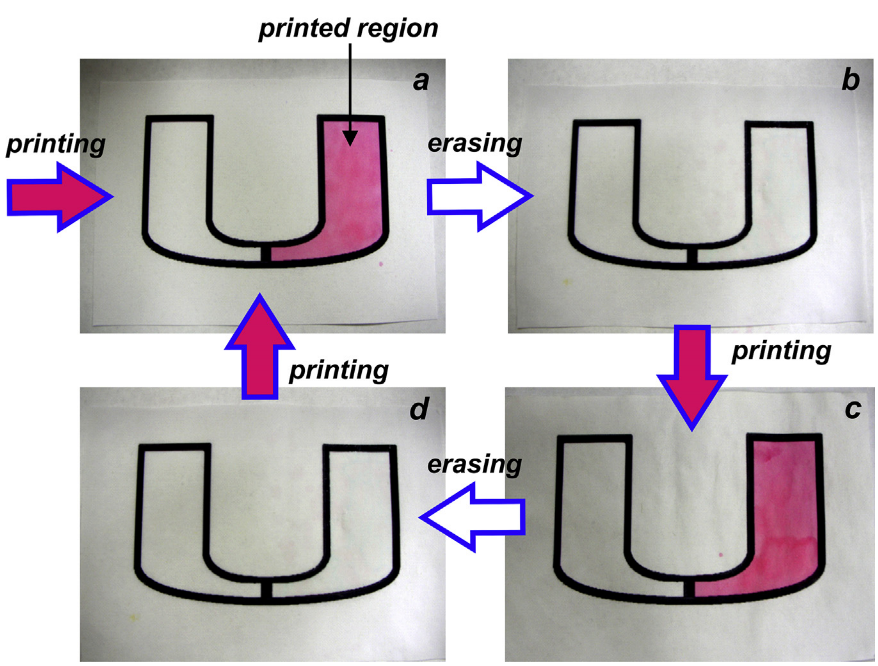

Fig. 2. Photos of a conventional sheet of paper after the application of a MeCN/EtOH (1:1, v/v) solution of **2** (1.2 mM) with a capillary tube exclusively in the indicated region (***a*** and ***c***) and immersion of the entire sheet in aqueous K_2CO_3 (15 mM) for 15 min and drying at 80 °C for 5 min (***b*** and ***d***).

Acknowledgments

The National Science Foundation (CAREER Award CHE-0237578, CHE-0749840 and CHE-1049860) is acknowledged for supporting our research program. JGA is grateful for a *Beatriu de Pinós* post-doctoral grant from the *Generalitat de Catalunya* (Spain, grant 2011 BP-A-00270).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2014.02.019.

References

[1] RISI. Annual historical data – world pulp; 2010.
[2] Feringa BL, Brown WL, editors. Molecular switches. Weinheim: Wiley-VCH; 2011.
[3] Drake JAG. Chemical technology in printing and imaging systems. Cambridge: RSC; 1993.
[4] Leach RH, Pierce RJ. The printing ink manual. London: Blueprint; 1993.
[5] (a) Kunjappu JT. Essays in ink chemistry. New York: Nova Science Publishers; 2001;
(b) Kunjappu JT. Ink chemistry. Chem Br 2003;39:22–5.
[6] Fudouzi H, Xia N. Photonic papers and inks: color writing with colorless materials. Adv Mater 2003;15:892–6.
[7] Kishimura A, Yamashita T, Yamaguchi K, Aida T. Rewritable phosphorescent paper by the control of competing kinetic and thermodynamic self-assembling events. Nat Mater 2005;4:546–9.
[8] Horiguchi T, Koshiba Y, Ueda Y, Origuchi C, Tsutsui K. Reversible coloring/decoloring reaction of leuco dye controlled by long-chain molecule. Thin Solid Films 2008;516:2591–4.
[9] Yamamoto S, Furuya H, Tsutsui K, Ueno S, Sato K. In situ observation of thermochromic behavior of binary mixtures of phenolic long-chain molecules and fluoran dye for rewritable paper application. Cryst Growth Des 2008;8:2256–63.
[10] Kohno Y, Tamura Y, Matsushima R. Simple full-color rewritable film with photochromic fulgide derivatives. J Photochem Photobiol A 2009;201:98–101.
[11] Yoon B, Ham DY, Yarimaga O, An H, Lee CW, Kim JM. Inkjet printing of conjugated polymer precursors on paper substrates for colorimetric sensing and flexible electrothermochromic display. Adv Mater 2011;23:5492–7.
[12] Sheng L, Li M, Zhu S, Li H, Xi G, Li YG, et al. Hydrochromic molecular switches for water-jet rewritable paper. Nat Commun 2014;5. 3044–1–8.
[13] (a) Tomasulo M, Sortino S, Raymo FM. A new family of photochromic compounds based on the photoinduced opening and thermal closing of [1,3]oxazine rings. J Photochem Photobiol A 2008;200:44–9;
(b) Deniz E, Tomasulo M, Cusido J, Sortino S, Raymo FM. Fast and stable photochromic oxazines for fluorescence switching. Langmuir 2011;27:11773–83.
[14] Although no change in color could be detected visually over this period of time, the actual image permanence rating was not determined and, at this stage, it is not clear how the lightfastness of this switchable formulation compares to that of commercial inks. For examples of the quantitative assessment of ink lightfastness, see: Chovancova A, Fleming III PD, Howell P, Rasmusson A. Color and lightfastness performance of different epson ink sets J Imaging Sci Technol 2005;49:652–9.