Hydrochromic molecular switches for water-jet rewritable paper

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1. Introduction

1.1. Paper

Paper prints retain 90% of information in business, but most of them are only used for one-time reading before disposal.[1]

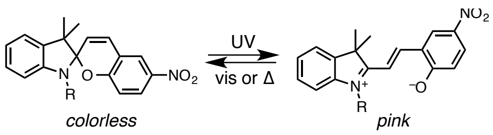
- Rewritable, and ink-free printable paper is desired for reduction of paper waste, cutting off ink cost, and forest conservation.

1.2. Switchable dyes for rewritable paper

Incorporation of switchable dyes as an imaging layer is an ideal economic approach for rewritable paper.

- Spiropyran-type molecular switches are well known to undergo light-stimulated reversible isomerization, accompanied by significant color change (*Scheme 1*).[2]
- The color switching stimuli is mainly UV/visible light or acids and bases, which limits the practical applications.[3]

Scheme 1. Light-stimulated reversible isomerization of spiropyran molecule.



1.3. Water as a switching trigger

Water is renewable resource with no risk for environment.

→ Ideal trigger for switching

Water also integrates well with ink-jet printing techniques.

→ *Water-triggered molecular switching by "water-jet" printing?*

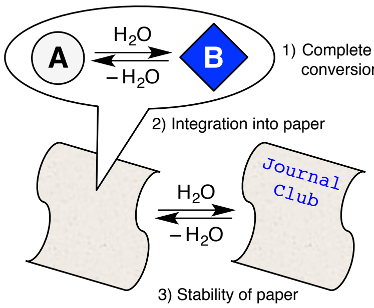


Figure 1. The application of the water-triggered switchable dyes to the rewritable paper.

Challenges for rewritable paper with water-triggered switchable dyes (*Figure 1*):

1) The dyes should exist in only one of its two states in the absence or presence of water.
2) The dyes should be capable of integration into paper based materials.
3) Resulting paper materials should be stable and robust enough to endure many write and erase cycles.

1.4. This work: Rewritable paper with hydrochromic dyes

- Water-triggered switchable dyes ("hydrochromic dyes") were designed and synthesized.
- The solid state properties of the hydrochromic dyes were investigated for paper application.
- Prototype of rewritable paper using hydrochromic dyes was developed.

2. Results and Discussion

2.1. Design for suitable hydrochromic dyes

To find suitable hydrochromic dyes, the authors focused on the previous reports about solvation effects on the isomerization of some spiropyrans in aqueous solutions.[2]

- ➢ The hydrochromic behavior is controlled thermodynamically (*Figure 2*).
  - Open-form (OF) has higher energy than closed-form (CF). → CF preferred
  - Hydrogen bonding reduces the energy of OF.
  - Certain amount of aqueous solvent makes OF energy lower than CF. → OF preferred

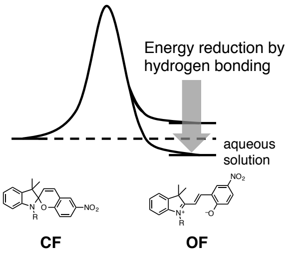


Figure 2. Energy diagram of the CF and OF of spiropyran.

Reported spiropyran-type molecular switches turns to colorless CF by visible light (*Figure 1*).

- ➢ Spiropyrans are sensitive to ambient light.

The conjugated push-pull zwitterionic structure of OF structures leads to the delocalization of molecular orbital.

- → The ring closing reaction is facilitated when light irradiated.

To break this conjugation, new oxazolidine-type switching molecules were designed and synthesized (*Figure 3*).

- → Similar switching molecules (oxazines, spiropyrans) were also synthesized following previous reports.

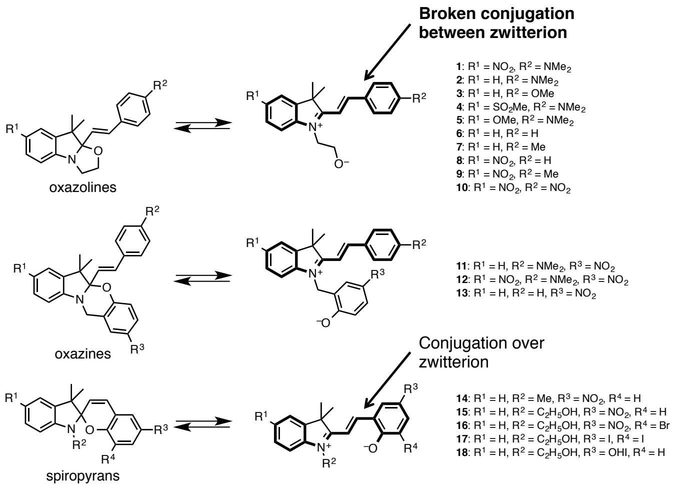


Figure 3. Oxazolines, oxazines and spiropyrans designed and synthesized in this work.

2.2. Investigation of the hydrochromism of oxazolidines

Solution test of the prepared 18 compounds was conducted (*Figure 4*).

- Oxazolidines and oxazines with electron donating groups (**1–5**, **11**, **12**) showed hydrochromic properties.
- Consistent to the previous reports, spiropyrans **14–18** did not show hydrochromism.
  - → Colored OF structures of spiropyrans are unstable against ambient light.

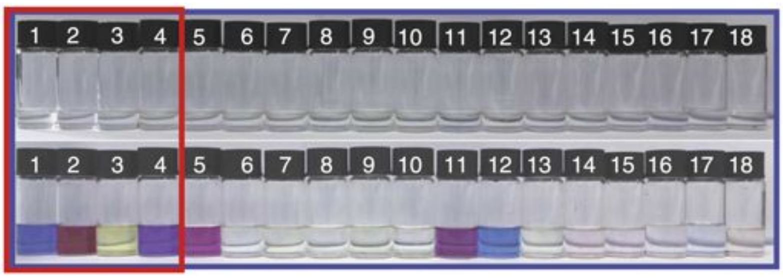
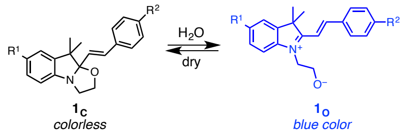


Figure 4. Photographs of 1×10^{-4} M 1,4-dioxane solutions of **1–18** before (above) and after (below) adding 2 mL of water at ambient conditions.

The reversible hydrochromic behavior was investigated on oxazolidine **1** (*Scheme 2*, *Figure 5*).

- Without water, absorption at 301 nm is found. → closed form $\mathbf{1_C}$
- As the water content increase, 588 nm peak appears while 301 nm peak decreses. → open form $\mathbf{1_O}$
- This 588nm peak decreases with water content decrease.
  → The hydrochromism of **1** is reversible.

Scheme 2. The hydrochromic behavior of oxazolidine **1**.



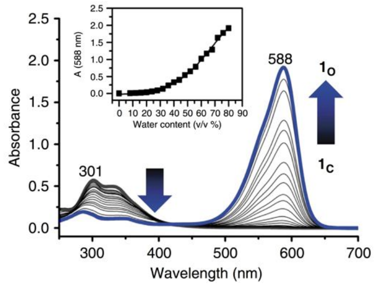


Figure 5. Absorption spectra of 2×10^{-5} M EtOH-H_2O solution of **1** with increasing ratio of water.

2.3. Properties of oxazolidine hydrochromic dye in solid state

To test the hydrochromism in the solid state, $\mathbf{1_C}$ was directly soaked into a paper substrate (*Figure 6*).

→ Blue color of $\mathbf{1_O}$ remained on paper, even without water.

- This phenomenon was also found in polyhydroxyl substrates (silica gel, polyvinyl alcohol).
- This was not found in non-hydroxyl substrates (glass non-cellulose filter paper, polyester, nylon).

➢ The blue $\mathbf{1_O}$ was stabilized by immobile hydroxyl groups (=hydrogen bond donor) on the substrate.

→ The passivation of the polyhydroxyls of paper is the key for the achievement.

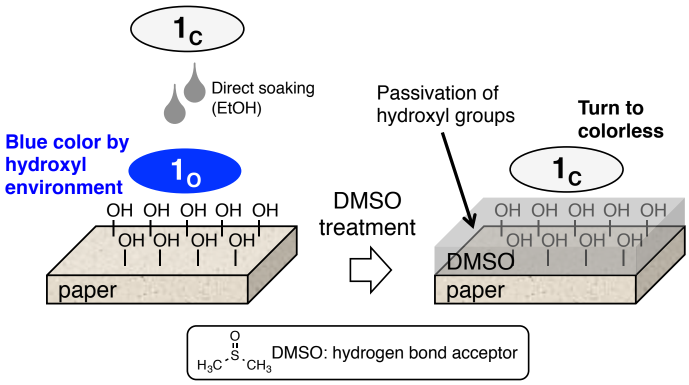


Figure 6. Blue color by direct soaking of **1c** on paper substrate, and its color fading by DMSO treatment.

$\mathbf{1_C}$ soaked paper was post-treated by hydrogen bond accepting DMSO for passivation (*Figure 6*).

→ The paper returned to colorless.

→ The blue color can be revived by water treatment.

➢ The passivation of the polyhydroxyls of paper by hydrogen bonding acceptor was successful.

2.4. Development of the water-jet rewritable paper

For the practical use, PEG instead of DMSO was chosen as a nonvolatile hydrogen bond acceptor.

Rewritable paper (**RP**) with four-layer structure of paper/PEG/PEG:hydrochromic dye/PEG was developed (*Figure 7*).

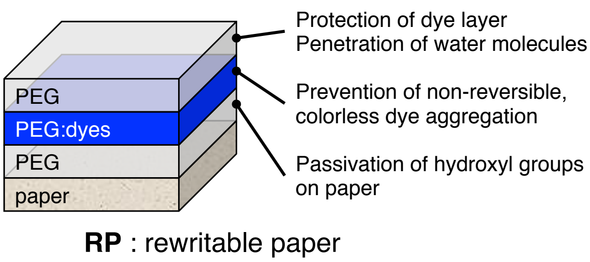


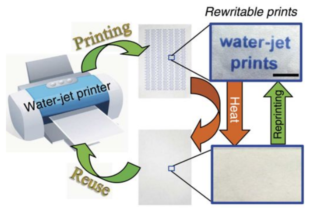
Figure 7. Schematic illustration of the four-layer structure of rewritable paper **RP**.

Water-jet printing on **RP** was successful by water-jet printing (*Figure 8*).

- Water was sprayed on dye-containing **RP** by replacing ink with water in the cartridges used in commercially available ink-jet printer.

  → **RP** turns to colorless by heat drying.

(a)



(b)

Legibility	22h under ambient condition
Color development	Less than 1s
Color vanishment	Heating at 70 °C for 30s

(c) (d)

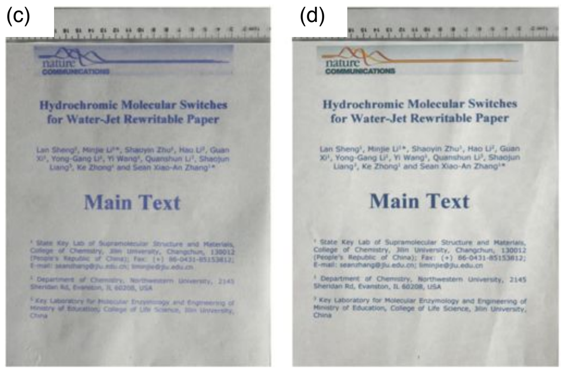


Figure 8. (a) Printing-reuse cycle of **RP** through water-jet printing. (b) Properties of water-jet printed **RP**. (c) Image of water-jet printed **RP**. (d) Image of ordinary ink-jet printed paper.

The reversibility of RP was tested by reflective UV-vis spectroscopy (*Figure 9*).

- In the absence of water, absorption at 301 nm can be observed. → $\mathbf{1}_C$ character
- Upon introduction of water, peak at 592 nm appears while 301 nm peak disappears. → $\mathbf{1}_O$ character
- This color change was observable for 10 cycles without significant decrease of color intensity.

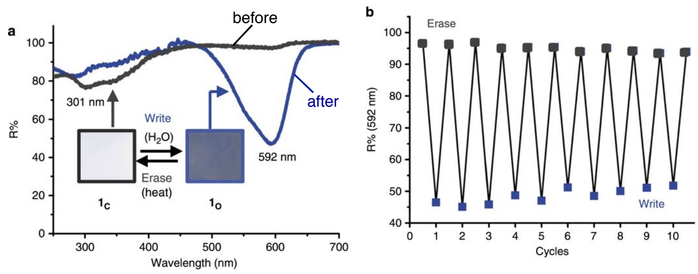


Figure 9. (a) Reflective UV-vis spectra of **RP** before and after addition of water. (b) The reflectivity change at 592 nm by cycles of water spraying (write) and water removal (erase) on **RP**.

Different colors of **RP** was also achieved by using suitable dyes (**2**–**4**) (*Figure 10*).

- Only monochromic **RP** is available, and multicolor **RP** is under investigation.

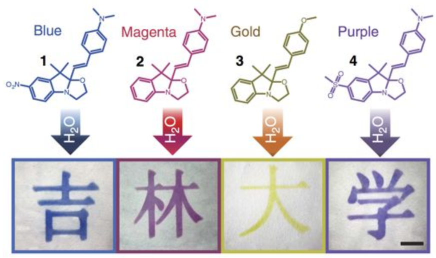


Figure 10. Water-jet prints with different colors.

3. Conclusion

- Water-triggered switchable dyes with stability against ambient condition were prepared.
- The incorporation of the hydrochromic dyes into paper substrate was achieved.
- Rewritable paper was demonstrated by water-jet printing techniques.

4. References

(1) Sarantis, H. *Business Guide to Paper Reduction* (*ForestEthics, 2002*).
(2) Shiraishi, Y.; Itoh, M.; Hirai, T. *Phys. Chem. Chem. Phys.* **2010**, *12*, 13737–13745.
(3) Klajn, R. *Chem. Soc. Rev.* **2014**, *43*, 148–184.