

## Synthesis of a Novel Fluorescent Reactive Dye Based on Coumarin-Benzimidazole for High Visibility Dyeing of Cotton

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### ABSTRACT

*Two fluorescent reactive dyes based on coumarin-benzimidazole derivatives were synthesized, characterized, and dyed cotton fabric. First, (3-(1H-benzo[d]imidazol-2-yl)-7-(diethylamino)-2H-chromen-2-one) (CB) was reacted with cyanuric chloride to produce primary colorant. Two fluorescent reactive dyes were created by separately substituting sulfanilic acid and nicotinic acid into the original material. The synthesized dyes were characterized by FTIR, <sup>1</sup>HNMR, <sup>13</sup>CNMR, elemental analysis, and UV-Vis spectroscopy. Both water-soluble dyes exhibited a positive solvatochromism response with considerable fluorescent intensity and quantum yield in photophysical evaluations. The nicotinic acid substituted reactive dye, 3-carboxy-1-(4-chloro-6-(2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-1H-benzo[d]imidazol-1-yl)-1,3,5-triazin-2-yl)pyridin-1-ium chloride (**D**<sub>3</sub>), showed the highest quantum yield (0.65 in aqueous form) and dyeing exhaustion (83 %) with a maximum emission wavelength of 512 nm when dyed on cotton fabric. High visibility and colorfastness assessments of the dyed fabrics confirmed, **D**<sub>3</sub> could be successfully introduced as the first highly visible coumarin-benzimidazole fluorescent reactive dye for cotton, according to the international standard of high visibility clothing, ISO 20471:2013. Prog. Color Colorants Coat. 15 (2022), 327-340© Institute for Color Science and Technology.*

### 1. Introduction

The synthesis and application of fluorescent dyes have received much interest in the textile industry. Several fluorescent dyes based on coumarin [1], xanthenes [2], hemicyanine [3], and naphthalimide [4] have been studied in textile applications. The fluorescent dyes are mainly used for security, safety, fashion, and high visibility clothing [5]. Coumarin, or 2H-chromen-2-one alone, has low fluorescence quantum yield, but suitable substitution can achieve strong fluorescence properties with good quantum yield [6]. Coumarin derivatives are suitable fluorophores with high quantum yield [7], high

molar extinction coefficient [8], and high Stokes shift and emission wavelength at range 490-500 nm [9]. In addition, they have good absorption and high luminescence in visible regions and good thermal stability [10].

Moreover, due to their excellent optical properties, coumarins have a wide variety of applications such as fluorescent dyes [11], optical brighteners [12], high-light ink marker, security inks [9], and laser dyes [13]. Coumarin-benzothiazole, Coumarin-benzimidazole, and Coumarin-benzoxazole derivatives of coumarins were reported in several studies as fluorescent dyes [14]. In

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addition, Coumarin-benzimidazole, which has an electron donor group such as *N,N*-diethylamino at position 7, and an electron acceptor ring at position 3, has promoted fluorescent efficiency [15].

Coumarin-benzimidazole (CB) commercial dyes have been applied in textile applications due to their exciting fluorescent and high visibility properties. The prominent examples are CI Disperse Yellow 82 for polyester, CI Acid Yellow 250 for wool, and CI Basic Yellow 40 for modacrylic fibers. No report on a fluorescent reactive dye synthesis based on CB has been published yet. Several reports on the synthesis of fluorescent reactive dyes with other structures, such as amino coumarin for wool [16], hemicyanine for wool and silk [3], and xanthenes for cotton [2], have been published. At present, the only available commercial fluorescent reactive dye is CI Reactive Yellow 78, which is based on the naphthalimide fluorophore and vinyl sulfone reactive group [17].

Highly visible fluorescent garments are usually made with a high visibility fluorescent background to increase the wearer's visibility during the day and

phosphorescence parts as retro-reflective tapes visible at night. They are evaluated according to the standard ISO 20471:2013 method [18]. Although research in this area is going on, there is no report of a highly visible fluorescent coumarin-benzimidazole reactive dye yet suitable for high visibility applications. The unavailability of different fluorescent reactive dyes can limit the application of cellulosic fibers in high visibility garments, needing further studies on the synthesis of new fluorescent reactive dyes adding to the value of any attempt in synthesizing novel structures. This paper describes the synthesis of novel fluorescent reactive dyes based on coumarin-benzimidazole for the dyeing of cotton fabrics for high visibility applications. In this case, For forming two fluorescent reactive species, as seen in Figure 1, CB fluorophore and cyanuric chloride reacted. Then, the product was separately substituted with sulfanilic acid and nicotinic acid. Both new dyes were applied on cotton fabrics, and their behavior for being used as high visibility reactive dye on cotton fabrics was assessed and reported.

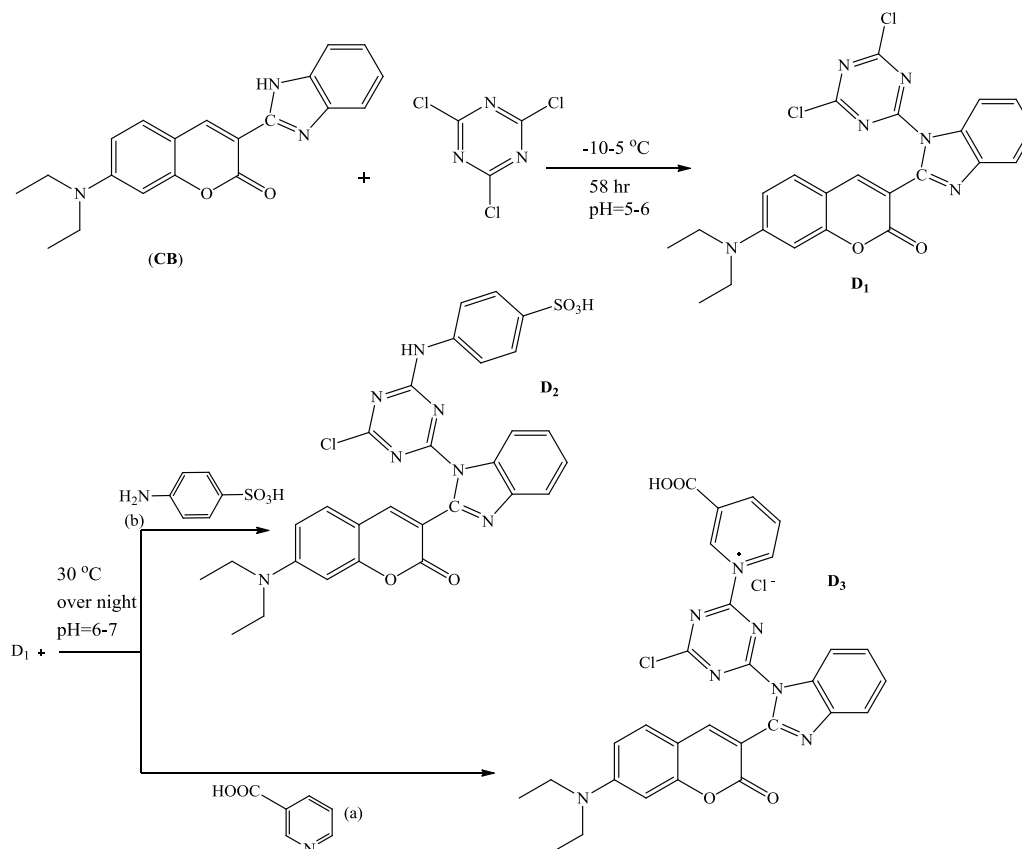


Figure 1: Synthesis of coumarin reactive dyes.

## 2. Experimental

### 2.1. Materials and instruments

All chemicals and solvents used to synthesize dyes were reagents or analytical grades obtained from Merck and Sigma group (Germany) and Jihua Group (China). Remazol Luminous Yellow FL (RY78) (CI Reactive Yellow 78) was acquired from Dystar Co. (Germany). The dyeing additives and textile auxiliaries were provided from Kima Kav Jahan Co. (Iran). 100% Gray knitted cotton fabric (200 g/m<sup>2</sup>) was supplied by Mahta Rang Toos (Iran). A Bruker DRX-AVANCE, Germany, with DMSO-d<sub>6</sub> as solvent at 250 MHz was used to obtain the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra. Elemental analysis of synthesized dyes was performed on Heraeus Elemental Analysis CHN-Rapid, USA. Perkin Elmer spectrum, USA, was used for FTIR analysis. Ci 4200-UV spectrophotometer, X-rite, USA, was used to measure the reflectance and absorption spectra of the dyed fabrics. CECIL 9200 Double Beam UV/Vis spectrophotometer, England, analyzed dye solutions. The emission properties were determined using the spectrofluorimeter (Perkin Elmer LS50B, USA).

Buchi Melting Point B-545, Switzerland, was used to measure the Melting points. Thin-layer chromatography (TLC) was performed on a silica gel layer, Fluka F60, 0.2 mm (toluene/ethyl acetate). A rotary sample-dyeing machine, Azar Delta, Iran, was used for the dyeing of cotton fabrics with the synthesized dyes. Colorfastness measurements performed on a: Crockmaster 255, for rubbing fastness, Xenon ArcLight and weathering fastness tester, James H. Heal, England, for light fastness, Washing and dry-cleaning colorfastness tester-Gyrowash 815/8, James H. Heal, England, for washing and laundry fastness, Fixotest 7501, Original Hanau Quarzlampen GMBH, Germany, for hot pressing fastness and Perspirometer HTC-006, Dongguan Hust Tony instrument Co., Hong Kong, for perspiration fastness.

### 2.2. Synthesis

#### 2.2.1. Synthesis of 3-(1-(4,6-dichloro-1,3,5-triazin-2-yl)-1H-benzo[d]imidazol-2-yl)-7-(diethylamino)-2H-chromen-2-one (D<sub>1</sub>)

The CB was purified with acetone in a Soxhlet extractor. First, 1.2 mmol (0.4 g) of CB was dissolved in 50 mL acetone in a 100 mL two-neck, round-bottom

flask equipped with a stirrer, thermometer, and reflux condenser. The temperature was set to -10 °C by an ice-salt bath containing 270 g/L salts. Then, 1.2 mmol (0.22 g) of cyanuric chloride was dissolved in 10 mL of cold acetone (0 °C) and added to the CB solution in a drop-wise manner [19]. The mixture was stirred at a constant temperature (-10 °C) for two hours. The temperature was gradually increased to 0 °C within one hour and kept for one extra hour. Then, 0.5 mmol sodium carbonate dissolved in 5 mL deionized water was added drop-wise in two hours [20], where the temperature was kept at 0-5 °C and continued at 10 °C for further 52 hours. The reaction was monitored by the TLC (toluene/ethyl acetate: 1/3) in a closed system. Finally, the mixture was poured into crushed ice, filtered, dried in a vacuum oven at room temperature, and recrystallized from hexane to obtain 0.51 g product as a yellow powder.

**D<sub>1</sub>:** Yield: 89 %; m.p: 288 °C; FT-IR (KBr), cm<sup>-1</sup>: 3129 (νC-H, str, Ar); 2963, 2926 (νC-H, str, aliphatic); 1720 (νC=O, str); 1620 (νC=N, str), 1592, 1465 (νC=C, str, Ar); 1260 (νC-O, str); 1095 (νC-N, str); 803 (νC-Cl, str). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) ppm: 1.46-1.52 (t, 6H, CH<sub>3</sub>); 3.48-3.53 (q, 4H, CH<sub>2</sub>); 6.7 (s, 1H, Ar-H); 6.82 (d, 1H, Ar-H); 7.35 (t, 1H, Ar-H); 7.38 (t, 1H, Ar-H); 7.43 (d, 1H, Ar-H); 7.75 (d, 1H, Ar-H); 8.05 (s, 1H, Ar-H); 8.55 (d, 1H, Ar-H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>) ppm: 12.91 (2C), 44.99 (2C), 108.4, 110.18, 113.84, 115.54, 117.73, 124.36, 124.9 (2C), 128.94, 129.71, 134.02, 139.07, 141.1, 143.91, 148.31, 149.91, 164.4, 170.22 (2C), 170.27, 182.63. Elemental analysis: (MW 481.33 g/mol); found: C, 57.25; H, 3.65; N, 17.28 %; C<sub>23</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>2</sub>; calculated: C, 57.39; H, 3.77; N, 17.46 %.

#### 2.2.2. Synthesis of 4-((4-chloro-6-(2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-1H-benzo[d]imidazol-1-yl)-1,3,5-triazin-2-yl)amino)benzenesulfonic acid (D<sub>2</sub>)

One mmol (0.48 g) of the synthesized dye (D<sub>1</sub>) was dissolved in 10 mL cold acetone (5-10 °C). Then one mmol (0.17 g) 4-aminobenzenesulfonic acid was dissolved in 10 mL cold deionized water adjusted at pH 5 (with 2.4% w/v sodium carbonate solution) and added gradually to D<sub>1</sub> solution. The solution was stirred in a 50 mL two-neck round-bottom flask with a reflux condenser. The pH was adjusted at 5-6 by adding 2.4% w/v sodium carbonate solution. The

temperature was kept constant at 5 °C for 1 hour by an ice-salt bath, then increased slowly to 30 °C at intervals of 5 °C each hour, and the mixture was kept overnight at 30 °C in a water bath. Consumption of **D<sub>1</sub>** was monitored by the TLC method (toluene/ethyl acetate: 1/3). Then the temperature was reduced to 0-5 °C, while 0.1N hydrochloric acid was added to adjust pH at 2-3. Finally, the product was filtered, dried in a vacuum oven at 40 °C, and recrystallized from methanol to obtain 0.52 g product as a yellow powder.

**D<sub>2</sub>**: Yield: 86 %; m.p: 347 °C; FT-IR (KBr), cm<sup>-1</sup>: 3417 (νO-H, str, SO<sub>3</sub>H); 3213 (νN-H, str); 3082 (νC-H, str, Ar); 2963, 2924 (νC-H, str, aliphatic); 1713 (νC=O, str); 1618 (νC=N, str); 1560 (νN-H, bend); 1587, 1461 (νC=C, str, Ar); 1416 (νO-H, bend); 1260 (νC-O, str); 1096 (νC-N, str); 1030 (νS=O); 802 (νC-Cl, str). <sup>1</sup>HNMR (DMSO-d<sub>6</sub>) ppm: 1.17-1.20 (t, 6H, CH<sub>3</sub>); 3.55-3.58 (q, 4H, CH<sub>2</sub>); 4.06 (s, 1H, NH); 6.93 (s, 1H, Ar-H); 6.95 (d, 1H, Ar-H); 7.2 (t, 2H, Ar-H); 7.28 (d, 1H, Ar-H); 7.3 (d, 2H, Ar-H); 7.56 (d, 2H, Ar-H); 7.6 (d, 1H, Ar-H); 8.06 (s, 1H, Ar-H); 8.56 (d, 1H, Ar-H). <sup>13</sup>CNMR (DMSO-d<sub>6</sub>) ppm: 12.81 (2C), 44.5 (2C), 107.83, 111.87, 113.29, 114.77, 115.39 (2C), 117.42, 122.67 (2C), 126.38 (2C), 131.96, 132.27, 133.69, 136.01, 139.12, 140.38, 142.77, 145.73, 147.19, 153.68, 164.55, 166.19, 168.49, 170.86. Elemental analysis: MW 618.06 g/mol; found: C, 56.27; H, 3.82; N, 15.65; S 5.17 %; C<sub>29</sub>H<sub>24</sub>ClN<sub>7</sub>O<sub>5</sub>S; calculated: C, 56.36; H, 3.91; N, 15.86; S, 5.19 %.

### 2.2.3. Synthesis of 3-carboxy-1-(4-chloro-6-(2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-1H-benzo[d]imidazol-1-yl)-1,3,5-triazin-2-yl)pyridin-1-ium chloride (**D<sub>3</sub>**)

One mmol **D<sub>1</sub>** (0.48 g) was dissolved in 20 mL cold acetone (5 °C) and a solution of one mmol pyridine-3-carboxylic acid (0.12 g) dissolved in 20 mL deionized water was added drop-wise within one hour into the **D<sub>1</sub>** solution while stirring at 5 °C. The temperature was raised to 30-35 °C gradually (5 °C per hour), and the mixture was maintained overnight. The disappearance of the **D<sub>1</sub>** was controlled by the TLC method (toluene/ethyl acetate: 1/3). In the next step, the temperature of the solution was reduced to 0-5 °C, and 0.1N hydrochloric acid was added to adjust pH at 3. Finally, the product was filtered, dried in a vacuum oven at 40 °C, and recrystallized from methanol to produce 0.48 g of a yellow powder dye.

**D<sub>3</sub>**: Yield: 85 %; m.p: 319 °C; FT-IR (KBr), cm<sup>-1</sup>: 3432 (νO-H, str, -COOH); 3076 (νC-H, str, Ar); 2923 (νC-H, str, aliphatic); 1719 (νC=O, str); 1622 (νC=N, str); 1580, 1466 (νC=C, str, Ar); 1418 (νO-H, bend); 1294 (νC-O, str); 1132 (νC-N, str); 809 (νC-Cl, str). <sup>1</sup>HNMR (DMSO-d<sub>6</sub>) ppm: 1.48-1.52 (t, 6H, CH<sub>3</sub>); 3.54-3.55 (q, 4H, CH<sub>2</sub>); 6.76 (s, 1H, Ar-H); 6.93 (d, 1H, Ar-H); 7.40 (d, 1H, Ar-H); 7.49 (t, 1H, Ar-H); 7.50 (t, 1H, Ar-H); 7.6 (t, 1H, Ar-H); 7.62 (d, 1H, Ar-H); 8.05 (s, 1H, Ar-H); 8.06 (d, 1H, Ar-H); 8.3 (d, 1H, Ar-H); 8.80 (d, 1H, Ar-H); 9.08 (s, 1H, Ar-H); 11.14 (s, 1H, COOH). <sup>13</sup>CNMR (DMSO-d<sub>6</sub>) ppm: 12.94(2C), 46.35(2C), 109.11, 111.38, 112.41, 114.16, 115.61, 123.68(2C), 127.47, 127.62, 128.04, 135.78, 136.13, 138.91, 141.02, 143.96, 145.92, 146.36, 148.18, 149.81, 159.81, 160.80, 168.56, 170.38, 171.22, 175.22. Elemental analysis: MW 604.44 g/mol; found: C, 57.78; H, 4.02; N, 16.48; C<sub>29</sub>H<sub>23</sub>Cl<sub>2</sub>N<sub>7</sub>O<sub>4</sub>; calculated: C, 57.62; H, 3.84; N, 16.22.

### 2.3. Dyeing of cotton fabrics

Cotton fabrics were scoured and bleached by treating in a solution containing 4.0 g/L sodium hydroxide, 0.8 g/L anionic detergents, 0.4 g/L sequestering agents, 5.0 g/L hydrogen peroxide, and 1.5 g/L sodium silicate at 94 °C for 60 min (liquor ratio of 1:30). Treated fabrics were then rinsed with hot and cold water, neutralized in a buffer solution containing 1.6 g/L sodium acetate and 1.2 g/L acetic acids for 30 min at 70 °C, then rinsed and dried at ambient condition.

One gram of scoured and bleached cotton fabric was dyed with a solution of each synthesized dyes **D<sub>2</sub>**, **D<sub>3</sub>**, and RY78 as a commercial dye in 2.5 and 6 (o.w.f % on the weight of fabric) separately. The pH of the dyeing liquors containing **D<sub>2</sub>** and RY78 was adjusted at 6-6.5, and the temperature was set at 30 °C. The temperature then was increased to 40 °C (1 °C/ min) before adding 1.2 g sodium sulfate (40 g/L) and continued at constant temperature for 20 more minutes. The temperature was then raised (1 °C/ min) to the fixation temperatures; to 80 °C for **D<sub>2</sub>** as a monochlorotriazine dye and 55 °C for RY78 as a vinyl sulfone reactive dye, and maintained for 30 min. Later on, in the fixing step, 0.6 gram (20 g/L) sodium carbonate was added in two steps every 20 min and continued for 30 more minutes [21]. Dyeing parameters for RY78 were followed according to the manufacturer's recommendations. The dyeing process of **D<sub>3</sub>** was the same as the **D<sub>2</sub>** with no addition of salt

and alkaline. The fixing temperature for the **D**<sub>3</sub>, a cationic reactive dye, was set at 100 °C [22]. After dyeing, all goods were given a hot wash at 95 °C for 20 min in a washing solution containing 1.0 g/L anionic detergent. The samples were then neutralized in a buffer solution containing 1.6 g/L sodium acetate and 1.2 g/L acetic acids, rinsed, and the samples were dried at room temperature. High visibility properties of the dyed cotton fabrics were further investigated according to ISO 20471: 2013 [23].

### 2.3.1. Determination of fixation, exhaustion, and total utilization of dyes on cotton fabrics

The dyeing performance of each synthesized dye on cotton fabrics was investigated using a transmittance spectrophotometer. Absorption of the dye solution before dyeing ( $A_0$ ), after dyeing ( $A_1$ ), and after soaping ( $A_2$ ) were measured to calculate exhaustion (E%), fixation (F%), and total utilization (T%) percentages according to Equations 1-3 [22]:

$$E\% = \frac{A_0 - A_1}{A_0} \times 100\% \quad (1)$$

$$F\% = \frac{A_0 - A_1 - A_2}{A_0 - A_1} \times 100\% \quad (2)$$

$$T = (E \times F) \times 100\% \quad (3)$$

## 3. Results and Discussion

### 3.1. Synthesis of the dyes

The reactions and chemical structures of the synthesized dyes are illustrated in Figure 1. **D**<sub>1</sub> was synthesized by the reaction of **CB** with cyanuric chloride in acetone at -10 to 0 °C. Also, the nucleophilic substitution was taken place at the N-H position on benzimidazole. Then, the **D**<sub>1</sub> was individually reacted with sulfanilic acid and nicotinic acid at 30 °C. These acids produced two monochlorotriazine reactive dyes (**D**<sub>2</sub> and **D**<sub>3</sub>). For two reasons, cyanuric chloride was substituted on **CB**: 1) as a reactive group 2) as a linker between soluble functional groups and fluorophore. The subsequent substitutions of sulfanilic acid and nicotinic acid add solubility to the synthesized dyes.

The chemical structures of the dyes were confirmed using <sup>1</sup>HNMR, <sup>13</sup>CNMR, FTIR, and elemental analysis. According to the NMR spectra, chemical shifts observed at 6.7-9.1 ppm and 107-182 ppm were attributed to aromatic protons and aromatic carbons of the synthesized dyes, respectively. Aliphatic protons

were detected in 1.1-3.6 ppm and 12-47 ppm for aliphatic carbons for all synthesized dyes. A chemical shift of protons in 11 ppm was related to COOH in the nicotinic acid ring confirmed the formation of the **D**<sub>3</sub> chemical structure. The FTIR analysis confirmed the C=O group of coumarin scaffold in 1713-1720 cm<sup>-1</sup> range, C-Cl functional groups in substituted cyanuric chloride at 802-809 cm<sup>-1</sup>, C-N at 1095-1132 cm<sup>-1</sup> range for all dyes. O-H group on **D**<sub>2</sub> and **D**<sub>3</sub> appeared at 3417-3432 cm<sup>-1</sup> (stretching) and 1416-1418 cm<sup>-1</sup> (bending). The existences of the sulfone and amine groups on **D**<sub>2</sub> were detected at 1030 cm<sup>-1</sup> and 3213 cm<sup>-1</sup> (stretching), 1560 cm<sup>-1</sup> (bending), respectively.

### 3.2. Spectral properties of synthesized dyes

#### 3.2.1. Fluorescence spectra

The fluorescence properties of the synthesized novel dyes were investigated in various solvents with different polarities (water, DMSO, DMF, methanol, ethanol, and acetone) at a concentration of 5×10<sup>-6</sup> mol/L. The excitation wavelength of the synthesized dyes to measure the fluorescence properties was the same as the absorption wavelength in each solvent. Fluorescence parameters such as maximum emission wavelength ( $\lambda_F$ ), Stokes shift ( $\nu_A - \nu_F$ ), quantum yield ( $\Phi_F$ ), energy yield ( $E_F$ ), and oscillator strength ( $f$ ) were studied. The results are shown in Table 1 and Figures 2-4.

The emission wavelengths are presented in Table 1 for all synthesized dyes in various solvents with different polarities. The results showed that the maximum emission wavelengths of **D**<sub>2</sub> (497, 509 nm) and **D**<sub>3</sub> (492, 500 nm) were increased compared to **D**<sub>1</sub> (482, 493 nm) in acetone and DMSO, respectively. The solvent's higher polarity creates a longer emission wavelength, resulting from the solvent rearrangement with a polar solute in the excited state [24]. This phenomenon is observed in the solution of **D**<sub>2</sub> (512 nm) and **D**<sub>3</sub> (503 nm) with solubilizing auxochrome groups (-SO<sub>3</sub>H, -COOH) in water. The solvent rearrangement was because of robust interaction in the excited state between the polar solvent and the polar dye molecules. It caused a decrease in the difference between the solute's excited state and ground state charge distribution. Shifts in the maximum emission wavelengths to longer wavelengths in more polar solvents are presented in Table 1 for the synthesized dyes, respectively.

The quantum yield of fluorophore indicates the number of emitted photons to the number of the absorbed photons [25], which was calculated by Eq. 4 [8]:

$$\Phi_F = \Phi_{ref} \left( \frac{I_{sam}/I_{ref}}{AF_{sam}/AF_{ref}} \right) \left( \frac{\eta_{sam}}{\eta_{ref}} \right)^2 \quad (4)$$

$\Phi_{ref}$  is the quantum yield of fluorescein, and the reference value is (0.95). The areas of fluorescence intensity for samples and references are  $I_{sam}$  and  $I_{ref}$ , respectively. The solvent refractive index of the sample and the fluorescein are given by  $AF_{sam}$  and  $AF_{ref}$ , respectively.  $\eta_{sam}$  and  $\eta_{ref}$  are the solvent refractive index of the sample and fluorescein, respectively.

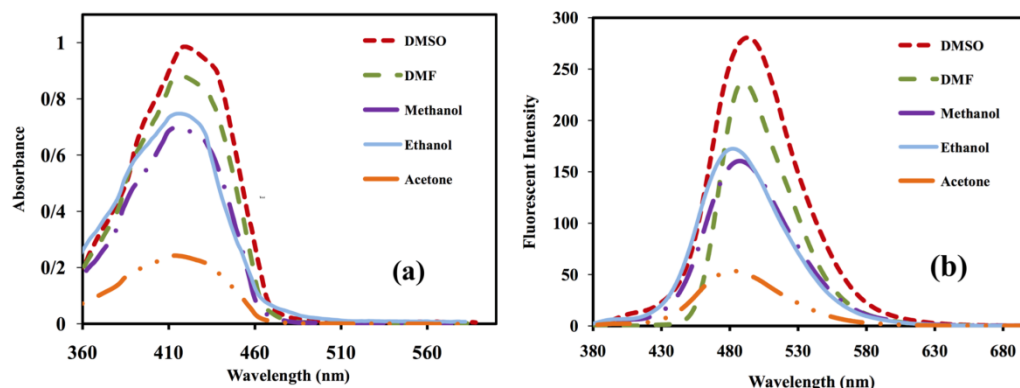


Figure 2: Absorption (a) and emission (b) spectra of **D<sub>1</sub>** in different solvents.

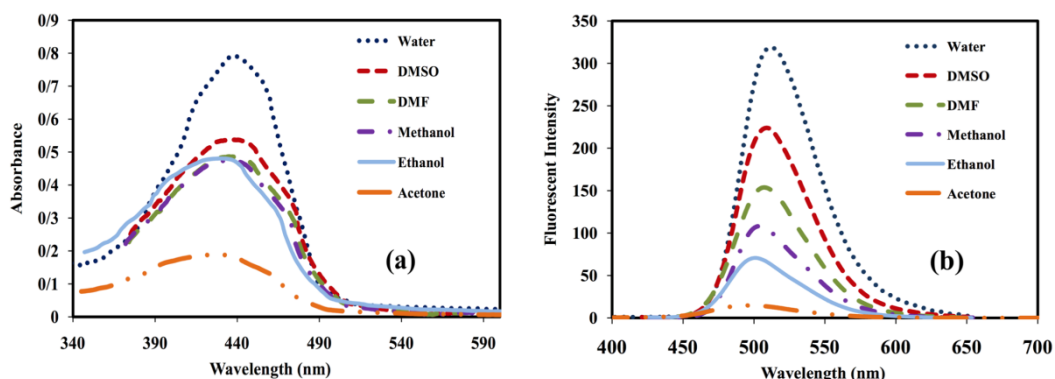


Figure 3: Absorption (a) and emission (b) spectra of **D<sub>2</sub>** in different solvents.

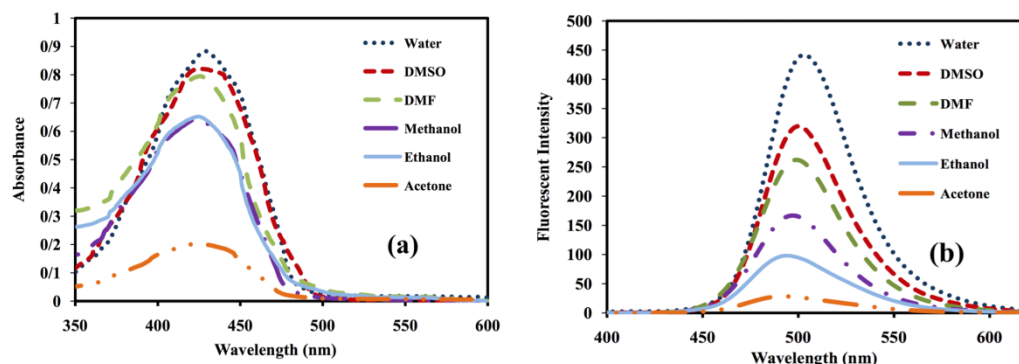


Figure 4: Absorption (a) and emission (b) spectra of **D<sub>3</sub>** in different solvents.

Table 1: Photophysical properties of novel fluorescent reactive dyes in different solvents.

Solvent / Dielectric constant		Water	DMSO	DMF	Methanol	Ethanol	Acetone
		80	46	38	35	25	20
$\lambda_A$ (nm)	CB	-	440	437	436	438	438
	D <sub>1</sub>	-	420	418	417	418	418
	D <sub>2</sub>	438	436	435	433	431	430
	D <sub>3</sub>	429	427	426	424	425	424
$\lambda_F$ (nm)	CB	-	495	490	487	486	484
	D <sub>1</sub>	-	493	490	487	485	482
	D <sub>2</sub>	512	509	507	504	501	497
	D <sub>3</sub>	503	500	497	495	494	492
$\Delta\nu_{1/2}$ (cm <sup>-1</sup> )	D <sub>1</sub>	-	3898	3955	3994	4337	4345
	D <sub>2</sub>	4323	4787	4854	4900	6045	6180
	D <sub>3</sub>	4155	4355	4428	4573	4450	4620
$\epsilon$ (Lmol <sup>-1</sup> cm <sup>-1</sup> )	D <sub>1</sub>	-	39872	35621	27694	30241	10672
	D <sub>2</sub>	21390	17843	14420	13190	13245	5637
	D <sub>3</sub>	24320	22515	21674	19630	20163	6841
$(\nu_A - \nu_F)$ cm <sup>-1</sup>	D <sub>1</sub>	-	3525	3515	3446	3304	3176
	D <sub>2</sub>	3299	3289	3264	3253	3241	3135
	D <sub>3</sub>	3429	3419	3353	3382	3286	3259
$\Phi_F$	D <sub>1</sub>	-	0.7	0.45	0.35	0.39	0.22
	D <sub>2</sub>	0.57	0.56	0.39	0.22	0.16	0.08
	D <sub>3</sub>	0.65	0.61	0.48	0.28	0.19	0.11
$E_F$	D <sub>1</sub>	-	0.59	0.38	0.30	0.33	0.20
	D <sub>2</sub>	0.49	0.48	0.33	0.19	0.13	0.06
	D <sub>3</sub>	0.55	0.52	0.41	0.24	0.16	0.1
$f$	D <sub>1</sub>	-	0.67	0.6	0.47	0.56	0.2
	D <sub>2</sub>	0.39	0.36	0.3	0.27	0.34	0.15
	D <sub>3</sub>	0.43	0.42	0.41	0.38	0.38	0.13

Studies of coumarins have shown an increase in their quantum yield in polar solvents [26]. The reported data confirmed that the quantum yield increased for **D<sub>2</sub>** and **D<sub>3</sub>** in solvents with more polarity. In acetone and water, these values were 0.08 and 0.57 for **D<sub>2</sub>**, 0.11,

and 0.65 for **D<sub>3</sub>**, respectively. The rigidity of fluorophore molecules increased with the interaction of more polar solvents with synthesized dyes due to the hydrogen bonding between hydrogen and nitrogen or oxygen atoms of solute and solvent. So, the quantum

yield of all three synthesized dyes is amplified in more polar solvents than less polar ones.

The Stokes shift shows the difference in the properties of fluorescent compounds in the ground state and excited state that was calculated using Eq. 5 [4]:

$$(\nu_A - \nu_F) = \left( \frac{1}{\lambda_A} - \frac{1}{\lambda_F} \right) \times 10^7 \quad (5)$$

Where  $\lambda_F$  and  $\lambda_A$  are the emission and absorption maxima wavelengths, respectively.

The Stokes shift of fluorescent materials is affected by the following process: a) electron redistribution in the solvent around the dipole moment of fluorophore in the excited state, b) particular interaction of solvent and fluorophore (hydrogen bonding and charge transfer creation), c) reorientation of solvent around dipole moment of fluorophore in the excited state [27]. The increase in Stokes shift occurred with an enhancement in the polarity of solvents, which presented the growing dipole moment in an excited state [28]. The Stokes shift values of **D**<sub>1</sub>, **D**<sub>2</sub>, and **D**<sub>3</sub> were 3500, 3300 and 3400 cm<sup>-1</sup> in DMSO as a polar solvent and 3200, 3100 and 3250 cm<sup>-1</sup> in acetone as a less polar solvent, respectively. This phenomenon was due to the  $\pi$ -conjugation effect that is transferred charge and indicating reorganization in the excited state. The higher Stokes shift value of fluorophores reduces the overlap of absorption and emission spectra and appears fluorescence due to decreasing interference [8]. The synthesized dyes' normalized absorption and emission spectra are illustrated in Figure 5 in more and less polar solvents, showing the minimum overlap between the two spectral.

Oscillator strength as a quantitative parameter explains the effectiveness of the number of excited

electrons from the ground state to the excited one, which is computed by Eq. 6 [2]:

$$f = 4.32 \times 10^{-9} \times \Delta\nu_{1/2} \times \epsilon_{max} \quad (6)$$

$\Delta\nu_{1/2}$  and  $\epsilon_{max}$  are the half bandwidth and molar extinction coefficient, respectively. The oscillator strength of synthesized dyes **D**<sub>1</sub>, **D**<sub>2</sub>, and **D**<sub>3</sub> were 0.67, 0.36, and 0.42 in DMSO and 0.2, 0.15, and 0.13 in acetone, respectively. The lower value of oscillator strength of **D**<sub>2</sub> and **D**<sub>3</sub> compared to **D**<sub>1</sub> can be explained by a) the lower molar extinction coefficient b) the redshift in fluorescence wavelength after substitution on **D**<sub>1</sub>.

The energy yield is another fluorescent property of fluorescent materials that depends on quantum yield and is calculated using Eq. 7 [29]:

$$E_F = \Phi_F \left( \frac{\lambda_A}{\lambda_F} \right) \quad (7)$$

The energy yield values of dyes are presented in Table 1. The results showed that energy yield has been changed with variation in quantum yield and has been more significant in more polar solvents. The energy yields of **D**<sub>1</sub>, **D**<sub>2</sub>, and **D**<sub>3</sub> were 0.2-0.59, 0.06-0.49, and 0.1-0.55 in less and more polar solvents, respectively.

### 3.2.2. UV-Vis properties

The absorption properties of fluorescent synthesized dyes such as maximum absorption wavelength, molar extinction coefficient, and the half bandwidth are presented in Table 1 and Figures 2-4 in different solvents in the concentration of  $5 \times 10^{-6}$  mol/L. The highest absorption wavelength was associated with more polar solvents for all dyes. This behavior is attributed to the solvatochromism effect of synthesized dyes.

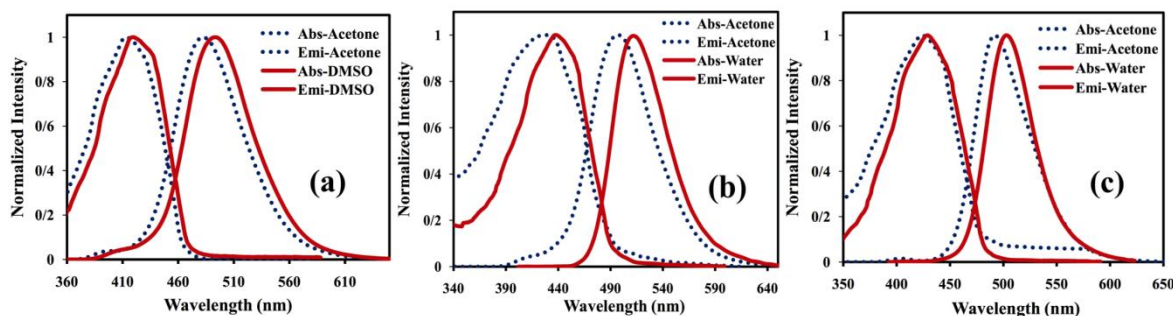


Figure 5: Normalized absorption and emission spectra of a) **D**<sub>1</sub>, b) **D**<sub>2</sub>, c) **D**<sub>3</sub> in more polar and less polar solvents.



The  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  bands illustrated a bathochromic shift (redshift) and hypsochromic shift (blue shift), respectively. By controlling the dipole-dipole and solute-solvent interactions in the excited state, the bathochromic shift is obtained by increasing the solvent polarity [30].

The maximum absorption wavelength of **D**<sub>1</sub> (420 nm) was less than **CB** (440 nm) in DMSO. The substitution of cyanuric chloride as an electron-withdrawing group caused a hypsochromic shift in **D**<sub>1</sub> compared to **CB**. It should be considered that the substitution of cyanuric chloride on the N-H position caused a minimal disturbance in charge transfer across the conjugated system and maximum absorption wavelengths. The absorption wavelength values of **D**<sub>1</sub>, **D**<sub>2</sub>, and **D**<sub>3</sub> were in the range 417-420 nm, 430-438 nm, and 424-429 nm, respectively. The maximum absorption wavelength of **D**<sub>2</sub> and **D**<sub>3</sub> were longer than **D**<sub>1</sub> mainly because of the electron-donating potential of the substituted groups on the triazine cycle (Redshift).

The half bandwidth ( $\Delta\nu_{1/2}$ ) is known as the brilliance factor and represents the absorption bandwidth at half of the height in the absorption profile. The hyperchromic effect and the narrow absorption peak in half bandwidth create the brilliance of shade. The half bandwidths of **D**<sub>1</sub>, **D**<sub>2</sub>, and **D**<sub>3</sub> were (3898-4345 cm<sup>-1</sup>), (4323-6180 cm<sup>-1</sup>), and (4155-4620 cm<sup>-1</sup>) in more polar solvents to less polar ones, as mentioned in Table 1, which concludes that **D**<sub>3</sub> is more brilliant than **D**<sub>2</sub>.

The molar extinction coefficient ( $\epsilon$ ) of the synthesized dyes **D**<sub>2</sub> and **D**<sub>3</sub> were 21390 and 24320 Lmol<sup>-1</sup>cm<sup>-1</sup> in water, respectively, as shown in Table 1. By increasing the molecular weight of the synthesized dyes, the molar extinction coefficient was decreased compared to **D**<sub>1</sub> (39872 Lmol<sup>-1</sup>cm<sup>-1</sup>).

### 3.3. Dyeing fixation, exhaustion, and the total utilization

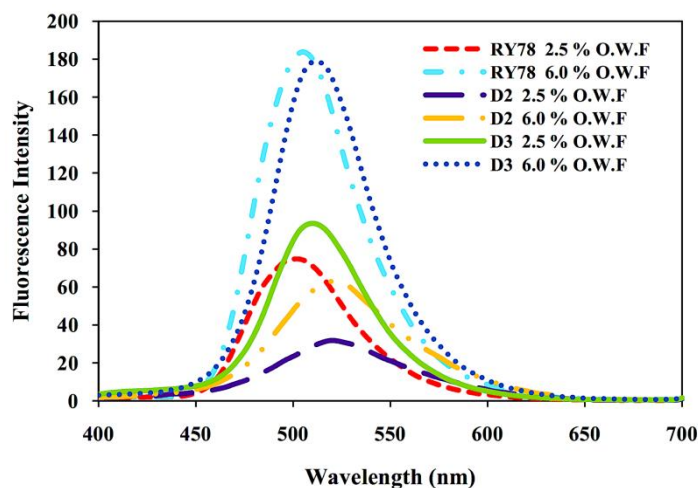
The exhaustion and fixation percentages of the synthesized dyes alongside the only commercially available reactive dye (RY78) on cotton fabric are indicated in Table 2. The fixation and exhaustion of **D**<sub>3</sub> were greater than **D**<sub>2</sub> because of the cationic Coulomb charges of **D**<sub>3</sub> present on the nicotinic acid group causing higher affinity and lower repulsion between the dye and cellulosic chains [31].

### 3.4. Fluorescent properties of the dyed cotton fabric

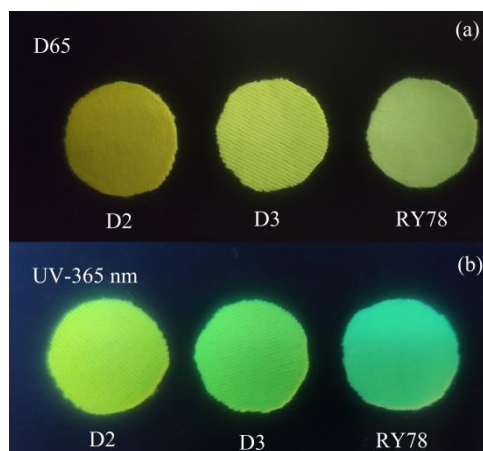
Fluorescent properties of cotton fabrics dyed with water-soluble synthesized reactive dyes **D**<sub>2</sub> and **D**<sub>3</sub> compared to RY78 are presented in Figures 6 and 7, and Table 3. The maximum emission wavelength and fluorescence intensity are the main factors of fluorescence properties. The fluorescent intensities were measured with 430, 440 and 450 nm excitation wavelengths for dyed samples with RY78, **D**<sub>3</sub> and **D**<sub>2</sub>, respectively. As can be seen from Figure 6, the maximum emission wavelengths of **D**<sub>2</sub> (520 and 522 nm) are higher than **D**<sub>3</sub> (510 and 512 nm) and RY78 (501 and 505 nm) in 2.5 and 6 % (o.w.f). It is also illustrated that the hue of RY78 is more green-emitting than the **D**<sub>3</sub> and **D**<sub>2</sub>, making the newly synthesized dyes better nominees for dyeing cotton in more pure yellow colors. The fluorescence intensity of **D**<sub>3</sub> (93.47, 178.63 nm) was higher than **D**<sub>2</sub> (31.87, 63.10 nm) in 2.5 and 6 % (o.w.f), respectively. Nicotinic acid leaving the group in **D**<sub>3</sub> leaves the scaffold of the fluorophore when it is substituted to the hydroxyl group of the cellulose during the dyeing process, justifying the excellent fluorescence intensity of **D**<sub>3</sub>.

**Table 2:** Fixation, exhaustion, and total utilization of the synthesized dyes at 2.5 and 6 % (o.w.f).

Dye (o.w.f)	Exhaustion (%)		Fixation (%)		Total utilization (%)	
	2.5	6	2.5	6	2.5	6
<b>D</b> <sub>2</sub>	77	72	78	73	60	53
<b>D</b> <sub>3</sub>	88	83	79	75	69	62
RY78	78	72	81	77	63	55



**Figure 6:** The emission spectra of **D<sub>2</sub>**, **D<sub>3</sub>**, and RY78 in 2.5 and 6 % (o.w.f).



**Figure 7:** The dyed cotton fabrics with **D<sub>2</sub>**, **D<sub>3</sub>** and RY78 a) in daylight (D65) and b) in UV-irradiation (365 nm) in 2.5 % (o.w.f).

**Table 3:** The fluorescent properties of the dyed cotton fabrics with **D<sub>2</sub>**, **D<sub>3</sub>**, and RY78.

Dye	o.w.f %	$\lambda_F$ (nm)	Fluorescence Intensity
RY78	2.5	501	74.81
	6	505	183.84
<b>D<sub>2</sub></b>	2.5	520	31.87
	6	522	63.10
<b>D<sub>3</sub></b>	2.5	510	93.47
	6	512	178.63

### 3.5. Color characteristics and high visibility properties of the dyed cotton fabrics

High visibility properties of the dyed cotton fabrics were studied according to the ISO 20471: 2013

standard authenticated for high visibility personal protective equipment (PPE) [32]. High visibility parameters including chromaticity coordinate (x, y), luminance factor ( $\beta$ ), CIE L\*a\*b\* (CIE 015: 2018-

colourimetry, 4<sup>th</sup> edition), K/S and R % values of the dyed cotton fabrics with **D**<sub>2</sub>, **D**<sub>3</sub>, and RY78 in 2.5 and 6 % (o.w.f) are reported in Table 4 and Figure 8, 9. According to Table 4, **D**<sub>3</sub> is lighter, more greenish, more yellowish, and purer than **D**<sub>2</sub> in both concentrations. Figure 8 illustrates that the reflectance values were decreased by increasing the dye concentration from 2.5 to 6% (o.w.f) for the synthesized dyes and the RY78.

Chromaticity diagrams of the dyed cotton fabrics with **D**<sub>2</sub>, **D**<sub>3</sub>, and commercially available fluorescent yellow dye (RY78) as standard are illustrated in Figure 9. The chromaticity coordinates x and y, which describe the chroma, saturation, and hue, are calculated

using Eq. 8 and 9:

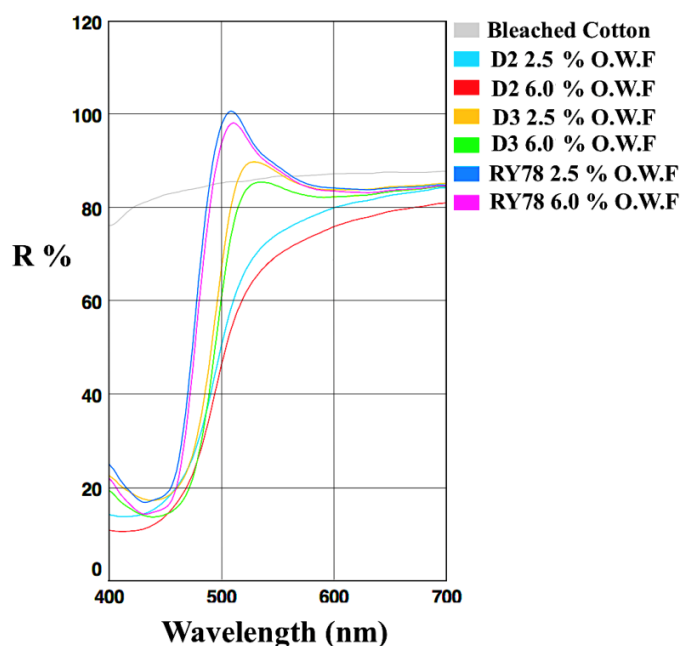
$$x = \frac{X}{X+Y+Z} \quad (8)$$

$$y = \frac{Y}{X+Y+Z} \quad (9)$$

where X, Y, and Z are the CIE tristimulus values of each fabric sample. Chromaticity boundaries for fluorescent yellow dyes suitable for use in high visibility protective equipment applications set by the ISO 20471: 2013 standard in clause 5.1.1 are shown in Table 4 and Figure 9. The results showed that the chromaticity coordinates (x, y) of **D**<sub>3</sub> was ideally

**Table 4:** Color characteristics of cotton fabrics dyed with synthesized and commercial dyes.

Dye	o.w.f (%)	L*	a*	b*	C*	h	K/S	R%	x	y	Y	β
RY78	2.5	93.96	-21.20	58.09	61.83	110.05	2.05	100.59	0.378	0.458	85.182	0.851
	6	93.34	-21.31	62.96	66.47	108.70	2.57	98.10	0.385	0.467	83.742	0.837
<b>D</b> <sub>2</sub>	2.5	86.20	-3.33	57.93	58.03	93.29	2.71	69.85	0.412	0.444	68.394	0.683
	6	84.01	-2.70	61.05	61.11	92.53	3.79	64.93	0.419	0.451	64.082	0.640
<b>D</b> <sub>3</sub>	2.5	91.74	-15.27	62.50	64.34	103.73	2.05	90.83	0.395	0.466	80.131	0.801
	6	89.36	-12.67	66.36	67.56	100.81	2.95	82.18	0.406	0.466	74.938	0.749



**Figure 8:** The R % spectra of **D**<sub>2</sub>, **D**<sub>3</sub>, and RY78 in 2.5 and 6 % (o.w.f).

located inside the accepted area in 2.5 to 6 (o.w.f %) concentration range. In contrast, the **D<sub>2</sub>** could not be found in the accepted area, even in higher concentrations. Reactive Yellow 78, the only commercial reactive dyes, could enter the accepted chromaticity boundaries set by the above standard in high concentrations.

The chromaticity coordinates (x, y) and the luminance factor ( $\beta$ ) of a fluorescent substrate are the essential factors to evaluate in the high visibility application [23]. The luminance factor of dyed fabrics is defined by Eq. 10 [5]:

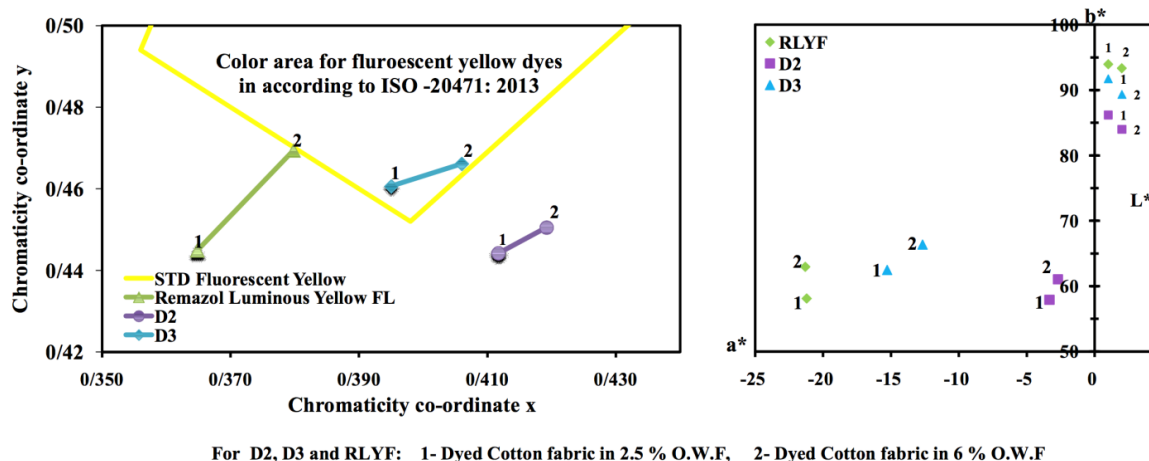
$$\beta = \frac{Y}{Y_0} \quad (10)$$

where Y and  $Y_0=100$  are the coordinates of the colored sample and a perfect reflective diffuser, respectively. According to the Iso standard mentioned above, the luminance factor of the samples should not be less than 0.7 to be accepted as a high visibility item. The luminance factor values of all dyed cotton fabrics

with synthesized dyes and RY78 are given in Table 4. The luminance factors of **D<sub>3</sub>** (0.801, 0.749) and RY78 (0.851 and 0.837) in both concentrations were more than 0.7. As a result, cotton fabrics dyed with the **D<sub>3</sub>** in 2.5 and 6 % o.w.f range and RY78 only in its 6 % o.w.f concentration are located inside the standard boundaries for use as high visibility fluorescent yellow dyes.

### 3.6. Color fastness

Color fastnesses were evaluated based on clauses 5.2, 5.3 of standard ISO 20471: 2013. The test methods of each fastness are described below in table 5. All samples in standard depth of 1/1 were used to evaluate their fastness properties. The fastnesses value of the dyed cotton fabrics with novel reactive dyes (**D<sub>2</sub>**, **D<sub>3</sub>**) and RY78 were reported in Table 5. The results showed that the cotton fabrics dyed with the synthesized novel reactive dyes could meet the minimum required fastnesses needed on backgrounds in standard ISO 20471: 2013.



**Figure 9:** I) Chromaticity coordinates (x, y) boundaries and locations and CIEL\*a\*b\* of the dyed cotton fabrics in 2.5 and 6 % o.w.f according to the ISO-20471: 2013 (clause 5.1.1).

**Table 5:** Fastness properties of the cotton fabrics dyed with the novel reactive dyes.

Dye	Laundry <sup>a</sup>		Light <sup>c</sup>	H.p <sup>d</sup>		Perspiration <sup>e</sup>		Dry Cleaning <sup>f</sup>	H.b <sup>g</sup>	Rubbing <sup>h</sup>	
	Change	St <sup>b</sup>		Dry	Wet	alkaline	acid			Wet	Dry
<b>D<sub>2</sub></b>	4-5	4	4	4-5	4-5	4-5	4-5	4-5	4	4	4-5
<b>D<sub>3</sub></b>	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
RY78	5	4-5	4	4-5	4-5	4-5	5	4-5	4-5	4-5	4-5

a: Home laundry (washing at 95 °C): ISO 105-C06-E2S: 2010, b: Staining on cotton fabric, c: light (xenon arc): ISO 105-B02: 2014

d: Hot pressing : ISO 105-X11: 1994, e: perspiration: ISO 105-E04: 2013, f: dry cleaning: ISO 105-D01:2010,

g: Hypochlorite bleaching: ISO 105-N01: 1993 h: rubbing: ISO 105-X12: 2016

#### 4. Conclusion

In the present research, two novel fluorescent reactive dyes were successfully designed and synthesized based on coumarin benzimidazole. Chemical structures of the synthesized dyes (**D<sub>2</sub>** and **D<sub>3</sub>**) were confirmed using FTIR, <sup>1</sup>HNMR, <sup>13</sup>CNMR, and elemental analysis. Photophysical properties of the synthesized dyes were investigated in six solvents with different polarities. **D<sub>2</sub>** and **D<sub>3</sub>** were soluble in water, and the solvatochromism effect was positive for all dyes. The emission and absorption wavelengths indicated that **D<sub>2</sub>** and **D<sub>3</sub>** had a bathochromic shift than the insoluble intermediate colorant (**D<sub>1</sub>**). Molar extinction coefficients of all synthesized dyes were higher in more polar solvents. Smaller half bandwidth and narrower absorption spectrums affirmed more brilliance of the **D<sub>3</sub>** compared to the **D<sub>2</sub>**.

Moreover, the amounts of the quantum yield for **D<sub>3</sub>** (0.65) and **D<sub>2</sub>** (0.57) illustrated that both products have considerable fluorescent properties in water. The exhaustion percentage of **D<sub>3</sub>** was greater than **D<sub>2</sub>** due to the cationic coulomb charge of the nicotinic leaving

group achieving a better total utilization than the other synthesized and commercially available reactive dye (RY78). Fluorescent properties of the dyed fabric proved that **D<sub>3</sub>** has higher fluorescent intensity than **D<sub>2</sub>** on cotton. This phenomenon is because of the detachments of the reactive group in **D<sub>3</sub>** leaving the original scaffold of fluorophore during the dyeing process.

Although both synthesized dyes revealed good fluorescence properties, the high visibility test results demonstrated that only **D<sub>3</sub>** in all concentrations dyed on cotton fabric was located in the high visibility boundary area set by the ISO standard. The fastness properties of both synthesized dyes on cotton fabrics satisfied the required fastness of the background material defined in the high visibility standard context.

A fluorescent reactive dye (**D<sub>3</sub>**) was introduced as the first high visibility reactive dye based on coumarin-benzimidazole derivative for dyeing of cellulosic fabrics, which successfully fulfills the criteria set of the international standard established in ISO 20471:2013 for high visibility clothing.

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