

## The Synthesis and Light Absorption Behaviour of Novel Coumarin Chromophores

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**ABSTRACT.** The synthetic route to coumarin systems is well established and one approach of particular interest leads to the intermediate 7-diethylamino-3-formylcoumarin. A combination of the *N,N*-diethylamino-coumarin donor with a wide range of acceptor groups of varying electron withdrawing strength should permit the synthesis of a series of extended coumarin dyes with absorption maxima range from 500 to 600 nm, or even beyond. In this communication, a novel efficient synthesis of indoles, benzothiazole and benzoxazole based on coumarin chromophores were achieved and the coloristic and fluorophoric properties of these chromophores were studied.

**Key words:** Coumarin, Knoevenagel condensation, Fluorescence, Chromophores

### INTRODUCTION

The synthetic coumarins are a colorless compound with intense fluorescence. Such coumarins have been reported to be useful in fluorescence probes, sensors, switches, solar collection and lasers.<sup>1-10</sup> The reasons for their wide range of applications are their spectral properties, mainly the intense fluorescence observed for many derivatives with appropriate substitution. For examples, the coumarins containing benzoxazolyl, benzothiazolyl and benzimidazolyl systems were reported in 1958.<sup>11</sup> The influence of environmental effects on the photophysics of substituted coumarins has been extensively studied with steady state and time resolved spectroscopy.<sup>12-16</sup> Therefore, the coumarin derivatives are widely used for monitoring the polarity and micro-viscosity of the environment in various simple, mixed or ionic solvents. Especially, it is worthy to note that, although hybrid coumarin-cyanine dyes have been broadly, used in fluorescent labeling, fluorescent imaging.<sup>17-21</sup>

### EXPERIMENTAL

All reagent and solvents were of chemical pure grade, purchased from Aldrich or Junsei and were used without further purification. UV/Vis spectra were determined on a Perkin-Elmer Lambda 15 spectrophotometer. The fluorescence was measured on a Luminescence Spectrometer (LS-50). <sup>1</sup>H NMR spectra were recorded on a Bruker AMX 300 MHz FT-NMR spectrometer. Mass spectrometric analyses were performed by a JNSDX 303 Mass spectrometer. Elemental analysis was performed on a PE-4000 instru-

ment. All synthetic reactions were monitored by thin layer chromatography. Melting points were determined on an Electro-thermal IA 900.

#### Synthesis of 7-diethylamino-3-formylcoumarin

4-Diethylaminosalicylaldehyde 17.92 g (93 mmole), diethylmalonate 16.33 g (10.2 mmole) and piperidine (20 ml) were stirred at 40 °C for 12 hours. To this mixture hydrochloric acid (18%) 94 ml was then added. The reaction mixture was stirred under reflux for 5 hours. On cooling the reaction mixture sodium acetate solution 14 ml was added and the pH carefully adjusted to pH 4-5 with aqueous sodium hydroxide solution (45%). The resultant precipitate was filtered off, washed with water, and dried in an oven at 50 °C to give 7-diethylaminocoumarin 17.2 g (77.7%). Dimethylformamide 7.14 g (98 mmole) was added dropwise to phosphorous oxychloride 16 g (104 mmole) at 40 °C. The mixture was then stirred at 50 °C for 45 minutes with exclusion of moisture. To this was added a suspension of the 7-diethylaminocoumarin 15 g (70 mmole) in *N,N*-dimethylformamide 18 g. The reaction mixture was heated to 60 °C and stirred for 2 hours. The orange colored reaction mixture was then poured into ice 150 g and stirred for a further 2 hours. The solid was filtered off, washed with water and dried in an oven at 50 °C, giving 7-diethylamino-3-formylcoumarin 9.6 g (56%). mp: 259-265 °C. Mass spectrum (EI): found *M* = 245 (excepted) required for *M*=245. Anal. Calcd for C<sub>14</sub>H<sub>15</sub>NO<sub>3</sub>: C, 68.56; H, 6.16; N, 5.71%. Found: C, 67.54; H, 5.91; N, 5.42%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 1.23 (t, 6H, *J* = 7.0 Hz), 3.45 (dd, 4H, *J* = 7.0 Hz), 6.45 (d, 1H, *J* = 2.5 Hz), 6.60 (dd, 1H, *J* = 7.2.5 Hz), 7.38 (d, 1H, *J* = 4.5 Hz), 8.22 (s, 1H), 10.09 (s, 1H).

**Synthesis of 2-(2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)vinyl)-1-ethyl-3,3-dimethyl-3H-indol-1-ium iodide (No.1)**

A mixture of 1-ethyl-3,3'-dimethylindolium iodide 18.9 g (60 mmole) and 7-diethylamino-3-formylcoumarin 12.25 g (50 mmole) in absolute ethanol and catalytic amount of piperidine (2 ml) were stirred at room temperature. The reaction mixture was stirred under reflux for 5 hours. The precipitated solid was filtered, washed with ethanol, dried and recrystallized from benzene to yield 22.5 g (83%) as crystalline solid, mp: 259–265 °C. Mass spectrum (EI): found M = 542 (excepted) required for M = 542. Anal. Calcd for C<sub>27</sub>H<sub>31</sub>IN<sub>2</sub>O<sub>2</sub>: C, 59.78; H, 5.76; N, 5.16%. Found: C, 59.99; H, 6.00; N, 4.98%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 1.29 (t, 6H, J = 7.10 Hz), 1.62 (t, 3H, J = 7.24 Hz), 1.84 (s, 6H), 3.52 (quart, 4H, J = 7.16 Hz), 4.86 (quart, 2H, J = 7.27 Hz), 6.46 (d, 1H, J = 2.31 Hz), 6.70 (dd, 1H, J = 9.15 Hz, J = 2.4 Hz), 7.43 (dd, 1H, J = 6.78 Hz, J = 1.53 Hz), 7.49 (multi, 3H), 8.00 (d, 1H, J = 15.9 Hz), 8.21 (d, 1H, J = 9.12 Hz), 8.60 (d, 1H, J = 15.9 Hz), 10.19 (s, 1H)

**Synthesis of 2-(2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)vinyl)-1-propyl-3,3-dimethyl-3H-indol-1-ium iodide (No.2)**

A mixture of 1-propyl-3,3'-dimethylindolium iodide 19.74 g (60 mmole) and 7-diethylamino-3-formylcoumarin 12.25 g (50 mmole) in absolute ethanol and catalytic amount of piperidine (2 ml) were stirred at room temperature. The reaction mixture was stirred under reflux for 5 hours. The precipitated solid was filtered, washed with ethanol, dried and recrystallized from benzene to yield 20.58 g (74%) as crystalline solid, mp: 258–263 °C. Mass spectrum (EI): found M = 556 (excepted) required for M = 556. Anal. Calcd for C<sub>28</sub>H<sub>33</sub>IN<sub>2</sub>O<sub>2</sub>: C, 60.43; H, 5.98; N, 5.03%. Found: C, 60.79; H, 6.20; N, 4.91%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 1.16 (t, 3H, J = 7.34 Hz), 1.28 (t, 6H, J = 7.03 Hz), 1.87 (s, 6H), 2.05 (multi, 2H), 3.52 (quart, 4H, J = 7.16 Hz), 4.77 (t, 2H, J = 6.87 Hz), 6.45 (d, 1H, J = 2.01 Hz), 6.69 (dd, 1H, J = 9.00 Hz, J = 2.22 Hz), 7.49 (multi, 4H), 8.05 (d, 1H, J = 15.8 Hz), 8.17 (d, 1H, J = 9.12 Hz), 8.61 (d, 1H, J = 15.9 Hz), 10.14 (s, 1H).

**Synthesis of 2-(2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)vinyl)-1-butyl-3,3-dimethyl-3H-indol-1-ium iodide (No.3)**

A mixture of 1-butyl-3,3'-dimethylindolium iodide 20.58 g (60 mmole) and 7-diethylamino-3-formylcoumarin 12.25 g (50 mmole) in absolute ethanol and catalytic amount of piperidine (2 ml) were stirred at room temperature. The

reaction mixture was stirred under reflux for 5 hours. The precipitated solid was filtered, washed with ethanol, dried and recrystallized from benzene to yield 22.25 g (78%) as crystalline solid, mp: 260–263 °C. Mass spectrum (EI): found M = 571 (excepted) required for M = 571. Anal. Calcd for C<sub>29</sub>H<sub>35</sub>IN<sub>2</sub>O<sub>2</sub>: C, 61.05; H, 6.18; N, 4.91%. Found: C, 61.23; H, 6.19; N, 5.01%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 1.01 (t, 3H, J = 7.27 Hz), 1.28 (t, 6H, J = 7.10 Hz), 1.61 (multi, 2H), 1.87 (s, 6H), 1.96 (multi, 2H), 3.52 (quart, 4H, J = 7.14 Hz), 4.77 (t, 2H), 6.45 (d, 1H, J = 2.31 Hz), 6.69 (dd, 1H, J = 9.12 Hz, J = 2.4 Hz), 7.47 (multi, 4H), 8.05 (d, 1H, J = 15.8 Hz), 8.17 (d, 1H, J = 9.12 Hz), 8.62 (d, 1H, J = 15.9 Hz), 10.14 (s, 1H).

**Synthesis of 2-(2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)vinyl)-1-hexyl-3,3-dimethyl-3H-indol-1-ium iodide (No.4)**

A mixture of 1-hexyl-3,3'-dimethylindolium iodide 22.26 g (60 mmole) and diethylamino-3-formylcoumarin 12.25 g (50 mmole) in absolute ethanol and catalytic amount of piperidine (2 ml) were stirred at room temperature. The reaction mixture was stirred under reflux for 5 hours. The precipitated solid was filtered, washed with ethanol, dried and recrystallized from benzene to yield 24.24 g (81%) as crystalline solid, mp: 145–155 °C. Mass spectrum (EI): found M = 598 (excepted) required for M = 598. Anal. Calcd for C<sub>31</sub>H<sub>39</sub>IN<sub>2</sub>O<sub>2</sub>: C, 62.20; H, 6.57; N, 4.68%. Found: C, 62.60; H, 6.36; N, 4.88%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 0.87 (t, 3H, J = 7.06 Hz), 1.29 (multi, 10H), 1.56 (multi, 2H), 1.88 (s, 6H), 1.97 (multi, 2H), 3.52 (quart, 4H, J = 7.16 Hz), 4.74 (t, 2H), 6.45 (d, 1H, J = 2.31 Hz), 6.69 (dd, 1H, J = 9.12 Hz, J = 2.4 Hz), 7.47 (multi, 4H), 8.04 (d, 1H, J = 15.81 Hz), 8.14 (d, 1H, J = 9.12 Hz), 8.62 (d, 1H, J = 15.84 Hz), 10.13 (s, 1H).

**Synthesis of 2-(2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)vinyl)-3-ethylbenzo[d]thiazol-3-ium iodide (No.5)**

A mixture of 3-ethylbenzothiazolium iodide 15.25 g (60 mmole) and diethylamino-3-formylcoumarin 12.25 g (50 mmole) in absolute ethanol and catalytic amount of piperidine (2 ml) were stirred at room temperature. The reaction mixture was stirred under reflux for 5 hours. The precipitated solid was filtered, washed with ethanol, dried and recrystallized from benzene to yield 22.36 g (84%) as crystalline solid, mp: 240–245 °C. Mass spectrum (EI): found M = 406 (excepted) required for M = 532. Anal. Calcd for C<sub>24</sub>H<sub>25</sub>IN<sub>2</sub>O<sub>2</sub>S: C, 54.14; H, 4.73; N, 5.26%. Found: C, 51.49; H, 4.80; N, 4.74%. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ (ppm) 1.15 (t, 6H, J = 6.90 Hz), 1.47 (t, 3H, J = 7.09 Hz), 3.52 (quart, 4H, J = 6.86 Hz), 4.78 (quart, 2H, J = 7.19 Hz), 6.66 (d, 1H, J

= 2.12 Hz), 6.86 (dd, 1H,  $J = 9.08$  Hz,  $J = 2.26$  Hz), 7.57 (d, 1H,  $J = 9.10$  Hz), 7.73 (t, 1H,  $J = 7.59$  Hz), 7.83 (t, 1H,  $J = 7.25$  Hz), 8.02 (s, 2H), 8.25 (d, 1H,  $J = 8.34$  Hz), 8.38 (d, 1H,  $J = 7.41$  Hz), 8.63 (s, 1H).

### Synthesis of 2-(2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)vinyl)-3-propylbenzo[d]thiazol-3-ium iodide (No.6)

A mixture of 3-propylbenzothiazolium iodide 19.14 g (60 mmole) and diethylamino-3-formylcoumarin 12.25 g (50 mmole) in absolute ethanol and catalytic amount of piperidine (2 ml) were stirred at room temperature. The reaction mixture was stirred under reflux for 5 hours. The precipitated solid was filtered, washed with ethanol, dried and recrystallized from benzene to yield 21.58 g (79%) as crystalline solid, mp: 235–240 °C. Mass spectrum (EI): found  $M = 546$  (excepted) required for  $M = 546$ . Anal. Calcd for  $C_{25}H_{27}IN_2O_2S$ : C, 54.95; H, 4.98; N, 5.13%. Found: C, 52.67; H, 5.88; N, 4.97%.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 1.17 (t, 3H,  $J = 7.37$  Hz), 1.27 (t, 6H,  $J = 7.14$  Hz), 2.07 (multi, 2H,  $J = 7.34$  Hz), 3.50 (quart, 4H,  $J = 7.15$  Hz), 4.89 (t, 2H,  $J = 7.26$  Hz), 6.46 (d, 1H,  $J = 2.31$  Hz), 6.67 (dd, 1H,  $J = 9.07$  Hz,  $J = 2.42$  Hz), 7.64 (t, 1H,  $J = 6.87$  Hz), 7.74 (multi, 2H), 7.87 (d, 1H,  $J = 9.08$  Hz), 8.15 (d, 1H,  $J = 7.72$  Hz), 8.34 (d, 1H,  $J = 15.21$  Hz), 8.53 (d, 1H,  $J = 15.23$  Hz), 9.54 (s, 1H).

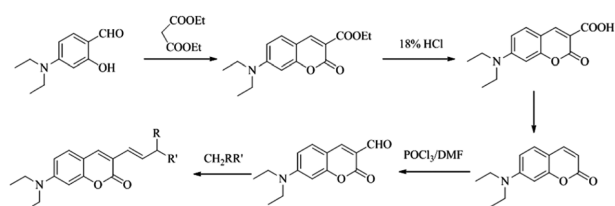
### Synthesis of 2-(2-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)vinyl)-3-hexylbenzo[d]oxazol-3-ium iodide (No.7)

A mixture of 1-hexyl-benzoxazole iodide 20.7 g (60 mmole) and diethylamino-3-formylcoumarin 12.25 g (50 mmole) in absolute ethanol and catalytic amount of piperidine (2 ml) were stirred at room temperature. The reaction mixture was stirred under reflux for 5 hours. The precipitated solid was filtered, washed with ethanol, dried and recrystallized from benzene to yield 26 g (76%) as crystalline solid, mp: 124–128 °C. Mass spectrum (EI): found  $M = 572$  (excepted) required for  $M = 572$ . Anal. Calcd for  $C_{28}H_{33}IN_2O_3$ : C, 58.74; H, 5.81; N, 4.89%. Found: C, 58.21; H, 5.63; N, 4.71%.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 0.87 (t, 3H,  $J = 6.93$  Hz), 1.30 (multi, 10H), 1.57 (multi, 2H), 2.03 (multi, 2H,  $J = 7.60$  Hz), 3.51 (quart, 4H,  $J = 7.13$  Hz), 4.89 (t, 2H,  $J = 7.23$  Hz), 6.45 (d, 1H,  $J = 2.30$  Hz), 6.68 (dd, 1H,  $J = 9.09$  Hz,  $J = 2.42$  Hz), 7.66 (multi, 3H), 7.82 (multi, 1H), 7.96 (d, 1H,  $J = 9.09$  Hz), 8.13 (d, 1H,  $J = 15.37$  Hz), 8.65 (d, 1H,  $J = 15.40$  Hz), 9.68 (s, 1H).

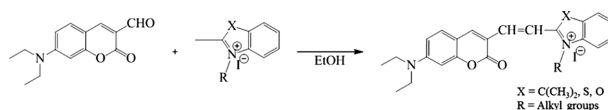
## RESULTS AND DISCUSSION

### Synthesis of Coumarin Derivatives

The general approach to 7-diethylamino-3-formylcoumarin and the derived coumarin dyes is summarized in



**Scheme 1.** The synthetic route of coumarin chromophores.

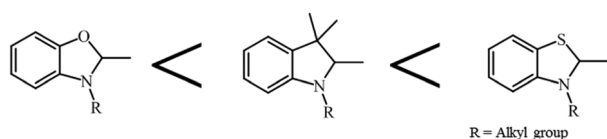


**Scheme 2.** The synthetic route of the new coumarin based chromophores.

*Scheme 1.* Reaction of 4-diethylaminosalicylaldehyde with diethylmalonate, under base catalyzed condition with piperidine gave 7-diethylaminocoumarin-3-carboxylic acid ethyl ester. The carboxylic ester could then be converted to 7-diethylaminocoumarin by refluxing in 18% hydrochloric acid solution, the reaction proceeding via decarboxylation of carboxylic acid intermediate. Vilsmeier formylation of then gave 7-diethylamino-3-formylcoumarin. By condensation the coumarin aldehyde with a suitable active methylene compounds could be synthesized. The new extended coumarin dyes prepared by this general method are listed in *Table 1*.

**Table 1.** Physical characterization data of coumarine compounds

No	Product	Mw (g/mol)	MP (°C)	Purity (%)
1		542.45	259–265	99.6
2		556.48	258–263	99.4
3		570.50	260–263	99.7
4		598.56	145–155	93.4
5		532.44	240–245	95.1
6		546.46	235–240	95.9
7		572.48	124–128	95.7



**Figure 1.** The nucleophilic effect of benzothiazole, indole and benzoxazole.

All compounds were confirmed by  $^1\text{H NMR}$ , MS and EA.

Coumarin aldehydes were synthesized by the conventional Vilsmeier reaction. A complication was encountered in the reaction of 7-diethylamino-3-formylcoumarin with Fisher's base, which gave dye (Fig. 1). The reaction of equimolar quantities of the two species gave pale yellow compounds which slowly turned green with intense fluorescence in the visible region.

### Visible Absorption Spectra of Coumarin Derivatives

The visible absorption spectra of the coumarin dyes were measured in dichloromethane, methanol and *N,N*-dimethylformamide, so giving an indication of solvatochromic behavior. The phenomenon of solvatochromism refers to the change in the ultraviolet, visible and fluorescence spectrum of a compound brought about a change in its surrounding medium, i.e. solvents. The spectral change can involve an alternation in the position, intensity and shape of absorption bands. The term "solvatochromism" was coined by Hantzsch in 1922.<sup>22</sup> Molar extinction coefficients of pure compounds were measured in methanol. The results of the spectral evaluation are summarized in Table 2.

It is a general feature that when the electron acceptor strength is increased within a donor-acceptor system a bathochromic shift is observed.<sup>23–25</sup> This is exemplified within the series of dyes. The bathochromic efficiency of this coumarin compounds is determined by the nucleophilicity of the activated methyl group, i.e. benzothiazole, indoline, benzoxazole. For example, the more electron donating strength (nucleophilicity) of the benzothiazole group in

these dyes affords a useful bathochromic shift compared to the other active methyl groups i.e. indoline and benzoxazole (Fig. 1).

The chromophoric system is typical of coumarin chromophores in that it shows relatively solvatochromism. This can be attributed to the electronic symmetry of such systems and the low dipole moment in the ground and excited states. However this is due to the presence of strong intermolecular hydrogen bonding, which influences the color, i.e. absorbing wavelength and is solvent dependent.

For example, the coumarin chromophores based on indoles (No 1–4) have max (maxima of wavelength) = 600–601 nm in dichloromethane as non-polar solvent, and whereas the coumarin dyes absorb max (maxima of wavelength) = 574–577 nm in methanol as polar solvent with slightly shorter wavelengths. The situation is the same that coumarin dyes containing benzothiazoles and benzoxazoles are absorption maxima in the range max (maxima of wavelength) = 563–581 nm and max (maxima of wavelength) = 534–546 nm in dichloromethane and methanol respectively. The results of the visible absorption spectra in various solvents were summarized in Table 2.

This is steric hindrance, leading to decreased molecular planarity and thus reduced  $\pi$ ,  $\pi$  overlap. Thus bathochromic shift in the series are smaller than expected. Positive solvatochromism (i.e. a bathochromic shift on going from a non-polar to polar solvent) is typical of most donor-acceptor chromophores, and indicates that the excited state is more polar than the ground state. In the series of coumarin dyes, bathochromic shifts vary from about 24–35 nm between methanol and methylene chloride as solvents.

### Fluorescence Emission Spectra of Coumarin Derivatives

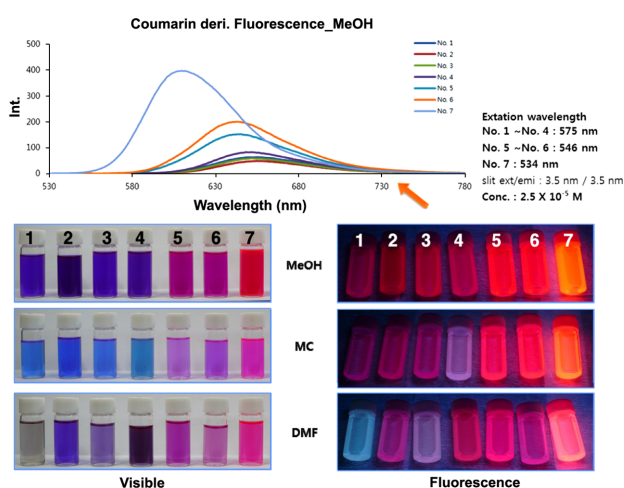
In general, traditional fluorescent dyes have spectral properties in the ultraviolet, visible region. Coumarin, Rhodamine and Phthalocyanine are common visible fluorophores. Fluorescent coumarins have the advantage over

**Table 2.** Light absorption and emission spectra data for coumarin compounds

	$\epsilon_{\text{max}}$ ( $\text{Lmol}^{-1}\text{cm}^{-1}$ ) in Methanol	Methanol			DMF			Dichloromethane		
		$\lambda_{\text{max}}$ (ex)	$\lambda_{\text{max}}$ (em)	Stokes shift	$\lambda_{\text{max}}$ (ex)	$\lambda_{\text{max}}$ (em)	Stokes shift	$\lambda_{\text{max}}$ (ex)	$\lambda_{\text{max}}$ (em)	Stokes shift
No. 1	60,240	574.5	658	83.5	579.5	663	83.5	600.5	669	68.5
No. 2	90,800	578.0	657	79	581.0	661.5	80.5	602.0	661.5	59.5
No. 3	83,920	578.0	656	78	581.0	661	80	602.0	656.5	54.5
No. 4	62,880	577.0	655	78	581.0	656	75	601.5	654.5	53
No. 5	18,623	546.5	645	98.5	553.5	655.5	102	581.0	644.5	63.5
No. 6	64,640	546.5	643	96.5	553.5	658	104.5	581.0	646	65
No. 7	70,080	534.0	609.5	75.5	538.0	627.5	89.5	563.0	610	47

conventional colorimetric indicators of much greater detection sensitivity. Consequently, these have been much recent interest in these, particularly from the biochemical and medical diagnostics areas. The following our experimental result may be adopted to provide this information. The spectral properties of the coumarins synthesized such as absorption maxima max (maxima of wavelength), emission maxima max (maxima of wavelength) were measured in methanol, *N,N*-dimethylformamide and dichloromethane. The coumarin compounds, having the indoline substituents, showed absorption maxima in the range of 574–578 nm in methanol. In *N,N*-dimethylformamide and dichloromethane, they displayed absorption maxima in the range of 579–581 nm and 600–602 nm, respectively. The coumarin based on benzothiazole typed showed absorption maxima at 546 nm in methanol compared to the absorption maxima at 553 and 581 nm in *N,N*-dimethylformamide and dichloromethane, respectively. Finally, the coumarin, having the benzoxazole, showed absorption maxima at 534 nm, 538 nm and 563 nm in methanol, *N,N*-dimethylformamide and dichloromethane, respectively. The indoline typed compounds displayed similar fluorescence spectra in the range of 600–658 nm and benzothiazoles showed in the range of 581–655 nm in a various solvents. In case of benzoxazole typed coumarin showed in the range of 538–609 nm. The coumarin compounds exhibited large Stokes shift of 98 nm and lowest Stokes shift of 53 nm. Thus fluorescence spectra were measured in dichloromethane, methanol and *N,N*-dimethylformamide. The fluorescence data for dyes are summarized in *Table 2*.

To investigate the influence of solvents, their visible



**Figure 2.** The fluorescence spectra of  $2.5 \times 10^{-5}$  M concentration in organic solution with an excitation at 575 nm, 546 nm and 534 nm respectively.

absorption and fluorescence spectra were measured in a series of different solvent such as methanol, dichloromethane and *N,N*-dimethylformamide. Although the bathochromic shift induced by solvatochromism is not large, the visual color change is very obvious for these dyes. For example, these dyes showed the color change in the range of 540–730 nm and the color changes to a more intense bright with almost fluorescent. The color change can be attributed extinction coefficients. The color change phenomenon is shown in *Fig. 2*.

## CONCLUSION

The synthetic route to coumarin systems is well established and one approach of particular interest leads to the intermediate 7-diethylamino-3-formylcoumarin. Knoevenagel type condensation of this aldehyde with active methylene compounds can lead to a coumarin systems with extended conjugation. A combination of the *N,N*-diethylamino-coumarin donor with a wide range of acceptor groups of varying electron withdrawing strength should permit the synthesis of a series of extended coumarin dyes with absorption maxima range from 500 to 600 nm, or even beyond. It was of interest to examine the fluorescence properties of the new coumarin dyes synthesized, as they could have technical value as long wavelength fluorophore. Also, it must be noted that the coumarin compounds did show dramatic color changes in solvent polarity and ability to form H-bond.

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