

Synthesis of Vapochromic Dyes with Highly Aggregative Characteristics and Their Application to Cotton-based VOC Sensors

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Abstract

The objective of this study was to fabricate cotton-based sensors exhibiting recognizable color change on exposure to vapor phase of volatile organic compounds (VOCs) at room temperature. Three vapochromic dyes (DiMo, MoMe, DiMe) with different substituents were synthesized and investigated on their color change properties after exposure to 32 organic solvents after dyeing on cotton fabrics. The cotton-based sensor exhibited strong sensing properties to polar solvents rather than non-polar solvents. Especially, N,N-dimethylformamide (DMF) detection was the best showing a color difference of 12.8 for DiMo, 21.4 for MoMe, and 25.8 for DiMe under 300ppm exposure. Even at as low concentration as 10ppm of DMF, the color change values were reached 7.3, 10.6, and 13.6 within an hour. The maximum absorption wavelength of the cotton-based sensor was shifted from 580nm to 560nm, 570nm to 560nm, and 560nm to 540nm, respectively, by the DMF exposure. The sensing mechanism was considered to depend on solvatochromism, aggregational properties of the dyes and adsorption amount of VOCs on textile substrates on which the dyes were applied. Finally, the reusability of the cotton-based sensor was tested for 10 cycles.

Introduction

A lot of chemicals are being used in various industrial and research fields. Most of them are harmful and toxic to human body as well as to environment. Especially, volatile organic compounds, called VOCs, have been getting a great attention recently. Therefore, many efforts are being made to monitor and reduce the concentration of VOCs.

The basic role of dyes was coloration of materials such as textiles, leather, paper, plastics, and so on. It has been expanding nowadays into organic sensors that detect target chemicals or physical stimuli (Ribeiro et al. 2013; Little and Christie 2016; De Meyer et al. 2016; Favaro et al. 2007; Chen et al. 2019; Hau et al. 2019; Ono et al. 2019; Beatty et al. 2019; Wang et al. 2019; Manjakkal et al. 2020). Those kinds of dyes are generally being called chemosensors which mean sensor materials detecting chemicals. In order for organic dyes to detect chemicals or physical stimuli, basically they must show color change after exposure to the stimuli. This phenomenon is called chromism and many instances are already well known such as solvatochromism, vapochromism, halochromism, ionochromism, electrochromism, thermochromism, and photochromism, to name a few. Since the sensor dyes cannot be used alone in practice, they need to be applied to substrates holding them inside like textile materials (Kim and Lee 2015a, b; Lee and Kim 2020, 2021; Lee et al. 2021; Kubota et al. 2021). In addition, the detection of vapor or gas phase will be more effective rather than liquid or solution phases. Unfortunately, however, the chromic properties of many sensor dyes are likely to be diminished or disappeared inside textile substrates. Because the stimulants such as VOCs or any toxic chemicals may not be penetrated into the substrates and in some cases the entrapment of sensor dyes inside compact molecular structure of substrates may cause the restriction of structural deformation of the dyes, which would have been induced by the stimulants.

In this study, several vapochromic dyes sensing vapor phase of VOCs were synthesized. They were direct dyes having planar structure and designed to show sensitive vapochromic properties to low concentration of vapor at room temperature. In order to show vapochromism, the dyes need to be solvatochromic at first and in addition high aggregative characteristics might increase their functions. Because the vapor phase of VOCs will penetrate between the dye molecules of aggregates or crystals, and it will cause spectral change of the dyes inside the textile substrates (Wenger 2013). This is why we determined to synthesize direct dyes. Direct dyes are very well known to be dyed easily to cellulosic fibers and to make aggregates in and on the fibers. We found a few direct dyes showing strong color change on exposure to vapor phase of VOCs inside cellulosic fibers at low concentration at room temperature. Therefore, the homologous series of the dyes were synthesized by replacement of substituents of the dyes and applied to cellulosic fibers to fabricate cotton-based VOC sensors (Scheme 1). The cotton-based VOC sensors were investigated in terms of sensing properties to 32 kinds of organic solvents and their sensing mechanism. The relationship between the chemical structure and sensitivity of the dyes were also studied. Finally, considering practical application, reusability was tested.

Experimental

Materials

To synthesize of the dyes, p-anisidine-sulfonic acid, 2,5-dimethoxyaniline, 2-methoxy-5-methylaniline, 2,5-dimethylaniline, 7-anilino-4-hydroxy-2-naphthalenesulfonic acid, sodium hydroxide, an aqueous of hydrochloric acid, sodium nitrite, and acetic acid were used. Various VOCs such as n-hexane, n-octane, cyclohexane, benzene, toluene, chlorobenzene, p-xylene, ethylbenzene, nitrobenzene, chloroform, dichloromethane, acetylene dichloride, dichloroethane, trichloroethane, tetrachloroethylene, ethylether, methyl t-butylether, formaldehyde, 1,4-dioxane, ethylacetate, propylene oxide, methanol (MeOH), iso-propanol (2-PrOH), acetone, methylethylketone, tetrahydrofuran (THF), acetic acid, acetaldehyde, acetonitrile, diethylamine, pyridine, N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), ethylene glycol, and water were used. For solvatochromism experiments, several solvents with different dielectric constants were especially selected. All reagents and solvents were commercially available and used without further purification.

Cotton standard fabric (ISO 105-F02, warp; 35 threads/cm, weft; 31 threads/cm, weight; 115 g/m²) was used as a cellulosic substrate for the fabricated sensors. A practical polycationic fixing agent was used for the aftertreatment to improve the wash fastness of the dyed fabric.

Instrumentation

HPLC from Waters 510 was utilized, and the column specification was C18, 5 μ m, 4.6 \times 150 mm and the flow rate was 1.0 mL/min with 55% methanol and 45% water added ammonium phosphate dibasic (20 mM) and UV detector spectrum was 254 nm. ¹H NMR (500 MHz) data were analyzed with Avance III 500, Bruker using DMSO-d₆ as solvents and TMS as an internal standard. The mass data (m/z) were obtained

on a XEVO-TQS micro, Waters LC/MS (ESI, Negative mode) with 3 kV of capillary voltage and 40 V of cone voltage, which flow rate was 0.2 mL/min under 50% methanol and 50% water. The absorption spectra and molar absorption coefficient were investigated by ultraviolet-visible spectrophotometer (Optizen 2010UV). X-ray diffraction analysis was performed using Malvern Panalytical EMPYREAN operating in the reflection mode with Cu-K α radiation (λ ; 1.540598 nm, $2^\circ \leq 2\theta \leq 100^\circ$).

Synthesis of dyes

Synthesis scheme of the three dyes **5a-c** is shown in Scheme 2. All three dyes were synthesized by twice diazotization and twice coupling.

Sodium 3-((E)-(2,5-dimethoxy-4-((E)-(4-methoxy-2-sulfonatophenyl)

diazenyl)phenyl)diazenyl)-4-hydroxy-7-(phenylamino)naphthalene-2-sulfonate (**5a, DiMo**)

To substitute a sulfonic acid group to sodium sulfonate in p-anisidine-sulfonic acid (**1**), the p-anisidine-sulfonic acid (**1**, 0.01 mol) was dissolved in sodium hydroxide (0.01 mol) aqueous solution (20 mL) and stirred at room temperature until a clear solution was obtained. Sodium nitrite (0.01 mol) aqueous solution (5 mL) was added to the mixture solution. The solution was placed in an ice-water bath and lowered temperature to 0 ~ 5°C and then an aqueous of hydrochloric acid (0.03 mol) was slowly put into the solution while maintaining 0 ~ 5°C and stirred for 1 h. As the diazonium reaction proceeds, the mixture turned into a white opaque solution. After the diazonium reaction, the reactant was slowly added to 2,5-dimethoxyaniline (**2a**, 0.01 mol) as the first coupler dissolved in acetic acid (5 mL) while maintaining 0 ~ 5°C. Upon addition, the reactants underwent azo coupling reaction and the solution turned red. After stirring for an hour, the product was filtered and washed with water several times. The product was dissolved in methanol (300 mL) and filtered to remove impurities and then the methanol with the product was partially evaporated to obtain a saturated solution, and an excess of ethylacetate (500 mL) as a non-solvent was added to precipitate a monoazo compound (**3a**, yield; 22%) and dried under vacuum. $^1\text{H NMR}$ (500 MHz, DMSO- d_6); δ (ppm) = 3.85 (s, 3H, CH $_3$), 3.92 (s, 3H, CH $_3$), 3.96 (s, 3H, CH $_3$), 6.42 (s, 1H, ArH), 6.92 (dd, 1H, ArH, J = 8.8 Hz), 7.20 (s, 1H, ArH), 7.37 (d, 1H, ArH, J = 8.8 Hz), and 7.43 (st, 1H, ArH, J = 2.9 Hz). Mass spectrometry (ESI, negative mode); m/z for C $_{15}$ H $_{16}$ N $_3$ O $_6$ S $^-$ (M-H) $^-$: calculated: 366.1, found: 366.0.

As the second diazotiation step, a sulfonic acid group of the monoazo compound (**3a**, 0.001 mol) was substituted to sodium sulfonate in sodium hydroxide (0.001 mol) aqueous solution (30 mL) and sodium nitrite (0.001 mol) aqueous solution (5 mL) was mixed and then an aqueous solution of hydrochloric acid (0.003 mol) was dropwise added with keeping 0 ~ 5°C. The mixture solution was slowly added to 7-anilino-4-hydroxy-2-naphthalenesulfonic acid (**4**, 0.001 mol) solution (10 mL), which sulfonic acid was substituted with sodium sulfonate in an aqueous sodium hydroxide as above, while maintaining 0 ~ 5°C and pH 9 ~ 10 with the aqueous sodium hydroxide (0.004 mol, 2 mL). The reaction was continued for an hour at that temperature and sodium chloride (20 g) was added to help precipitation of the synthesized

dye (**5a**). After filtering, an excess of methanol (300 mL) was poured to dissolve DiMo and unreacted compounds except for sodium chloride, followed by filtering again. The methanol solution was partially evaporated to obtain a saturated solution, and then about 0.5 mL aqueous of hydrochloric acid were added to substitute sodium sulfonate with sulfonic acid to diminish ionization of the dye. An excess of water (500 mL) as a nonsolvent was added to precipitate a blue disazo compound named DiMo (**5a**, yield; 9%) and dried under vacuum. $^1\text{H NMR}$ (500 MHz, DMSO- d_6); δ (ppm) = 3.74 (s, 3H, CH₃), 3.85 (s, 3H, CH₃), 3.92 (s, 3H, CH₃), 6.65 (s, 1H, ArH), 6.99 (dd, 2H, ArH, J = 9.0 Hz), 7.05 (t, 1H, ArH, J = 7.4 Hz), 7.29 (d, 2H, ArH, J = 8.5 Hz), 7.37 (t, 2H, ArH, J = 8.1 Hz), 7.49 (sd, 1H, ArH, J = 2.7 Hz), 7.5 (dd, 1H, ArH, J = 8.8 Hz), 7.64 (s, 2H, ArH), 7.94 (s, 1H, ArH), and 8.10 (d, 1H, ArH, J = 8.3 Hz). Mass spectrometry (ESI, negative mode); m/z for C₃₁H₂₅N₅NaO₁₀S₂⁻ (M-Na)⁻: calculated: 714.1, found: 714.0, C₃₁H₂₆N₅O₁₀S₂⁻ (M-2Na + H)⁻: calculated: 692.1, found: 692.0.

Sodium 4-hydroxy-3-((E)-(2-methoxy-4-((E)-(4-methoxy-2-sulfonato

phenyl)diazenyl)-5-methylphenyl)diazenyl)-7-(phenylamino)naphthalene-2-sulfonate (**5b**, MoMe)

The p-anisidine-sulfonic acid (**1**, 0.01 mol) was dissolved in an aqueous of sodium hydroxide (0.01 mol, 10 mL) and stirred at room temperature. Sodium nitrite (0.01 mol) aqueous solution (5 mL) was added to the mixed solution. The solution was placed in an ice-water bath and lowered the temperature to 0 ~ 5°C and then an aqueous of hydrochloric acid (0.03 mol) was slowly added to the solution while maintaining 0 ~ 5°C and stirred for 1h. After the first diazonium reaction, the reaction solution was slowly put into the first coupler (2-methoxy-5-methylaniline (**2b**, 0.01 mol)) which was dissolved in acetic acid (3 mL) while maintaining 0 ~ 5°C. After stirring for an hour, the product was filtered and washed with water several times. The product was dissolved in methanol (300 mL) and filtered to remove impurities and then the methanol solution was partially evaporated to make a saturated solution, and an excess of water (500 mL) was poured to precipitate a monoazo compound (**3b**, yield; 16.1%) and dried under vacuum. $^1\text{H NMR}$ (500 MHz, DMSO- d_6); δ (ppm) = 2.37 (s, 3H, CH₃), 3.83 (s, 3H, CH₃), 3.88 (s, 3H, CH₃), 6.72 (s, 1H, ArH), 7.05 (s, 1H, ArH), 7.08 (dd, 1H, ArH, J = 8.9 Hz), 7.30 (sd, 1H, ArH, J = 2.9 Hz), and 7.68 (d, 1H, ArH, J = 9.0 Hz). Mass spectrometry (ESI, negative mode); m/z for C₁₅H₁₆N₃O₅S⁻ (M-H)⁻: calculated: 350.1, found: 350.0.

In the second diazotization step, the sulfonic acid group of the monoazo compound (**3b**, 0.001 mol) was substituted to sodium sulfonate in an aqueous of sodium hydroxide (0.001 mol, 20 mL) and sodium nitrite (0.001 mol) aqueous solution (5 mL) was added and then an aqueous solution of hydrochloric acid (0.003 mol) was dropwise added with keeping 0 ~ 5°C. The mixture solution was slowly added to the 7-anilino-4-hydroxy-2-naphthalenesulfonic acid (**4**, 0.001 mol) solution (10 mL), which sulfonic acid was substituted with sodium sulfonate in an aqueous sodium hydroxide as above, while maintaining 0 ~ 5°C and pH 9 ~ 10 with the aqueous sodium hydroxide (0.004 mol, 2 mL). The reaction was continued for an hour at that temperature and sodium chloride (20 g) was added to help precipitation of the synthesized dye (**5b**). After filtering, an excess of methanol (300 mL) was poured to dissolve MoMe and impurities

except for sodium chloride and filtered again. The methanol solution was partially evaporated to obtain a saturated solution, and then 0.5 mL of hydrochloric acid were added to substitute sodium sulfonate with sulfonic acid for the same reason as above and an excess of water (500 mL) was added to precipitate a purple dye, MoMe (**5b**, yield; 38%) and dried under vacuum. $^1\text{H NMR}$ (500 MHz, DMSO- d_6); δ (ppm) = 2.67 (s, 3H, CH₃), 3.86 (s, 3H, CH₃), 3.95 (s, 3H, CH₃), 7.01 (dd, 1H, ArH, J = 8.9 Hz), 7.04 (tt, 1H, ArH, J = 7.3 Hz), 7.12 (dd, 1H, ArH, J = 8.7 Hz), 7.17 (sd, 1H, ArH, J = 2.3 Hz), 7.29 (dd, 2H, ArH, J = 8.7 Hz), 7.37 (m, 2H, ArH), 7.49 (sd, 1H, ArH, J = 2.9 Hz), 7.55 (d, 1H, ArH, J = 8.8 Hz), 7.64 (s, 2H, ArH), 7.90 (s, 1H, ArH), and 8.11 (d, 1H, ArH, J = 8.8 Hz). Mass spectrometry (ESI, negative mode); m/z for $\text{C}_{31}\text{H}_{25}\text{N}_5\text{NaO}_9\text{S}_2^-$ (M-Na) $^-$: calculated: 698.1, found: 698.0, $\text{C}_{31}\text{H}_{26}\text{N}_5\text{O}_9\text{S}_2^-$ (M-2Na + H) $^-$: calculated: 676.1, found: 676.0.

sodium 4-hydroxy-3-((E)-(4-((E)-(4-methoxy-2-sulfonatophenyl)

diazenyl)-2,5-dimethylphenyl)diazenyl)-7-(phenylamino)naphthalene-2-sulfonate (**5c**, DiMe)

The synthesis procedure was the same as compound **5b** (MoMe). For the monoazo compound and disazo compound colored violet were obtained 13% and 32%, respectively. $^1\text{H NMR}$ (500 MHz, DMSO- d_6); δ (ppm) = 2.22 (s, 3H, CH₃), 2.33 (s, 3H, CH₃), 3.97 (s, 3H, CH₃), 7.17 (sd, 1H, ArH, J = 2.3 Hz), 7.29 (dd, 1H, ArH, J = 8.9 Hz), 7.64 (s, 1H, ArH), 7.91 (s, 1H, ArH), and 8.12 (d, 1H, ArH, J = 8.8 Hz). Mass spectrometry (ESI, negative mode); m/z for $\text{C}_{15}\text{H}_{16}\text{N}_3\text{O}_4\text{S}^-$ (M-H) $^-$: calculated: 334.1, found: 334.0.

$^1\text{H NMR}$ (500 MHz, DMSO- d_6); δ (ppm) = 2.43 (s, 3H, CH₃), 2.69 (s, 3H, CH₃), 3.85 (s, 3H, CH₃), 6.99 (dd, 1H, ArH, J = 9.0 Hz), 7.05 (tt, 1H, ArH, J = 7.4 Hz), 7.13 (dd, 2H, ArH, J = 8.9 Hz), 7.20 (sd, 1H, ArH, J = 2.3 Hz), 7.30 (td, 2H, ArH, J = 8.5 Hz), 7.50 (d, 2H, ArH, J = 8.8 Hz), 7.61 (s, 2H, ArH), 7.99 (s, 1H, ArH), and 8.14 (d, 1H, ArH, J = 8.7 Hz). Mass spectrometry (ESI, negative mode); m/z for $\text{C}_{31}\text{H}_{25}\text{N}_5\text{NaO}_8\text{S}_2^-$ (M-Na) $^-$: calculated: 682.1, found: 682.0, $\text{C}_{31}\text{H}_{26}\text{N}_5\text{O}_8\text{S}_2^-$ (M-2Na + H) $^-$: calculated: 660.1, found: 660.0.

Solvatochromism

To investigate solvatochromism, nine solvents such as water (78.40), DMSO (47.24), ethylene glycol (41.40), DMF (38.25), acetonitrile (36.64), MeOH (33.00), acetone (21.01), pyridine (13.26), and THF (7.52) with different dielectric constants were selected. The three dyes were dissolved in each solvent and absorption spectra were investigated and color change according to the dielectric constants was observed.

To obtain a deeper insight into the solvatochromic properties of the dyes, density function theory (DFT) calculation was performed. Geometry optimization was performed at the B3LYP/6-31 + G(d,p) level. Electron transitions were also calculated using the time dependent DFT method at the B3LYP/6-31 + G(d,p) level and additionally using solvation model, the integral equation formalism variant polarizable continuum model (IEFPCM), at the 9 kinds solvents. From the calculation, the HOMO and LUMO energy values were obtained and compared to the experimental values of maximum absorption wavelength of the dyes in each solution.

Application of the dyes to cellulosic substrates

To determine the optimal concentration of the dyes to show the largest color change when exposed to VOCs, the three dyes were applied at concentrations of 0.5 ~ 30% owf. A certain concentration of dye and 3g of sodium sulfate were added to 60 mL of deionized water and stirred for 30 min at room temperature. The 1.2g of cellulosic substrates were dyed in the solutions at 100°C for an hour. After dyeing the dyed fabrics were washed 5 times with water at room temperature.

Measurement of color strength and color change

The color strengths and spectra of cotton-based VOC sensors were measured using a color measurement instrument (spectrophotometer CM-3600, Konica Minolta) and expressed by K/S values based on the reflectance (R) of a single wavelength obtained at every 10 nm in the range of 360 ~ 740 nm using Eq. (1). The viewing angle was 10° and illuminant was the standard light D₆₅ (Koh 2006; Baumann et al. 1987).

$$K/S = (1-R)^2 / 2R \quad (1)$$

To measure a color change upon exposure to VOCs, the concept of color difference (ΔE) was employed. There are several color formulas for specification of color differences. Herein, the CIELAB color space was used, which comprises L^* , a^* , and b^* factors. The three values are plotted at three dimensions corresponding to the lightness (L^*), red to green (a^*), yellow to blue (b^*) of the color vision. The color difference (ΔE) was calculated by Eq. (2) (Hunt 1991; Fairchild 2005):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

2

,where Δ indicates the difference before and after exposure to VOCs. To examine the detection of 32 VOCs qualitatively, 2mL of VOCs were added in a 20mL vial and a cotton samples (15 mm × 20 mm) dyed with the three dyes was hanged inside each vial under the condition of saturated vapor without direct contact with the liquid phase of VOCs at the bottom of the vials. The vials were sealed completely with sealing film and left for 24 hours at room temperature. Then, the color difference values of the samples before and after exposure were measured. The selected 5 from 32 VOCs, which showed relatively strong color change, were quantitatively investigated at various concentration of 10 ~ 300ppm at exposure time range of 10 ~ 200min. Since the boiling points of the 5 VOCs are different and higher than room temperature, the test vials containing a cotton-based sensor (dyed sample) and the VOCs were heated in the quantitative experiment up to 30°C for acetone, MeOH, and acetonitrile, 50°C for pyridine, and 70°C for DMF, respectively. The maximum concentration, 300ppm, of the VOCs was completely vaporized at those temperatures during experiments.

Adsorption of VOCs for cellulosic substrates

The concept of this study is to detect VOCs by adsorbing to cotton-based sensor and changing color. Therefore, the amount of adsorption of VOCs may have a great influence on the sensing performance. The amounts of VOCs adsorbed to the pristine cotton fabrics were obtained by a gas chromatography (GC-2030, Shimadzu, column; dimethylpolysiloxane, 30 m, 0.25 mm, I.D. 0.25 μ m, PerkinElmer, detector; FID). To obtain a calibration curve of the VOCs, various concentrations of VOCs were prepared and measured their area of the gas chromatography. To verify the relationship between the adsorption amount of VOCs on cotton fabrics and color change, the especially selected 11 VOCs ranging from the well-detected and the poorly-detected were used. They were as follows; acetone, acetonitrile, benzene, dichloromethane, DMF, 1,4-dioxane, ethylacetate, n-hexane, MeOH, pyridine, and THF. The pristine cotton fabrics (0.05g) were exposed to the 11 VOCs (300ppm) without direct contact for 200min at 30 ~ 70°C as described above. After that, the fabrics containing VOCs were immersed in extraction solvent, DMF, to desorb the VOCs out of the cotton fabrics. However, in case that a VOC itself is the DMF, MeOH was used as the extraction solvent not to interfere between the VOC and an extraction solvent in gas chromatography. By analyzing the area of the VOCs extracted from the cotton fabrics in gas chromatography, the adsorbed amounts of the VOCs could be obtained quantitatively.

Repeatability and reusability of the cotton-based VOC sensors

One of the practical demands for cotton-based sensors, repeatability or reusability was examined. The one cotton-based sensor was exposed to 300ppm of DMF, which was the best detected VOC, at 70°C for 200min, and measured its color change. And then the sensor kept inside a vacuum chamber for minimum 24 hours to desorb the adsorbed DMF from the sensor completely. The process was repeated 10 times.

Aftertreatment

To improve wash fastness, the cotton-based sensor was aftertreated with a conventional polycationic fixing agent generally used for direct dyes. The 5% of the polycationic fixing agent was used (liquor ratio; 1:30) at 40°C for 20 min. To confirm the color change property after this treatment, the color difference of the samples was measured after exposure to 300ppm of DMF at 70°C for 200min and compared with the color difference before treatment. The durability of the dyed fabrics against washing, rubbing, and light fastness were examined by the procedure of textile standard test methods, ISO 105-C06 A1S, ISO 105-X12, and ISO 105-B02, respectively.

Results And Discussion

Absorption properties of the dyes

Absorption spectra of the three dyes (DiMo, MoMe, DiMe) were measured in water. The maximum absorption wavelength of DiMo, MoMe, DiMe were 571 nm, 558 nm, and 542 nm, which means blue, purple, and violet colors. The DiMo, MoMe, DiMe are compounds with substituents of dimethoxy, methoxy-methyl, and dimethyl, respectively, which means that the maximum absorption wavelength

appears at a longer wavelength as they have polar substituents. The molar absorption coefficient of the DiMo, MoMe, DiMe are 29,205, 35,024, and 33,339, respectively.

Application of the dyes to cellulosic substrates

To fabricate a cotton-based sensor showing color change on exposure to VOCs in a vapor state, the synthesized dyes were applied to standard cotton fabrics and the sensing properties were investigated. To determine an optimal concentration of the dyes showing the maximum color change upon exposure to VOCs, the dyes were applied in the range of 0.5 ~ 30% owf and then the dyed samples were exposed to saturated vapor of DMF. Color strength and color difference values according to the dye concentrations were presented in Fig. 3. The color strengths (Fig. 3a) increased with increase of dye concentration and reached equilibrium at about 10% owf. However, the color differences between before and after exposure (Fig. 3b) showed the maximum value at 2% owf and then decreased as the dye concentration increased more. The color of the fabric was too light at lower range of concentration and too dark at higher concentration to be recognized visually. Therefore, the optimal concentration of all the dyes was determined to be 2% owf.

VOC sensing properties of the dyes on cellulosic substrates

The cotton fabrics (15 mm × 20 mm) dyed with the 2% owf of the three synthesized dyes (DiMo, MoMe, DiMe) were placed inside a sealed vials containing saturated vapors of each VOC without direct contact to the liquid VOCs and exposed at room temperature for 24 hours to observe color change. The results were shown in Fig. 4.

The three cotton-based sensors dyed with the synthetic dyes showed similar sensing behavior to 32 types of VOCs. Compared to the non-polar VOCs, the color change was large for relatively polar VOCs. It is thought that the three dyes are polar compounds soluble in polar solvents, and the substrate through which the dyes were permeated was also a polar material, cellulosic fabrics, so it has good affinity for polar VOCs.

Among them, quantitative experiments were conducted according to exposure time (10 ~ 200min) and concentration (10 ~ 300ppm) for selected 5 VOCs that frequently used and showed strong color change such as acetone, MeOH, acetonitrile, pyridine, and DMF. In contrast to the previous experiment carried out under saturated vapors at room temperature, each test vial was heated up to 30°C for acetone, MeOH, and acetonitrile, 50°C for pyridine, and 70°C for DMF, respectively in order to make sure that all VOCs were evaporated completely in the test vials. Even though the temperature was lower than their boiling points, it was enough to evaporate the maximum 300ppm of VOCs to vapor phase in the vials. Among the 5 VOCs, the color change properties of the cotton-based sensor on exposure to DMF, which caused the strongest color change, was shown Fig. 5 and the results of the other 4 VOCs were presented in Fig. S1. According to the Fig. 5 (a), the color change increased as the increase of the concentration of DMF and exposure time and reached equilibrium finally. There are various indicators of toxicology of VOCs. In this study, the sensitivity and effectiveness of the sensors were investigated with regard to threshold limit

value-time weighted average (TLV-TWA), which represents the maximum allowable exposure concentration during normal work based 8 hours a day, 5 days a week (Lee et al. 2011; Park et al. 2011; Kim et al. 2011). In the case of DMF, the TLV-TWA is well known to 10 ppm. From the Fig. 5 (a), it can be seen that even at the allowable exposure concentration of 10 ppm, the color differences were obtained 7.3 for DiMo, 10.6 for MoMe, and 13.6 for DiMe within an hour. It is generally known that the more than 1.0 of color difference can be easily recognizable with naked eyes. This means that the dyes exhibit strong sensing performance even inside cellulosic substrate under very low concentration of VOCs. Figure 5 (b) and (c) display the K/S spectral shift and change of L^* , a^* , and b^* values when three cotton-based sensors were exposed to DMF.

The K/S spectral shift of each VOC also showed the same trend. When all of the cotton-based sensors dyed with the three dyes were exposed to VOCs, a hypsochromic shift (DiMo; from 580 nm to 560 nm, MoMe; from 570 nm to 560 nm, DiMe; from 560 nm to 540 nm) and a hyperchromic shift occurred. The L^* , a^* , and b^* values for dyed sample with DiMo were 31.51, 5.41, and - 16.19 before exposure and 34.62, 17.56, and - 11.01 after exposure. For MoMe, the L^* , a^* , and b^* values were 28.12, 12.30, and - 27.93 before exposure and 27.75, 32.60, and - 19.02 after exposure. For DiMe, the values were from 25.19, 20.55, and - 24.33 to 27.96, 42.47, and - 8.88. It means that all cotton-based sensors dyed with the three dyes change from blue or purple to violet or red when exposed to VOCs. All the three dyes exhibited almost very similar sensing behavior except for the sensitivity. The DiMe exhibited the best sensing ability and the DiMo showed the relatively lower sensitivity. It was thought to be due to the different substituents of the dyes structure, for example, dimethoxy groups were substituted for DiMo, methoxy and methyl groups for MoMe, and dimethyl groups for DiMe. The more hydrophobic substituents, the better the sensing ability to VOCs.

To visualize the performance of the cotton-based VOC sensor, we dyed cotton filament yarn with the synthesized vapochromic dye (DiMe) and then embroidered it as the lettering "VOCs" on a sheet of polyester fabric dyed with a conventional non-vapochromic disperse dye of the same color as DiMe dye, as depicted in Fig. 6. The cotton-based sensor was put in a closed acrylic box containing 200ppm of DMF gas for 200min, and the cotton-based sensor displayed the lettering (VOCs) by changing the color.

The sensing mechanism could depend on three factors, such as the solvatochromism, the aggregative properties of dyes, and the adsorption amount of the VOCs on cellulosic substrates. Therefore, the sensing performance was investigated in terms of the three as below.

Sensing mechanism: Solvatochromism

The solvatochromism was investigated by dissolving the synthesized dyes in the solvents (water, DMSO, ethylene glycol, DMF, acetonitrile, MeOH, acetone, pyridine, and THF). The shift of the absorption spectrum according to the polarity of the solvents was shown in Fig. 7a. In this case, the polarity was expressed by the dielectric constant, which was one of the indicators of the polarity of a material. Figure 7b is the result of the relationship between the dielectric constant of the solvent and the maximum

absorption wavelength. All the dyes showed the positive solvatochromism that exhibits a bathochromic shift as the solvent polarity increases.

From this result, the first reason of color change of this cotton-based VOC sensors was attributable to the solvatochromism of the dyes inside the fiber. The cotton fabric used as a substrate of the sensor is hydrophilic and normally contains about 7 ~ 10% of water at standard condition. This means that the dye molecules are placed at water-rich environment inside cellulose structure and exhibits an absorption spectrum similar to that of inside liquid water which is the most polar solvent than any other organic solvents. However, on exposure to VOCs that are less polar than water, the internal condition of cellulose will change to less polar environment, and this bring about the shift of absorption spectra of the dyes from longer wavelength to shorter ones as same as shown in solvatochromism of Fig. 7. This result agrees well with that of Fig. 5.

To obtain a deeper insight into the solvatochromic properties of the dyes, density function theory (DFT) calculation was performed. After geometry optimization was performed, additionally solvation effect was calculated for the 9 kinds of solvents that were used in the solvatochromism experiments. From the calculation, the HOMO and LUMO energy values were obtained and compared to the experimental values of maximum absorption wavelength of the dyes in each solution. According to Fig. 8, the energy gap between HOMO and LUMO of DiMo, MoMe, and DiMe dyes became narrow as the dielectric constants, namely polarity, of the solvents increases. This means that the maximum absorption wavelength of the dyes in solvents are shifted to the longer wavelength, and it agrees well with the experimental results of the Fig. 7.

Sensing mechanism: Aggregative characteristics

The direct dyes have planar structures and thus have high aggregative properties. Exposure to VOCs may cause color change by penetration of them between dye molecules of aggregates or crystals and change the crystallinity of the dyes. To verify the change in the distance between the dye molecular planes due to exposure to VOCs, XRD analysis was performed. Figure 9 depicts the XRD patterns of DiMo, MoMe, and DiMe before and after exposure to DMF.

The XRD peak patterns of all three dyes before exposure are very similar. Since the chromophore was almost the same except for substituents in the middle of the molecular structures, it is considered that the interplanar distances are almost the same. The dyes showed diffraction peaks at 27.3°, 31.7°, 45.5°, 53.9°, 56.4°, 66.2°, 75.3°, and 83.9° before exposure and it can be calculated the molecular interplanar distance using the Bragg Equation as 3.26 Å, 2.82 Å, 1.99 Å, 1.63 Å, 1.41 Å, 1.26 Å, and 1.15 Å, respectively. After exposure to DMF, the intensity of the peaks decreased, and new peaks appeared. In DiMo, a broad peak was observed near 11.2° and 19.5°, for MeMo, existing peaks disappeared, and new small peaks were appeared on the side with the lower 2 theta value. Similarly in the case of DiMe, the existing peaks were greatly reduced, and new peaks are created in 4.3°, 4.9°, and 9.2°. It indicates that the DMF molecules disrupt the regularity of dye aggregates.

Most organic dye molecules are dissolved as a monomer state in good solvents but aggregate in poor solvents. The aggregate is theoretically divided into two forms; J- and H-aggregates. According to the exciton theory, the excitonic states of the dye aggregate splits into two levels through the interaction of their transition dipoles (Kasha 1965). The molecules may form head-to-tail arrangement (end-to-end stacking) in J-aggregates. It can be simplified two levels of the excitonic state in the molecule arrangements through the interaction of their transition dipoles, such as unstable aggregation exhibiting higher transition energy by charge repulsion and stable aggregation with lower transition energy by charge attraction compared to the monomeric state. In H-aggregate, the molecules may aggregate in a parallel way (side-by-side stacking) and it also can be simplified as two arrangements. However, the unstable aggregative form in J-aggregates and the stable aggregative form in H-aggregates are forbidden transitions according to the exciton theory. Therefore, J-aggregates show the red shifted absorption and H-aggregates show the blue shifted absorption based on free molecules (monomeric state) absorbance spectrum (Wurthner et al. 2011). When the dyed cotton fabrics were exposed to the vapor of DMF, the DMF molecules adsorbed to the dyes aggregated at the internal substrate, and then, the dye molecules become to more monomeric state as increasing the aggregation distance. The cotton-based sensors, which were dyed with three synthesized dyes, showed a hypsochromic and hyperchromic shift on exposure to DMF. Based on this, the dyes formed J-aggregates in the cellulosic fiber and it was disrupted by penetration of vapor of VOCs, and finally they changed to more monomeric states, which caused the color of cotton-based sensor a hypsochromic and hyperchromic shift (Fig. 5b). Therefore, the color change behavior due to VOC exposure was attributed to not only the solvatochromism but also the deformation of aggregates of the dye molecules.

Sensing mechanism: Adsorption amount of VOCs on cellulosic substrates

As mentioned above, the main causes of color change by VOC exposure were solvatochromism and the change of aggregation property. In order for a cotton-based sensor to detect vapor of VOCs, most of all, it is necessary for the textile substrates to adsorb the VOCs. Therefore, affinity of VOCs for cellulosic substrates and sensing performance were also closely related. The relationship between the amounts of VOCs adsorbed on cotton fabrics and color difference before and after exposure to vapor phase of VOCs were in Fig. 10. The adsorption amount of VOCs to the cellulosic substrates and the color difference were linearly proportional. This means that the greater the amount of VOCs adsorbed to the substrates, the greater the color difference.

Figure 11 presents the relationship between the rate of adsorption of VOCs on to cellulosic fabric and color change under 300 ppm of DMF. The adsorbed amount of VOCs and the color change show the very similar increasing behaviors according to exposure time. This means that there is a close relationship between the adsorption amount for VOCs and the color difference of the cotton-based sensors. The results of the other 4 VOCs were presented Fig. S2.

Summarizing the above results, it can be concluded that the sensing performance of the cotton-based VOC sensors of this study is affected by the three factors together: solvatochromism, aggregative

properties of the dyes, and adsorption amount of VOCs on to substrates.

Repeatability

One of advantages of the cotton-based sensor using DiMo, MoMe, and DiMe is that it can be reused continuously and repeatedly. The color of the sensor changed on exposure to VOCs can be returned to its original colors by desorption of the VOCs out of the cotton-based sensors. This is because the solvatochromism disappeared and the aggregates of dye molecules were restored as the VOCs were desorbed. It was confirmed that the sensitivity was maintained even after the cotton-based sensor repeated VOC adsorption and desorption 10 times (Fig. 12).

Aftertreatment

Although direct dyes have advantages on the cellulosic fibers, including the simplicity of the dyeing process, varieties of colors, and reasonable price, they exhibit poor washing fastness. The aftertreatment process is needed to improve the wash fastness. cotton-based sensors were employed the aftertreatment by a practical polycationic fixing agent and evaluated the durability of the dyed fabrics against washing, rubbing, and light fastness by the procedure of textile standard test methods and summarized in Table S1. Fastness ratings were improved by about 1 level. The color difference values of the treated cotton-based sensors applied with DiMo, MoMe, and DiMe were 10.3, 16.6, and 19.6, respectively. Compared to the untreated samples, the sensing performance retained at about 80%.

Conclusion

The cotton-based vapochromic sensors were designed to detect low concentrations of VOCs in the vapor phase. To fabricate the sensors, the three dyes (DiMo, MoMe, DiMe) having planar structures for good aggregative properties were synthesized and they were dyed on cellulosic fabrics. The maximum absorption wavelength of each of the three dyes applied to the cellulosic fabrics was 580 nm for DiMo (blue), 570 nm for MoMe (purple), and 560 nm for DiMe (violet). When exposed to VOCs, it changed to 560 nm, 560 nm, and 540 nm, respectively, that is, the color changed to violet or red. As for the sensitivity to VOCs, the DiMe of the violet color was the best. It was found that the sensing performance was maintained even after 10 repeat cycles. In addition, aftertreatment was performed to improve wash fastness, and the sensing behavior and ability were almost maintained about 80% after the treatment.

Declarations

Acknowledgements

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References

Ribeiro LS, Pinto T, Monteiro A, Soares OSGP, Pereira C Freire C, Pereira MFR (2013) Silica nanoparticles functionalized with a thermochromic dye for textile applications. *J Mater Sci* 48:5085-5092. <https://doi.org/10.1007/s10853-013-7296-7>

Little AF, Christie RM (2016) Textile applications of commercial photochromic dyes. Part 6: photochromic polypropylene fibres. *Color Technol* 132:304-309. <https://doi.org/10.1111/cote.12221>

De Meyer T, Steyaert I, Hemelsoet K, Hoogenboom R, Van Speybroeck V, De Clerck K (2016) Halochromic properties of sulfonphthaleine dyes in a textile environment: The influence of substituents. *Dyes Pigments* 124:249-257. <https://doi.org/10.1016/j.dyepig.2015.09.007>

Favaro G, Clementi C, Romani A, Vickackaite V (2007) Acidichromism and ionochromism of luteolin and apigenin, the main components of the naturally occurring yellow weld: A spectrophotometric and fluorimetric study. *J Fluoresc* 17:707-714. <https://doi.org/10.1007/s10895-007-0222-0>

Chen X, Yang M, Xu W, Qu Q, Zhao Q (2019) Broadly absorbing bluish black-to-transmissive sky blue electrochromic polymer based on 3,4-dioxythiophene. *J Solid State Electrochem* 23:19-25. <http://doi.org/10.1007/s10008-018-4106-9>

Hau FK, Cheung K, Zhu N, Yarm VW (2019) Calixarene-based alkynyl-bridged gold(i) isocyanide and phosphine complexes as building motifs for the construction of chemosensors and supra molecular architectures. *Org Chem Front* 6:1205-1213. <https://doi.org/10.1039/C9QO00258H>

Ono T, Tsukiyama Y, Hatanaka S, Sakatsume Y, Ogoshi T, Hisaeda Y (2019) Inclusion crystals as vapochromic chemosensors: fabrication of a mini-sensor array for discrimination of small aromatic molecules based on side-chain engineering of naphthalenediimide derivatives. *J Mater Chem C* 7:9726-9734. <https://doi.org/10.1039/C9TC03140E>

Beatty MA, Selinger AJ, Li Y, Hof F (2019) Parallel synthesis and screening of supramolecular chemosensors that achieve fluorescent turn-on detection of drugs in saliva. *J Am Chem Soc* 141:16763-16771. <https://doi.org/10.1021/jacs.9b07073>

Wang X, Lin Q, Ramachandran S, Pembouong G, Pansu RB, Leray I, Lebental B, Zucchi G (2019) Optical chemosensors for metal ions in aqueous medium with polyfluorene derivatives: Sensitivity, selectivity and regeneration. *Sens Actuators B Chem* 286:521-532. <https://doi.org/10.1016/j.snb.2019.01.013>

Manjakkal L, Dervin S, Dahiya R (2020) Flexible potentiometric pH sensors for wearable systems. *RSC Adv* 10:8594-8617. <https://doi.org/10.1039/D0RA00016G>

Kim T, Lee S (2015) Characteristics and application of the highly-durable and highly-sensitive super hydrophobic acid-gas sensing dye. *Text Color Finish* 27:105-112.

<https://doi.org/10.5764/TCF.2015.27.2.105>

Kim T, Lee S (2015) Synthesis and application of acid-gas sensing dyes having alkyl groups symmetrically substituted on monoazo chromophore. *Fiber Polym* 16:2106-2111.

<https://doi.org/10.1007/s12221-015-5428-1>

Lee J, Kim T (2020) Synthesis of an acid-gas sensing fluorescence dye showing change of both color and fluorescence emission spectrum inside polyethylenic fiber on exposure to gas phase strong acid for application to washable textile sensors. *Fiber Polym* 21:2275-2284. <https://doi.org/10.1007/s12221-020-1094-z>

<https://doi.org/10.1007/s12221-020-1094-z>

Lee J, Kim T (2021) Synthesis of novel coumarin-based acid vapochromic fluorescence dye showing change of both color and fluorescence emission spectrum for application to sensitive, reusable, and washable textile sensors. *Text Res J* 91:613-623. <https://doi.org/10.1177/0040517520955232>

Lee J, Jun H, Kubota Y, Kim T (2021) Synthesis of red fluorescent dye with acid gas sensitive optical properties and fabrication of a washable and wearable textile sensor. *Text Res J* 91:2036-2052. <https://doi.org/10.1177/0040517521994496>

<https://doi.org/10.1177/0040517521994496>

Kubota Y, Nakazawa M, Lee J, Naoi R, Tachikawa M, Inuzuka T, Funabiki K, Matsui M, Kim T (2021) Synthesis of near-infrared absorbing and fluorescent bis(pyrrol-2-yl)squaraines and their halochromic properties. *Org Chem Front* 8:6226-6243. <https://doi.org/10.1039/D1QO01169C>

Wenger O (2013) Vapochromism in organometallic and coordination complexes: Chemical sensors for volatile organic compounds. *Chem Rev* 113:3686-3733.

<https://doi.org/10.1021/cr300396p>

Koh J (2006) Alkali-clearable disperse dyeing of poly(ethyleneterephthalate) with azohydroxypyridone dyes containing a fluorosulfonyl group. *Dyes Pigments* 69:233-238. <https://doi.org/10.1016/j.dyepig.2005.03.003>

<https://doi.org/10.1016/j.dyepig.2005.03.003>

Baumann W, Groebel B, Kraymer M (1987) Determination of relative colour strength and residual colour difference by means of reflectance measurements. *J Soc Dyers Colour* 103:100-105. <https://doi.org/10.1111/j.1478-4408.1987.tb01101.x>

<https://doi.org/10.1111/j.1478-4408.1987.tb01101.x>

Hunt RWG (1991) *Measuring colour*. Ellis Horwood, New York, pp.71-77.

Fairchild MD (2005) *Color appearance models*. John Wiley, Chichester, pp.183-195.

Lee H, Kim E, Park J, Kang S (2011) Cancer mortality and incidence in Korean semiconductor workers. *Saf Health Work* 2:135-147.

<https://doi.org/10.5491/SHAW.2011.2.2.135>

Park H, Jang J, and Shin J (2011) Quantitative exposure assessment of various chemical substances in a wafer fabrication industry facility. *Saf Health Work* 2:39-51. <https://doi.org/10.5491/SHAW.2011.2.1.39>

Kim E, Lee H, Ryu H, Park S, Kang S (2011) Cases series of malignant lymphohematopoietic disorder in Korean semiconductor industry. *Saf Health Work* 2:122-134. <https://doi.org/10.5491/SHAW.2011.2.2.122>

Kasha M, Rawls H, El-Bayoumi M (1965) The exciton model in molecular spectroscopy. *Pure Appl Chem* 11:371-392. <https://doi.org/10.1351/pac196511030371>

Wurthner F, Kaiser T Saha-Moller C (2011) J-aggregates: From serendipitous discovery to supra-molecular engineering of functional dye materials. *Angew Chem Int Ed* 50:3376-3410. <https://doi.org/10.1002/anie.201002307>

Supplementary Information

Supplementary information (Table S1, Figures S1-S2) is not available with this version.

Figures

Figure 1

Scheme 1. Schematic illustration of cotton-based VOC sensor.

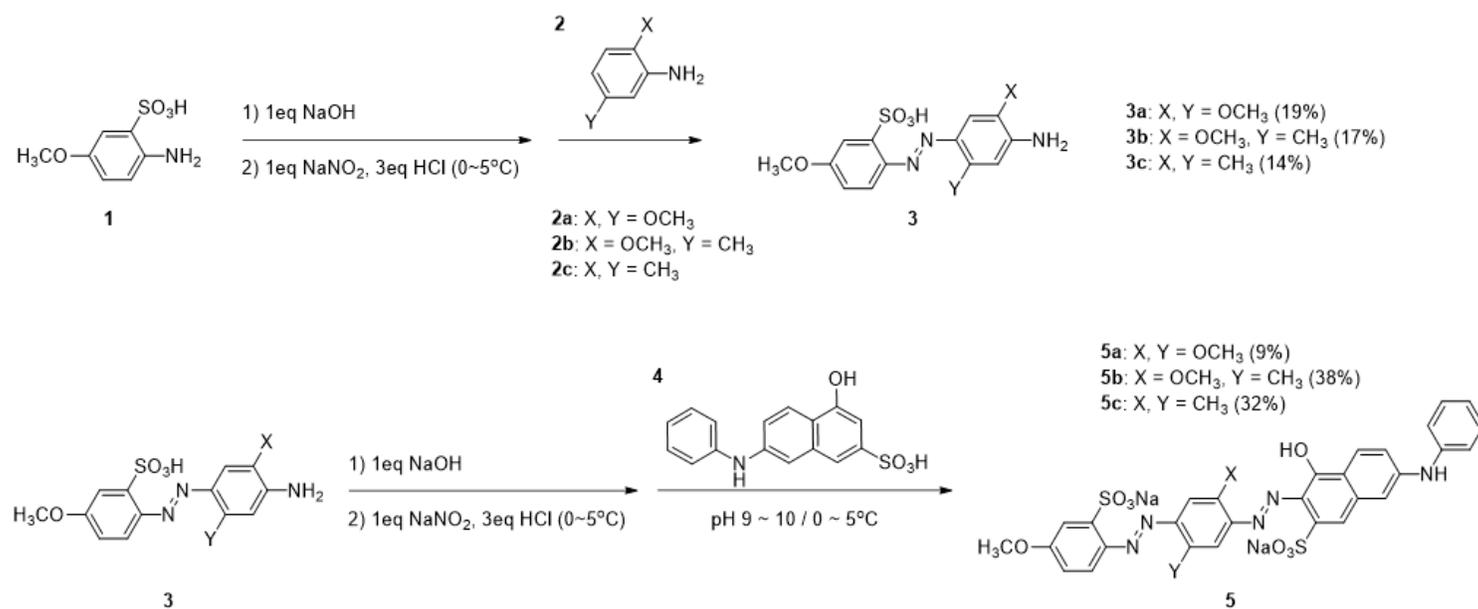


Figure 2

Scheme 2. Synthetic procedure of VOC sensing chromogenic dyes.

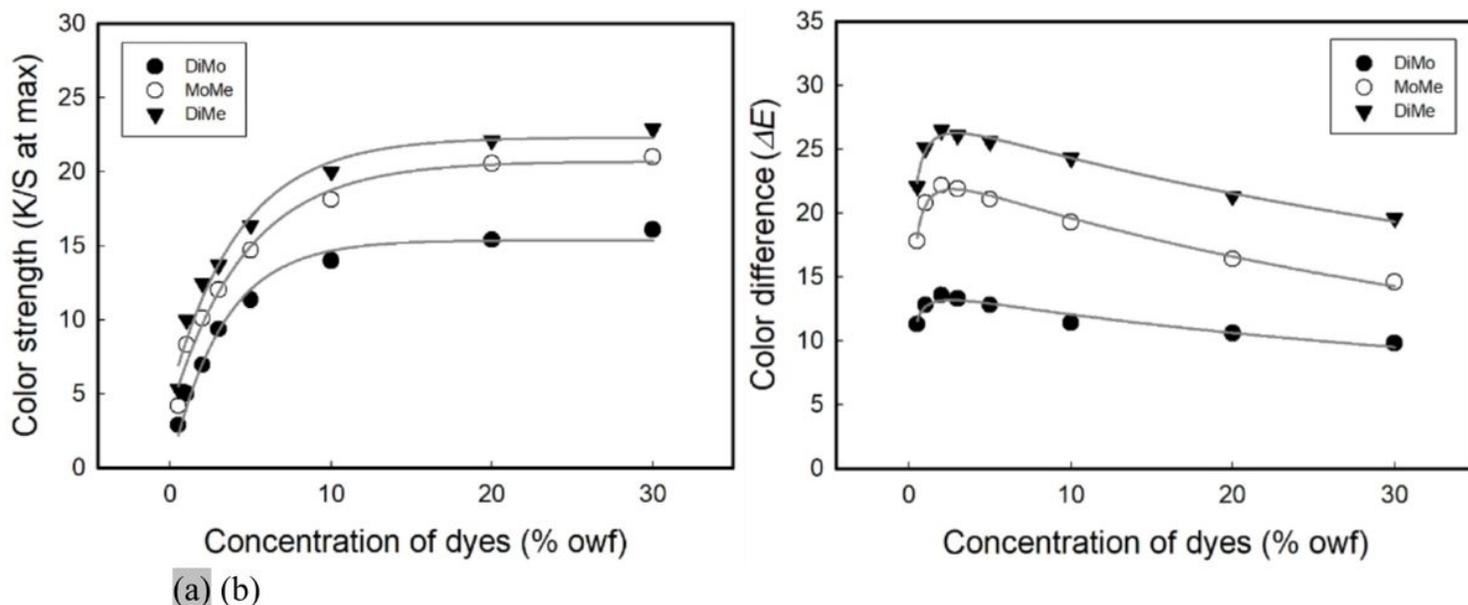


Figure 3

a Color strengths at λ_{max} and **b** color differences (ΔE) of cellulosic substrate dyed with DiMo, MoMe, and DiMe before and after exposure to DMF.

Figure 4

Color difference (ΔE) of cellulosic substrates dyed with DiMo, MoMe, and DiMe before and after exposure to 32 kinds of VOCs.

Figure 5

a Rate of color change in cellulosic substrates dyed with DiMo, MoMe, and DiMe on exposure to DMF. **b** Change in color spectra of dyed fabrics exposed to 300 ppm DMF for 24 h. **c** Color coordination before and after exposure to DMF.

Cotton fibers dyed with the vapochromic dye



Figure 6

Visualization of the concept of cotton-based VOC sensor.

Figure 7

a Absorption spectra of DiMo, MoMe, and DiMe dissolved in solvents with different polarities, and **b** Relationship between the maximum absorption wavelengths and VOC dielectric constants.

Figure 8

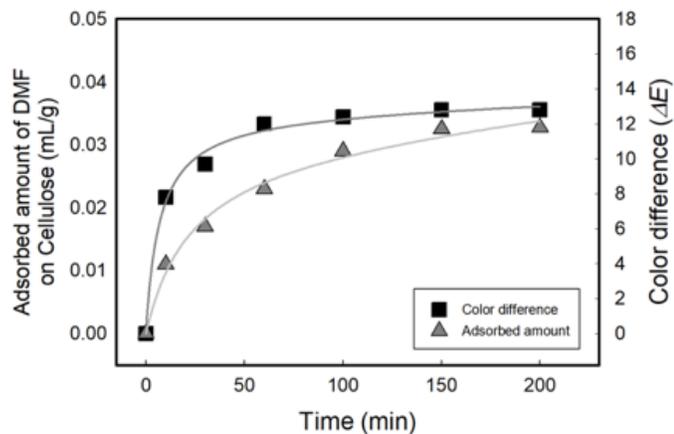
a, c Molecular orbital energy diagrams and isodensity surface plots of DiMo, MoMe, and DiMe and **b** relationship between molecular orbital energy gap and VOC dielectric constants.

Figure 9

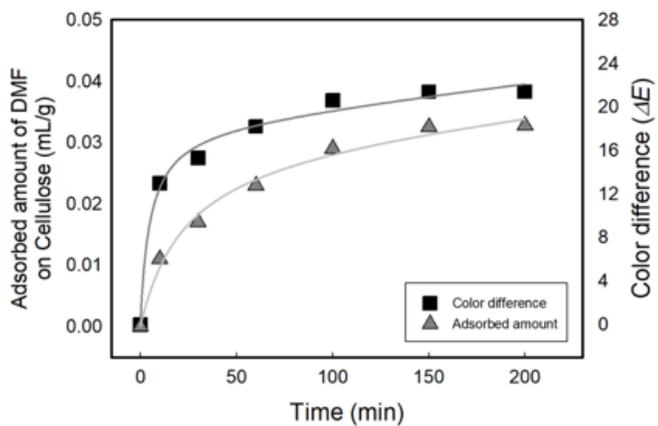
XRD patterns of DiMo, MoMe, and DiMe before and after exposure to DMF.

Figure 10

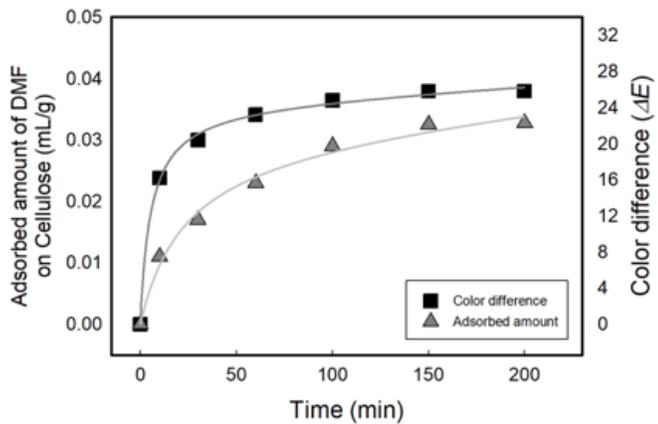
Relationship between the adsorption amount of VOCs on cellulosic substrates and color change before and after exposure to the VOCs.



DiMo



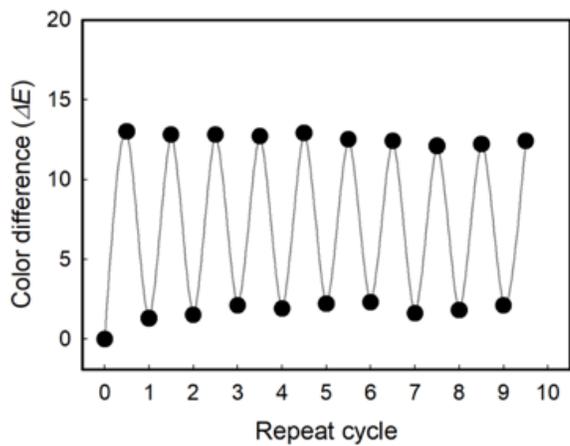
MoMe



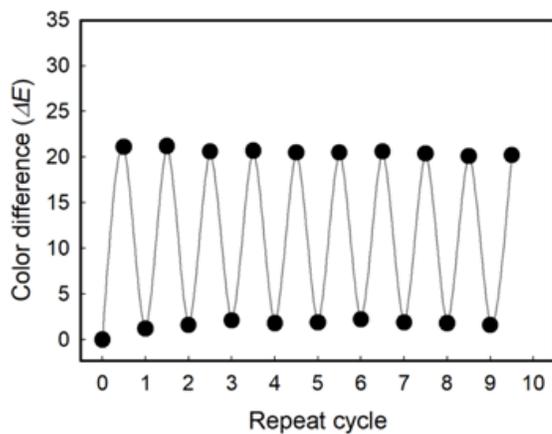
DiMe

Figure 11

Relationship between the rate of adsorption of DMF to substrates and the rate of color change.



DiMo



MoMe



Figure 12

Repeatability of the cotton-based VOC sensors.