

## Synthesis and Application of a Novel Fluorescent Reactive Dye Based on Fused Iminocoumarin on Cotton Fabric

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### ARTICLE INFO

#### Article history:

Received: 1 Nov 2021

Final Revised: 11 Feb 2022

Accepted: 13 Feb 2022

Available online: 25 Oct 2022

#### Keywords:

Fused iminocoumarin

Nicotinic acid

Spectral properties

Fluorescent reactive dyes

Dyeing

### ABSTRACT

**T**his research has studied the synthesis and characterization of two novel red dyes based on fused iminocoumarin. For this purpose, 3-(diethylamino)-7-imino-7H-benzo[4,5]imidazo[1,2-a]chromeno[3,2-c]pyridine-6-carbonitrile) was reacted with cyanuric chloride. The product was then substituted with nicotinic acid to obtain a novel fluorescent reactive dye (E)-3-carboxy-1-(4-chloro-6-((6-cyano-3-(diethylamino)-7H-benzo[4,5]imidazo[1,2-a]chromeno[3,2-c]pyridin-7-ylidene)amino)-1,3,5-triazin-2-yl)pyridin-1-ium chloride. FTIR, <sup>1</sup>HNMR, <sup>13</sup>CNMR, and elemental analysis studied the characterization of the synthesized dyes. The spectral properties of novel dyes such as absorption and emission wavelengths, molar extinction coefficients, half bandwidth, quantum yields, Stokes shifts, and oscillator strength were investigated in four different solvents (water, dimethyl sulfoxide, methanol, and acetone). The absorption and emission wavelength of dyes were in the range of 525-547 nm and 581-596 nm in different polarities of solvents, respectively. The results demonstrated a positive solvatochromism effect for both dyes. However, a more bathochromic shift occurred for the nicotinic acid derivative. The cationic water-soluble dye was treated on cotton fabrics. The exhaustion, fixation, color characteristics, fastness properties, and fluorescent intensity of dyed fabrics were evaluated as a new fused iminocoumarin fluorescent reactive fluorescent dye in red gamut. Prog. Color Colorants Coat. 16 (2023), 71-81 © Institute for Color Science and Technology.

### 1. Introduction

In recent years, the synthesis and use of fluorescent dyes have attracted much attention [1]. Coumarin derivatives are among the most popular and common classes of fluorescent dyes [2]. These dyes are used for many applications such as textiles [3], cell biology [4], medical analysis [5], sensors [6], and lasers [7]. Coumarin alone is non-fluorescent, but the presence of different electron donor and electron acceptor groups at various positions can cause the emission and increase

in fluorescent intensity on it [8]. The change in the fluorescence properties of coumarins is due to the strength of the electron donor and acceptor groups. Recently, fused coumarins have been considered for various applications to prevent the intersystem crossing and increase the fluorescence intensity with high Stokes shift [9].

Some coumarin and iminocoumarin derivatives have an electron donor and an electron acceptor. An electron donor (N,N-dialkylamino, or julolidine) was at

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Doi: 10.30509/pccc.2022.166910.1139

position 7 [10]. Benzimidazole, benzothiazole, or cyano group were electron acceptor at position 3 [9, 11]. They are more common than other derivatives for fluorescent usage (Figure 1) [10].

Iminocoumarin is a coumarin derivatives class with high quantum yield [12] and fluorescence properties [2]. Iminocoumarins have been used for metal sensors [11], biological systems [13], and lasers [14]. The flat structure of the fused iminocoumarin prevents the rotation of groups at position 3 and internal conversion and increases the electron flow of the conjugated system [9]. Furthermore, various substitutions can modify iminocoumarins at the imino position on the fluorescent moiety. Therefore, these methods produce a new invention, fluorescent dyes [2].

Fluorescent dyes have high popularity because of their high brightness. Most fluorescent dyes are produced for textile usage based on various fluorophores such as coumarin (CI 551200), fused iminocoumarin (CI 505720), xanthenes (CI 45100 and CI 45350), and naphthalimide (CI 56205) [15]. The only commercially available fluorescent reactive dye based on vinyl sulfone reactive group is Remazol Luminous Yellow FL [16].

However, a recent publication reported fluorescent reactive dyes such as bi-functional reactive dyes with xanthene fluorophore for cotton in yellow gamut [17, 18]. Furthermore, hemicyanine fluorophore and  $\alpha$ -bromo-acrylamide as a reactive group for wool and silk [19], xanthene with vinyl sulfone for cotton [20], and a bi-functional reactive dye based on amino coumarin fluorophore [21] for wool in red gamut have also been introduced. While the coumarin derivatives are fluorophores with an emission wavelength in the range of 500 nm [22], iminocoumarin products have been studied to achieve longer emission wavelengths in the close range of 600 nm [23]. A new fluorescent iminocoumarin reactive dye is synthesized in the present study that exhibited a longer emission wavelength in the red gamut. Although substitution on the imino group of iminocoumarin derivatives using nucleophilic substitution had been reported [24], it has not been used to add a reactive group to the structure to react with cellulosic fibers. Therefore, this is the first report synthesizing an iminocoumarin based fluorophore reactive dye for dyeing cotton fabric.

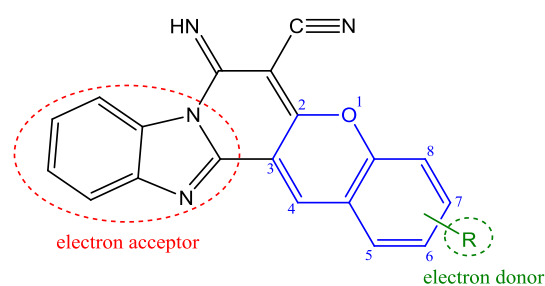
This research described the synthesis of two novel fluorescent dyes based on fused iminocoumarin. In this way, cyanuric chloride was substituted on the imino

group of fused iminocoumarin by a nucleophilic substitution reaction with minimum disturbance in the conjugated system. Then the product was reacted with nicotinic acid to create a new fluorescent reactive dye (Figure 2). Characterization and photophysical properties of the synthesized dyes were investigated. Fixation, exhaustion, and fastness properties of the water-soluble reactive dyes were also reported on cotton fabric.

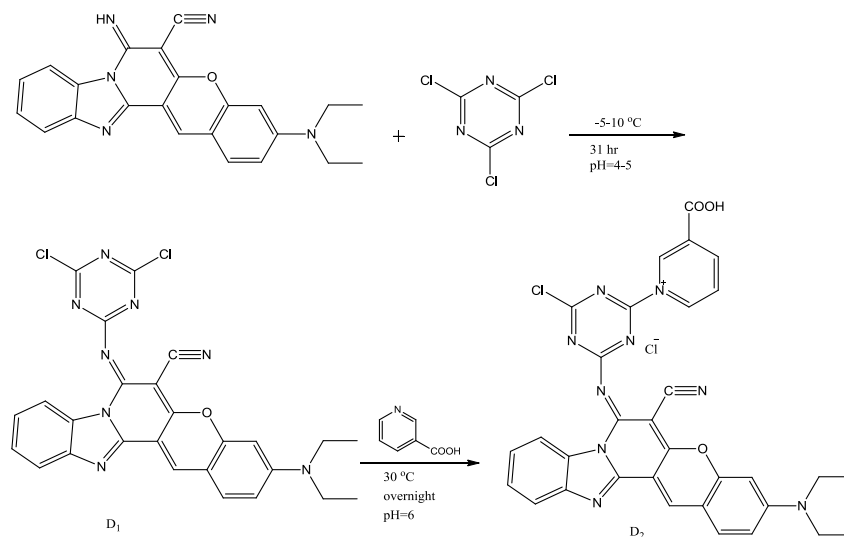
## 2. Experimental

### 2.1. Materials and instruments

Nicotinic acid, 3-(diethylamino)-7imino-7H-benzo [4,5]imidazo[1,2-a]chromeno[3,2-c] pyridine-6-carbonitrile (fused iminocoumarin) and cyanuric chloride were obtained from Lonsen Group, China. The following substances were purchased from Merck Chemical Industry Co., Ltd.: ethyl acetate, n-hexane, acetone, toluene, methanol, dimethylformamide (DMF), sodium carbonate, and TLC Silica gel 60 F 254. All chemicals and additives for the dyeing process were attained from Kimia Kav Jahan, Iran. The  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR spectra (Bruker DRX-AVANCE instrument, Germany) were obtained with DMSO- $d_6$  as solvent at 250 MHz. Heraeus Elemental Analysis CHN-Rapid, USA, was used to analyze the elemental contents of synthesized dyes. The Perkin Elmer spectrum, USA, attained FTIR spectrums. Double Beam CECIL 9200: England was used to determining the absorption of dyes solutions. Fluorescence properties were investigated by a spectrofluorimeter (Perkin Elmer LS50B, USA). Buchi melting point B-545, Switzerland, was utilized to measure the melting points of dyes. The light, rubbing, and washing fastnesses were taken on Xenon ArcLight, James H. Heal, England, Crockmaster 255, and Gyrowash 815/8, James H. Heal, England instruments, respectively.



**Figure 1:** The chemical structure of fused iminocoumarin.



**Figure 2:** The synthesis process of fused iminocoumarin dyes.

## 2.2. Synthesis of (E)-7-((4,6-dichloro-1,3,5-triazin-2-yl)imino)-3-(diethylamino)-7H-benzo[4,5]imidazo[1,2-a]chromeno[3,2-c]pyridine-6-carbonitrile (D<sub>1</sub>)

A solution of 1 mmol (0.38 g) fused iminocoumarin in 300 mL acetone was poured in a 500 mL two neck round-bottom flask equipped with a thermometer and stirrer located in an ice salt bath (270 g/L NaCl) to maintain the flask temperature at  $-5-0\text{ }^{\circ}\text{C}$ . First, 1.1 mmol (0.2 g) cyanuric chloride was weighed under fume hood condition and dissolved in 50 mL cold acetone, then the cyanuric chloride solution was added dropwise into the flask while stirring. The temperature was controlled for two hours at  $-5-0\text{ }^{\circ}\text{C}$ , then 0.4 mmol sodium carbonate solution 10% (w/v) was added in a dropwise manner during one hour. The process was continued for two additional hours; then, the temperature was increased to  $5-10\text{ }^{\circ}\text{C}$  by adding water to the bath and kept this condition for 26 hours. The consumption of the primary substance was checked by thin-layer chromatography (TLC) (n-hexane/ethyl acetate: 2/5). Finally, the product was dried at room temperature, washed with 10 mL cold acetone, and recrystallized from toluene to earn 0.49 g red powder.

**D<sub>1</sub>:** Yield: 89 %; m.p.  $286\text{ }^{\circ}\text{C}$ ; FT-IR (KBr),  $\text{cm}^{-1}$ : 3078 ( $\nu\text{C-H}$ , str, Ar); 2921 ( $\nu\text{C-H}$ , str, Alkane); 2232 ( $\nu\text{C}\equiv\text{N}$ , Nitril); 1652 ( $\nu\text{C}=\text{N}$ , str); 1461 ( $\nu\text{C}=\text{C}$ , str, Ar); 1111 ( $\nu\text{C-O}$ , str); 1055 ( $\nu\text{C-N}$ , str); 800 ( $\nu\text{C-Cl}$ , str).  $^1\text{H}$ NMR (DMSO- $d_6$ ) ppm: 1.26 (t, 6H,  $\text{CH}_3$ ); 3.41 (q, 4H,  $\text{CH}_2$ ); 6.62 (s, 1H, Ar-H); 6.77 (d, 1H, Ar-H); 7.37 (d, 1H, Ar-

H); 7.40 (s, 1H, Ar-H); 7.42 (t, 2H, Ar-H); 7.75 (d, 2H, Ar-H).  $^{13}\text{C}$ NMR (DMSO- $d_6$ )ppm: 12.71(2C), 46.30 (2C), 73.76, 92.91, 105.72, 106.23, 114.88, 115.25, 115.91, 123.77 (2C), 129.47, 129.83, 130.57, 138.53, 138.80, 141.40, 149.68, 150.18, 154.25, 169.46, 170.49, 170.73 (2C). Elemental analysis: MW 529.38 g/mol; found: C, 58.62; H, 3.15; N, 21.35.  $\text{C}_{26}\text{H}_{18}\text{Cl}_2\text{N}_8\text{O}$ ; Calculated: C, 58.99; H, 3.43; N, 21.17.

## 2.3. Synthesis of (E)-3-carboxy-1-(4-chloro-6-((6-cyano-3-(diethylamino)-7H-benzo[4,5]imidazo[1,2-a]chromeno[3,2-c]pyridin-7-ylidene)amino)-1,3,5-triazin-2-yl)pyridin-1-ium chloride (D<sub>2</sub>)

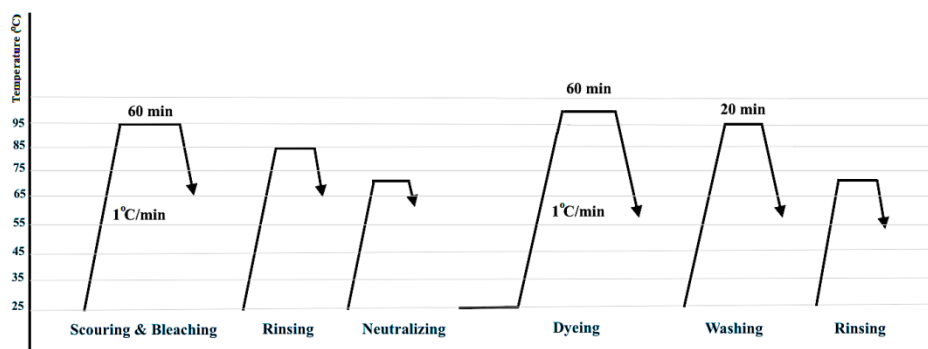
0.8 mmol (0.42 g) of D<sub>1</sub> in 150 mL cold acetone was dissolved in a 250 mL two round-bottom neck flask fitted with a magnetic stirrer, thermometer, and condenser at  $10\text{ }^{\circ}\text{C}$ . The nicotinic acid (0.8 mmol (0.1 g)) was solved in 20 mL deionized water, then added to D<sub>1</sub> gradually and maintained the condition for one hour. The pH was controlled by adding sodium carbonate solution (10 % w/v) for one hour. The temperature was increased to  $30\text{ }^{\circ}\text{C}$  at an interval of 5 degrees each hour and continued overnight. TLC method (toluene/ethyl acetate: 2/5) was used to determine the reaction's endpoint. The product was dissolved in hydrochloric acid 0.1 N, pH=3 at  $0-5\text{ }^{\circ}\text{C}$ , filtered, dried, and recrystallized from methanol. 0.45 g product as the red powder was obtained.

**D<sub>2</sub>:** Yield: 87%; m.p.  $297\text{ }^{\circ}\text{C}$ ; FT-IR (KBr),  $\text{cm}^{-1}$ : 2600-3500 ( $\nu\text{O-H}$ , str, broad); 3073 ( $\nu\text{C-H}$ , str, Ar); 2923( $\nu\text{C-}$

H, str, Alkane); 2252 ( $\nu\text{C}\equiv\text{N}$ , Nitril); 1716 ( $\nu\text{C}=\text{O}$ , carboxylic acid); 1643 ( $\nu\text{C}=\text{N}$ , str); 1464 ( $\nu\text{C}=\text{C}$ , str, Ar); 1405 ( $\nu\text{O}-\text{H}$ , bend); 1278 ( $\nu\text{C}-\text{O}$ , carboxylic acid); 1113 ( $\nu\text{C}-\text{O}$ , str); 1060 ( $\nu\text{C}-\text{N}$ , str); 805 ( $\nu\text{C}-\text{Cl}$ , str).  $^1\text{H}$ NMR (DMSO- $d_6$ ) ppm: 1.27 (t, 6H,  $\text{CH}_3$ ); 3.41 (q, 4H,  $\text{CH}_2$ ); 6.71 (s, 1H, Ar-H); 6.86 (d, 1H, Ar-H); 7.40 (d, 2H, Ar-H); 7.42(s, 1H, Ar-H); 7.45 (t, 2H, Ar-H); 7.80 (d, 1H, Ar-H); 8.45 (t, 1H, Ar-H); 9.08 (d, 1H, Ar-H); 9.18 (d, 1H, Ar-H); 9.43 (s, 1H, Ar-H); 11.17 (s, 1H, COOH).  $^{13}\text{C}$ NMR (DMSO- $d_6$ ) ppm: 12.58 (2C), 46.52 (2C), 73.18, 92.50, 105.79, 106.33, 114.25, 115.31, 115.74, 123.97 (2C), 128.79, 129.09, 129.80, 130.48, 137.44, 138.45, 139.10, 141.58, 142.78, 147.21, 148.43, 149.32, 150.19, 154.85, 164.76, 169.70, 169.87, 169.97, 171.44. Elemental analysis: MW 652.49 g/mol; found: C, 58.45; H, 3.22; N, 19.01.  $\text{C}_{32}\text{H}_{23}\text{Cl}_2\text{N}_9\text{O}_3$ ; Calculated: C, 58.90; H, 3.55; N, 19.32.

## 2.4. Dyeing of cotton fabrics with synthesized reactive dye

$\text{D}_2$  was nominated for the dyeing application of cotton fabric due to its water solubility. The dyeing process was treated according to Table 1 and Figure 3 with a liquor ratio of 1:30. First, the cotton fabrics were scoured and bleached at 95 °C for 1 hour. Next, the samples were rinsed and neutralized at 70 °C for 30 min. Then the scoured cotton fabrics were dyed with the novel fluorescent reactive dye based on nicotinic acid ( $\text{D}_2$ ) at 0.5, 1, 2, and 4 % o.w.f. The dyeing fixation temperature was 100 °C in neutral conditions and salt-free [25]. Finally, the dyed cotton fabrics were washed at 95 °C for 20 min and rinsed. Dyed cotton fabric is evaluated for color, fixation, exhaustion, and fluorescent properties.



**Figure 3:** The scouring, bleaching, neutralizing, dyeing, washing, and rinsing diagram of synthesized dye ( $\text{D}_2$ ).

**Table 1:** The materials used in the dyeing process of  $\text{D}_2$ .

Process	Materials	g/L
Scouring and bleaching	Sodium hydroxide	4.0
	Anionic detergent	0.8
	Sequestering agent	0.4
	Hydrogen peroxide	5.0
Neutralizing	Sodium silicate	1.5
	Sodium acetate	1.6
Dyeing Buffer	Acetic acid	1.2
	Disodium hydrogen phosphate	5.5
Dyeing	Citric acid	0.5
	Synthesized dye $\text{D}_2$	X %
Washing after dyeing	Anionic detergent	1.0

### 3. Results and Discussion

#### 3.1. Synthesis of dyes

The chemical structures of novel fluorescent dyes based on fused iminocoumarin are illustrated in Figure 2. D<sub>1</sub> is synthesized by the reaction of cyanuric chloride with fused iminocoumarin at -5-10 °C. Then nicotinic acid was added to D<sub>1</sub> at 10-30 °C to synthesize D<sub>2</sub>. Structures of the two dyes were characterized by FTIR, <sup>1</sup>HNMR, <sup>13</sup>CNMR, and elemental analysis. The N-H bond of the imino group at 3412 cm<sup>-1</sup> (stretching) 1577 cm<sup>-1</sup> (bending) was eliminated. The C-Cl bond of D<sub>1</sub> was confirmed at 800 cm<sup>-1</sup>. The C≡N group of fused coumarin is observed at 2232 and 2252 cm<sup>-1</sup> for D<sub>1</sub> and D<sub>2</sub>, respectively. The C=O and C-O of the carboxylic acid group of D<sub>2</sub> were confirmed at 1716 and 1278 cm<sup>-1</sup>, separately. The O-H group's broad stretching and bending were appeared at 2600-3500 cm<sup>-1</sup> and 1405 cm<sup>-1</sup> for D<sub>2</sub>, respectively. The COOH group proton of nicotinic acid was seen at 11.17 ppm in <sup>1</sup>HNMR analysis related to D<sub>2</sub>. The aromatic and aliphatic protons were at 6.62-9.43 and 1.26-3.41 ppm, respectively. The <sup>13</sup>CNMR spectra confirmed the presence of aromatic and aliphatic carbons in structures of dyes sections (2.2 and 2.3).

#### 3.2. Photophysical properties

The photophysical properties of synthesized dyes were investigated in four different solvents; water, DMSO, methanol, and acetone at 5×10<sup>-6</sup> mol/L concentration. The emission properties such as maximum emission wavelength, quantum yield, energy yield, Stokes shift, and oscillator strength were studied. Furthermore, the absorption parameters as maximum absorption wavelength, the half bandwidth, and the molar extinction coefficient were measured (Table 2). The excitation wavelengths in different solvent polarities were measured close to the maximum absorption wavelength of studied fluorescent dyes.

The absorption spectra of fused iminocoumarin (D) showed a maximum wavelength at 544-551 nm with a shoulder peak at 509-515 nm in less polar and more polar solvents. After excitation in a specific wavelength, only one emission spectra was observed. It should be noted that the photophysical calculations are reported based on the maximum absorption wavelength [23].

Maximum absorption wavelengths of D<sub>1</sub> were 525 and 529 nm, while the shoulder peaks were observed at 493 and 497 nm in acetone and DMSO, respectively.

On the other hand, D<sub>2</sub> had the bathochromic shift in maximum absorption (in range of 537-547 nm) and emission (583-596 nm) wavelengths in acetone as a less polar solvent than water. These behaviors are shown a positive solvatochromism effect with both dyes at absorption and emission wavelengths (Figure 4 (a, b)). When the interaction of solute and solvent increases, the positive solvatochromism effect happens. On the other hand, the excited molecule becomes more stable in polar solvents.

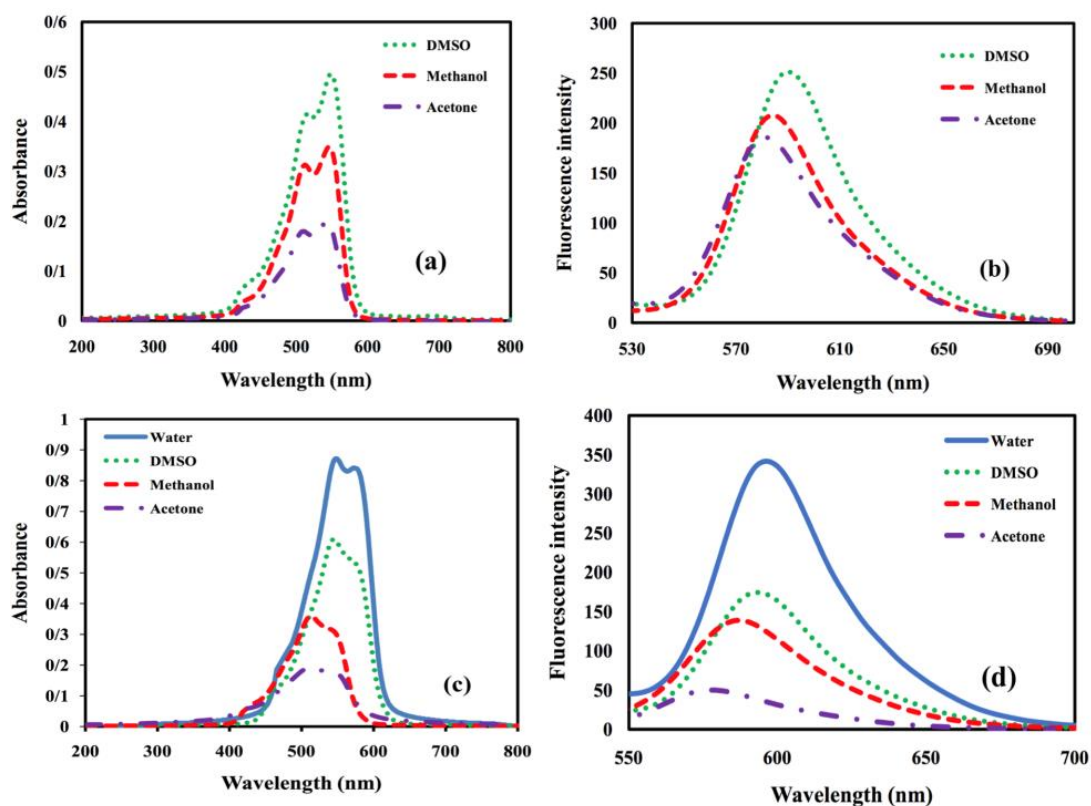
The substitution of polar groups on organic chromophores caused the redistribution of electron density in the ground and excited states, which improved absorption and emission properties [2]. In addition, the dielectric constant of solvents caused an increase in intermolecular charge transfer in the excited state, which made emission with lower energy and higher wavelength [17]. In more polar solvents, the fluorophore in the excited state is stabilized. So, the energy difference between the molecule's ground state and excited state decreased, so the absorption wavelength increased and shifted to the higher wavelengths (redshift) [26].

The molar extinction coefficients of dyes were 18250 Lmol<sup>-1</sup>cm<sup>-1</sup> in DMSO for D<sub>1</sub> and 16430 Lmol<sup>-1</sup>cm<sup>-1</sup> for D<sub>2</sub> in water as red dyes. The half bandwidths show the brilliancy of the dyes, which were 3117-3313 cm<sup>-1</sup> and 3054-3934 cm<sup>-1</sup> for D<sub>1</sub> and D<sub>2</sub> in different solvents, respectively (Table 2). Based on the results, it can be shown that D<sub>2</sub> had higher half bandwidth than D<sub>1</sub>, exhibiting the hypochromic effect [27] and being more opaque than D<sub>1</sub>. This result attributed to nicotinic acid as an auxochrome and increased molecular weight.

The quantum yield is explained as the number of photons emitted to photons absorbed. The quantum yields of synthesized dyes have been measured by the following Equation 1:

$$\Phi_F = \Phi_{ref} \left( \frac{S_{sam}}{S_{ref}} \right) \left( \frac{A_{ref}}{A_{sam}} \right) \left( \frac{n_{sam}}{n_{ref}} \right)^2 \quad (1)$$

where S<sub>sam</sub>, S<sub>ref</sub>, A<sub>sam</sub>, A<sub>ref</sub>, n<sub>sam</sub>, and n<sub>ref</sub> are the emission spectra area, the absorption factor, and refractive index for sample and fluorescein as the reference, respectively.



**Figure 4:** a,b) absorption and emission spectra of D1, c,d) absorption and emission spectra of D2 in different solvents at  $5 \times 10^{-6}$  mol/L concentration.

**Table 2:** The absorption and emission parameters of the synthesized dyes in different solvents.

Solvent		Water	DMSO	Methanol	Acetone
Dielectric constant		80	46	35	20
$\lambda_A$ (nm)	D	---	551	548	544
	D <sub>1</sub>	---	529	527	525
	D <sub>2</sub>	547	545	540	537
$\lambda_F$ (nm)	D	---	595	592	587
	D <sub>1</sub>	---	590	584	581
	D <sub>2</sub>	596	593	587	583
$\epsilon$ (l mol <sup>-1</sup> cm <sup>-1</sup> )	D	---	16738	18976	20435
	D <sub>1</sub>	---	18250	15461	10380
	D <sub>2</sub>	16430	14924	11562	7371
$\Delta\nu_{1/2}$ (cm <sup>-1</sup> )	D	---	2576	2559	2777
	D <sub>1</sub>	---	3117	3196	3313
	D <sub>2</sub>	3054	3079	3139	3934
$(\nu_A - \nu_F)$ (cm <sup>-1</sup> )	D	---	1375	1356	1346
	D <sub>1</sub>	---	1954	1853	1835
	D <sub>2</sub>	1503	1485	1482	1469



Table 2: Continue.

Solvent		Water	DMSO	Methanol	Acetone
$\phi_F$	D	---	0.44	0.50	0.55
	D <sub>1</sub>	---	0.53	0.44	0.27
	D <sub>2</sub>	0.47	0.34	0.32	0.18
E <sub>F</sub>	D	---	0.41	0.46	0.51
	D <sub>1</sub>	---	0.47	0.39	0.24
	D <sub>2</sub>	0.43	0.31	0.29	0.17
$f$	D	---	0.18	0.20	0.24
	D <sub>1</sub>	---	0.24	0.21	0.14
	D <sub>2</sub>	0.21	0.19	0.15	0.12

-D<sub>1</sub> was insoluble in water.

-D: fused iminocoumarin

The value of quantum yield is obtainable in Table 2. The results showed that the quantum yields of the synthesized novel dyes were increased by increasing the dielectric constant of solvents and were 0.27-0.53 and 0.18-0.47 in less polar solvents and more polar solvents for D<sub>1</sub> and D<sub>2</sub>, respectively. This phenomenon is related to the lower aggregation of dye molecules in polar solvents. Furthermore, the interaction between the polar solvents and dye caused the rigidity of dye molecules and increased the quantum yield in polar solvents compared to less polar solvents [18].

The Stokes shift is the term used to describe the difference in the wavelength at which a molecule emits light is relative to the wavelength at which the molecule was excited. This value is calculated by Equation 2 [28]:

$$(v_A - v_F) = \left(\frac{1}{\lambda_A} - \frac{1}{\lambda_F}\right) \times 10^7 \quad (2)$$

Where  $\lambda_F$  and  $\lambda_A$  are the emission and absorption wavelength, respectively. The Stokes shift depends on the solvent polarity and fluorophore environment. When the emitted photons have less energy than the absorbed photons, this energy difference is called the Stokes shift. The solvent polarity, hydrogen bonding, and intermolecular charge transfer influence Stokes shift [29]. Stokes shifts of the synthesized dyes increased by growing the polarity of solvents and were 1835-1954 cm<sup>-1</sup> and 1469-1503 cm<sup>-1</sup> for D<sub>1</sub> and D<sub>2</sub> in a more polar and less polar solvent, respectively. The more significant Stokes shift in more polar solvents is related to the hydrogen bonding interaction between polar solvent and fluorophore and  $\pi \rightarrow \pi^*$  transition.

The energy yield is directly related to quantum yield and changes with the quantum yield changes. This value depends on absorption and emission wavelength values and is calculated by Equation 3 [30]:

$$E_F = \phi_F \left(\frac{\lambda_A}{\lambda_F}\right) \quad (3)$$

The energy yields of D<sub>1</sub> and D<sub>2</sub> were 0.24-0.47 and 0.17-0.43 range in polar and less polar solvents. Those increased with the increment of the polarity of solvents and fluorescence quantum yield.

The oscillator strength was defined as the number of transferred electrons from the ground state to the excited state, measured by Equation 4 [30]:

$$f = 4.32 \times 10^{-9} \times \Delta v_{1/2} \times \varepsilon \quad (4)$$

Where  $\varepsilon$  and  $\Delta v_{1/2}$  are molar extinction coefficients and the half bandwidth of synthesized dyes. The oscillator strengths of novel dyes were in the range of 0.12-0.21 and 0.14-0.24 for D<sub>1</sub> and D<sub>2</sub> in different solvents with different dielectric constants, respectively.

### 3.3. Fixation, exhaustion, and total utilization of dyed cotton fabrics

The scoured and bleached cotton fabrics were dyed with D<sub>2</sub> at 0.5, 1, 2, and 4 % o.w.f. The absorbance of the dye bath solution before dyeing, after dyeing, and after the washing process was measured as A<sub>0</sub>, A<sub>1</sub>, A<sub>2</sub>,

respectively. The percentage of exhaustion (E%), fixation (F%), and total utilization (T%) of dyed cotton fabrics were calculated according to Equations 5-7 [25]:

$$E\% = \frac{A_0 - A_1}{A_0} \times 100\% \quad (5)$$

$$F\% = \frac{A_0 - A_1 - A_2}{A_0 - A_1} \times 100\% \quad (6)$$

$$T = (E \times F) \times 100\% \quad (7)$$

The results showed that the exhaustion of novel cationic fluorescent reactive dye (D<sub>2</sub>) was more than 80 % in all concentrations of dyebath (Figure 5). On the other hand, the fixation of dyed cotton fabrics was reported in the range of 76 – 85 %, which is decreased

by increasing the dye percentage in dyebath's solution due to the growing probability of hydrolysis in water.

### 3.4. Color characteristics

The color characteristics of dyed cotton fabrics (CIEL\*a\*b\*C\*h°- CIE 015: 2018-colourimetry, 4<sup>th</sup> edition) have been illustrated in Figure 6 and Table 3 at 0.5, 1, 2, and 4 % o.w.f. The values of samples have shown that the a\* and b\* values were in a positive and negative region, which expressed that the samples had a blueish red hue. The dyed samples' K/S (color strength) showed the highest K/S for 4 % o.w.f close to 2 % o.w.f at 550 nm as an absorption wavelength. Growing the color strength has enhanced the values of a\*(redness), and b\* (blueness) and reduced the brightness (L\*).

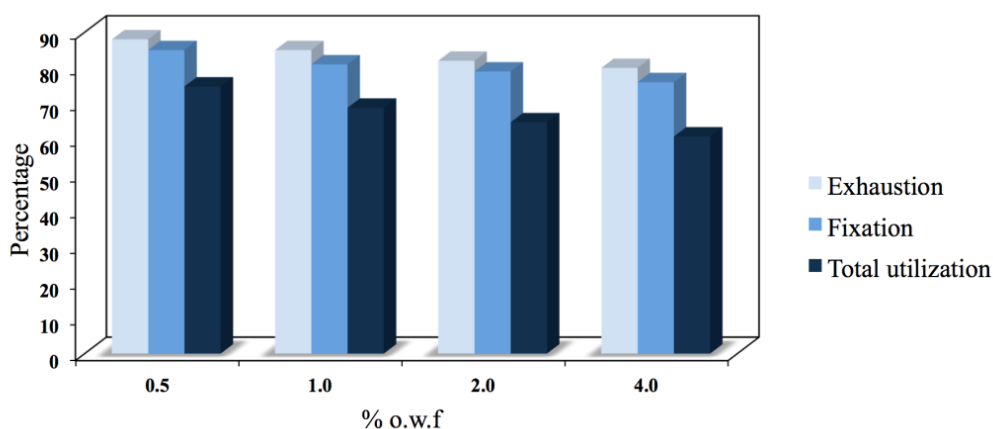


Figure 5: The exhaustion, fixation, and total utilization of dyed cotton fabrics with different concentration.

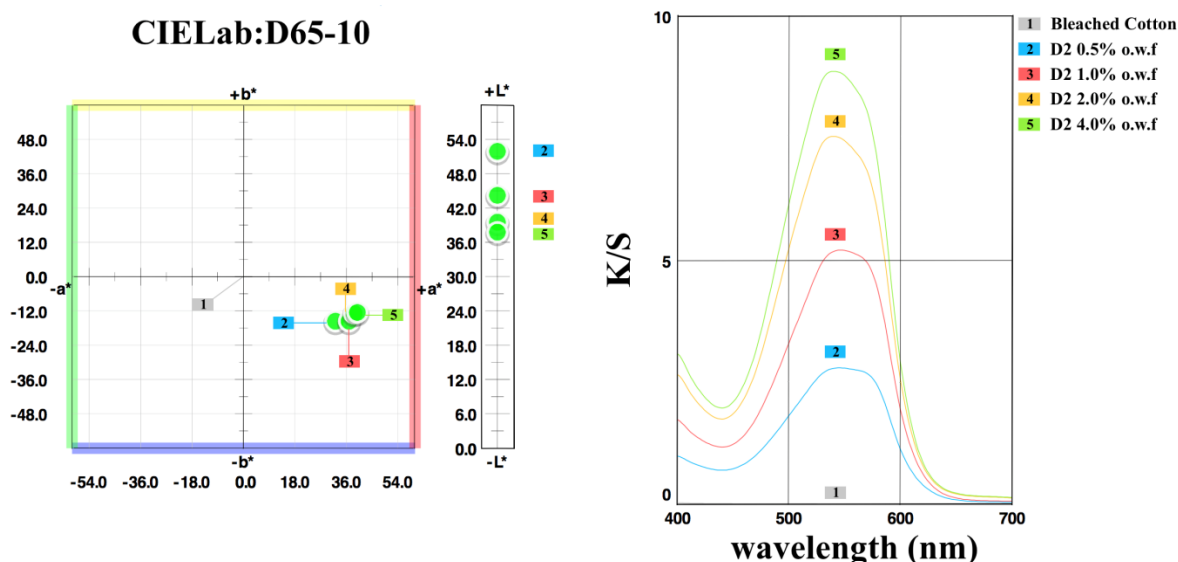


Figure 6: The color characteristics and K/S values of D2 on cotton fabrics in different concentration.



**Table 3:** The color characteristics of dyed cotton fabric with D2 at different concentrations.

o.w.f (%)	L*	a*	b*	C*	h°	K/S
Substrate	91.16	0.99	7.30	7.37	82.80	0.03
0.5	51.92	32.14	-15.56	35.71	334.16	2.79
1.0	44.23	36.90	-15.51	40.03	337.20	5.20
2.0	39.54	38.70	-12.84	40.78	341.65	7.53
4.0	37.79	39.81	-12.50	41.73	342.57	8.86

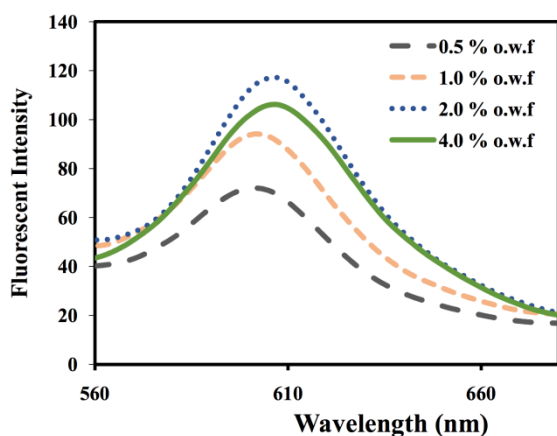
**Table 4:** The colorfastness of dyed cotton fabric with D2.

Light fastness	Rubbing fastness		Washing fastness		Hypochlorite bleaching
(ISO 105-B02: 2014)	(ISO 105-X12: 2016)		(ISO 105-C10: 2006)		(ISO 105-N01: 1993)
	Dry	wet	CH <sup>a</sup>	St <sup>b</sup>	
4-5	4	4-5	4-5	4-5	4

a: Change of shade b: Standing on cotton fabric

### 3.5. Fluorescent properties

The fluorescent properties of dyed cotton fabrics with D<sub>2</sub> have been illustrated in Figure 7. The excitation wavelength in fluorescent intensity measurement was 546 nm. The results showed that the fluorescence intensity has increased with increasing the dye concentration on cotton fabric up to 2 % o.w.f, then decreased in the dyed sample at 4 % o.w.f. This phenomenon indicated the aggregation of dye in higher concentrations on the fiber, which reduced the fluorescence intensity of the dyed fabric.


**Figure 7:** The fluorescent intensity of dyed cotton fabrics with D2 at different concentration.

### 3.6. Color fastness

The color fastnesses of dyed cotton fabrics with D<sub>2</sub> have been evaluated according to light (ISO 105-B02: 2014), rubbing (ISO 105-X12: 2016), washing (ISO 105-C10:2006), and hypochlorite bleaching fastness (ISO 105-N01: 1993). The results demonstrated the light fastness in the range of 4-5 with good rubbing (4-5), washing (4-5), and hypochlorite bleaching (3-4) fastness (Table 4).

## 4. Conclusion

Two novel fluorescent red dyes based on fused iminocoumarin were synthesized. The emission and absorption properties were studied in four solvents with different dielectric constants. The solvatochromism effect of dyes was investigated, which revealed a positive effect. The absorption and emission wavelength of the synthesized dyes were 525-547 nm and 583-596 nm in different solvents, respectively. The product solubility in water was obtained by substituting a nicotinic acid group on D<sub>1</sub>. However, it led to redshift (bathochromic shift) in absorption and emission spectra.

The Stokes shifts of synthesized dyes were higher in the more polar than less polar solvent (1835-1954 cm<sup>-1</sup> for D<sub>1</sub> and 1469-1503 cm<sup>-1</sup> for D<sub>2</sub>). The half bandwidth of D<sub>1</sub> was lower than D<sub>2</sub>, which showed the

brilliance shade due to its narrow absorbance peak. The highest quantum yield of D<sub>1</sub> and D<sub>2</sub> were observed in DMSO (0.53) and water (0.47), respectively. The oscillator strengths of D<sub>2</sub> were lower than D<sub>1</sub> in different polarities of solvents because of its lower molar extinction coefficient. The synthesized water-soluble dye (D<sub>2</sub>) was performed well in dyeing cotton fabrics. The exhaustion and fixation were in the range of 80-88 % and 76-85 % in different depths of dyeing

(% o.w.f), which confirmed the dyeing ability of D<sub>2</sub> as a reactive dye on cotton. The increasing rate of K/S from 2.0 to 4.0 % o.w.f was slower than 0.5 to 2.0 % o.w.f. The dyed sample at 2.0 % o.w.f showed the maximum fluorescent intensity value. Thus D<sub>2</sub> could be introduced as a novel fused iminocoumarin reactive dye with fluorescent properties for dyeing application on cotton fabrics in bluish-red gamut.

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How to cite this article:

M. Souhangir, S. M. Bidoki, K. Gharanjig, Synthesis and Application of a Novel Fluorescent Reactive Dye Based on Fused Iminocoumarin on Cotton Fabric. *Prog. Color Colorants Coat.*, 16 (2023), 71-81.

