

# Preparation of photochromic silk fabrics based on thiol-halogen click chemistry

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**Abstract:** In this study, we have synthesized a photochromic compound 9'-(2-bromo-2-methylethoxycarbonyl)-1,3,3-trimethyl-spiro[2H-indole-2,3'-[3H]naphtha[2,1-b][1,4]oxazine] and applied it to the silk fabric to acquire photochromic properties. First, tris (2-carboxyethyl) phosphine (TCEP) was used as a reducing agent to produce thiol groups on the surface of silk fabric. Then, these thiol groups will react with -Br groups of the spirooxazine via thiol-halogen click chemistry. The spirooxazine was characterized by FTIR and UV. And the color change properties of the as-prepared silk fabrics were evaluated by the color measurement methods. The results indicated that treated silk fabric has excellent photochromic properties.

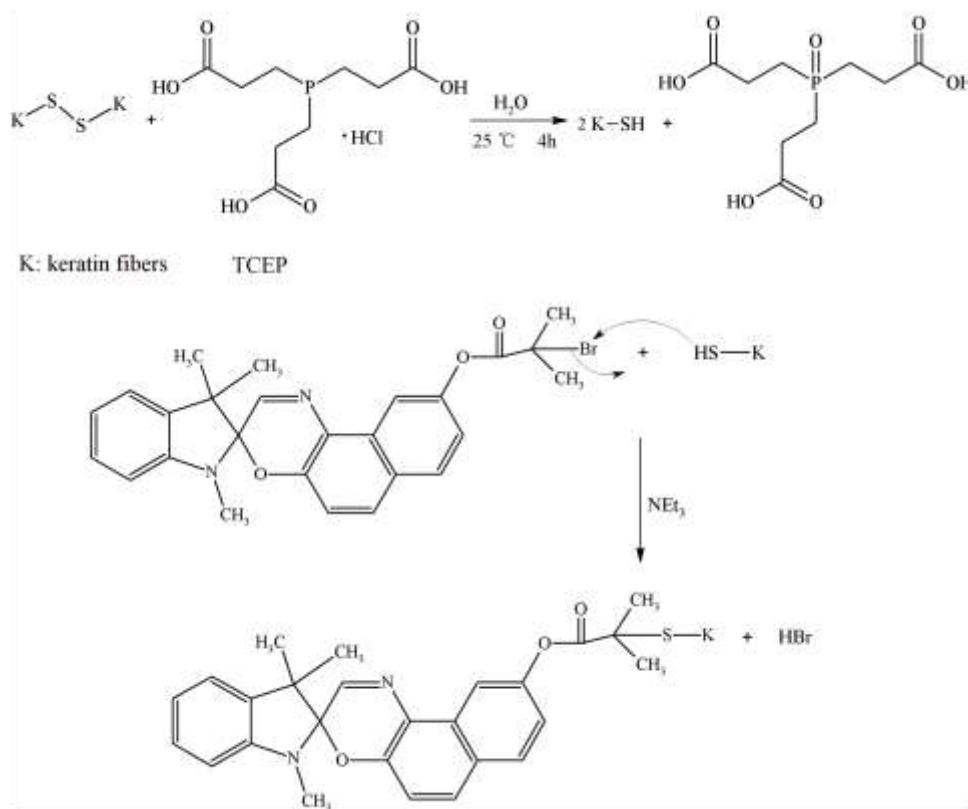
## 1. Introduction

In recent decades, photochromic compounds have been extensively studied for their applications in many areas [1, 2]. Several methods of preparing photochromic textiles using spirooxazine have been reported, including conventional dyeing techniques and screen printing [3, 4]. However, the conventional preparation methods of the photochromic fabric have the disadvantages like complicated preparation process, slower color switching speed and rough handle. In addition, the spirooxazine and the fabric mainly relied on physical adsorption or hydrogen bonding, so it is easy to be removed after washing and affected the photochromic effect [5, 6]. Peng [7] et al. has synthesized N-methyl-3,3-dimethyl-9'-dichloro-s-triazine group spiro [2H-indole-2'-[3H]naphtho[2,1-b][1,4]oxazine] and applied it to cotton fabrics, using the -Cl groups on the spirooxazine derivative to react with -OH groups in the cotton fibers. The experimental results demonstrate that the cotton fabric has good photochromic properties and better washing resistance after dyeing. Currently, other photochromic textiles have not been reported, especially those could be easily prepared and with good durability. Therefore, our target of this paper is to find a novel chemical method of preparing photochromic textiles with durable properties.

In this paper, a novel photochromic compound with a halogen end group was firstly synthesized. The silk fabric was then treated by TCEP to generate reactive thiol groups. The synthetic photochromic compound was finally grafted onto the silk fabric through the thiol-halogen click



chemistry to form a covalent bond, and the reaction mechanism of the photochromic compound with silk fabric was shown in figure 1. In addition, the photochromic properties, fatigue resistance and washing fastness of photochromic silk fabrics were evaluated.



**Figure 1.** Mechanism of reacting wool with photochromic compound.

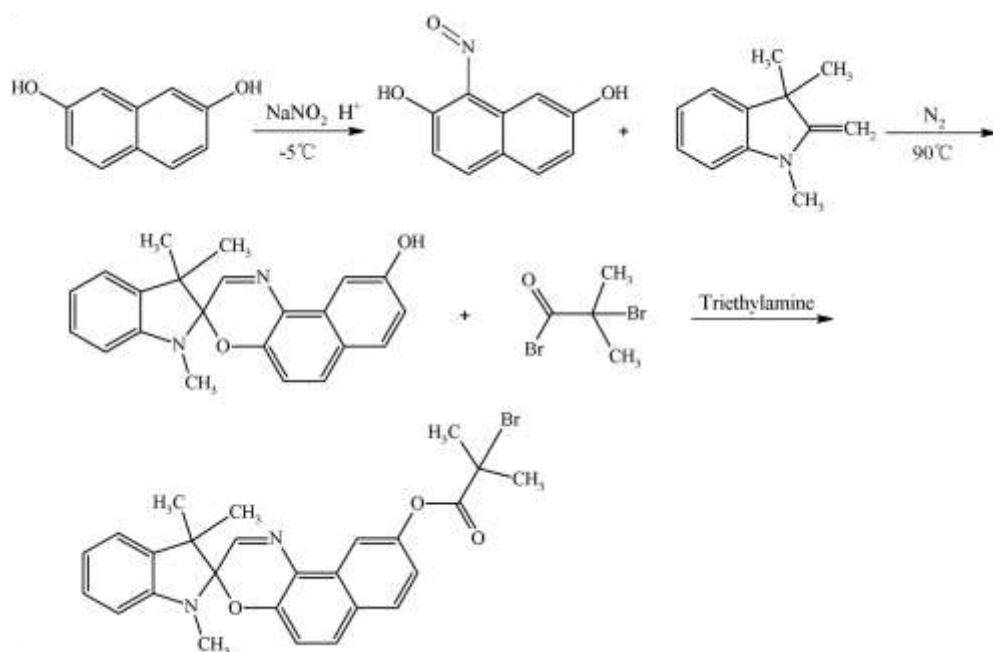
## 2. Experimental

### 2.1 Materials

Degummed silk fabric was purchased from Yufeng Co. Ltd. 1,3,3-trimethyl-2-methyleneindoline (97 %) was purchased from Shanghai Jiuding Chemical Technology Co., Ltd. 2-bromoisobutyryl bromide (98 %) was purchased from Beijing InnoChem Science & Technology Co., Ltd. Tris (2-carboxyethyl) phosphine hydrochloride (TCEP) was purchased from Sigma Aldrich. Other chemicals used in the experiment were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were analytic grade reagents, and used without further purification.

### 2.2 Synthesis of spirooxazine compound

The synthesis process of spirooxazine compound was shown in figure 2. 9'-hydroxy-1,3,3-trimethyl-spiro[2H-indole-2,3'-[3H]naphtha[2,1-b][1,4]oxazine] was synthesized by Kakishita et al and carefully characterized it in the article [8]. And 9'-(2-bromo-2-methylethoxycarbonyl)-1,3,3-trimethyl-spiro[2H-indole-2,3'-[3H]naphtha[2,1-b][1,4]oxazine] was synthesized and described in detail by Such et al [9].



**Figure 2.** Synthesis process of spirooxazine.

### 2.3 Pretreatment of silk with TCEP

A pretreatment solution was prepared by dissolving TCEP in an alcohol-water mixture (v/v=1:1) to form a 20 mmol/l TCEP solution. The liquor ratio was 50:1 and the pH values were adjusted by the buffer ( $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ ) pH=7.0. And pretreated with TCEP solution at 25 °C for 4 h [10].

### 2.4 Application of spirooxazine to the silk fabrics

The final synthesized spirooxazine was dissolved with dichloromethane, and the pretreated silk fabric was added into the prepared solution at 25 °C for 1 h with a small amount of triethylamine as a catalyst. After treatment, washed the silk fabric with standard detergent thoroughly and rinsed with clean water and dried to obtain the final product.

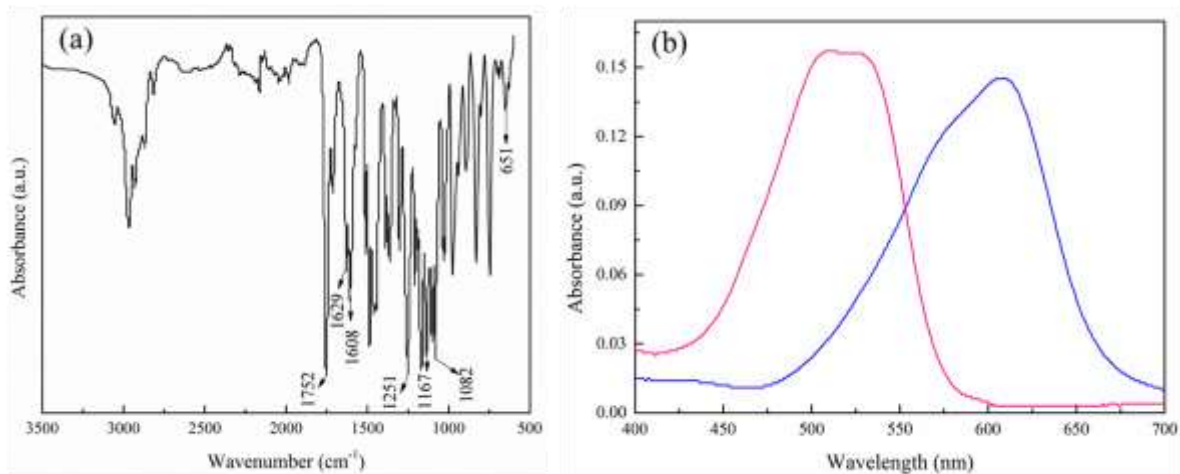
### 2.5 Characterization

The chemical structure of spirooxazine was investigated by fourier transform infrared analysis (Nicolet 6700, Thermo Fisher, America). The UV absorption spectrum of spirooxazine dissolved in ethanol solution was tested by using a UV/Vis spectrophotometer (UV-3600, Japan) with the wavelength changed from 400 to 700 nm. The color yields (K/S values) of the photochromic silk fabrics were carried out by Datacolor 650 (Datacolor, USA).

## 3. Results and discussion

Figure 3(a) showed the FTIR spectrum of spirooxazine. The peak at  $1752\text{ cm}^{-1}$  is assigned to the stretching vibration of the C=O bonds. The peak at  $1629\text{ cm}^{-1}$  is attributed to the stretching vibration of C=N, while the peaks at  $1608\text{ cm}^{-1}$  and  $1511\text{ cm}^{-1}$  are assigned to the stretching vibrations of C=C in the naphthalene ring. Two peaks appeared in the region of  $1251\text{ cm}^{-1}$  and  $1082\text{ cm}^{-1}$ , which are attributed to the stretching vibration of the functional groups  $\text{C}_{\text{spiro}}\text{-O-C=}$  [11]. At  $1167\text{ cm}^{-1}$ , the peak belongs to the stretching vibration of Ar-O, and that at  $651\text{ cm}^{-1}$  is assigned to the stretching vibration of C-Br. The results demonstrate the spirooxazine compounds were successfully synthesized. Figure 3(b) showed the UV spectrum of the spirooxazine compound under UV irradiation. When the spirooxazine solution was irradiated with UV light at 365 nm, it was observed that the wavelength

became longer and the solution turned blue. This is because the molecular structure of spirooxazine is changed from closed loop to open loop under the UV irradiation, resulting in a significant change in color.



**Figure 3.** (a) FTIR spectra of spirooxazine and (b) UV spectra of spirooxazine.

In order to prove the mechanism of photochromism, the color change was evaluated from  $L^*$ ,  $a^*$ ,  $b^*$  values by using CIE color space, and the test results are listed in table 1. It can be observed that the brightness of the original silk fabric ( $L^*$ ) was highest, but it decreased obviously after treated with spirooxazine. The redness ( $a^*$ ) of photochromic silk fabric was increased but the blueness ( $b^*$ ) was decreased. It is indicated that the color of the silk fabric is blue after UV irradiation.

**Table 1.** Color properties of the sample.

Samples		$L^*$	$a^*$	$b^*$
Original silk		92.01	0.01	4.06
Pretreated silk		-5.11	2.56	-0.25
Photochromic silk	Before irradiation	-35.27	16.15	0.06
	After irradiation	-37.15	9.49	-3.44

#### 4. Conclusion

This paper introduces a method for preparing photochromic silk fabrics by thiol-halogen click chemistry. The method comprises the following three steps: firstly synthesizing the spirooxazine compound with photochromic properties, and then the silk fabric was pretreated with TCEP. Finally, the synthetic spirooxazine compound was reacted with the reduced silk fabric via thiol-halogen click chemistry. It was confirmed by FTIR and UV that the spirooxazine compound was synthesized and it was successfully grafted onto the silk fibers. The results indicated that treated silk fabric has excellent photochromic properties.

#### Acknowledgements

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