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Synthesis of Alkoxy-Based Terpyridine to Produce Viscose Fabric with Antibacterial Properties

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Synthesis of Alkoxy-Based Terpyridine to Produce Viscose Fabric with Antibacterial Properties

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Abstract

A new alkoxy-containing terpyridine was synthesized and completely characterized by elemental analysis, FTIR, ^{1}H- and ^{13}C-NMR, and GC-MS spectral analysis. The alkoxy terpyridine was applied on viscose fabric via spray-coat processing and screened for its antibacterial performance against some pathogens including *S. aureus* and *E. coli*. The alkoxy terpyridine treatment was acceptable in terms of antibacterial activity of the treated viscose. Additionally, the treated viscose demonstrated antibacterial and ultraviolet protection properties without weakening its mechanical or whiteness characteristics. The surface morphological properties of the spray-coated viscose samples were characterized by scanning electron microscopy (SEM). The comfort properties were explored by testing their bending length and air permeability.

Key words: Terpyridine; Spray-coat; Viscose; Antibacterial; Ultraviolet protection

1. Introduction

Smart materials and technical textiles have been considered of significance due to their application in different fields, such as medical applications. Textile customers are currently becoming alert of the harmful effect that pathogenic organisms may have on textiles and human sanitation [1-3]. Medical technical textiles have particularly received great applicability of antibacterial finishes to stop the probability of bacterial infections [4-13]. Bacterial multiplication on clothing may cause discoloration, bad odor and reduced mechanical properties, which may harmfully influence human health [14, 15]. Thus, diverse antibacterial agents, such metal oxides, quaternary ammonium salts and metal-based nanoparticles, were applied on textiles fibers to impart them antibacterial character [16-21]. However, there was a permanent and vital need to explore novel antibacterial agents of various chemical structures and different functional mechanisms due to the alerting increment in the occurrence of new infectious diseases. Additionally, the bacterial pathogens develop resistance to currently employed antibacterial agents [22-24].

Recently, terpyridine-based compounds have been investigated as novel antibacterial agents [25, 26]. Terpyridines are polypyridyl heterocyclic compounds derived from pyridine and comprising aromatic nitrogen atoms acting as multiple active sites with beneficial structure for a variety of applications, such as drug design, coordination chemistry and supramolecular architectures [27-29]. Terpyridines are tridentate ligands with the ability to bind to metals at three sites producing coordination complexes with the majority of transition metal ions with distinguished optical and electrochemical characteristics and reversible oxidation/reduction behavior [30, 31].

In this study, the viscose fabric loaded with alkoxy terpyridine (Figure **1**) were synthesized and fully characterized to possible production of antibacterial and ultraviolet protective clothing.

An international standard testing was applied to describe the antibacterial performance of the treated viscose fabric against both *S. aureus* (gram +ve) and *E. coli* (gram -ve). We applied the spray-coat method to load the alkoxy terpyridine substance on the viscose fabric. The ultraviolet shielding efficiency of the treated fabrics along with washing durability was also explored.

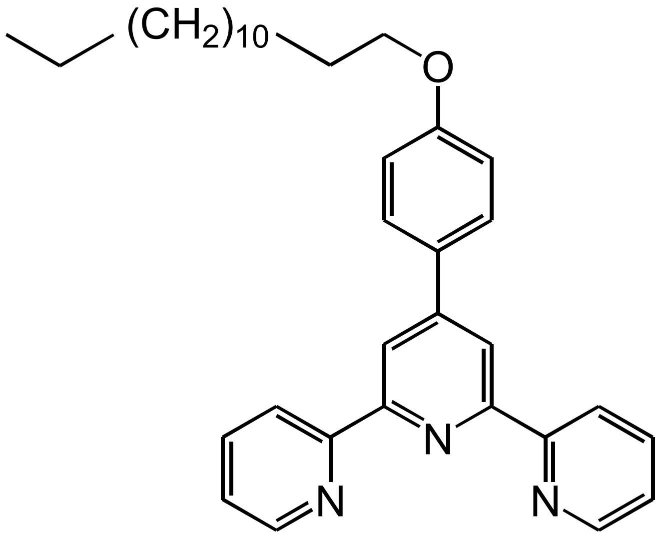


Figure 1: Chemical structure of alkoxy terpyridine

2. Experimental details

2.1. Materials and reagents

Mercerized an bleached viscose fabric (Lenzing Viscose®) characterized by a linear density of 1.3dtex and a length of 38mm, was supplied by Misr Spinning and Weaving Company (El-Mahalla El-Kobra, Egypt). The fabric did not include any spin finish and were applied without additional curing. Solvents employed in this research study were purchased from Fluka and Aldrich. Compounds **1** and **2** were synthesized according to literature methods [32, 33].

The progress of reactions was visually monitored under UV lamp (254 or 365nm) by Merck TLC aluminum plates coated by silica gel PF254.

2.2. Apparatus and methods

Melting point (°C) of alkoxy-substituted terpyridine was recorded uncorrected on Stuart SMP30. FTIR spectra were reported on JASCO FTIR-4700 spectrophotometer. Elemental analyses were performed on PerkinElmer 2400 analyzer (PerkinElmer, Norwalk, CT, United States). Mass spectra were monitored on from a Shimadzu GCMS-QP-1000 EX spectrometer in (70 ev) mode. NMR spectra were explored on BRUKER AVANCE 400 spectrometer at 400 MHz; chemical shift were determined in ppm relative to TMS internal standard. The surface morphological features of the treated viscose substrates were tested on a scanning electron microscope (SEM; Quanta FEG-250, Czech Republic).

2.3.Characterization of hydroxy-substituted terpyridine intermediate 1

The hydroxy-substituted terpyridine intermediate **1** was re-crystallized from a mixture of $CHCl_3$/Methanol (1:1) to give a white powder. ^1H NMR (400 MHz, DMSO-d_6) ppm: 8.76 (d, 2H), 8.64 (d, 2H), 8.62 (s, 2H), 8.01 (t, 2H), 7.63 (d, 2H), 7.49 (t, 2H), 6.70 (t, 2H).

2.4. Preparation of alkoxy-substituted terpyridine 2

A mixture of compound **1** (5 mmol), anhydrous potassium carbonate (20 mmol), potassium iodide and 1-bromotetradecane (5 mmol) was stirred under nitrogen in dry dimethylformamide (15 mL) at 80ºC for 14 hours. The reaction mixture was then added to cold water to give solid precipitate which was isolated by filtration and washed with water then hexane. White powder was obtained (yield 83%). m.p. 202-204ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.75 (d, 2H), 8.73 (s, 2H), 8.68 (d, 2H), 7.89 (dd, 4H), 7.36 (dd, 2H), 7.04 (d, 2H), 4.04 (t, 2H), 1.84 (m, 2H), 1.49 (m, 2H), 1.28 (s, 20H), 0.90 (t, 3H); ^{13}C NMR (400 MHz, DMSO-d_6) δ ppm: 160.14, 156.42, 155.80, 149.80, 149.08, 136.82, 130.45, 128.47, 123.72, 121.36, 118.23, 114. 86, 68.14, 34.00, 32.68, 31.94, 29.71, 29.25, $^{-1}$): 2225 (CN), 1585 (C=N); MS *m/z* (%): 521 [*M*]$^{+}$. Elemental analysis calculated for $C_{35}H_{43}N_3O$ (521.74): C 80.57, H 8.31, N 8.05; Found: C 81.02, H 8.26, N 8.12

2.5. Treatment of viscose fabric

The viscose fabric was subjected to spray-coating by an aqueous solution of alkoxy terpyridine at different concentrations (0.1, 0.5, 1, 2, 4, and 6wt%) and polyacrylate-based binder additive (10wt%) in distilled water. The spray-coated fabrics were then passed through a padding mangle to get rid of excess solution. The treated samples were air-dried at ambient conditions and then cured at 140^{o}C for 3 minutes. Samples were then immersed in an aqueous solution of sodium lauryl sulfate (2 g/l) for 5 minutes to take away the unbound alkoxy terpyridine, rinsed with running water to take away the soap solution and finally air-dried at ambient conditions.

2.6. Evaluation of UV protection

Ultraviolet Protection Factor was explored employing AS/NZS 4399:1996 standard method on UV/Vis spectrophotometer (AATCC 183:2010, UVA Transmittance).

2.7. Evaluation of antimicrobial performance

The antimicrobial activity of the spray-coated viscose samples was tested quantitatively against *E. coli* and *S. aureus* applying standard procedure (AATCC 100-1999).

2.8. Whiteness index

The whiteness of both treated and pristine substrates were explored by the color coordinates (L^*, a^*, b^*) on spectrophotometer with pulsed xenon lamps (UltraScanPro, Hunter Lab, United States) with d/2 viewing geometry, illuminant of D65 with 10° observer, and 2mm area. An average of five measurements reported at different locations of the examined viscose fabric, was taken as the major value.

2.9. Bend length

Bend length was evaluated depending on British Standard method 3356:1961 employing Shirley stiffness tester. The bend length was recorded as an average of five readings at five different locations for every sample.

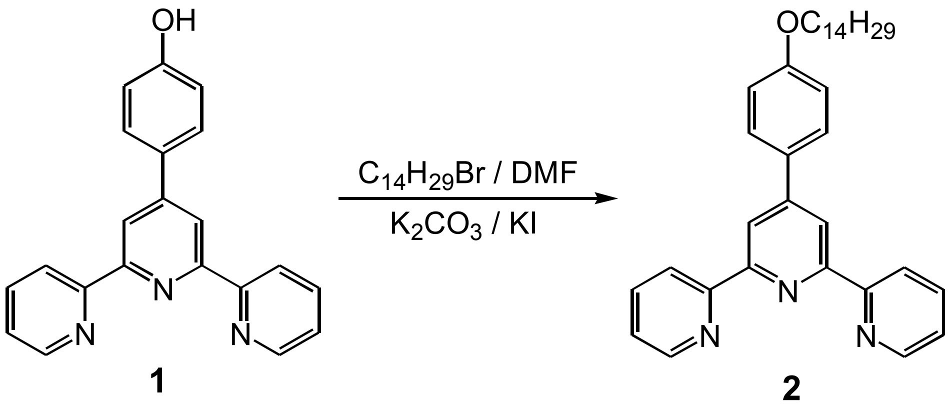
2.10. Air permeability

The air permeability was recorded depending on ASTM Standard D-737 using Textest FX 3300 (the pressure gradient was 100Pa). The final measurement was reported as an average of three readings at five different locations for every sample.

3. Results and discussion

3.1. Synthesis and characterization

As demonstrated in Scheme **1** and according to literature procedures [32, 33], the hydroxy-substituted terpyridine intermediate **1** was prepared. Our target compound alkoxy-substituted terpyridine compound **2** was synthesized by heating a mixture of the hydroxy-substituted terpyridine intermediate **1**, anhydrous potassium carbonate, 1-bromotetradecane and potassium iodide, in dry dimethylformamide at 60ºC to give a white powder in a good yield reaching 83%.



Scheme 1. Preparation of alkoxy-substituted terpyridine **2**.

Form the ^{1}H-NMR spectrum of the tetrazine compound **3**, the three peaks at 8.16, 7.87, 7.13 ppm were attributed to the four phenyl azo moieties, while the ^{13}C-NMR displayed nine signals in the aromatic area and nine signals for the aliphatic moieties. In conclusion, a new bis-azo *sym*-tetrazine was effectively prepared and verified according to FT-IR, elemental analysis, and ^{1}H- and ^{13}C-NMR spectroscopic methods.

3.2. Surface morphological

The morphological features of the alkoxy terpyridine spray-coated viscose fabric surface were explored by scanning electron microscopy. Figure **2** demonstrates the scanning electron micrograph images of treated viscose. Treatment of viscose fibers with alkoxy terpyridine resulted in the development of a heterogeneous film on the fabric surface. The alkoxy terpyridine particle size was in the range between 350nm to 1μm.

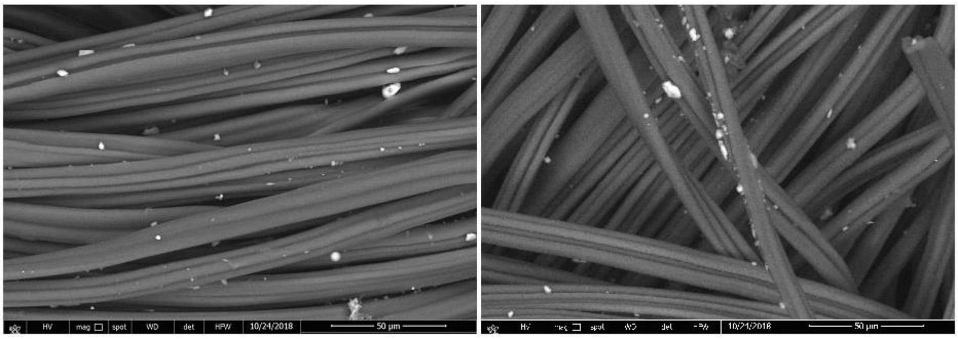


Figure 2. SEM images of treated viscose fibers.

3.3. UV-protection and antibacterial performance

The UV-shielding performance of the spray-coated viscose fabrics was directly evaluated as shown in Table **1.** The Ultraviolet Protection Factor (UPF) values of the spray-coated viscose substrates were found to increase as the alkoxy-substituted terpyridine concentration increase. The improvement of ultraviolet protection of the spray-coated viscose substrates could be attributed to the ultraviolet absorption ability of the alkoxy-substituted terpyridine.

Table 1: Ultraviolet protection of blank and spray-coated viscose fabrics

alkoxy terpyridine wt%	UPF
0	**37**
0.1	**77**
0.5	**92**
1.0	**116**
2.0	**121**
4.0	**129**
6.0	**131**

The antibacterial performance of the spray-coated viscose fabrics against some pathogens including *E. coli* and *S. aureus* were tested using plate agar count approach as displayed in Table **2.** The hydroxyl-substituted terpyridine intermediate did not show any antibacterial activity. The blank viscose fabric showed no inhibition result on the reduction of all pathogens. Additionally, the spray-coated viscose substrates demonstrated different antibacterial activity result depending on the alkoxy terpyridine concentration.

Table 2: Antibacterial performance (bacterial reduction %) of blank and spray-coated viscose fabrics

alkoxy terpyridine wt%	*E. coli* (–ve)	*S. aureus* (+ve)
0	**0.00**	**0.00**
0.1	**12±1.1**	**11±1.3**
0.5	**17±1.0**	**18±1.2**
1.0	**23±1.2**	**21±1.1**
2.0	**25±1.3**	**23±1.4**
4.0	**27±1.0**	**22±1.2**
6.0	**28±1.2**	**25±1.0**

3.4. Mechanical and colorimetric properties

The main reason of using spray-coat process was to present a smooth thin layer with lowest optimum rough surface, whilst maintain the breathability and flexibility of the treated viscose samples. Both bend length and air permeability for spray-coated viscose fabrics are shown in Tables **3** and **4**. The spray-coat procedure did not considerably influence on the air permeability of the treated fabrics while increasing the alkoxy terpyridine content.

Table 3. Effect of spray-coat on viscose air permeability upon raising the concentration of alkoxy terpyridine.

alkoxy terpyridine wt%	air permeability ($cm^3\ cm^{-2}\ s^{-1}$)
0.1	59.21
0.5	58.82
1.0	58.10
2.0	57.68
4.0	57.19
6.0	56.73

On the contrary, the bend length of the spray-coated viscose in both warp and weft direction was considerably improved relative to the pristine sample. The influence of spray-coating viscose with alkoxy terpyridine demonstrated that viscose lost some of its whiteness upon increasing the alkoxy terpyridine concentration. On the other hand, no considerable influence on the burst strength was detected (Table **5**).

Table 4: Mechanical properties of pristine and alkoxy terpyridine spray-coated viscose.

sample	whiteness index	burst strength (KPa)	bend length (cm)	
			Warp	Weft
Pristine	32.9	291.3	2.3	2.7
0.1	29.7	288.2	2.9	3.1
0.5	29.3	286.7	3.1	3.2
1.0	28.6	287.9	3.4	3.5
2.0	28.1	287.0	3.5	3.6
4.0	28.0	286.3	3.5	3.6
6.0	28.0	286.3	3.4	3.5

To assess the coloration measurements as a result of alkoxy terpyridine spray-coating, the CIE color coordinates (L^*, a^*, b^*) were recorded and displayed in Table **5**. As anticipated, no considerable color change was detected for the treated fabrics fabrics. This was confirmed by the closely related magnitudes of the CIE color coordinates before and after spray-coating.

Table 5. Coloration measurements of blank and spray-coated viscose upon increasing alkoxy terpyridine concentration.

Sample (Conc.)	L^*	a^*	b^*
pristine viscose	95.28	0.04	2.36
0.1	**94.87**	**- 0.12**	**2.29**
0.5	**94.51**	**- 0.19**	**2.78**
1.0	**93.24**	**-0.08**	**2.17**

2.0	**92.31**	**0.15**	**2.65**
4.0	**92.85**	**0.12**	**2.38**
6.0	**91.37**	**0.31**	**2.98**

4. Conclusion

A spray-coat was deposited on viscose substrates using alkoxy terpyridine in combination with polyacrylate binder additive to impart antibacterial and UV protection characteristics. By varying the concentration of the alkoxy-terpyridine in the deposition solution, antibacterial and UV protection performance were customized. The results were proved by exploring surface morphology of the spray-coated viscose fabric employing scanning electron microscopy (SEM). The produced antibacterial viscose fabrics were found to exhibit sufficient shielding against ultraviolet electromagnetic radiation without considerably weakening the mechanical features of viscose. The comfort properties of spray-coated viscose were evaluated to show acceptable results of bend length and air permeability. This spray-coat procedure was characterized by relative stability to wash, easy to handle, and bath preparation and almost no deterioration in tensile strength or air permeability.

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