

Photophysical Responses of Benzimidazolic and Benzoxazolic Hydroxy Coumarin Dyes

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ARTICLE INFO

Article history:

Received: 05-07-2015

Final Revised: 15-05-2015

Accepted: 01-08-2015

Available online: 01-08-2015

Keywords:

Benzoxazole

Benzimidazole

Coumarin dye

DFT

Fluorescence

ABSTRACT

Four novel benzoxazolic and benzimidazolic derivatives of 6-hydroxycoumarin were synthesized and their photophysical properties were studied as well. The products with brilliant yellow color shades revealed green fluorescence. The emission peaks of the products appeared at 456–474 nm. The important characteristics of fluorescent compounds, including the Stokes shift ($\nu_A - \nu_F$), oscillator strength (f), and fluorescence quantum yield (Φ_F) were measured. Furthermore, their photophysical and electronic properties have been theoretically investigated using density functional theory. Dyeing of nylon fabrics was also carried out by the synthesized fluorescent dyes. The build-up curves of the synthesized dyes generally flatten off at dye concentrations of 2–3 % owf. Prog. Color Colorants Coat. 8 (2015), 247-257 © Institute for Color Science and Technology.

1. Introduction

Due to their intense fluorescence, Coumarin derivatives are known commercially in a broad range of applications [1-6]. These significant fluorescent materials are widely used in laser dyes, fluorescent whiteners, and organic nonlinear optical technologies as important materials in industry [7-10]. Different

biological effects and diverse pharmacological properties are reported for coumarin derivatives as well [8, 11-14].

In addition, applications of these dyes in the coloring or fluorescent whitening of textiles are particularly important. Recently, development of an

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easy microwave assisted method for synthesis of coumarin derivatives was reported [15, 16]. Many interesting molecules having coumarin based-ring systems have been synthesized utilizing novel synthetic techniques. Some new coumarin derivatives were hybrid with the benzoxazoles and benzimidazoles.

To continue our previous studies on Coumarins [1, 16-18] and based on the above cited findings and the potential activity of benzoxazolic and benzimidazolic coumarin derivatives, [5, 12, 19-26] we directed to the synthesis of four novel benzoxazolic and benzimidazolic derivatives of 6-hydroxycoumarin as a key starting material. The targeted compounds **1-4** were synthesized as depicted in Scheme 1 and then their photophysical properties were studied. Due to the application of coumarin derivatives in the coloring or fluorescent whitening of textiles [27], their applications as fluorescent dyes on nylon fiber were also studied.

2. Experimental

2.1. General

Chemicals were purchased from Merck, and used without further purification. $^1\text{H-NMR}$ spectra were measured at 300MHz, using a Bruker 300-Avance Fourier transform (FT-NMR) instrument with dimethyl sulfoxide (DMSO-D_6) as solvent and ^{13}C NMR spectra was measured at 75.5 MHz. Melting points were measured with a Buchi melting-point B-545 apparatus. Elemental analysis for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were measured on a Perkin-Elmer Spectrum One BX FT-IR spectrometer. UV/Vis spectra were recorded using a UV/VIS spectrophotometer, Multispec-1501 Shimadzu. Fluorescence spectra were

measured using Fluorescence Spectrometer Perkin Elmer LS 55. The reflectance characteristics of the dyed samples were measured on a Grating Macbeth 7000 A, color eye reflection spectrophotometer (D65 illumination, 10° observer). Nylon knitted fabric (101 g m^{-2}) was used in this study. Nonionic detergents (Lotensol, Hansa) were utilized for scouring the fabrics. The dyeing of the fabrics was fulfilled in acidic media (glacial acetic acid, Merck) by using the laboratory HT dyeing machine.

2.2. Computational modeling

The structures of coumarin dyes **1-4** were optimized by density functional theory (DFT) level with hybrid functional (B3LYP) and 6-31+G (d) as a basis set without applying restrictions on the symmetry of molecules. Gaussian03 (Revision A.01) program package were used for calculations.

2.3. Dyeing of nylon fabrics and measuring fastness properties

Nylon fabrics (1 g) were treated with 5 g L^{-1} nonionic detergent at 60°C for 20 min in a liquor ratio (L.R) of 50:1 after which, the substrate was rinsed and dried.

Dyeing of nylon fabrics was carried out in a liquor ratio of 50: 1 at 30°C and pH 5-5.5. The temperature of the dye bath was increased to 100°C in 45 min. Then, the dyeing was done for 60 min in 100°C (Figure 1); the dyed samples were then cooled down to room temperature and washed with an aqueous solution of a nonionic detergent (5 g L^{-1}) at 50°C for 20 min.

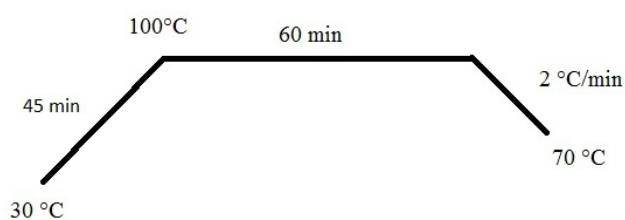


Figure 1: Dyeing procedure of nylon fabrics.

The color strength of dyed fabrics expressed as K/S was measured by the light reflectance technique [28-30], and the relative color strength was calculated by applying the Kubelka-Munk Eq. (1):

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \quad \text{Eq. (1)}$$

where K is the absorbance coefficient, S is the scattering coefficient, R is the reflectance value at λ_{max} (wavelength of maximum absorption). K/S data were directly correlated with the dye concentration present on the dyed substrate.

Light and wash fastnesses of dyed samples were assessed in accordance with ISO 105/B and ISO 105/C2S standards, respectively. The rubbing fastness test was carried out using a crockmeter in accordance with ISO 105-X12:1993.

2.4. General procedure for the preparation of compounds 1-4

A mixture of ortho-phenylenediamine or ortho-phenylenediamine derivatives **c** (5.7 mmol) and ethyl cyanoacetate **b** (0.65 g, 5.7 mmol) and 2,4-dihydroxybenzaldehyde **a** (0.8 g, 5.7 mmol) in n-pentanol (2 ml) containing benzoic acid (0.7 g, 5.7 mmol) were mixed well and irradiated under microwave at atmospheric pressure for 8-10 min at 110 °C, and completion of the reaction was monitored by TLC. The contents were cooled down to room temperature; the solid mixture was suspended in water, filtered and washed with excess water. Finally, pure products **1-4** were obtained by recrystallization in ethanol.

7-Hydroxy-3-(5-methylbenzo[d]oxazol-2-yl)-2H-chromen-2-one, 1. Yellow powder; mp 328-329 °C; IR (KBR) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3425 (OH), 3050 (=C-H Alken), 2978 (CH=), 1721 (C=O), 1602 (C=N). ¹H-NMR (300MHz, DMSO-*d*₆): δ_{H} 2.42 (3H, s, CH₃), 4.35 (1H, bs, OH), 6.77 (1H, s, CH), 6.86 (1H, d, J_{HH} 3 Hz, CH), 7.22 (1H, d, J_{HH} 8.24 Hz, CH), 7.56 (1H, s, CH), 7.62 (1H, d, J_{HH} 8.3 Hz, CH), 7.79 (1H, d, J_{HH} 8.56 Hz, CH), 8.9 (1H, s, CH); ¹³C-NMR (75.5 MHz, DMSO): δ_{C} (CH₃), 101.92 (CH), 109.21 (C), 110.17

(CH), 111.02 (C), 114.11 (CH), 119.46 (CH), 126.62 (CH), 131.7 (CH), 134.3 (C), 141.42 (C), 146.41 (CH), 148.21 (C), 156.35 (C), 156.46 (C), 159.11 (C=O), 163.64 (C).

3-(benzo[d]oxazol-2-yl)-7-Hydroxy-2H-chromen-2-one, 2. Yellow powder; mp 310 °C; IR (KBR) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3435 (OH), 1740 (C=O), 1608 (C=N), 1455 (C-C in ring), 1231 (C-O), 778 (CH Aromatic). ¹H-NMR (300MHz, DMSO-*d*₆): δ_{H} 6.77 (1H, d, J_{HH} 1.75 Hz, CH), 6.86 (1H, dd, J_{HH} 6 Hz, J_{HH} 2.02 Hz, CH), 7.4 (3H, m, CH), 7.7 (3H, m, CH), 8.91 (1H, s, CH); ¹³C-NMR (75.5 MHz, DMSO): δ_{C} 101.94 (CH), 109.04 (C), 110.77 (CH), 110.98 (CH), 114.18 (CH), 119.72 (C), 124.88 (CH), 125.61 (CH), 131.74 (CH), 141.23 (C), 146.61 (CH), 149.93 (C), 156.35 (C), 156.53 (C), 159.06 (C=O), 163.64 (C).

3-(5-chlorobenzo[d]oxazol-2-yl)-7-Hydroxy-2H-chromen-2-one, 3. Orange powder; mp 329 °C; IR (KBR) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3418 (OH), 1732 (C=O), 1615 (C=N), 1232 (C-O), 1186 (C-N), 846 (C-Cl). ¹H-NMR (300MHz, DMSO-*d*₆): δ_{H} 6.75 (1H, s, CH), 6.85 (1H, d, J_{HH} 8.57 Hz, CH), 7.42 (1H, dd, J_{HH} 9 Hz, J_{HH} 1.7 Hz, CH), 7.77 (1H, dd, J_{HH} 9 Hz, J_{HH} 3.75 Hz, CH), 7.85 (1H, s, CH), 8.90 (1H, s, CH); ¹³C-NMR (75.5 MHz, DMSO-*d*₆): δ_{C} 101.94 (CH), 108.50 (C), 110.92 (C), 112.10 (CH), 114.24 (CH), 119.30 (CH), 125.54 (CH), 129.06 (C), 131.88 (CH), 142.48 (C), 147.11 (CH), 148.72 (C), 156.14 (C), 156.65 (C), 160.62 (C=O), 164.07 (CH).

3-(1H-benzo[d]imidazol-2-yl)-7-Hydroxy-2H-chromen-2-one, 4. Yellow powder; mp 381 °C; IR (KBR) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3432 (OH), 1712 (C=O), 1621 (C=N), 1560 (NH), 1251 (C-O), 1129 (C-N aliphatic amine), 741 (CH aromatic). ¹H-NMR (300MHz, DMSO-*d*₆): δ_{H} 6.84 (1H, s, CH), 6.88 (1H, d, J_{HH} 8.59 Hz, CH), 7.18 (2H, m, 2CH), 7.63 (2H, m, 2CH), 7.81 (1H, d, J_{HH} 8.53 Hz, CH), 9.02 (1H, d, J_{HH} 9 Hz, CH), 10.93 (1H, s, OH), 12.42 (1H, bs, NH); ¹³C-NMR (75.5 MHz, DMSO-*d*₆): δ_{C} 101.99 (CH), 111.64 (CH), 111.76 (C), 114.16 (C), 115.38 (C), 122.14 (2CH), 128.56 (C), 129.26 (C), 131.17 (2CH), 143.04 (CH), 146.44 (C), 155.52 (C), 159.69 (C=O), 162.68 (CH).

3. Results and discussion

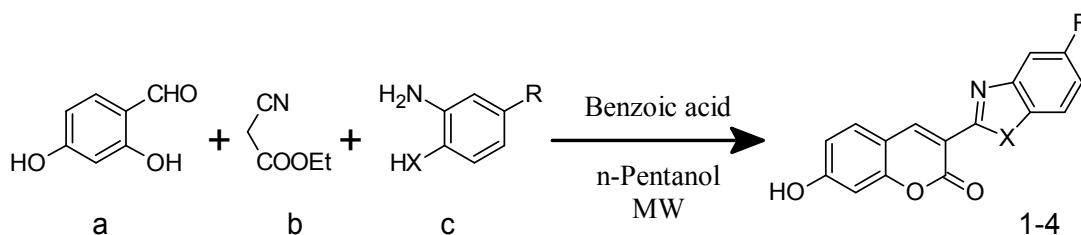
The solvent-free reaction of 2,4-dihydroxybenzaldehyde (**a**) with ethyl cyanoacetate (**b**) and ortho-phenylenediamine or ortho-phenylenediamine derivatives (**c**) in the presence of Benzoic acid under microwave irradiation leads to the corresponding 3-(5-substituted-2-benzoxazolyl)-7-hydroxycoumarin **1-3** and 3-benzimidazolyl-7-hydroxy-Coumarin **4** within less than 10 min (Table 1). The results of the CHN elemental analysis, FT-IR, and ^1H and ^{13}C -NMR spectroscopy clearly confirmed the formation of structures **1-4**. For example, in compound **1**, the peak at 3425 cm^{-1} is due to OH stretch, the peaks at 3050 and 2978 are due to $=\text{C-H}$ alkene, and $\text{CH}=\text{C}$ stretching respectively, $\text{C}=\text{O}$ stretching is indicated at 1721 cm^{-1} , and $\text{C}=\text{N}$ stretching at 1602 cm^{-1} .

The ^1H -NMR spectrum (Figure 2) in $\text{DMSO-}d_6$ shows a singlet at 2.42 ppm for CH_3 protons, a multiple at $6.77\text{--}7.79\text{ ppm}$ for CH protons of phenyls according to the structure as discussed in experimental section in detail, as well as a singlet at 8.9 for CH group on

coumarin moiety. In ^{13}C -NMR, carbons of a coumarin moiety of **1** appeared at 101.92 (CH), 111.02 (C), 114.10 (CH), 131.69 (CH), 134.3 (C), 146.41 (CH), 156.46 (C), 159.11 (C), and 163.06 (C) (Figure 2).

The maximum absorption wavelength of products **1-4** were in the range of $370\text{--}384\text{ nm}$ (Table 1). The color shades of these products were brilliant yellow with reasonably high extinction coefficients of $2.08\text{--}4.07 \times 10^4\text{ (L.M}^{-1}\text{.cm}^{-1}\text{)}$.

Figure 3 shows the excitation and fluorescence emission spectra of the $10^{-5}\text{ mol.L}^{-1}$ concentration of the hydroxycoumarin dyes in acetone at 293 K . All the dyes **1-4** were excited at $370\text{--}384\text{ nm}$ and showed fluorescence emission at a range of $456\text{--}474\text{ nm}$. These products with brilliant yellow color shades revealed green fluorescence. The emission peaks of the products appeared in the same area and similar emission intensities were found for **1-4**.



| Dye | X | R | Time*(min) |
|-----|----|-----------------|------------|
| 1 | O | CH ₃ | 10 |
| 2 | O | H | 13 |
| 3 | O | Cl | 14 |
| 4 | NH | H | 9 |

*The 900W was used as microwave power

scheme 1: Synthesis of hydroxycoumarin dyes **1-4**.

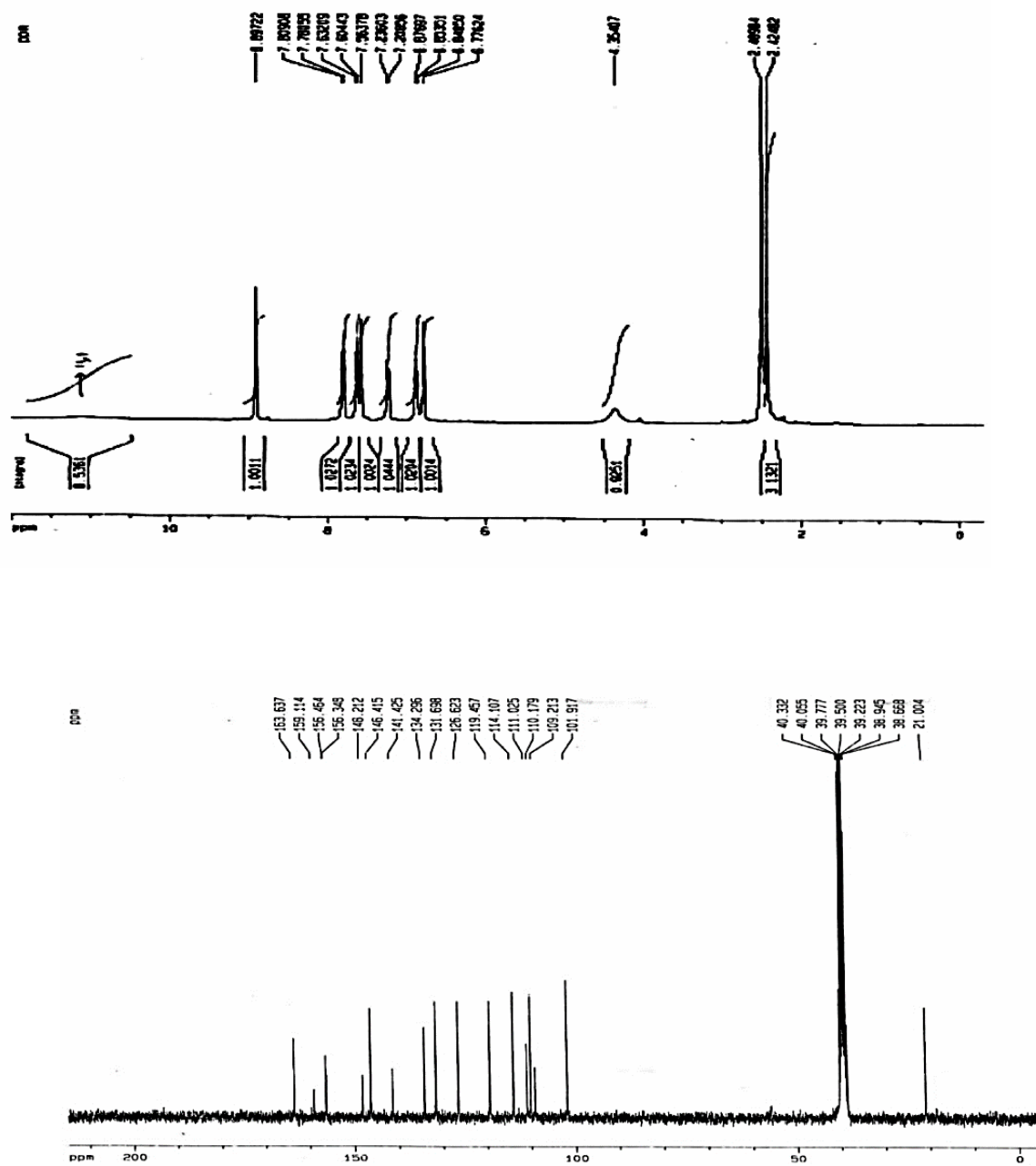


Figure 2: $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectrum of dye 1.

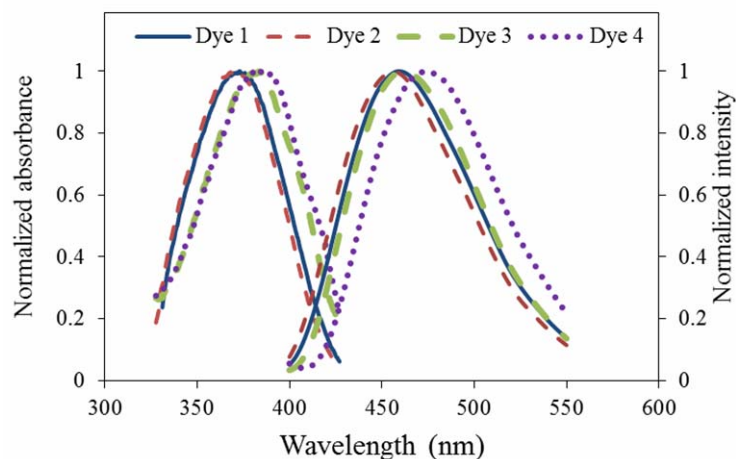


Figure 3: The excitation and fluorescence emission spectra of the hydroxycoumarin dyes in acetone at 293 K.

Two important characteristics of fluorescent compounds, i.e. the Stokes shift ($\nu_A - \nu_F$) and oscillator strength (f) [31, 32] have been studied for the synthesized dyes. The Stokes shift is a parameter that indicates the difference in the properties and structure of the fluorophores between the ground state S_0 and the first excited state S_1 . The Stokes shifts values of the dyes under study were observed between 4148 cm^{-1} and 5024 cm^{-1} (Table 1).

The oscillator strength (f) shows the effective number of electrons whose transition from ground to excited state gives the absorption area in the electron spectrum. The values of the oscillator strength are related to the full width at half maximum absorption band (at ϵ_{max}). The obtained values of oscillator strengths in range of 0.43–0.74 for the hydroxycoumarin dyes are summarized in Table 1.

The fluorescence quantum yield (Φ_F) is the ratio of photons absorbed to photons emitted through fluorescence. As a result, the quantum yield gives the ability of molecules to emit the absorbed light energy. The quantum yield of the dyes was calculated using 1,1,4,4-tetraphenyl-1,3-butadiene ($\Phi_{\text{ref}} = 0.7$) as a reference, and the results are presented in Table 1.

3.1. Molecular modeling

To demonstrate the effect of structural variation on final photophysical properties, molecular modeling was carried out on the new coumarin structures. Results of optimization at the B3LYP/6-31+G(d) level of theory is shown in Figure 4 and Table 2. Dihedral angles and dipole moments revealed that replacing the oxygen atom in 1–3 by NH in 4, due to hydrogen bonding between hydrogen of imidazole and carbonyl of coumarin moiety, improved the molecular planarity, which causes about 18 nm bathochromic shift. This theoretical red shift prediction was confirmed by experimental data (Table 1).

Comparing 1, 2 and 3 structures, electronegativity inductive effect of chlorine reduced both HOMO and LUMO energies, and also coumarin-benzoxazole dihedral angle, which caused more planarity in 3 than 1 and 2.

Table 1: Absorption and fluorescence characteristics of the hydroxycoumarin dyes; 1×10^{-5} molL⁻¹ in acetone at 293 K.

| Dye | λ_{\max}^a (nm) | λ_{em} (nm) | $\epsilon^b \times 10^4$ (L.M ⁻¹ .cm ⁻¹) | $\nu_A - \nu_F$ (cm ⁻¹) | Intensity (au) | f | Φ_F |
|-----|-------------------------|----------------------------|---|-------------------------------------|----------------|------|----------|
| 1 | 373 | 460 | 3.78 | 4439 | 610 | 0.77 | 0.12 |
| 2 | 370 | 456 | 4.07 | 5024 | 696 | 0.84 | 0.12 |
| 3 | 383 | 461 | 2.14 | 4148 | 590 | 0.43 | 0.19 |
| 4 | 384 | 474 | 2.08 | 4610 | 286 | 0.43 | 0.10 |

Acetone was used as solvent; λ_{\max} : wavelength of maximum absorption; λ_{em} : wavelength of maximum emission; ϵ : molar absorption coefficient

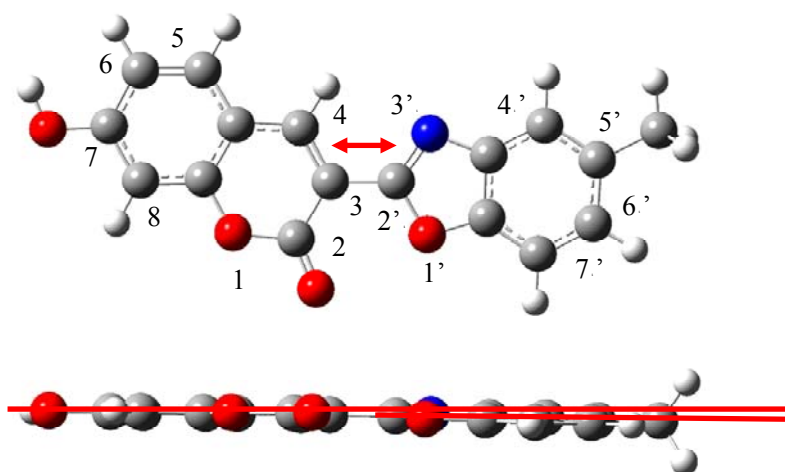

Figure 4: Front and side view of optimized structure of dye 1.

Table 2: Computed parameters for coumarin 1-4 at the B3LYP/6-31+G (d) level of theory.

| Dye | Dipole moment | HOMO | LUMO | λ_{onset}^1 | Bond Length(Å) ² | Dihedral angle ³ |
|-----|---------------|-------|-------|----------------------------|-----------------------------|-----------------------------|
| 1 | 5.62 | -6.06 | -2.56 | 354 | 1.460 | 3.50 |
| 2 | 5.73 | -6.15 | -2.61 | 350 | 1.460 | 3.05 |
| 3 | 6.34 | -6.31 | -2.75 | 348 | 1.459 | 1.04 |
| 4 | 4.95 | -5.89 | -2.52 | 368 | 1.462 | 0.17 |

¹ λ_{onset} : absorption band right edge, ²Bond C3-C2', ³Angle C2-C3-C2'-C1'

3.2. Dyeing properties

All the synthesized dyes were applied to nylon fabrics as explained in section 2.3. Figure 5 illustrates the build-up curves of dyes 1-4. As it is clear from Figure 5, they generally flatten off at dye concentrations of 2-3 % owf. Dyes 2, 3 and 4 have an 'excellent' build-up capability on the nylon fabric samples ($K/S > 30$ where K and S are absorption coefficient and the scatter

coefficient of dyed sample, respectively), whereas dye 1 has a 'very good' build-up property ($K/S > 20$).

The color properties of the dyed nylon samples at 1/1 standard depth according to ISO 105-A06 were measured (Table 3). The leveling properties of the dyes were excellent for all the synthesized dyes. The dye 1 produced yellowish cream hue.

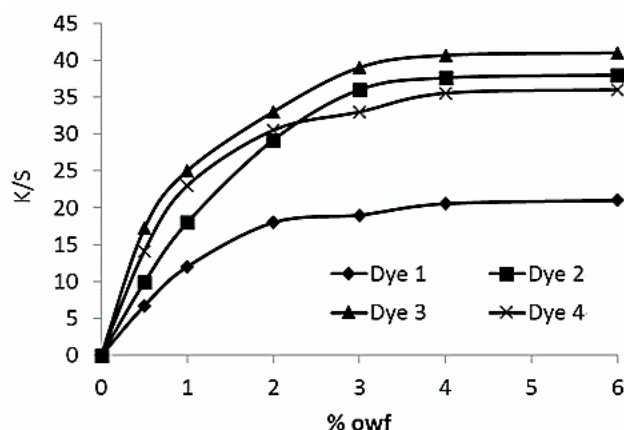


Figure 5: The buildup curves of Dyes 1-4 on nylon fabrics.

Table 3: Color characteristics of dyed nylon fabrics in various concentrations of dyes.

| Dye | % owf | L^*a | a^{*b} | b^{*c} | C^{*d} | h^{*e} | $\lambda_{max}(nm)$ | K/S |
|-----|-------|--------|----------|----------|----------|----------|---------------------|--------|
| 1 | 0.5 | 81.377 | -15.118 | 41.147 | 43.836 | 110.174 | 390 | 6.691 |
| | 2 | 76.294 | -10.051 | 59.135 | 59.984 | 99.646 | 400 | 18.001 |
| | 4 | 72.816 | -7.528 | 58.525 | 59.007 | 97.330 | 400 | 20.541 |
| 2 | 0.5 | 63.962 | -6.065 | 41.277 | 41.720 | 98.359 | 400 | 9.861 |
| | 2 | 55.430 | 1.292 | 48.728 | 48.745 | 88.480 | 400 | 29.194 |
| | 4 | 46.968 | 9.135 | 42.915 | 43.877 | 77.982 | 400 | 37.622 |
| 3 | 0.5 | 73.669 | -4.099 | 49.260 | 49.430 | 94.757 | 390 | 17.161 |
| | 2 | 67.775 | 2.270 | 63.701 | 63.741 | 87.958 | 400 | 33.016 |
| | 4 | 60.118 | 10.462 | 60.058 | 60.962 | 80.118 | 410 | 40.665 |
| 4 | 0.5 | 69.748 | -8.509 | 48.002 | 48.751 | 100.052 | 400 | 14.115 |
| | 2 | 58.032 | -1.721 | 47.553 | 47.584 | 92.0737 | 400 | 30.521 |
| | 4 | 46.110 | 3.103 | 40.209 | 40.329 | 85.586 | 400 | 35.529 |

a: Lightness, b: Red-green coordinate, c: Blue-yellow coordinate, d: Chroma, e: Hue

3.3. Fastness properties

Color fastness properties to light, washing and rubbing were assessed using ISO standard fastness test protocol. The staining, taking place on the dyed cotton fabric was evaluated according to the subsequent gray scale: 1= poor, 2= fair, 3= moderate, 4= good, 5= excellent. The measurement of light fastness of the all dyes on nylon fabrics demonstrated that their light

fastness is less than moderate (4-5). Novel synthesized dyes showed fairly good (4-5 values in grayscale) for the washing and rubbing fastness properties (Table 4).

Fluorescence emission of the dyed nylon fibers was also measured (Figure 6). The dye 1 revealed maximum emission on the nylon and quenched very fast by increasing of the concentration.

Table 4: Color fastness of dyed nylon fabrics with dyes at 1/1 standard depth.

| Dye | L. F ^a | W. F ^b | | | R. F ^c | |
|-----|-------------------|-------------------|----------------|--------|-------------------|-----|
| | | C ^d | N ^e | Change | Dry | Wet |
| 1 | 5 | 4-5 | 4 | 4-5 | 5 | 5 |
| 2 | 4 | 4 | 4 | 4-5 | 4-5 | 4-5 |
| 3 | 4 | 4 | 4 | 4-5 | 5 | 5 |
| 4 | 4 | 4 | 4 | 4-5 | 5 | 5 |

a: Light Fastness; b: Washing Fastness; c; Rubbing Fastness; d: Cotton and e: Nylon.

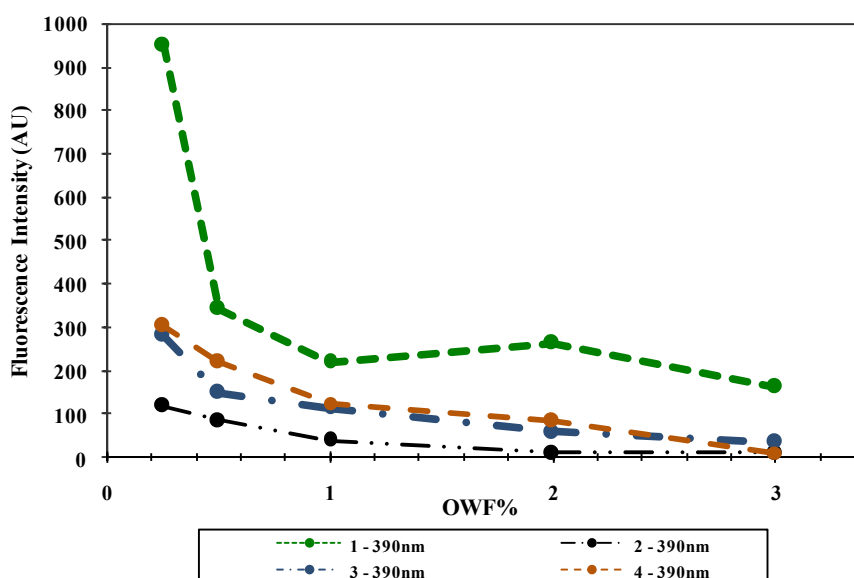


Figure 6: Fluorescence emission of the dyed nylon fibers.

4. Conclusions

Consequently, four fluorescent dyes based on benzoxazolic and benzimidazolic derivatives of 6-hydroxycoumarins were synthesized using solvent-free reaction under microwave irradiation within less than 10min and characterized by FT-IR, ¹H, ¹³C-NMR, and CHN analysis. The emission spectra of the products with brilliant yellow color shades with reasonably high extinction coefficients $2.08 - 4.07 \times 10^4$ (L.M⁻¹.cm⁻¹) and green fluorescence were found in the range of 456–474 nm.

The oscillator strength (f) values of the hydroxycoumarin dyes was 0.43-0.74. The fluorescence quantum yield (Φ_F) using 1,1,4,4-tetraphenyl-1,3-butadiene ($\Phi_{ref}=0.7$) as a reference was

in the range of 0.1-0.19.

Computed photophysical characteristics of the imidazolin based molecule confirmed intramolecular hydrogen bond causing the molecule planar, and red shift in absorption than oxazole based structures. The calculated predictions were in agreement with the obtained experimental data.

The applications of the synthesized compounds as a fluorescent dyes on nylon fiber were illustrated by the build-up curves which generally flatten off at dye concentrations of 2-3 % owf. Dyes 2, 3 and 4 have an excellent build-up capability on the nylon fabric samples (K/S >30), whereas dye 1 has a very good build-up property (K/S >20).

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