

## Efficient Dyeing of Silica Fiber Using Metal-Coordinated Polymeric Dye Rotaxane

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**ABSTRACT:** We prepared an azo dye rotaxane and its polymeric metal complex and successfully demonstrated their useful application for dyeing silica fiber, which exhibited high-color strength and fairly good color fastness. These benefits were made possible by the hydrogen bonding between SiO<sub>2</sub> and hydroxyl groups (—OHs) on  $\alpha$ -cyclodextrin ( $\alpha$ -CD). Spectroscopic evidence supports the formation of polymeric metal-complexed rotaxanes within the silica fiber. The current results are meaningful because they indicate that the proper adjustment of the interaction between CD and SiO<sub>2</sub> can produce CD-encapsulated dyes that provide an effective platform for depositing various metal ions on silica surfaces, which will be useful in numerous promising applications. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** polyrotaxanes; dyes/pigments; supramolecular structures; silica fiber; metal complex

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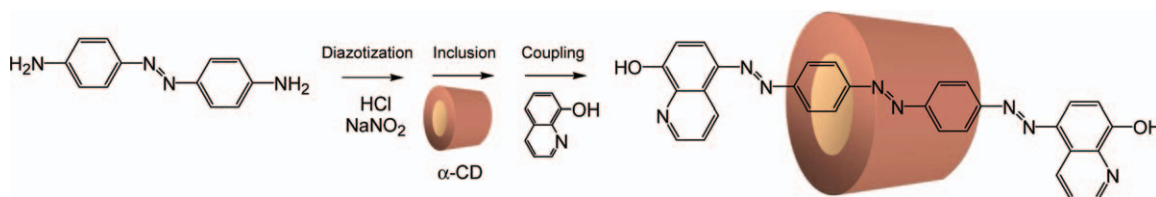
### INTRODUCTION

Silica fiber has drawn considerable interest for a broad range of conventional textile applications because of its inherent flame retardancy. Many textile products, especially sleepwear, mattresses, and curtains, require lower flammability, so conjugated mixtures with silica have been implemented in various forms.<sup>1–3</sup> Meanwhile, silica fiber doped with organic materials is considered an important modified functional extension of conventional fibers, ever since the introduction of specialty fiber doped with various organic or inorganic materials.<sup>4–8</sup> Meanwhile, with the advent of novel synthetic micro-sized or nano-sized fibers, the demand for the development of after-treatment techniques has steadily increased. However, the application of such fibers invokes the tricky problem of their poor dyeability, because they generally assume high crystalline morphology, which means that only a small portion of their total volume is accessible to dyes.<sup>9–11</sup> In fact, silica fiber has generally been considered undyeable. Although several efforts have been made to improve the dyeability by increasing sites for dye attraction, none of these efforts have succeeded in providing full color depth.

A rotaxane is a supramolecular assembly shaped like a dumbbell, featuring a macrocycle around its molecular axis. A

rotaxane is formed when a molecule threads the cavity of macrocycles and bulky terminal groups on both sides, thereby preventing the threaded molecule from escaping.<sup>12</sup> We used cyclodextrins (CDs) as a macrocycle in the synthesis of an azo dye rotaxane. CDs have hydrophobic interiors and hydrophilic exteriors and are widely used as hosts for various organic molecules, including polymers.<sup>13</sup> CDs include numerous hydroxyl (—OH) groups, with the primary —OHs on the narrow side of the conical cylinder and the secondary —OHs on the wider side. According to previous reports, azo dye rotaxanes were successfully prepared by the hydrophobic effect, in which rotaxane encapsulation enhances the stability of azo dye without preventing the dye from binding to cellulosic fibers.<sup>14</sup>

In effort to develop a new dyeing method for silica fiber, we used an azo dye rotaxane formed with  $\alpha$ -CD, because it has been reported that —OH groups strongly adsorb to SiO<sub>2</sub>.<sup>15–17</sup> In this article, we describe the synthesis of an azo dye rotaxane (ADR hereafter) by coupling 8-hydroxyquinolines (8-HQs) with diazo components in the presence of  $\alpha$ -CD. Using the ability of 8-HQs to form metal chelates, we prepared the polymeric metal complex of CD-rotaxanated azo dye, which was found to be useful in providing a deeper shade on silica fiber.



**Scheme 1.** Synthesis of azo dye rotaxane. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## EXPERIMENTAL

### Materials

All chemicals used in the synthesis and purification, including 4,4'-diaminoazobenzene; 8-HQ; sulfanilic acid;  $\alpha$ -CD; HCl (37%);  $\text{NaNO}_2$ ; sodium acetate; methanol; ethanol; silica; and  $\text{DMSO-d}_6$ , were of laboratory reagent grade. The silica fiber was obtained from Yoo-Jin Textile (Korea) and used without any further treatment.

### Synthesis of Dye Rotaxane and Its Polymeric Metal Complex

4,4'-diaminoazobenzene (240 mg, 1.12 mmol) was dissolved in water (10 mL) with 1 N HCl (6.8 mL) and 10%  $\text{NaNO}_2$  (1.6 mL), and the solution was stirred at 0–5°C for 1 h to complete diazotization. Next,  $\alpha$ -CD (4.668 g, 4.8 mmol) was added dropwise to water (15 mL) followed by stirring for another 1 h at 0–5°C. 8-HQ (0.488 mg, 3.36 mmol) in 2 N NaOH (2 mL) was slowly added to the above prepared diazonium salt solution over 30 min whilst maintaining pH at 9.5—the azo coupling proceeded at room temperature overnight. After the reaction, the mixture was treated with aqueous alkaline solution (30 mL, pH 11 by NaOH) and the free dye was removed by filtration. The pH of the filtrate was then adjusted to neutral condition, and the residue was collected, washed with water, and dried in air. Dissolving and precipitating were repeated twice. Collected crude product was refluxed in ethanol and methylene chlorider for 12 h, respectively, followed by hot filtration and washing with hot ethanol. The product was isolated using column chromatography on silica using methylethylketone/ammonium hydroxide/1-propanol (1/1/1 vol %) as an eluent (ADR hereafter, yield 9%) (Scheme 1).

8-HQ was dissolved in NaOH to give a solution of pH 10 and then the above prepared diazonium salt solution slowly added to this 8-HQ solution over 30 min whilst maintaining pH at 10(?)—the azo coupling proceeded and was left overnight.

In preparation of the polymeric metal complex, ADR (0.2245 g, 0.15 mmol) in hot ethanol (10 mL) was slowly mixed with  $\text{CuSO}_4$  (0.0319 g, 0.20 mmol) followed by reflux for 6 h. After the reaction, half the solvent was removed and the solution cooled down to room temperature. The dye precipitate was collected by filtration, washed with a mixture of cold water and ethanol (1/1 vol %), and dried overnight in vacuum.

### Dyeing of Silica Fiber

Dyeing experiments were performed at 90°C in a closed flask. A silica fiber sample of about 1 g was immersed into a water bath (100 mL) containing 30 mg dye (3% on the weight of fiber) and 0.5 g NaOH. After 3 h, the dyed sample was washed profusely with water and dried in air overnight. For post-metal

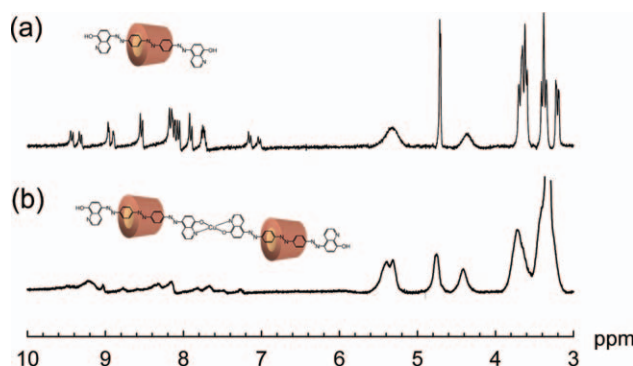
complexing, an aqueous solution (10 mL) of 30 mg  $\text{CuSO}_4$  was added after 1.5 h at 90°C and maintained for another 1.5 h.

### Property Investigation

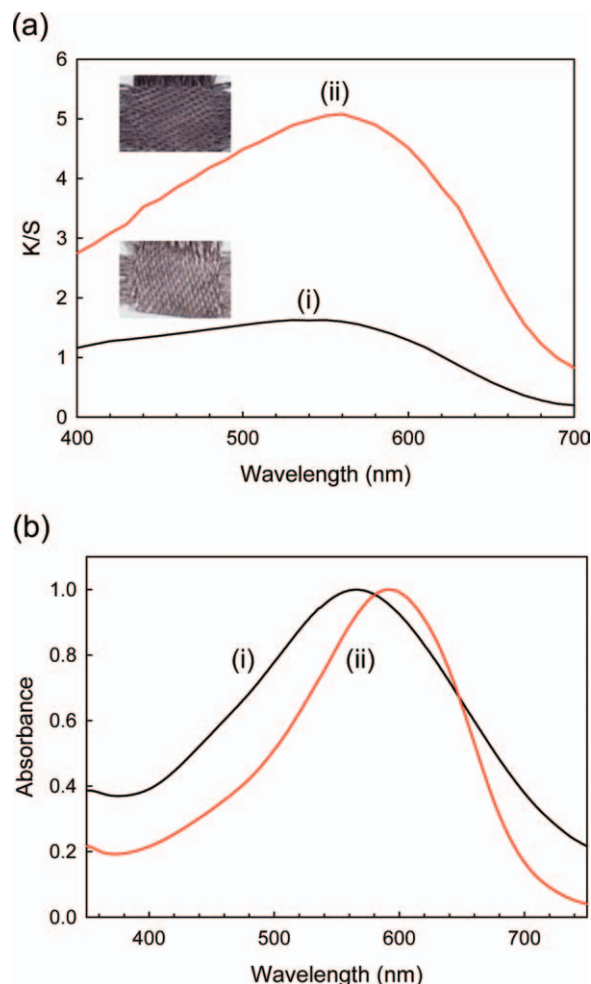
The  $^1\text{H-NMR}$  spectra were measured in solvents of  $\text{DMSO-d}_6$  using Mercury VXx 300 (Varian, 300 MHz). The reflectivities of dyed samples were measured using spectrophotometer (CE-3000, Macbeth), and their  $K/S$  (absorption to scattering coefficient) values were calculated using the Kubelka-Munk equation,  $K/S = (1-R)^2/2R$ .<sup>18</sup> We measured the XPS (Theta Probe XPS System, Thermo Fisher), photoluminescence (LS-45 spectrofluorophotometer, Perkin-Elmer) of the dyed silica fiber. To understand the metal complexing behavior of an azo dye rotaxane, we used UV-Vis (Lambda 7 spectrometer, Perkin Elmer), NMR spectroscopies, and elemental analysis.

## RESULTS AND DISCUSSION

The formation of ADR was confirmed by  $^1\text{H-NMR}$  spectroscopy [Figure 1(a)]. ADR experiences a nonequivalent environment from the threaded  $\alpha$ -CD at both ends of the dye molecule, resulting in more split and complex peaks. This is attributed to the conical shape of  $\alpha$ -CD, which confirms the threading of the azo chromophore within the cavity of  $\alpha$ -CD. From the relative integrals, the ratio between the chromophore and CD is found to be 1 : 1, indicating the formation of the azo dye rotaxane.<sup>2</sup> In previous report, elemental analysis confirmed the formation of metal-ligand (ADR- $\text{Cu}^{2+}$ ) binding, indicating the formation of linear polymeric metal complexes based on equal stoichiometry of azo dye rotaxane and copper (II).<sup>19</sup> In  $^1\text{H-NMR}$  spectra, the peaks of  $\alpha$ -CD are observed to be much broader when complexed with copper(II) [Figure 1(b)], which is attributed to the fact that metal coordination leads to a reduced conformational flexibility of CDs in the polymeric architecture. It is known that CDs adopt



**Figure 1.**  $^1\text{H-NMR}$  spectra of (a) azo dye rotaxane (ADR) and (b) its polymeric metal complex prepared with copper(II). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



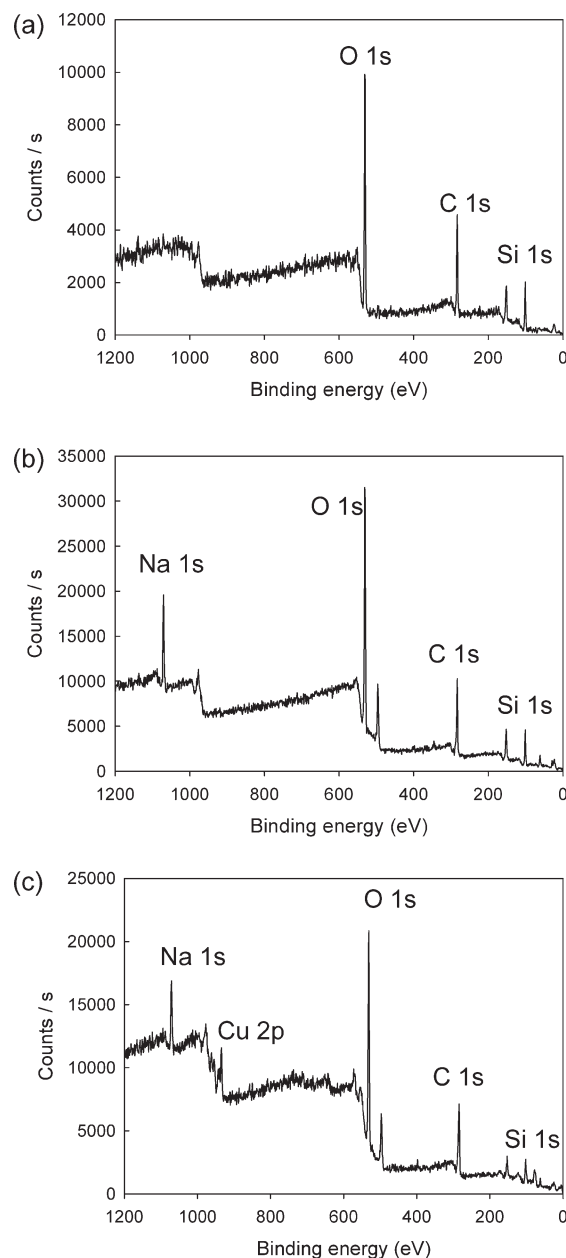
**Figure 2.** (a)  $K/S$  curves of silica fibers (i) dyed with ADR and (ii) dyed with ADR, and then complexed with  $\text{CuSO}_4$ , and (b) absorption spectra of (i) ADR and (ii) its copper complex, in mixed solvent (DMF/pH 9.6 buffer, 8:2 vol %). Absorbances in (b) were normalized and concentrations were  $[\text{ADR}] = 1.0 \times 10^{-5} \text{ M}$  and  $[\text{Cu}^{2+}] = 1.0 \times 10^{-5} \text{ M}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

a more symmetric cyclic conformation in solid crystalline polymer-CD inclusion complexes, leading to a reduced splitting in NMR spectra,<sup>20</sup> and we observed the same behavior in the extended and linear structure of the soluble dye-metal complexes.

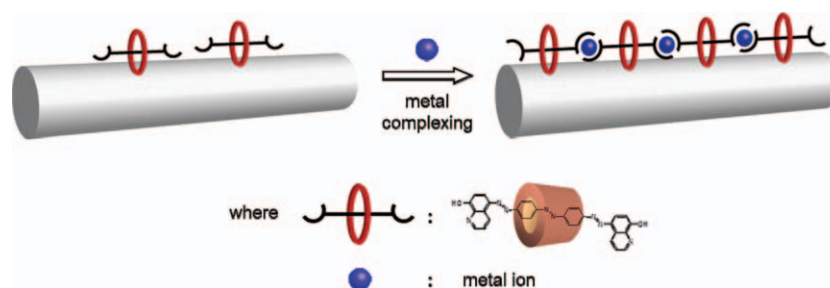
We now turn to the dyeing of silica fiber using the azo dye rotaxane. In actual dyeing experiments, ADR enables the dyeing of silica fiber, showing a pale violet color in the substrate. In terms of reflectivity and the calculation of  $K/S$  values, the ADR-dyed sample shows its absorption maximum ( $\lambda_{\text{max}}$ ) around 550 nm [Figure 2(a)]. We believe that this comes from the existence of numerous -OH groups on  $\alpha$ -CD surrounding the chromophore, leading to the formation of hydrogen bonds with the inorganic component,  $\text{SiO}_2$ . As noted, the chemical structure of the threaded chromophore resembles that of disperse dyes, and because it has no ionic functional groups, it hardly shows any stainings on the fiber surface. Copper-complexing increased the color strength of the fiber by three times, coupled with a slight red shift. A metal-coordinated dye devel-

ops a larger molecular size that causes deeper shades on the fiber, making it difficult to remove the dye molecules from the fiber, even with repeated washings.<sup>21,22</sup> By a similar process, the azo dye rotaxane, after being metallized, shows higher color strength on silica fiber. In addition, the metal complex exhibited a spectral shift in absorption. On complexing, its  $\lambda_{\text{max}}$  shifts to a slightly longer wavelength at 560 nm (a difference of 10 nm), because of the complex formation between terminal HQs and metal ions, forming linear and extended structures of the rotaxanated dye molecules.

To understand the complexing behavior between azo dye rotaxane and metal ions, the absorption spectra in aqueous solution were investigated [Figure 2(b)]. In the absence of copper (II), the



**Figure 3.** XPS spectra of silica fibers (a) before dyeing, (b) dyed with ADR, and (c) dyed with ADR and then complexed with  $\text{CuSO}_4$ .



**Figure 4.** Schematic representation of the dyeing behaviors of ADR on silica fiber (only one possible structure is shown). In the presence of metal ions, it is proposed that ADR forms linear polymeric metal-complexed architecture. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$\lambda_{\max}$  of ADR occurs at 565 nm, which corresponds to the typical  $\pi \rightarrow \pi^*$  transition of  $-\text{N}=\text{N}-$  group in azo dyes.<sup>23,24</sup> With the addition of copper, the  $\lambda_{\max}$  shifts to 590 nm, with a red shift by 25 nm. This color change is easily noticeable in the solution and can even be observed with the naked eye. The color change is irreversible, because a dye-Cu(II) complex forms a precipitate over time, due to its reduced aqueous solubility. The absorption maximum in solution (565 nm) appears at higher wavelengths compared with that in silica fiber (550 nm), which is attributed to the high pH of the solutions in which absorption spectra were measured (pH 9.6). ADR exhibited pH sensitivity, and, as noted, its absorption maximum shifts to a longer wavelength (red shift) at high pHs. In dyeing tests, residual alkalis were thoroughly removed by repeated washing in water, and thus the  $\lambda_{\max}$  occurs at a shorter wavelength. Notably, considering that such a red shift became negligible in DMF, we assume that ADR is more sensitive to pH condition than to the polarity of the solvent system.

We observe that the binding between the azo dye rotaxane and  $\text{SiO}_2$  is quite strong. Even after a week in water at room temperature, the dyed fibers showed no color changes. As previously reported, CD binding to  $\text{SiO}_2$  surface induces high adsorption of organic molecules and directs a multilayer assembly of  $\text{SiO}_2$  nanoparticles.<sup>15–17</sup> Thus, bonds between  $\alpha$ -CD and  $\text{SiO}_2$  should be strong enough to provide a durable color on silica fibers containing  $\text{TiO}_2$ .

XPS spectra of silica fibers were recorded after dyeing with ADR in both the absence and presence of  $\text{CuSO}_4$  (Figure 3). Peaks at 100.8 eV and 530.4 eV correspond to Si 2P and O 1s spectra, respectively, and these peaks exhibit no difference before and after dyeing. The XPS surface O/Si ratio of the ADR-dyed fiber increased from 2.09 to 2.61 in the case of undyed silica, indicating that the fiber surface was more or less covered by dye molecules. After Cu-complexing, we observed the appearance of the characteristic Cu 2p peak at 933.9 eV, and the O/Si and Cu/Si ratios were measured to be 4.04 and 0.50, respectively. These measurements suggest that polymeric metal-complexing allowed the dye species to become highly enriched on the surface of the silica fiber. Another noteworthy aspect of this method is that various metal ions can be deposited on the surface of inorganic fibers when adopting different chelating metals.

Based on the above results, it is obvious that terminal HQs form coordinated bonds in the presence of metal ions, leading

to the development of large extended structures for the metal-complexed dye molecules, whereas each  $\alpha$ -CD strongly binds to the  $\text{SiO}_2$  on the silica fiber surface. Therefore, we can reasonably deduce the dyeing behavior of the azo dye rotaxane and the formation of its metal complex on the surface of silica fiber (Figure 4). In the model, polymeric architecture was formed by the metal-dye complex, which attached to the fiber surface by hydrogen bonding of CD-silica attractions.

We observe that binding of the azo dye rotaxane to  $\text{SiO}_2$  is quite strong. No color change in Cu-complexed sample has been observed in water at room temperature after a week. Thus we consider that bonds between  $\alpha$ -CD and  $\text{SiO}_2$  are strong enough to provide a durable color on silica fibers. It is also believed that the binding stability of CD-rotaxanated dyes in a polymer host can be controlled by chemical modification of CD -OH groups, which could control interactions with polymer matrices. Therefore, we believe that the proper adjustment of the interaction between CD and  $\text{SiO}_2$  should enable CD-encapsulated dyes to be used for many more promising applications. Furthermore, our preliminary experiments indicate that the surface of silica fiber can be deposited with many different kinds of metals, including ruthenium and osmium, which are useful for various electrochemical applications, and such applications will be elaborated in subsequent reports.

In summary, we prepared an azo dye rotaxane and its polymeric metal complex. We successfully demonstrated the use of a metallized dye rotaxane for dyeing silica fiber, which offered a fairly good color fastness. This was made possible by the hydrogen bonding between  $\text{SiO}_2$  and -OHs on  $\alpha$ -CD. Spectroscopic evidence indicated that polymeric metal-complexed dye structures formed within the silica fiber.

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