

Thioxanthylum Cations: Highly Reversible Hydrochromic Materials with Tunable Color and Moisture Sensitivity

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Abstract: Hydrochromic materials, which change color in response to moisture, are highly sought-after due to some unique applications such as moisture detection, humidity monitoring, anti-counterfeiting, and sweat-pore mapping. We herein report a new thioxanthene-9-ols/thioxanthylum cations hydrochromic system. The hydrochromic thioxanthylum cations can be generated/regenerated by exposing a chemically stable thioxanthene-9-ol to trifluoroacetic acid (TFA). The intensely colored thioxanthylum cations can be chemically reverted to the colorless thioxanthene-9-ol. Interestingly, the conversion between thioxanthene-9-ol and its cation species was found to be highly reversible in most cases (up to 50 activation-deactivation cycles). The color and moisture-sensitivity of thioxanthylum cations were also validated to be tunable via functionalization of the thioxanthene core with different aliphatic and aromatic groups at its 9 or 2,7-positions. Finally, paper probes were prepared using solution-immersion and inkjet-printing techniques to demonstrate the system's potential applications in humidity sensing and anti-counterfeiting

Introduction

Hydrochromic materials exhibit color change upon interaction with water molecules. Hydrochromism is a fairly rare phenomenon, found in only limited classes of nanocrystals,^[1] carbon dots,^[2] metal complexes,^[3] and organic dyes^{[4] [5]}. They are found useful for moisture/humidity sensing, leakage detection, anti-counterfeiting, rewritable paper, finger-printing and sweatpore mapping^[6]. The most common hydrochromic materials are perhaps CoCl_2 and CuCl_2 , which exhibit blue-to-pink and yellow-to-blue colour changes, respectively, and are often found in self-indicating desiccants and humidity indicator cards for electronics packaging. However, their toxicity limits their use in other applications.

Comparatively, organic hydrochromic systems may serve as better and safer alternatives. These include 4-((anthracen-9-yl)methylamino)butanoic acid,^[7] boron-bisavobenzene salts,^[8] fluorans,^[9] squaric acid-functionalized perylene bisimide,^[10]

naphthalimide-pyridinium fluorophore-receptors pair,^[11] and 3,6-bis(5-bromothien-2-yl)diketopyrrolopyrrole^[12]. The mechanisms of hydrochromism for these examples include hydroxy group deprotonation,^[10] rearrangement of molecular packing structures,^[12] excited state charge transfer,^[11] and zwitterion formation.^[7] Two notable examples were the polydiacetylene - based supramolecular systems studied by Kim and Park et al.,^[4] and a series of oxazolidine, oxazine, spiropropan-based molecular switches reported by Zhang et al.^[5] The former undergoes blue-to-red color change and fluorescence "turn-on", owing to partial distortion of the polymer backbone when exposed to water, whereas the latter undergoes reversible water-triggered ring-opening reactions to generate intensely colored zwitterions.

The usefulness of hydrochromic materials for a wide range of applications signals the need to develop such materials, desirably with high moisture-sensitivity, low toxicity, wide color availability, fast response, easy recovery, and high reversibility. Thioxanthylum cations have been reported as photosensitizers for biological applications^[13] and organo-photoredox catalysis for cycloaddition reactions,^[14] but their use as hydrochromic materials has not been investigated. Hori et al. earlier showed that thioxanthylum cations undergo nucleophilic additions with Grignard reagents, amines, phenolates and thiophenolates nucleophiles at the 9-position carbocation site.^[15] Similar reactivity towards diazomethane,^[16] dimethylmercury,^[17] aromatic amines,^[18] imidazoles and benimidazoles,^[19] have also been reported. Water, being a nucleophile, may therefore also react with thioxanthylum cations in a similar fashion.

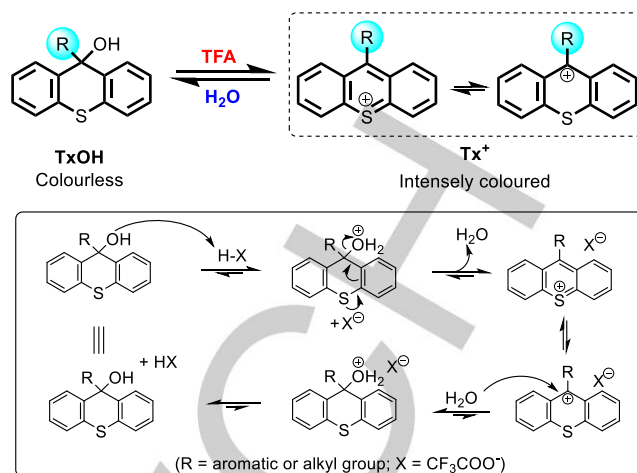
Herein, we report the unprecedented discovery of hydrochromism in thioxanthylum (Tx^+) cations, with residual water in solvent and atmospheric moisture sufficient to cause dramatic decolorization. Tx^+ can be easily generated by exposing chemically-stable thioxanthene-9-ol (TxOH) precursors to common strong organic acids such as tetrafluoroboric acid,^[20] triflic acid,^[21] and in this work, TFA.

Results and Discussion

First, 9-phenyl-thioxanthen-9-ol (**TxOH-a**) was prepared via a simple Grignard reaction between thioxanthenone and phenylmagnesium bromide. The corresponding 9-phenyl-thioxanthylium cation (**Tx⁺-a**) was then generated by adding a few drops of TFA into the colorless **TxOH-a** solution, leading to immediate intense orange coloration. The subsequent addition of water resulted in the rapid decolorization, indicating a chemical reaction between water and **Tx⁺-a**. Interestingly, when the water layer was removed and a few more drops of TFA were added into the remaining organic solution, intense coloration was recovered, signifying the possible regeneration of **Tx⁺-a**.

Spectrophotometric titration studies were performed by first adding incremental amounts of TFA into **TxOH-a** solution (0.1 mM in chloroform) and changes in absorption spectra were observed due to the formation of **Tx⁺-a**. **TxOH-a** showed an absorption maximum (λ_{abs}) at 269 nm, with no absorption beyond 325 nm. Introduction of TFA led to the emergence of new absorption bands with λ_{abs} at 280, 386 and 497 nm (**Figure 1a**). TFA was added until no further increase in the intensities of the new absorption bands, thus suggesting the full conversion of **TxOH-a** into **Tx⁺-a**. Thereafter, water (diluted in THF) was incrementally added and the absorption spectra were observed to gradually change back to that of **Tx-OH** (**Figure 1b**).

Proton NMR titration studies were then performed with **TxOH-a** in THF-*d*⁸ with changes in NMR spectra in the aromatic region of 6.8



Scheme 1. Generation and hydrochromism mechanism of **Tx⁺** cation.

– 9.0 ppm recorded. **TxOH-a** displays two sets of NMR signals at 6.88 and 7.11 ppm, corresponding to the five protons on the phenyl ring, and another three sets of signals at 7.30, 7.42 and 8.02 ppm, accounting for the eight protons on the thioxanthenone core. As TFA is added, the NMR signals belonging to **TxOH-a** gradually diminish while new NMR signals appear further downfield. The NMR signals of **TxOH-a** eventually disappear, are replaced by new NMR signals belonging to **Tx⁺-a** (**Figure 1c**). There are three sets of signals at 7.75, 7.80 and 8.25 ppm belonging to the phenyl ring protons, and the remaining four sets

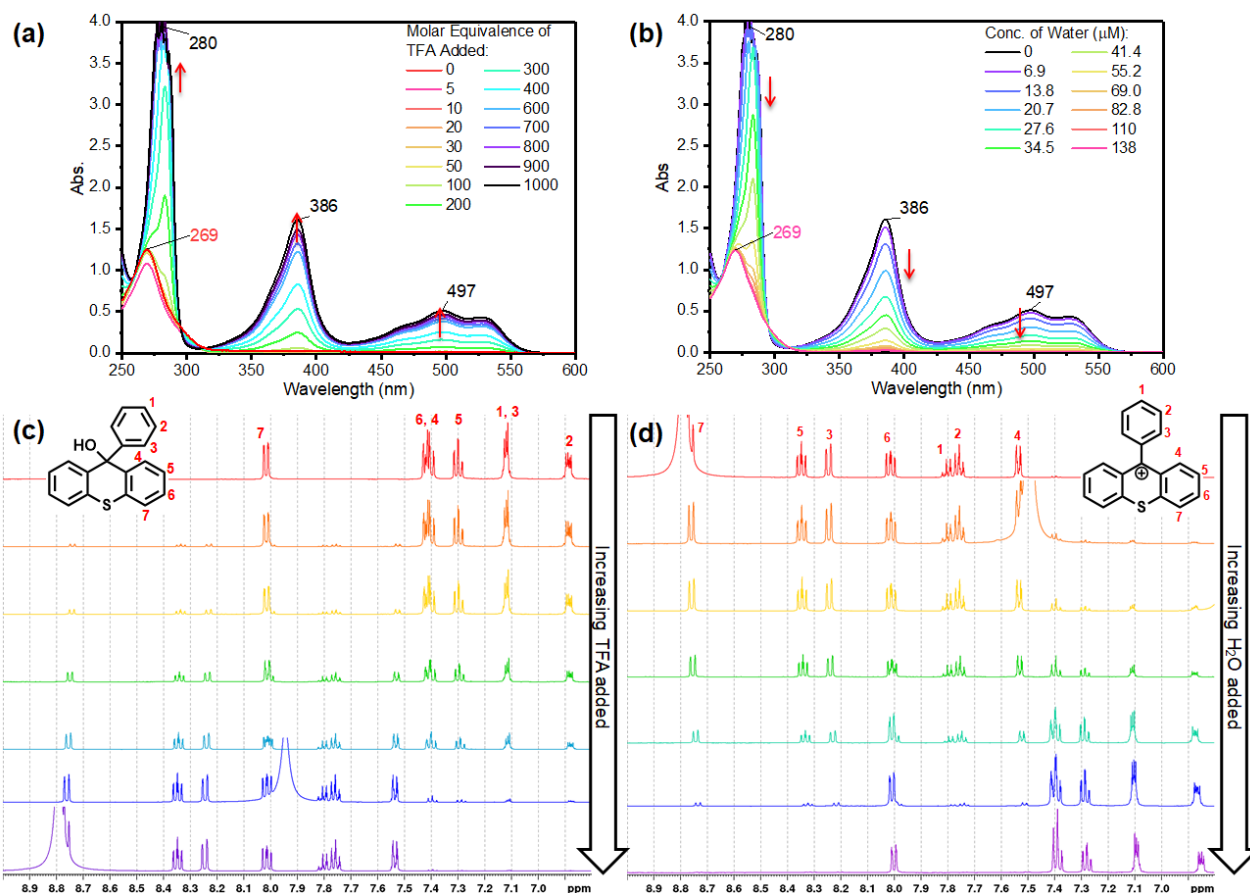
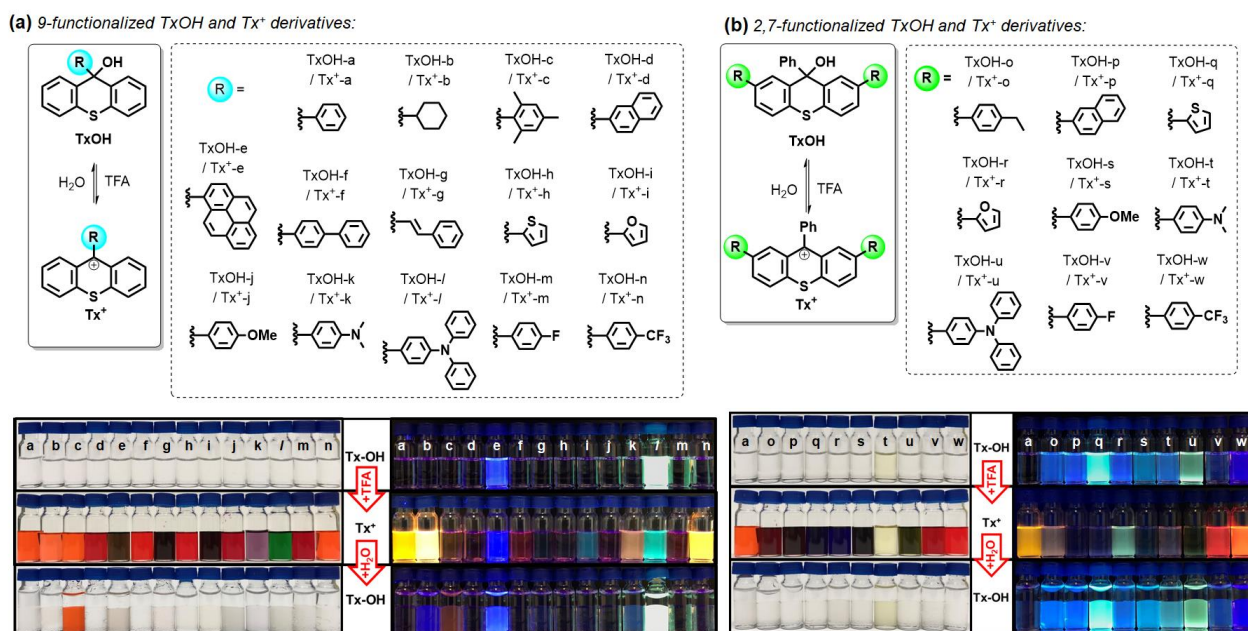


Figure 1. UV-Vis absorption spectra changes when an incremental amount of TFA was added to **TxOH-a** solution to generate **Tx⁺-a** (a) and the subsequent addition of water (dissolved in THF) into the same solution (b). The concentration of water in (b) was estimated from Karl Fisher titration and volume of water/THF solutions added with respect to overall volume. Changes in proton NMR spectra when incremental amounts of TFA was added to **TxOH-a** solution to generate **Tx⁺-a** (c) and the subsequent addition of water into the same solution (d).

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at 7.54, 8.02, 8.35 and 8.76 ppm that are assigned to the protons on the thioxanthene core. Next, when deionized water is added dropwise, the downfield NMR signals of **Tx⁺-a** gradually disappears and the upfield NMR signals of **TxOH-a** re-emerge (**Figure 1d**). Both spectrophotometric and proton NMR titration

studies therefore confirm the mechanism and reversibility of the **TxOH/Tx⁺** hydrochromism system, where **TxOH** undergoes a protonation-induced dehydration by TFA to generate **Tx⁺**, which can undergo a nucleophilic addition reaction by water at the 9-position to regenerate **TxOH** (**Scheme 1**).



Bedlek^[22] and Erabi^[23] earlier respectively demonstrated how different aromatic substituents at the 9-position could affect the photophysical properties and frontier molecular orbital energies of thioxanthylum cations. On this basis, we synthesized two series of **TxOH** derivatives with different substituent groups at the 9- and 2,7-positions, respectively, (**Figure 2**) to study the effects of structural functionalization on **Tx⁺** hydrochromic properties. The different substituent groups consist of aliphatic (cyclohexyl) and aromatic groups (different electron-rich and electron-poor aromatic groups, aromatic heterocycles, and fused aromatic systems). 9-functionalized derivatives (**TxOH-a** - **TxOH-n**) were synthesized by a simple one-pot Grignard reaction, while 2,7-functionalized derivatives (**TxOH-o** - **TxOH-w**) were obtained by first pre-functionalizing thioxanthenes, followed by the Grignard reaction with phenylmagnesium bromide (**Scheme S1**, *ESI*).

The **TxOH** derivatives appear colorless in chloroform solution but on the addition of a few drops of TFA, intense colorations were observed due to the formation **Tx⁺** (**Figure 2**). Different aromatic substituents at the 9-position lead to extension of π -conjugation of **Tx⁺** cations and even intramolecular charge transfer for some **Tx⁺** (eg. **Tx⁺-k**), and thus **Tx⁺** cations show different colors. On the other hand, the disparity in color range and intensities between 2,7-functionalized and 9-functionalized **Tx⁺** derivatives could be attributed to the former having more extended π -conjugation network. For the same reason, all 2,7-functionalized **TxOH** show blue-to-green fluorescence while all 9-functionalized **TxOH** are non-fluorescent except for **TxOH-e** and **TxOH-l** that emit blue/green fluorescence due to the presence of pyrene and

triphenylamine moieties, respectively. Addition of TFA led to the emergence of a range of different fluorescence colors and intensities associated with the **Tx⁺** formation (**Figure 2**).

Subsequent addition of a large excess of water to **Tx⁺** solutions led to dramatic decolorization in most cases, due to the regeneration of **TxOH** which effectively disrupts the aromatic π -conjugation of **Tx⁺** (**Figure 2**). Likewise, solution fluorescence also mostly disappeared, corresponding to the formation of **TxOH**. One notable exception is the **Tx⁺-c**, which is non-responsive to water due to sterically bulky mesityl groups hindering the carbocation center from nucleophilic attack by water molecules. Herein, we therefore demonstrated the colors and fluorescence tunability of **TxOH/Tx⁺** system via structural functionalization. These observations were supported by spectrophotometric titration studies (**Figure S1–S22**, *ESI*) in which significant absorption changes can be observed in the presence of water concentration as low as 10^{-5} to 10^{-6} M.

Then, we studied the moisture-sensitivities of **Tx⁺** derivatives in the solid states. To begin with, **TxOH** derivatives were spin-coated onto glass substrates and exposed to the TFA fume. Their absorption spectra were recorded over 30 minutes at 2.5 minutes intervals (**Figures S25 – S26**, *ESI*). Changes in the absorption were observed, generally showing collapse or decrease in intensities of absorption bands, reflecting the conversion of **Tx⁺** back to **TxOH** upon interaction with atmospheric moisture. The rate of changes in absorption spectra generally reflects the moisture-sensitivities, correlating to the functionalization of each

different speeds, which correlates with structural functionalization. For instance, absorption band of 9-cyclohexyl-functionalized $\text{Tx}^+\text{-b}$ collapsed within 5 minutes, much shorter than that of 9-phenyl-functionalized $\text{Tx}^+\text{-a}$ (27.5 minutes), while pyrene and biphenyl functionalized $\text{Tx}^+\text{-e}$ and $\text{Tx}^+\text{-f}$ experienced more gradual and incomplete collapse of absorption bands over 30 minutes.

Moisture-sensing via spin-coated thin film is limited by its low porosity which discourages interactions of Tx^+ film with water vapor. As an alternative, paper probes were prepared by immersing cellulose based Whatman® filter paper into TxOH solutions and then air-dried. The highly porous, white-colored probes revealed immediate intense coloration when exposed to TFA fume. To assess the moisture-sensitivities of “activated” probes, decolorization was monitored over 24 hours in a controlled laboratory environment at 24 °C and relative humidity (RH) of 70 % (Figure 3). In general, functionalization with aliphatic group (at 9-position) and electron-deficient aromatic groups tends to elevate moisture-sensitivities of Tx^+ cations by reducing cation-stabilities and increasing Tx^+ electrophilicities to be attacked by water nucleophiles. Meanwhile, functionalization with electron-rich and fused aromatic groups resulted in the opposite trend. 2,7-functionalization with aromatic groups also generally appeared to have greater cation-stabilization effect, and hence lower Tx^+ moisture-sensitivities compared to 9-functionalization, due to the former with extension of π -conjugated network of Tx^+ cations.

To quantify the above observations and to further explore the TxOH/Tx^+ system for potential humidity monitoring applications, colorimetric studies were performed with paper probes coated with TxOH-a , TxOH-e , TxOH-j , TxOH-n , TxOH-s , and TxOH-w . Reflectance-mode colorimetric measurements were obtained at regular intervals over two hours with the probes being placed in a humidity chamber with RHs controlled at 50–55 %, 70–75 % and 85–90 %, respectively, in-between readings. The reflectance

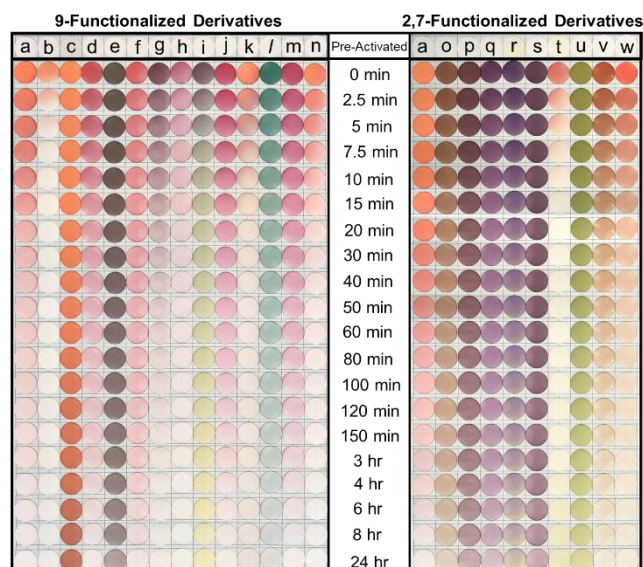
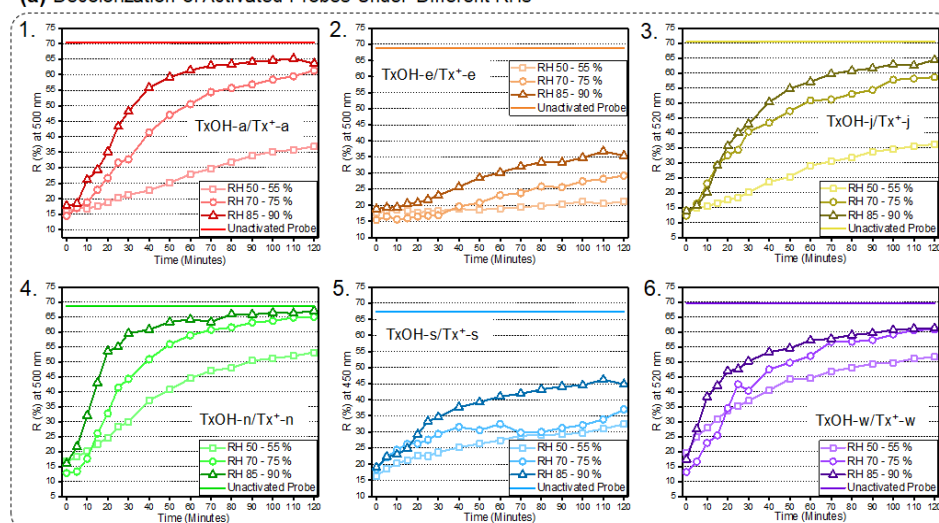


Figure 3. Activation of paper probes coated with TxOH-a to TxOH-w , and the decolorization of activated paper probes over time on standing in a controlled laboratory environment and exposure to atmospheric moisture.

(R%)-vs-wavelength spectra and corresponding color coordinates values, according to the CIE 1976 $L^*a^*b^*$ color space, are collated (Figures S29 – S36, ES). The gradual decolorization of activated probes upon humidity exposure caused increase in R% and L^* with time. Evidently, higher RHs led to faster and more significant increase in both R% and L^* values across all six probes (Figure 4a; Figures S29–S34, ES). Slow and modest changes in R% and L^* prevailed for activated probes containing pyrene- and 4-methoxyphenyl- functionalized $\text{Tx}^+\text{-e}$ and $\text{Tx}^+\text{-s}$ while faster changes were recorded for activated probes containing 4-(trifluoromethyl)phenyl-functionalized $\text{Tx}^+\text{-n}$ and $\text{Tx}^+\text{-f}$ (Figure 4a and Figure S36, ES).

(a) Decolorization of Activated Probes Under Different RHs



(b) Reversibility of Hydrochromism

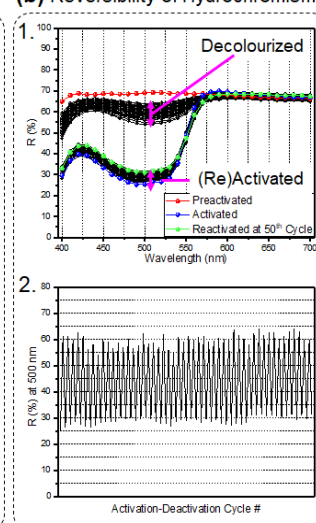


Figure 4. (a) Changes in reflectance (R%) of paper probes containing derivatives 1. TxOH-a , 2. TxOH-e , 3. TxOH-j , 4. TxOH-n , 5. TxOH-s , and 6. TxOH-w , over time, at 500, 500, 520, 500, 450 and 520 nm, respectively, under different RH at 25 °C. Also included were the respective R% of un-activated probes at the selected wavelengths. The wavelengths were chosen based on the largest difference in R% between freshly-activated and un-activated probes. (b) Reversibility study of $\text{TxOH-a}/\text{Tx}^+\text{-a}$ hydrochromism: 1. Reflectance spectra of paper probe containing TxOH-a before activation and after (re)activation and decolorization for 50 cycles; 2. R% of paper probe at 500 nm over 50 cycles of reactivation and decolorization/deactivation.

The reversibility of **TxOH/Tx⁺** hydrochromic system was then studied. The probes were repeatedly reactivated over TFA fume and then were exposed to atmospheric moisture for 24 hours, for ten cycles (**Figures S27 & S28, ES**). Throughout the ten cycles, most probes (except for **TxOH-c**, **TxOH-g**, **TxOH-i**, and **TxOH-r**) are able to reveal coloration on exposure to TFA fume, with color intensities comparable with that of the first activation. Meanwhile, significant decolorization can be achieved by most probes except for those coated with **TxOH/Tx⁺** derivatives functionalized with mesityl, fused aromatic and electron-rich substituents. The reversibility of **Tx⁺-a**-based probe's hydrochromism was further validated with colorimetric measurements, which was able to undergo 50 activation/decolorization cycles (**Figure 4b**).

The good solubility of **TxOH** hydrochromic system allows it for different applications such as humidity indicator cards and anti-counterfeiting markings. We therefore attempted inkjet printing on common printing paper using **TxOH-a**, **TxOH-j** and **TxOH-s**. With inks facilely prepared by dissolving each derivative in propylene glycol monomethyl ether (PGME), a 2.5-by-5.0 cm logo was printed over normal printing paper. The printed papers appeared blank with no trace of printed logo but exposure to TFA fume instantaneously revealed the intensely coloured logo (**Figure 5; ES/ Video 1**). The printed logo may even be revealed by simply blowing TFA vapor over the paper using a plastic dropper (**ES/ Video 2**). Likewise, exposure of the activated paper to ambient humidity resulted in the disappearance of the coloured logo and the time taken is affected by the functionalization on **TxOH** (**Figure 5c**). In this case, functionalization with electron-rich 4-methoxyphenyl group resulted in **Tx⁺-s** and **Tx⁺-j** being less moisture-sensitive than **Tx⁺-a**, thus the partial disappearance of the corresponding purple and red logos after an hour.



Figure 5. Paper probes (2.5 x 5.0 cm) inkjet-printed with **TxOH-a**, **TxOH-s** and **TxOH-j** before (a) and after exposure to TFA fumes (b), as well as 1 hour on standing in ambient laboratory humidity after exposure to TFA fumes (c).

Conclusion

In summary, we discovered a new hydrochromic system consisting of **TxOH/Tx⁺** that could be switched by organic acid and water. This system exploits a simple chemistry involving the reversible conversion between acidochromic **TxOH** precursors and hydrochromic **Tx⁺**. The **TxOH/Tx⁺** system presents several unique key features and advantages compared to other reported organic hydrochromic systems. Our **TxOH/Tx⁺** system is easily activated by exposing chemically-stable **TxOH** to organic acid like

TFA, thus generating **Tx⁺** only at the point of use. This facilitates easy storage and handling of the materials without requirement of any strict inert and anhydrous environment. Exposure to water regenerates **TxOH**, resulting in a dramatic decolorization of **Tx⁺** cations. The hydrochromic mechanism is unique compared to reported hydrochromic systems, which generally reveal colourization or colour changes on exposure to water. In our system, the conversion between **TxOH** and **Tx⁺** promoted by acid and water can be considered an equilibration between the protonation-induced dehydration of **TxOH**, and the nucleophilic addition of water molecules to **Tx⁺** cations. Therefore, the recovery of the hydrochromic species also does not involve in a drying process but rather acid reactivation.

In addition, we have demonstrated the ability to tune colour, fluorescence, and moisture-sensitivity of **Tx⁺** via facile structural modification, such as the use of different aliphatic, aromatic, fused aromatic, electron-rich, and electron-deficient groups functionalized at the 9- or 2,7- positions of the thioxanthene core. While colour-tuning has been reported in some systems such as the spiro-compounds molecular switches^[5a, 5b] and PDA-based system^[4], the modulation of moisture-sensitivity has not been explicitly studied in other reported hydrochromic systems. Many of our **Tx⁺** cations are extremely moisture-sensitive, and an ambient humidity level or a trace amount of water in organic solvents (~1 – 10 mM) being sufficient to fully decolorize them. Moreover, the **TxOH/Tx⁺** system is generally highly reversible, and able to undergo up to 50 activation-decolorization cycles. Finally, **TxOH** derivatives are generally highly soluble in common organic solvents, which renders them solution processable for real-life applications. Simple solution-immersion as well as ink-jet printing technique was used to fabricate paper probes, which are potentially useful as moisture indicators or anti-plagiarism encryption labels. In conclusion, the discovery of hydrochromism in the **TxOH/Tx⁺** system is exciting, potentially creating vast opportunities for numerous applications. We believe this hydrochromic system has potential for a wide range of industry applications, able to offer customized solutions owing to their colour and sensitivity tuneability, low-cost, easy storage and handling of hydrochromic materials and large-scale production.

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Keywords: Hydrochromic • Thioxanthylum • Moisture Sensor • Humidity Sensor • Paper Probe

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Entry for the Table of Contents



Hydrochromism of thioxanthyl cations/ thioxanthen-9-ol can be tuned by structural functionalization to offer diverse colors and moisture-sensitivities. This reversible hydrochromic system is easily activated with organic acid from chemically stable precursors, allowing for possible uses in moisture-sensing and anti-counterfeiting encryption.