Anthracene-Oxazine based reversible ink

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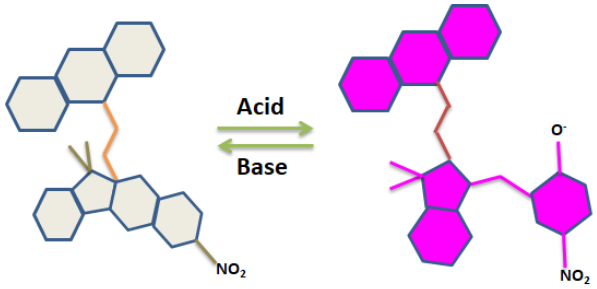
Abstract:

An Anthracene fluorophore and an oxazine chromophore get coupled within the same molecular configuration to produce a molecular machine based receptor **1**. On treatment with TFA, the oxazine closed form gets open in conjugation with the 1, 3, 3-Trimethylindoline species. This molecular change produces a bathochromic shift of 140nm directly from UV to Visible region in association with intense pink color. This molecule can be used as molecular ink to print a different colored decoration on paper. Upon addition with TEA, the colored open form of the receptor **1** reverts to colorless form to rub the printed impression. Thus, the simple paper can be used for multiple times to achieve the write-read-erase strategy. This photo-switchable molecular motif can evolve many opportunities in the industry for acid-jet printing purpose and huge paper consumption.

Keywords: Anthracene-Oxazine conjugate • Reversible • Molecular Ink • Saving paper

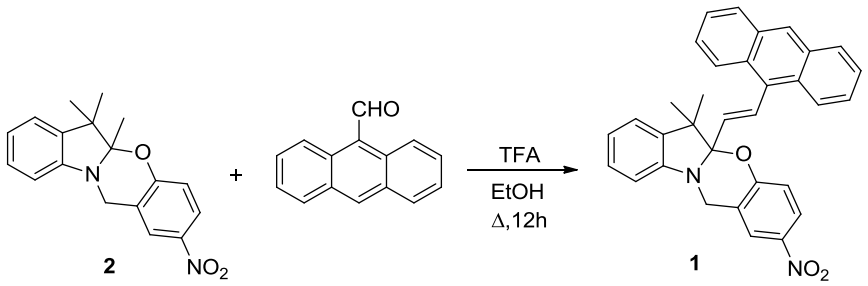


1. Introduction

T The world is currently suffering a load of consumption of paper is around 400 million tons per year.[1] According to US Environmental Protection Agency, consumption of paper is high in school or offices for printouts and notebooks, comprises the largest category.[2] Although, paper is significant to the society. For the purpose of printing and writing, it is now became a serious threat to the environment as well. The environmental influence of paper is pervasively valuable. Because of the pudgy use of paper, heavy efforts are demanded to ascertain that the environment is trouble free. The trailing is gone, we have time to transform our near future, with the usage of present day technologies such as electronic devices or photo-switchable molecular inks,[3] we can minify the regular use of paper. In today's era, digital revolution and the use of electronic devices in our routine life, we are rely much on magazines, books, xerox and any plausible journey of printed papers on a steady basis. A feasible plan to reduce the stress call for paper, its natural material, is an evolution of photo-switchable reversible inks.[3] There are several molecular ink based probes reported in the literature.[4-7] However, these systems suffered from many challenges like hard to synthesize, easy to use, on site demand etc. In order to achieve the development of an oxazine based reversible ink, there is a quick need to develop a simple, chemically induced fastness based sensing materials with an optical colorimetric signal.[8, 9] The system with different colorimetric signals and sensitivity are demanding in other printing devices. Although, reversible molecular inks are widely reported in the literature.[10] Many of these reported receptors are not well routed and less sensitive to impart an optical signal. [4, 11, 12] Therefore, we have designed a molecular key ring with a fluorophore anthracene and auxochrome oxazine within same skeleton and synthesized in a one step process. Upon treatment with acid, the closed form gets converted to open form and the anthracene unit is in conjugation with 1, 3, 3-Trimethylindoline cation. This structural alteration is supported by naked eye detection in the visible region, with a dark pink color.

2. Results and Discussions

In order to develop a reversible method for molecular ink,[13] we envisaged anthracene-oxazine conjugate molecular switch based upon the ring opening and ring closing of the receptor **1** upon the treatment of acid and base alternatively. In a single step process, we have synthesized and developed a covalent linkage between a fluorophore (anthracene) and 1,3-oxazine ring (Scheme 1; Figure S1-S4). The receptor **1** gets open to the form **2** upon addition of trifluoroacetic acid which in turn, conjugated with 1, 3, 3-trimethyl indolinium cation.



Scheme 1. Synthesis of the molecular receptor **1**.

2.1 UV-Vis Spectroscopy

The UV-Vis spectrum of the receptor **1**, when dissolved with CH_3CN at 298K, shows no significant absorption band in the region of 500-600nm and hence, revealed that the receptor **1** is present in the solution as its closed form. Simultaneously, three main bands positioned at 350nm, 368nm and 388 nm with ε (9456, 10184 and 8760 M^{-1} cm^{-1}) in **1** contributes by the fluorophore anthracene coupled with the oxazine ring (Figure S5). Upon treatment of TFA, the [1, 3]-oxazine ring of the receptor **1** gets to produce the open form. This molecular change provided a bathochromic shift of 140nm which brings the chromophore anthracene unit of the receptor **1** in conjugation with the indoline moiety with an appearance of intense pink color (Figure S6). The titration of receptor **1** with TFA yields pink coloration in CH_3CN solution, which in turn, results in the unusual detection limit of 76nM (Figure S7). In order to check the reversibility of the receptor, **1** (1.2mg, 0.0001M) was dissolved in acetonitrile and on treatment

with the vapors of TFA, the solution immediately turned to pink color and then treatment with the vapor of tri-ethyl amine, the receptor **1** turned back to its closed form. This spectral transformation can be reversible using TEA. Under the influence of TEA, the open form of the receptor **1** reverts to its original state. In order to check the reversibility of the receptor, we consequently evaluated the receptor using an acid and base repeatedly for five times (Figure S8). The foremost significant change in color in the receptor **1** in association with the reversibility of the molecular ink can be further used for the development of smart molecular based reversible ink.

2.2 Fluorescence Studies

In order to understand the emission spectrum, we have performed the experiments under the light of excitation wavelength at 420nm, the receptor **1** shown a broader emission band was observed at 470nm which on subsequent treatment with TFA shifts the emission band towards the red region and appeared at 570nm (Figure 1). The titration profile tells us about the appearance of isosbestic point at 530nm and the detection limit of receptor **1** which was observed to be 11nM in CH_3CN solution (Figure S9).

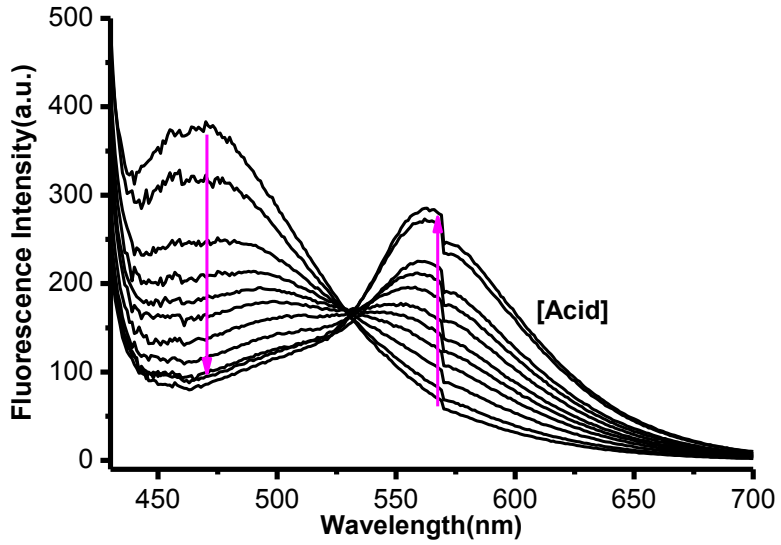


Figure 1. Fluorescence spectrum of receptor **1** after the addition of TFA (0.0001M) in aliquots.

2.3 Excitation Spectra

Further, the excitation spectra of receptor **2** revealed that the structural information with the corresponding bands observed at 349nm, 365nm, 385nm is of anthracene unit attached to the base skeleton of the receptor **2.** The peak observed at 444nm is of the base skeleton of the oxazine ring. No significant change in the excitation spectra was observed of the receptor **2** with the consecutive treatment of TFA and TEA alternatively (Figure 2). But, the receptor **1** shown significant changes on treatment with TFA due to which, the emission intensity of **1** lowers down at 444nm because of the protonation of the closed form of the oxazine ring, results in pink coloration (Figure 2).

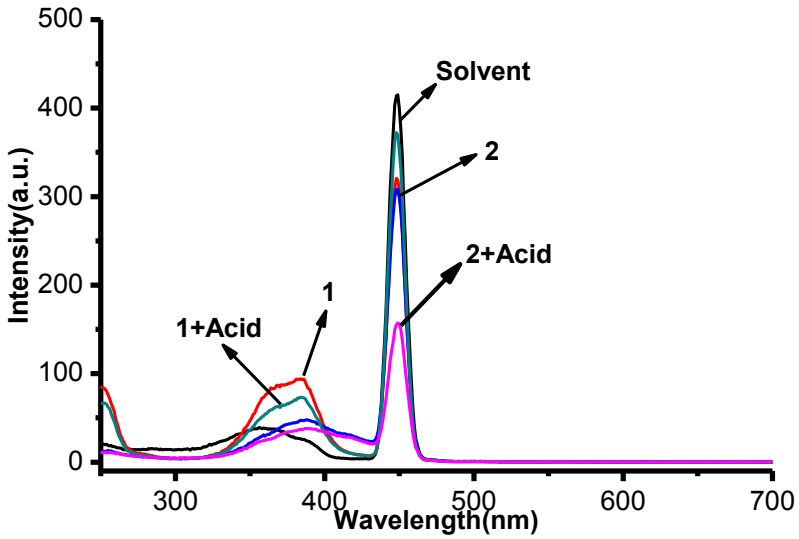


Figure 2. Comparison of the excitation spectra of the receptor **1**, **2** and Solvent (Acetonitrile). λ_{em} = 425nm. Slit Width = 10nm.

2.4 Practical Utility

Our research group developed a novel switchable ink[13] that depends upon the closing and opening of [1, 3]-oxazine rings upon treatment with trifluoroacetic acid and triethylamine base consecutively. The process can be fully reversed between the closed and open form, the awakening color changes with this switchable alteration between the closed and open form can be used to develop reversible inks.

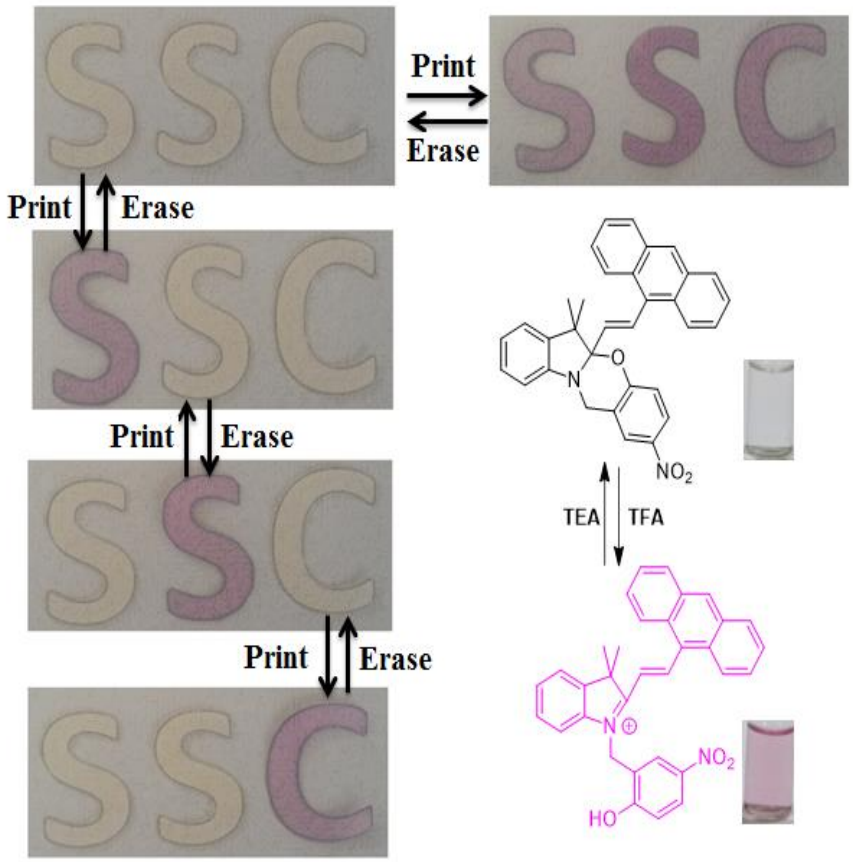


Figure 3. Reversible printed decoration of "SSC" on paper strips under TFA and TEA and snapshot of switching in Acetonitrile.

With a large change in absorption and development of a pale pink color. The protonated pink colored form can be used for printing purpose on a simple paper which in turn, reverses the colored form to its original state and information can be erased. Paper can be tuned to recycled multiple times using TFA and TEA alternatively (Fig. 3). Interestingly, a solution of the receptor **1** can be used to imprint the on demand pattern of "SSC" on a simple blotting paper. The colored form of the receptor turned colorless in the presence of one equivalent of base (Figure 3).

3. Conclusions

In conclusion, our study on this molecular probe **1** can be a pillar in the development of reversible ink. It also provides an opportunity for the paper industry to follow up the write-read-erase strategy consecutively on a model paper, hence to reuse it for manifold purposes. The above mentioned results may bring a dramatic change in paper industry by reducing the depletion of paper.

Conflict of Interest

The authors declare no conflict of interest.

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Appendix A. Supplementary Information

Supplementary data is freely available and can be found at the given website.

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