Quinaldine and Indole based pH Sensitive Colorimetric Chemosensor and their application of nanofiber

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ABSTRACT

Colorimetric chemosensors are now considered as one of the most effective analytical method used in the environment monitoring. Colorimetric chemosensors for pH sensing can easily detect the primary danger or change of the surrounding environment pollution and source of infection and can prevent danger in the various fields.

Quinaldine and Indole based colorants having the function of colorimetric chemosensors were synthesized. Synthesized colorants were characterized by 1H NMR, GC-Mass, EA and UV-Vis spectroscopy. Especially UV-Vis spectroscopy revealed that the color of each colorant solution was changed in basic conditions while no changes were observed in acidic condition. And then synthesized colorants were mixed with poly-acrylonitrile for electrospinning. Electrospun fibers containing each colorant were used as pH textile sensors and they were analyzed by Spectrophotometer.

Keywords: quinaldine, indole, nanofiber, chemosensor, pH sensor

1 INTRODUCTION

Colorimetric chemosensors are now considered as one of the most effective analytical method used in the environment monitoring [1-3]. Among lots of dangers threatening our environment, pH is a very important factor not only in the research area such as environmental, medical, and industrial area but also in our daily life. Many studies using some appliances have been conducted to detect pH but those methods have disadvantages such as complex procedure or high price. In this regard, colorimetric chemosensors for pH detection which make up for this disadvantage have received attention. Colorimetric chemosensors for pH sensing can easily detect the primary dangers or changes of the surrounding environmental pollution and source of infection. They also can prevent danger in the various fields [4-6].

In this study, Quinaldine and Indole based colorants were synthesized to detect pH changes easily with naked eyes and evaluated as pH sensors. Synthesized colorants were characterized by 1H NMR, GC-Mass, Elementary Analysis (EA) and UV-Vis spectroscopy. UV-Vis spectroscopy was measured to evaluate the synthesized colorants as pH sensing chemosensors. This change was considered that the color changes are due to the change of arrangement of electron in the colorants with regard to acidic or basic conditions. And then nanofiber containing each colorant were prepared as pH textile sensors. Electrospun fibers were obtained by electrospinning method with poly-acrylonitrile and analyzed by a variety of methods such as Scanning Electron Microscope (SEM), and Spectrophotometer. So, it was anticipated that they can be applied in many fields because they have advantages environmentally and economically.

2 EXPERIMENTAL

2.1 Materials

Iodomethane, 2-methylquinoline, Indole-3-carboxaldehyde, 2-methyl benzothiazol and Piperidine were purchased from Sigma-Aldrich chemical. Acetonitrile was purchased from Burdick & Jackson chemical. Chloroform, 1-propanol and Hexane were supplied by Duksan. Poly-acrylonitrile with a molecular weight of 150,000 g/mol was supplied by Sigma-Aldrich. All the chemicals were used without further purification.

2.2 Synthesis of Quinaldine based dye

4.5g of Iodomethane and 5g of 2-methylquinoline was refluxed with acetonitrile solvent in round flask for 7hr. After reflux, quinaldinium salt was obtained by removing solvent in evaporator followed by washing using chloroform and drying. 0.5g of quinaldium salt was put in flask with 0.225g of indole-3-carboxaldehyde and 20ml of 1-propanol. By adding 2-5 drop of piperidine, color change was observed immediately. The solution was refluxed for 7 hours in ambient temperature and cooled for 1 day. The colorant was obtained after filter and washed with hexane followed by drying. Yield: 81%; mass (m/z): 284.1(M^+). ^{1}H NMR (400MHz, chloroform-d_6): δ 4.47(s, 3H, -NCH_3), 7.29(m, 2H), 7.54(m, 2H), 7.82(t, 1H, J=7.84), 8.06(t, 1H, J=8.84), 8.20(m, 1H), 8.23(d, 1H, J=8.12), 8.39(s, 1H), 8.43(d, 1H, J=8.84), 8.59(d, 1H, J=9.08), 8.63(d, 1H,

J=15.4), 8.81(d, 1H, J=9.08), 12.32(s, 1H, -NH)ppm. EA: Anal. calcd. : C, 58.27; H, 4.16; N, 6.79. Found: C, 58.33; H, 4.18; N, 6.83%. m.p: 258℃

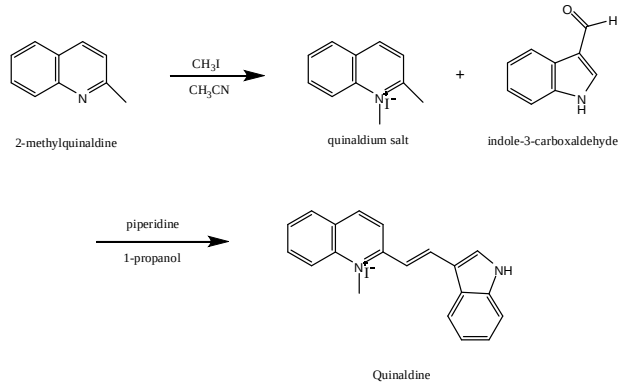


Figure 1. Structure of Quinaldine based dye

2.3 Synthesis of Indole based dye

The Indole intermediate was synthesized with similar method with Quinaldine based colorants. 2-Methylbenzothiazol 5g was added instead of 2-methylquinoline. 0.2g of benzothiazole iodide and 0.1g of indole-3-carboxaldehyde was dissolved in 10ml of 1-propanol. By adding 3-5 drop of piperidine, color change was observed immediately. The solution was refluxed for 3 hours and cooled after TLC confirmation. The colorant was obtained by filter and drying. Yield: 68%; mass (m/z): 290.1(M^+). ^{1}H NMR (400MHz, chloroform-d_6): δ 4.28(s, 3H, -NCH_3), 7.34(m, 2H), 7.49(d, 1H, J=15.4), 7.57(t, 1H, J=4.8), 7.67(t, 1H, J=8.08), 7.77(t, 1H, J= 8.6), 8.13(d, 1H, J=8.32), 8.26(t, 1H, J=3.8), 8.31(d, 1H, J=8.08), 8.42(d, 1H, J=15.64), 8.47(s, 1H), 12.52(brs, 1H, -NH)ppm. EA: Anal. calcd. : C, 51.68; H, 3.61; N, 6.70; S, 7.67. Found: C, 51.60; H, 3.61; N, 6.84; S, 7.83%. m.p: 263℃.

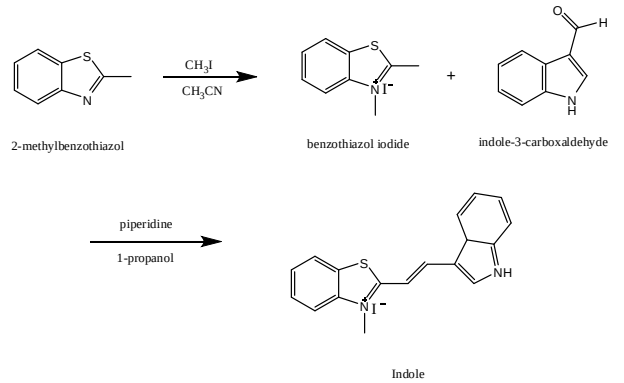


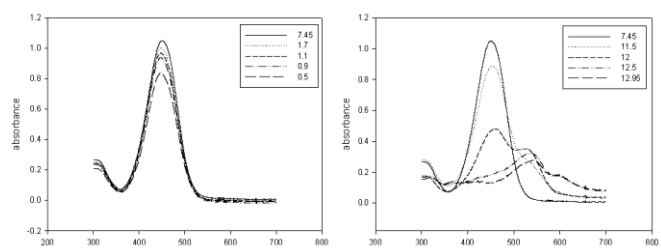
Figure 2. Structure of Indole based dye

2.4 Formation of Nanofiber

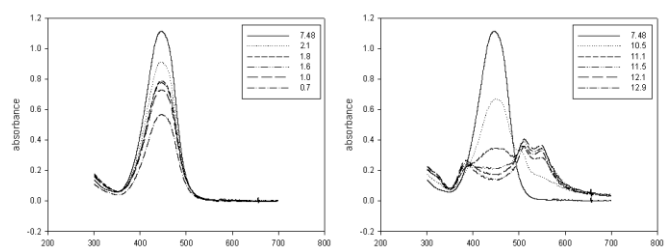
At first, we made polymer solution for electrospinning. PAN was dissolved in DMF at a concentration of 10 wt% and colorants were added in 10 wt% solutions. Each colorants concentration was various; 1%, 5%, 10%, 15%, 20% for PAN weight. And to make nanofibers, we carried out electrospinning. The applied voltage and the distance between the tip of the spinneret and the collector were maintained at 22Kv and 20cm, respectively. The flow rate was set to 10μm/min and nozzle diameter was 21G(0.51mm).

3 RESULTS

In case of quinaldine based colorant, the maximum absorption peak was shown at 450nm. The color was not changed in lower pH; however significant color change was shown by moving higher pH. In other words, shifted maximum absorption peak to longer wavelength by moving to basic condition, called bathochromic shift was took place, and the color of solution was changed from yellow to red.
In case of Indole based colorant, the result was very similar with that of quinaldine based colorant. The maximum absorption peak was shown at 447nm. In addition, rapid color change was shown by moving to basic condition while there is no color change at acidic condition. The bathochromic shift was also observed in Indole based colorant.



(a) Quinaldine based dye

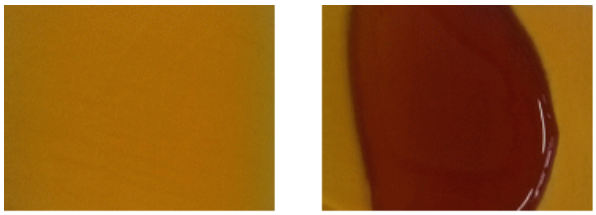


(b) Indole based dye

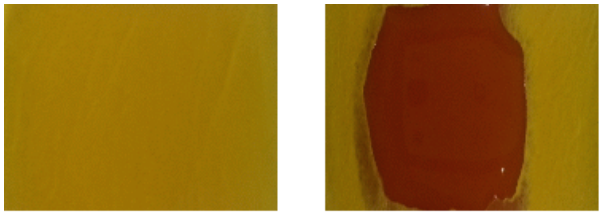
Figure 3. UV-Vis. absorbance spectra of Quinaldine and Indole based colorant

When alkali solution was dropped on nanofibers, it changed the color of surface. In other words, orange nanofiber containing quinaldine based colorant turned redder orange. So, we could realize that the condition became alkali and we called it 'Textile sensor'. In case of Indole based colorant contained nanofiber, it was similar to quinaldine based colorant. The surface was yellow, but it turned orange when alkali solution was dropped. All

nanofiber containing colorants were change their surface color as becoming alkali condition and return to initial colors with the change of acidic condition; the reaction was reversible.



(a) Quinaldine based dye contained nanofiber



(b) Indole based dye contained nanofiber

Figure 4. The Color change of nanofiber containing Quinaldine (a) and Indole (b) based colorants (5%)

We got 10 samples each colorant through electrospinning and it seemed like having different colors. So, through analysis of spectrophotometer, the differences in colors of nanofibers made clear. In case of quinaldine based colorant containing nanofiber, the lightness was decreased and total K/S was increased with adding more colorants or changing alkali condition. In an aspect of color, when alkali solution was dropped, the value of b^* was decreased and actually we could see orange nanofiber became red with naked eye. Indole based colorant containing nanofiber had similar results of the lightness and total K/S. Because of concentration of colorants and alkali condition, the lightness was decreased and total K/S was increased. In an aspect of color, as becoming alkali condition, the value of a* was increased, on the other hand, the value of b* was decreased. These changes of values showed the color change of nanofibers well; yellow nanofiber became red.

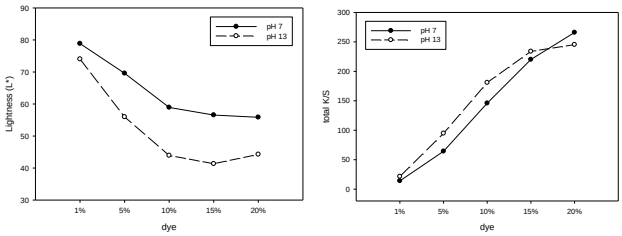


Figure 5. The colormetric data graphs of nanofiber containing Quinaldine based colorant

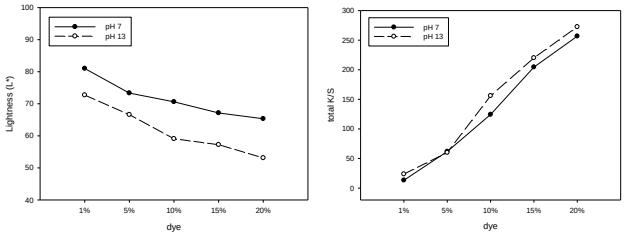


Figure 6. The colormetric data graphs of nanofiber containing Indole based colorant

4 CONCLUSION

New Quinaldine and Indole based colorants having halochromic properties were prepared and applied to textiles to identify pH change easily with naked eyes. The color changes of solution and textile were measured by various methods. Especially UV-vis. Spectroscopy and spectrophotometer evaluated the synthesized colorants and electrospund nanofiber as pH sensing chemosensors. Electrospinning was the proper way to make the pH detecting nanofiber which was applied by quinaldine and indole based colorants. The colors of the solution and nanofiber were sharply changed in the alkaline condition. This change is due to the rearrangement of electrons in the dye molecules with regard to acidic or basic conditions. By adopting theses colorants to various kinds of materials, it can be applied to several environmental monitoring fields because it has lots of advantages.

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