

Investigation of synthesis two novel fluorescent dyes and their properties

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Abstract—Two novel fluorescent naphthalimide dyes with acetyl amino and amino groups were prepared for the first time by imidation, reduction and acetylation reactions from 4-nitro-1,8-naphthalic anhydride as a starting material. The synthesized dyes were characterized by FTIR, differential scanning calorimetry (DSC), ¹HNMR, ¹³CNMR, Uv-visible and fluorometry spectroscopic techniques. The absorption spectra of the dyes were examined in DMF and wavelength maxima and molar extinction coefficients of dyes were obtained. The fluorescence properties of dyes were evaluated in DMF and their Stokes shift were determined.

Keywords—Synthesis, Fluorescent naphthalimide dye, Characterization, Stock's shift.

I. Introduction

Organic fluorescent dyes have a wide range of applications in cosmetics, paint and coatings, food, inks and textile industries [1]. Moreover they have been specialized in high technology industries such as donor acceptor pairs in fluorescence resonance energy transfer, sensors, solar cells and liquid crystal displays [2,3]. By far many chemical structures of organic fluorescent dyes were synthesized and their properties were studied. One group of fluorescent dyes are 1,8-naphthalimide derivatives which form a distinctive class of compounds with a wide range of applications [4]. 1,8-Naphthalimide derivatives are used as fluorescent dyes for solar energy collectors [5]. They can also be used as yellow daylight fluorescent pigments, fluorescent dichroic dyes in liquid crystal displays and fluorescent brighteners in

detergents, textiles, papers, plastics and paints [6]. Naphthalimide compounds have also been described as an intermediate for the synthesis of derivatives with photosensitizing or chemiluminescent properties for molecular biology markers, potential photosensitive biologically units, analgesics in medicine, light emitting diodes, electroluminescent materials, ion probes and sensors [7]. 1,8-Naphthalimide derivatives with amino groups in the C-4 position have a bright yellow color and show very intense yellow-green fluorescence [6]. Whereas, 4-alkoxy derivatives of 1,8-naphthalimide are well established as a fluorescent brightening agents for polymers with an intensive blue fluorescence [1]. Substitution of an electron donor group at the C-4 position of naphthalimide compounds with amino and acetyl amino groups leads to a large bathochromic shift in both absorption and emission. The length of the shift depends on the strength of the electron donor. For instance alkylamino groups in the C-4 position of naphthalimides display bathochromic shifts up to 50 nm in absorption band and over 100 nm in emission [8]. There have been previous studies about synthesis and properties of 1,8-naphthalimide derivatives and the possibility of obtaining colored or fluorescent polymers [8, 9]. In this study, we report the synthesis and investigation of spectral and fluorescence properties of two novel 4-amino(acetyl amino)-3-aminomethylpyridine-1,8-naphthalimide derivatives using 4-nitro-1,8-naphthalic anhydride and 3-aminomethylpyridine as starting materials. The final products were purified by chromatography method and identified by FTIR, DSC, ¹HNMR and ¹³CNMR techniques.

II. Experimental

Materials and apparatus

Acenaphthene and 3-aminomethylpyridine (Aldrich and Merck, respectively) in pure analysis grade were obtained. All organic solvents (Aldrich, Merck) used in this study were of spectroscopic grades. Melting points (m.p) were determined using a PerkinElmer Pyris used 6 differential scanning calorimeter (DSC). The NMR spectra were recorded with a Bruker DRX AVANCE spectrometer, operating at 500MHz and 125MHz for ¹HNMR and ¹³CNMR, respectively, using a dual 5mm probe head. The measurements were carried out in DMSO-d₆ solution at ambient conditions. The FTIR spectra were recorded on a Perkin Elmer Spectrum One. The UV-visible spectra of dyes were measured with a Cecil 9200 double beam spectrophotometer and then fluorescence spectra

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of dye solutions were evaluated by Osea Optics Usb2000flg Fluorometer. Fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra, using fluorescein as standard ($\Phi_{ref} = 0.95$).

A. Syntheses of intermediates

5-nitroacenaphthene and 4-nitronaphthalic anhydride were prepared according to the literature procedures [6, 8, 10, 11].

B. Synthesis of 4-nitro-N-3-aminomethylpyridine-1,8-naphthalimide

To a solution of 4-nitro-1,8-naphthalic anhydride (1.2 g, 5 mmol) in tetrahydrofuran (20 ml), 3-aminomethylpyridine (0.54 g, 5 mmol) was added dropwise at room temperature. The solution was stirred for 6 h and then filtered. The precipitation was collected and washed with THF (15 ml) to obtain a pale yellow powder. Then the crude product was recrystallised from a mixture of ethanol and dichloromethane (3:7 ratio). A pale-yellow solid (yield: 83%) was obtained.

Mp: 170 °C; $R_f = 0.31$ (ethyl acetate:n-hexane = 2:1); FTIR (KBr, cm^{-1}): 3076 (C–H str. Ar), 2975 (C–H str. Aliphatic), 1706, 1670 (C=O str. Carbonyl groups), 1587 (C=C str. Aromatic ring), 1533, 1337 (NO_2 str. unsym. And sym.); $^1\text{H NMR}$ (500 MHz, DMSO): 5.26 (s, 2H, CH₂), 7.31–7.34 (t, 1H, J = 7.9 Hz, C-5'), 7.79–7.81 (d, 1H, J = 7.9 Hz, C-4'), 8.06–8.09 (t, 1H, J = 8 Hz, C-6), 8.45–8.46 (d, 1H, J = 4.64 Hz, C-6'), 8.52–8.54 (d, 1H, J = 8 Hz, C-3), 8.59 (s, 1H, C-2'), 8.61–8.69 (3H, C-2, C-7, C-5); $^{13}\text{C NMR}$ (125 MHz, DMSO): 42.0, 123.5, 123.6, 124.4, 125.1, 125.4, 127.4, 129.4, 129.8, 130.7, 130.9, 132.8, 133.4, 136.5, 149.3, 150.2, 163.2, 164.0.

C. Synthesis of 4-amino-N-3-aminomethylpyridine-1,8-naphthalimide

A mixture of 5.9 g (18 mmol) 4-nitro-N-3-aminomethylpyridine-1,8-naphthalimide, 20.31 g (90 mmol) stannous chloride and 22.5 ml hydrochloric acid in 90 ml methanol was refluxed for 3 h. The reaction mixture was poured into 300 ml of water and then the precipitated solid filtered off. The crude product was purified by silica gel column chromatography with acetone as eluant. An orange solid (yield: 78%) was obtained. Mp: 350 °C; $R_f = 0.54$ (ethyl acetate:n-hexane = 4:1); FTIR(KBr, cm^{-1}): 3344, 3240 (N–H str. Primary amino group), 1693, 1655 (C=O str. Carbonyl groups), 1580 (C=C str. Aromatic ring); $^1\text{H NMR}$ (500 MHz, DMSO): 5.33 (s, 2H, CH₂), 6.86–6.88 (d, 1H, J = 8.4 Hz, C-3), 7.2–7.23 (t, 1H, J = 6.1 Hz, C-5'), 7.66–7.7 (t, 1H, J = 7.7 Hz, C-6), 7.77 (s, 2H, NH₂), 7.87–7.89 (d, 1H, 7.5 Hz, C-4'), 8.17–8.18 (d, 1H, J = 8.4 Hz, C-2), 8.41–8.42 (2H, C-5, C-7), 8.67–8.69 (2H, C-2', C-6'); $^{13}\text{C NMR}$ (125 MHz, DMSO): 42.8, 103.1, 109.6, 119.1, 120.2, 121.3, 122.3, 122.9, 125.2, 131.5, 133.5, 133.9, 136.8, 154.8, 157.8, 161.2, 162.9, 164.4.

D. Synthesis of 4-acetylaminomethylpyridine-1,8-naphthalimide

4-Amino-N-2-aminomethylpyridine-1,8-naphthalimide (240 mg, 0.8 mmol) was suspended in a mixture of acetic acid (4 ml) and acetic anhydride (2 ml). The suspension of mixture was refluxed for 5 h. Then it was cooled down to room temperature and neutralized with 20 ml of a 10% sodium hydroxide solution and the desired product was precipitated. The crude product was recrystallised in ethanol. A pale yellow solid (yield: 66%) was obtained. Mp: 276 °C; $R_f = 0.86$ (methanol: chloroform = 1:1); FTIR (KBr, cm^{-1}): 3450 (N–H str. Secondary amino group), 1762, 1727 (C=O str. Carbonyl groups), 1676 (C=O str. Acetyl amino group), 1586 (C=C str. Aromatic ring); $^1\text{H NMR}$ (500 MHz, DMSO): 2.29 (s, 3H, CH₃), 5.4 (s, 2H, CH₂), 7.2–7.5 (2H, C-3, C-5'), 7.8–7.94 (2H, C-6, C-4'), 8.37–8.39 (d, 1H, J = 8.2 Hz, C-2), 8.49–8.55 (2H, C-5, C-7), 8.7–8.8 (2H, C-2', C-6'), 10.48 (s, 1H, NH); $^{13}\text{C NMR}$ (125 MHz, DMSO): 25.0, 42.01, 114.4, 119.8, 119.9, 121.4, 122.9, 124.6, 127.4, 131.2, 131.6, 133.4, 134.45, 136.76, 142.3, 154.8, 157.8, 161.0, 161.8, 170.6.

III. Results and discussion

The two novel fluorescent dyes were synthesized by using 4-nitro-1,8-naphthalic anhydride as starting material. The preparation of these dyes was carried out by imidation, reduction and acetylation reactions. The process of reactions is illustrated in Figure 1. Dye 2 is synthesized through reduction of 4-nitro-N-3-aminomethylpyridine-1,8-naphthalimide. The reduction of nitro group on naphthalimide ring was carried out by stannous chloride and hydrochloric acid in alcoholic medium under reflux conditions. The results of DSC, R_f values, color and yield of reaction of the prepared dyes are represented in Table I. The FTIR spectra of the synthesized dye 2 showed primary amino group (NH₂) in 3344, 3240 cm^{-1} . Also, the $^1\text{H NMR}$ spectra of the dye 2 demonstrated the presence of primary amino group protons as a singlet peak in 7.77 ppm. The dye 3 was prepared through acetylation reaction of dye 2. Dye 2 reacted with acetic anhydride under reflux conditions for 6 h. The FTIR spectrum of the dye 3 was confirmed by the presence of secondary aromatic amine (NH-R) in 3450 cm^{-1} . The difference data of $^1\text{H NMR}$ spectra between dye 2 and 3 was confirmed the presence of the singlet peak in region 10.48 ppm which is related to the proton of acetyl amino (NHCOCH₃) group in dye 3. The FTIR, $^1\text{H NMR}$ and $^{13}\text{C NMR}$ of two dyes (2 and 3) are demonstrated in Table II.

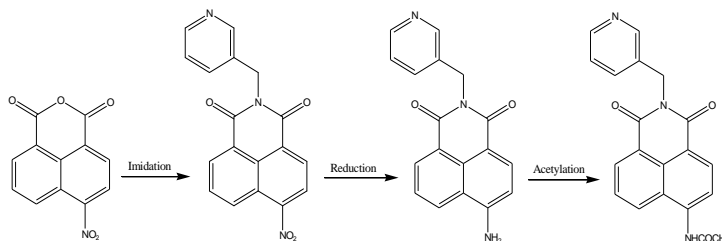


Fig. 1. The route of synthesis of dyes

Table I. The yield of reaction, melting point, R_f values, color synthesized dyes and intermediate

Dye	Yield (%)	M.p. (°C)	R_f	Color
1	83	170	0.31	Pale yellow
2	78	350	0.54	Orange
3	66	276	0.86	Pale yellow

TABLE II. The FTIR, ^1H NMR and ^{13}C NMR spectra of final dyes and intermediate

Dye	FTIR	^1H NMR	^{13}C NMR
1	1706, 1670 (C=O str. Carbonyl groups), 1533, 1337 (NO ₂ str. Nitro)	5.26 (H, Aliphatic), 7.31-8.69 (H, Aromatic)	42 (C,aliphatic) 123.5-164 (C,Aromatic)
2	3370, 3211 (NH ₂ str.) 1688,1659(C=O str. Carbonyl)	5.32 (H, Aliphatic) 7.48 (2H, NH ₂) 6.85-8.66 (H, Aromatic)	44.9 (C,aliphatic) 108-165 (C,Aromatic)
3	1655 (C=O str. Acetyl) 1740,1694 (C=O str.carbonyl) 3440 (N-H str.)	2.29,5.36(H,Aliphatic) 7.21- 8.57 (H, Aromatic) 10.42 (H, NH)	25,45(C,aliphatic) 118-170 (C,Aromatic)

The spectrophotometric and fluorescent data of dyes solutions in DMF is shown in Table 2. The absorption bands of these dyes were in 427 and 372 nm for dyes 2 and 3, respectively.

In DMF solution, dye 2 shows intense yellow-green fluorescence due to the charge transfer in the naphthalimide units from the electron donating amino group at C-4 position to the accepting carbonyl groups. Whilst dye 3 demonstrates blue emission at 372 nm.

The maximum wavelengths of naphthalimide dyes are related to the charge transfer of electron donating group from C-4 position to carbonyl groups as accepting groups. In dye 2 the electron donor group is amino group which is a strong donor group, whereas in dye 3 the substitution on naphthalimide ring in C-4 position is an acetylamino group, which is a weak electron donating group. Therefore, the dye 3 display a hypsochromic effect compared to the dye 2. The hypsochromic shift of dye 3 in DMF is shown in Figure 2. The extinction coefficients of dyes 2 and 3 solutions in DMF are 1.5×10^4 and $1.6 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$, respectively.

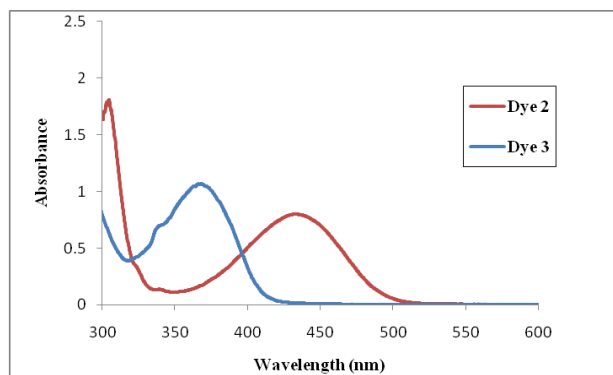


Fig. 2. The absorption spectra of dyes 2 and 3 at concentration of $10^{-4} \text{ mol l}^{-1}$ in DMF

The Stokes shift ($\nu_A - \nu_F$), oscillator strength (f) and quantum yield (Φ_F) are important properties for the fluorescent dyes. The Stokes shift is a parameter that represents the differences in the properties and structure of the fluorescent compounds between the ground state and the first excited state. The Stokes shifts of dyes 2 and 3 were determined by Eq. (1) [12].

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

Where $\nu_A - \nu_F$ is Stokes shift, λ_A and λ_F are absorption and fluorescence maxima, respectively. The Stokes shift value of the acetylamino substituted 1,8-naphthalimide dye 3 (6600 cm^{-1}) was higher than amino derivative of 1,8-naphthalimide substituted dye 2 (4620 cm^{-1}).

As the dipole moment of the molecule is enhanced upon excitation due to electron density redistribution, the excited molecule is more stabilized in polar solvents, such as DMF, because of stronger interaction with the solvent dipoles [6]. This effect cause the red shift in the fluorescence maxima resulting in large-scale addition of the Stokes shift value for acetylamino substituted 1,8-naphthalimide [13].

The oscillator strength (f) demonstrates the effective number of electrons which their transition from ground to excited state gives the absorption area in the electron spectrum. Values of oscillator strength were calculated by Equation 2 [6].

$$f = 4.32 \times 10^{-9} \Delta \nu_{1/2} \epsilon_{\max} \quad \text{Eq.2}$$

Where $\Delta \nu_{1/2}$ is the width of the absorption band at $1/2 \epsilon_{\max}$. For the dye 3 which has acetylamino group as a substituent at the C-4 position, the f value is higher than dye 2 with NH₂ group in C-4 position. The fluorescence quantum yield of fluorescent compounds evaluates by the capability of the molecules to emit the absorbed light energy. The quantum yield of fluorescent compound was calculated using fluorescein ($\Phi_{\text{ref}} = 0.95$) as a standard material according to Equation 3 [13].

$$\Phi_F = \Phi_{ref} \left(\frac{S_{sample}}{S_{ref}} \right) \left(\frac{A_{ref}}{A_{sample}} \right) \left(\frac{n_{sample}^2}{n_{ref}^2} \right) \quad \text{Eq. 3}$$

Where, Φ_F is quantum yield of samples, Φ_{ref} is quantum yield of fluorescein, A_{ref} , S_{ref} , n_{ref} and A_{sample} , S_{sample} , n_{sample} are the absorbance at the excited wavelengths, the integrated emission band area and the solvent refractive index of the standard and the sample, respectively. The quantum yields of synthesized dyes 2 and 3 are 0.54 and 0.33, respectively. The energy yield of fluorescence was obtained by using Eq. 4 [13].

$$E_F = \Phi_F \frac{\lambda_A}{\lambda_F} \quad \text{Eq. 3}$$

The spectrophotometric and fluorescent data of dyes 2 and 3 are depicted in Table III.

TABLE III: The spectrophotometric and fluorescent data of dyes 2 and 3 in DMF

Dye	$\nu_A - \nu_F (cm^{-1})$	f	Φ_F	$\lambda_F (nm)$	$\lambda_A (nm)$
2	4620	0.492	0.54	532	427
3	6600	0.525	0.33	493	372

IV. Conclusions

Two novel fluorescent dyes based on naphthalimide derivatives containing amino and acetylamino groups were synthesized by using imidation, reduction and acetylation processes. The dyes and intermediate were characterized by DSC, FTIR, ¹HNMR, ¹³CNMR and UV-visible techniques. The spectrophotometric and fluorescence properties of the synthesized dyes in DMF solvent were examined. The results showed that dye 2 containing amino group in C-4 position of naphthalimide ring has fluorescence wavelength higher than dye 3 containing acetylamino group. Dye incorporated with amino group in C-4 position of naphthalimide ring has quantum yield higher than that containing acetylamino group. The Stokes shift value of the acetylamino substituted 1,8-naphthalimide of dye 3 was higher than amino derivative of 1,8-naphthalimide substituted of dye 2.

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