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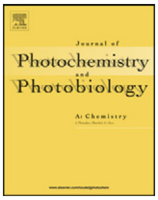

Synthesis and photophysical properties of some novel fluorescent dyes based on naphthalimide derivatives

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ABSTRACT

A series of novel naphthalimide dyes with amino and acetylamino functional groups were synthesized through imidation, reduction and acetylation reactions on 4-nitro-1,8-naphthalic anhydride. The synthesized dyes were characterized by DSC, TLC (R_f values), FTIR, ^{1}HNMR, ^{13}CNMR, UV–visible and Fluorometery. Molar extinction coefficients and wavelength maxima were obtained by examining dye solutions in DMF and THF. The results demonstrated that the synthesized dyes have wavelength maxima ranging from 372 to 433 nm in DMF and 370 to 419 nm in THF and molar extinction coefficients 1.1×10^4–1.9×10^4 l mol^{-1} cm^{-1} in DMF and 0.84×10^4–1.4×10^4 l mol^{-1} cm^{-1} in THF. The absorption spectra of dyes showed that grafting N-substituted naphthalimides does not affect their color whilst the type of substitutions in C-4 position of naphthalimide very effectively changes the color. The fluorescency of these dyes was evaluated and their Stokes shift values were determined as DMF and THF solutions. The results demonstrated that all dyes had fluorescence properties and Stokes shift values were between 4000 and 6600 cm^{-1} in DMF and 3880 cm^{-1} and 6400 cm^{-1} in THF. Measuring of quantum yields of dyes showed that dyes containing N-ester group had the highest and dyes containing 4-acetylamino group had the lowest quantum yield.

1. Introduction

Organic fluorescent dyes have a wide range of applications in cosmetics, paint and coatings, food, inks and textile industries [1,2]. 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 [3–13]. By far many chemical structures of organic fluorescent dyes were synthesized and their properties studied. One group of fluorescent dyes are 1,8-naphthalimide derivatives which form a distinctive class of compounds with a wide range of applications [14,15]. 1,8-Naphthalimide derivatives are used as fluorescent dyes for solar energy collectors [16]. 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 [17–21].

Naphthalimide compounds have also been described as an intermediate for the synthesis of derivatives with photosensiting or chemiluminescent properties for molecular biology markers, potential photosensitive biologically units, analgesics in medicine, light emitting diodes, electroluminescent materials, ion probes and sensors [22–26].

1,8-Naphthalimide derivatives with amino groups in the C-4 position have a bright yellow color and show very intense yellow-green fluorescency [27]. Whereas, 4-alkoxy derivatives of 1,8-naphthalimide are well established as 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 acetylamino 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 [28]. There have been previous studies about synthesis and properties of 1,8-naphthalimide derivatives and the possibility of obtaining colored or fluorescent polymers [26,27]. Besides of improvement of the range of fluorescent dyes based on naphthalimides with donor groups in C-4 position, the aim of this research is investigation of color and fluorescent properties of some of these dyes containing N-aminomethylpyridine group. The presence of aminomethylpyridine group in N-position of naphthalimides has provided new applications of these dyes. Cationization of

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aminomethylpyridine group in these dyes might be cause antimicrobial properties which is very significant in dyeing of textiles. The authors report the synthesis procedure and characterization of some novel 4-amino(4-acetylamino)-N-aminomethylpyridine-1,8-naphthalimide derivatives using 4-nitro-1,8-naphthalic anhydride and aminomethylpyridine as starting materials. All products were purified and characterized with FTIR, TLC (R_f values), ^{1}HNMR, ^{13}CNMR, DSC, UV–visible and Fluorometery. The absorption and emission spectra of the synthesized dyes have also been investigated and compared with spectral properties of 4-amino-N-ethylglycinate-1,8-naphthalimide.

2. Experimental

2.1. Materials

The synthesis methods of 5-nitroacenaphthene, 4-nitro-1,8-naphthalic anhydride, 4-nitro-N-ethylglycinate and 4-amino-N-ethylglycinate-1,8-naphthalimide are reported in the literature [29–31]. Acenaphthene, 2-aminomethylpyridine and 3-aminomethylpyridine (Aldrich and Merck, respectively) in pure analysis grade were used as obtained. All organic solvents (Aldrich, Merck) used in this study were of spectroscopic grades.

2.2. Instrumentation

Melting points (m.p) were determined using a PerkinElmer Pyris 6 differential scanning calorimeter (DSC). The NMR spectra were recorded with a Bruker DRX AVANCE spectrometer, operating at 500 MHz and 125 MHz for ^{1}HNMR and ^{13}CNMR, respectively, using a dual 5 mm 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. TLC was performed on silica gel, Fluka F60 254, 20 × 20, 0.2 mm, using the solvent systems of ethyl acetate:n-hexane = (2:1) and methanol:chloroform = (1:1) as eluants. All dyes were used as DMF and THF solutions with five different concentrations of 2×10^{-5} M, 4×10^{-5} M, 6×10^{-5} M, 8×10^{-5} M and 1×10^{-4} M. The UV–visible spectra of dyes were measured with a Cecil 9200 double beam spectrophotometer and then fluorescence spectra of dye solutions were evaluated by Osean Optics Usb2000flg Fluorometer. Fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra, using fluorescein as standard ($\Phi_{ref} = 0.95$). To obtain quantum yield for each dye, a solution of the synthesized dyes were prepared in DMF and THF solutions with concentration of 10^{-4} M and then absorption and emission values of them were assessed by absorption spectrophotometer and fluorometer in maximum wavelength, separately. The quantum yields of dyes were determined by using Eq. (3).

2.3. Synthesis of dyes and their intermediates

2.3.1. Synthesis of 4-nitro-N-2-aminomethylpyridine-1,8-naphthalimide (2)

To a solution of 4-nitro-1,8-naphthalic anhydride (1.2 g, 5 mmol) in tetrahydrofuran (20 ml), 2-aminomethylpyridine (0.54 g, 5 mmol) was added dropwise at room temperature. The solution was stirred for 5 h to obtain a pale yellow powder. The precipitate was collected and washed with THF (10 ml). Then the crude product was recrystallised from a mixture of ethanol and dichloromethane (2:8 ratio). Yield: 85%; m.p: 191 °C; $R_f = 0.66$ (ethyl acetate:n-hexane = 2:1); FTIR (KBr, cm^{-1}): 3073 (C–H str. Ar), 2928 (C–H str. Aliphatic), 1708, 1668 (C=O str. Carbonyl groups), 1590 (C=C str. Aromatic ring), 1528, 1339 (NO_2 str. unsym. and sym.); ^{1}HNMR (500 MHz, DMSO): 5.36 (s, 2H, CH_2), 7.22–7.25 (t, 1H, $J = 6.1$ Hz, C-5′), 7.43–7.45 (d, 1H, $J = 7.9$ Hz, C-3′), 7.72–7.75 (t, 1H, $J = 7.7$ Hz, C-4′), 8.05–8.08 (t, 1H, $J = 8$ Hz, C-6), 8.39–8.4 (d, 1H, $J = 4.5$ Hz, C-6′), 8.51–8.53 (d, 1H, $J = 8$ Hz, C-3), 8.56–8.59 (2H, C-2, C-7), 8.67–8.69 (d, 1H, $J = 8.6$ Hz, C-5); ^{13}CNMR (125 MHz, DMSO): 45.4, 121.9, 123.1, 123.3, 123.6, 125.2, 127.1, 129.2, 129.9, 130.8, 131, 132.8, 137.6, 149.8, 150.1, 156.3, 162.9, 163.7.

2.3.2. Synthesis of 4-nitro-N-3-aminomethylpyridine-1,8-naphthalimide (5)

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. A pale yellow precipitate was obtained. The solid was washed with THF (10 ml). Then the precipitate was recrystallised from a mixture of ethanol and dichloromethane (3:7). Yield: 83%; m.p: 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}HNMR (500 MHz, DMSO): 5.26 (s, 2H, CH_2), 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}CNMR (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.

2.3.3. Synthesis of 4-amino-N-2-aminomethylpyridine-1,8-naphthalimide (3)

A mixture of 5.9 g (18 mmol) 4-nitro-N-2-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 water and the precipitated solid filtered off. The crude product was purified by silica gel column chromatography with acetone as eluant. Yield: 82%; m.p: 288 °C; $R_f = 0.74$ (ethyl acetate:n-hexane = 2:1); FTIR (KBr, cm^{-1}): 3370, 3211 (N–H str. Primary amino group), 1688, 1659 (C=O str. Carbonyl groups), 1579 (C=C str. Aromatic ring); ^{1}HNMR (500 MHz, DMSO): 5.32 (s, 2H, CH_2), 6.85–6.87 (d, 1H, $J = 8.3$ Hz, C-3), 7.19–7.22 (t, 1H, $J = 6.2$ Hz, C-5′), 7.24–7.26 (d, 1H, $J = 7.9$ Hz, C-3′), 7.48 (s, 2H, NH_2), 7.65–7.71 (2H, C-4′, C-6), 8.18–8.2 (d, 1H, $J = 8.3$ Hz, C-2), 8.39–8.43 (2H, C-5, C-7), 8.64–8.66 (d, 1H, $J = 8.4$ Hz, C-6′); ^{13}CNMR (125 MHz, DMSO): 44.9, 108.3, 109.1, 120.3, 121.5, 122.6, 122.8, 124.9, 130.4, 130.8, 132.1, 135.0, 137.5, 149.7, 153.8, 157.5, 163.7, 164.7.

2.3.4. Synthesis of 4-amino-N-3-aminomethylpyridine-1,8-naphthalimide (6)

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 water and the precipitated solid filtered off. The crude product was purified by column chromatography (silica gel, eluant: acetone). Yield: 78%; m.p: 350 °C; $R_f = 0.54$ (ethyl acetate:n-hexane = 2:1); 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}HNMR (500 MHz, DMSO): 5.33 (s, 2H, CH_2), 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, NH_2), 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}CNMR (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.

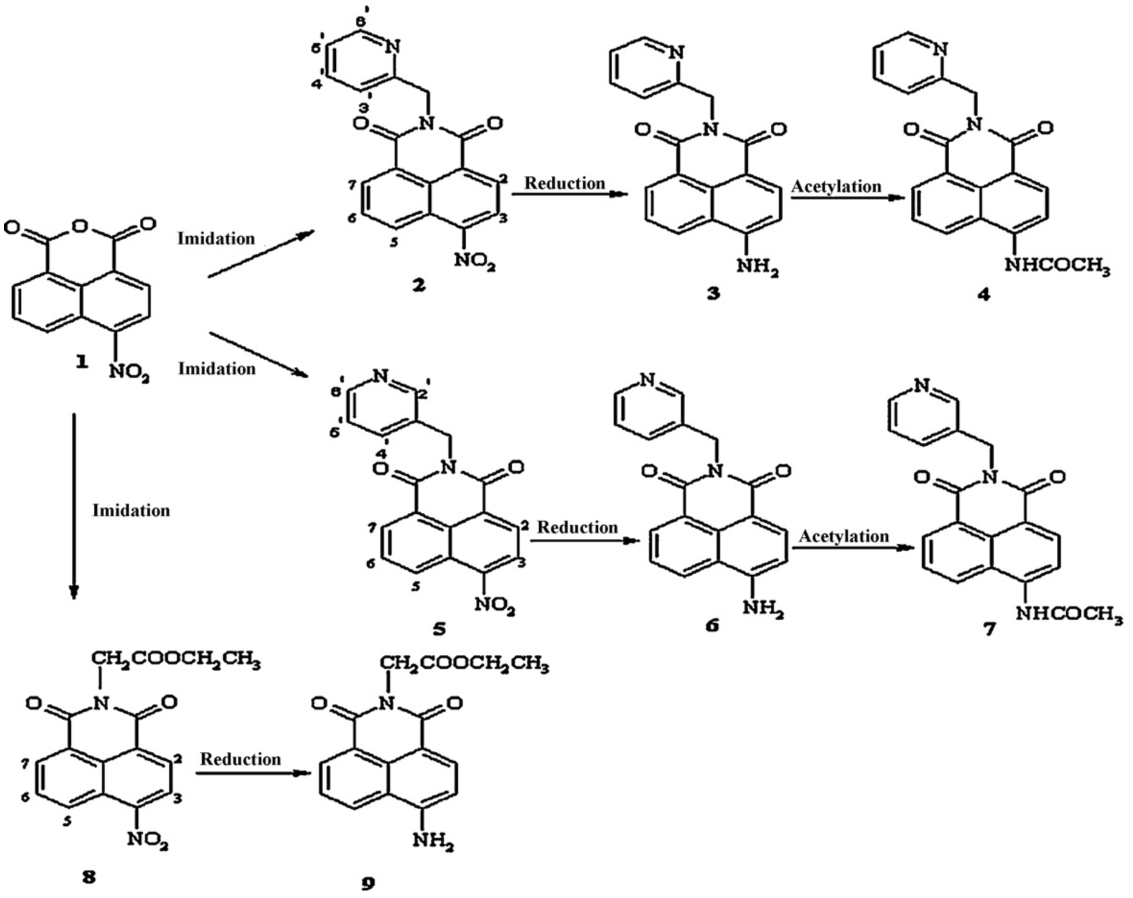

Fig. 1. Synthesis of dyes and their intermediates.

2.3.5. *Synthesis of 4-acetylamino-N-2-aminomethylpyridine-1,8-naphthalimide (4)*

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 was refluxed for 5 h. Then it was cooled down to room temperature and neutralized with 10 ml of a 10% sodium hydroxide solution and the desired product precipitated. The crude product was recrystallised in ethanol. Yield: 63%; m.p: 232 °C; $R_f = 0.81$ (methanol:chloroform = 1:1); FTIR (KBr, cm^{-1}): 3440 (N–H str. Secondary amino group), 1740, 1694 (C=O str. Carbonyl groups), 1655 (C=O str. Acetylamino group), 1592 (C=C str. Aromatic ring); ^{1}HNMR (500 MHz, DMSO): 2.29 (s, 3H, CH_3), 5.36 (s, 2H, CH_2), 7.21–7.24 (d, 1H, $J = 6.7$ Hz, C-3), 7.36–7.38 (t, 1H, $J = 7.9$ Hz, C-5′), 7.71–7.74 (d, 1H, $J = 7.6$ Hz, C-3′), 7.88–7.89 (t, 1H, $J = 8$ Hz, C-4′), 8.32–8.34 (t, 1H, $J = 8.2$ Hz, C-6), 8.38–8.39 (d, 1H, $J = 8.1$ Hz, C-2), 8.46–8.48 (d, 1H, $J = 8.2$ Hz, C-5), 8.51–8.53 (d, 1H, $J = 7.2$ Hz, C-7), 8.73–8.75 (d, 1H, $J = 8.5$ Hz, C-6′), 10.42 (s, 1H, NH); ^{13}CNMR (125 MHz, DMSO): 24.98, 45.09, 118.12, 120.12, 121.76, 122.94, 123, 124.8, 127.2, 129.3, 130.3, 131.9, 132.7, 137.5, 141.4, 149.7, 156.9, 163.7, 164.3, 170.5.

2.3.6. *Synthesis of 4-acetylamino-N-3-aminomethylpyridine-1,8-naphthalimide (7)*

4-Amino-N-3-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 was refluxed for 5 h, then it was cooled down to room temperature and neutralized with 15 ml of a 10% sodium hydroxide solution and the desired product precipitated. The precipitate was recrystallised in ethanol. Yield: 66%; m.p: 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. Acetylamino group), 1586 (C=C str. Aromatic ring); ^{1}HNMR (500 MHz, DMSO): 2.29 (s, 3H, CH_3), 5.4 (s, 2H, CH_2), 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}CNMR (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.

3. Results and discussion

3.1. *Synthesis of dyes*

The five dyes were synthesized using 4-nitro-1,8-naphthalic anhydride as starting material (Fig. 1). This compound reacted separately with 2-aminomethylpyridine and 3-aminomethylpyridine in tetrahydrofuran at room temperature. In this reaction which called imidation, the amino compound attacked the carbonyl groups in naphthalic anhydride. The mechanism of imidation reaction is a nucleophilic addition and leaving group displacement.

The reactions between 4-nitro-1,8-naphthalic anhydride with 2-aminomethylpyridine and 3-aminomethylpyridine in tetrahydrofuran, results in separate pale yellow compounds with high yields. The reactions were monitored by thin layer chromatography on silica gel eluded with a mixture of 2:1 ethyl acetate:n-hexane. The reaction yields, melting points, R_f values, color and crystal shapes of the synthesized intermediates are shown in Table 1. The FTIR spectra showed the elimination of anhydride group (1800 cm^{-1}) in 4-nitro-1,8-naphthalic anhydride in products which considers to be a proof of reaction completion. The anhydride group of 4-nitro-1,8-naphthalic anhydride in final product disappears.

Table 1
The yield of reaction, melting point, R_f values, color and crystal's shape of synthesized dyes and their intermediates.

Compounds	Yield (%)	M.p. (°C)	R_f	Color	Crystal shapes
2	85	191	0.66[a]	Pale yellow	Flake
3	82	288	0.74[a]	Orange	Needle
4	63	232	0.81[b]	Yellow	Needle
5	83	170	0.31[a]	Pale yellow	Needle
6	78	350	0.54[a]	Orange	Needle
7	66	276	0.86[b]	Cream	Needle
8	92	168	0.48[a]	Pale yellow	Needle
9	89	228	0.55[a]	Orange	Needle

[a] TLC in a solvent system ethyl acetate: n-hexane = (2:1).
[b] TLC in a solvent system methanol: chloroform = (1:1).

Dyes 3 and 6 are synthesized through reduction of 4-nitro-N-2-aminomethylpyridine(3-aminomethylpyridine)-1,8-naphthalimide. The reduction of nitro group on naphthalimide ring was performed by stannous chloride and hydrochloric acid in alcoholic medium under reflux conditions. The completion of reactions was determined by TLC on silica gel with a mixture of ethyl acetate and n-hexane (2:1) as eluant.

The FTIR spectra of the synthesized dyes showed primary amino group (N–H stretch) in 3370, 3211 cm^{-1} and 3344, 3240 cm^{-1} for compounds 3 and 6, respectively. Also, the ^{1}HNMR spectra of the dyes 3 and 6 demonstrated the presence of primary amino group protons as a singlet peaks in 7.4 ppm and 7.7 ppm regions, respectively, which there are not these two singlet peaks in the intermediate compounds of 2 and 3.

The synthesis of dyes 4 and 7 were done through acetylation of dyes 3 and 6. Both dyes reacted with acetic anhydride under reflux conditions for 5 h. The crude products were purified by recrystalisation in ethanol. The reactions were monitored by thin layer chromatography on silica gel eluded with a mixture of 1:1 methanol:chloroform. The FTIR spectra of the dyes confirmed the presence of secondary aromatic amines in 3340 and 3450 cm^{-1} for compounds 4 and 7, respectively. The difference data of ^{1}HNMR between dyes (3, 6) and (4, 7) confirmed the presence of the singlet peaks in regions 10.42 and 10.48 ppm which are related to the protons of acetylamino ($NHCOCH_3$) groups in dyes 4 and 7, respectively. The yield of these reactions, melting points, R_f values, color and crystal shapes of the synthesized dyes are shown in Table 1.

3.2. Spectrophotometric properties of dyes

3.2.1. Absorption spectra

The spectrophotometric data of all dye solutions in DMF and THF is shown in Table 2. The absorption bands of these dyes range from 370 to 435 nm. The absorption peaks of dyes containing amino group were located at 427–433 nm in DMF and 417–419 nm in THF and dyes containing acetylamino group peaked at 372–374 nm in DMF and 370–371 nm in THF. The difference between maximum wavelengths of dyes is due to various substitutions on C-4 position of naphthalimide ring. The dyes containing acetylamino group as electron donor in C-4 position have the lowest maximum wavelengths, whilst dyes containing $-NH_2$ group in C-4 position have higher maximum wavelengths. The maximum wavelengths of naphthalimide dyes are related to the electron donating and accepting power of substituents in C-4 position and carbonyl groups. In dyes 3, 6 and 9 the electron donor group is amino which is a strong donor group, whereas in dyes 4 and 7, the substitution on naphthalimide ring in C-4 position is an acetylamino group, which is a weak electron donating group. Therefore, these dyes (4 and 7) display a hypsochromic effect compared to the synthesized other dyes (about 60 nm difference). The hypsochromic shifts of these dyes in DMF are shown in Fig. 2.

In this category, the maximum wavelength of dyes 3, 6 and 9 with various N-substituted compounds (N-ester and N-aminomethylpyridine) are roughly identical and do not change by altering the N-substituted compound in naphthalimide ring (Fig. 2). In fact, the nature of imide groups has no effect on the color. The extinction coefficients of these dye solutions in DMF are between 1.1×10^4 and 1.9×10^4 $\text{l mol}^{-1}\,\text{cm}^{-1}$ and in THF between 0.84×10^4 and 1.4×10^4 $\text{l mol}^{-1}\,\text{cm}^{-1}$.

Table 2
The absorption data of dyes at five different concentrations in DMF and THF solutions.

Dye	Concentration (mol l^{-1})	Absorbance		$\varepsilon_{\max}$ ($10^4\,\text{M}^{-1}\,\text{cm}^{-1}$)		$\lambda_{\max}$ (nm)		R^2	
		DMF	THF	DMF	THF	DMF	THF	DMF	THF
3	2×10^{-5}	0.21	0.19	1.1	0.84	432	418	098	0.99
	4×10^{-5}	0.41	0.34						
	6×10^{-5}	0.62	0.53						
	8×10^{-5}	0.83	0.69						
	1×10^{-4}	1.22	0.83						
4	2×10^{-5}	0.40	0.21	1.9	1.4	374	371	0.95	0.97
	4×10^{-5}	0.75	0.41						
	6×10^{-5}	1.48	0.75						
	8×10^{-5}	1.67	0.84						
	1×10^{-4}	1.76	0.97						
6	2×10^{-5}	0.24	0.20	1.5	0.92	427	417	0.95	0.99
	4×10^{-5}	0.49	0.39						
	6×10^{-5}	0.73	0.58						
	8×10^{-5}	0.92	0.78						
	1×10^{-4}	1.60	0.90						
7	2×10^{-5}	0.34	0.30	1.6	1.2	372	370	0.99	0.96
	4×10^{-5}	0.68	0.61						
	6×10^{-5}	1.02	0.93						
	8×10^{-5}	1.29	1.09						
	1×10^{-4}	1.58	1.26						
9	2×10^{-5}	0.27	0.20	1.3	0.91	433	419	0.99	0.98
	4×10^{-5}	0.54	0.42						
	6×10^{-5}	0.84	0.61						
	8×10^{-5}	1.10	0.75						
	1×10^{-4}	1.31	0.90						

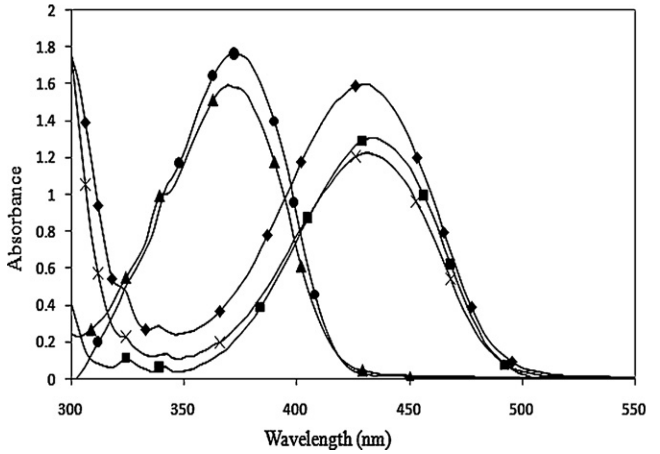

Fig. 2. The absorption spectra of dyes at concentration 10^{-4} mol l^{-1} in DMF solution: dye 3 (×); dye 4 (●); dye 6 (♦); dye 7 (▲); dye 9 (■).

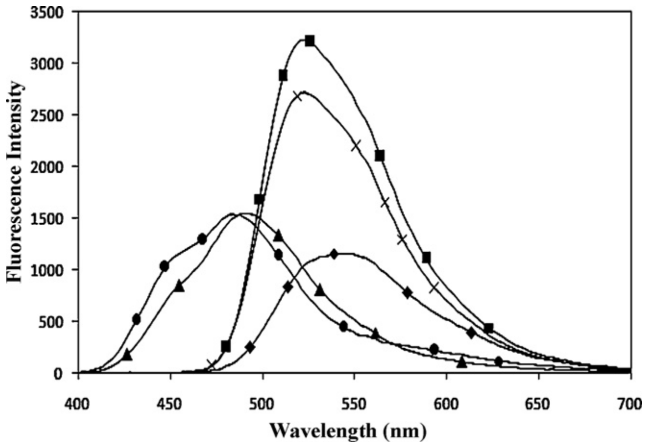

Fig. 3. The emission spectra of dyes at concentration 10^{-4} mol l^{-1} in DMF solution with $\lambda_{Ex,\text{ dye }3} = 435$ nm, $\lambda_{\text{Ex, dye }4} = 375$ nm, $\lambda_{\text{Ex, dye }6} = 430$ nm, $\lambda_{\text{Ex, dye }7} = 375$ nm and $\lambda_{\text{Ex, dye }9} = 436$ nm: dye 3 (×); dye 4 (●); dye 6 (♦); dye 7 (▲); dye 9 (■).

Investigation of spectrophotometric properties of the synthesized dyes in THF and DMF solutions shown positive solvatochromic effects (Table 2). The wavelengths maxima of all dyes increased with changing media from THF to DMF. On the other hand, all dyes showed bathochromic shift in the DMF comparison to THF. The values of bathochromic shift for dyes were 2–14 nm. The highest and lowest bathochromic shifts were in dyes 3, 9 and 7, respectively.

3.2.2. Fluorescent properties

The fluorescent characteristics of all these dyes were measured in DMF and are represented in Table 3. In DMF solutions, dyes 3, 6 and 9 show 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. The emission of dyes is in the visible region at about 524–532 nm (Fig. 3), whilst dyes 4 and 7 demonstrate blue emission at 484–493 nm. It says that dyes 3, 6 and 9 have similar fluorescent behaviour. Also, dyes 4 and 7 have extremely identical emitting wavelengths. These results show that various substitutions on imide group have no fluorescence-related effects on naphthalimide derivatives' wavelengths. These findings are also obvious in other naphthalimide compounds [32]. In this research, it could be concluded that the presence of electron amino donating groups in C-4 position naphthalimide derivatives result in a red shift. In comparison with dyes containing primary amino groups, dyes consisting of secondary amino groups (acetylaminoes) have blue shifts due to their weak electron donating characteristics.

Table 3
The fluorescent characteristics of dyes at concentration 10^{-4} mol l^{-1} in DMF and THF solutions.

Solvent	$\nu_A - \nu_F$ (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	f	λ_F (nm)	Φ_F	E_F
3						
DMF	4100	4100	0.356	524	0.38	0.31
THF	4000	3950	0.272	505		
4						
DMF	6070	4600	0.517	484	0.26	0.20
THF	5900	4580	0.381	478		
6						
DMF	4620	4300	0.492	532	0.54	0.44
THF	4400	4260	0.330	513		
7						
DMF	6600	4900	0.525	493	0.33	0.25
THF	6400	4820	0.388	483		
9						
DMF	4000	3900	0.353	527	0.80	0.65
THF	3880	3860	0.267	507		

DMF: $\lambda_{Ex,\text{ dye }3} = 435$ nm, $\lambda_{\text{Ex, dye }4} = 375$ nm, $\lambda_{\text{Ex, dye }6} = 430$ nm, $\lambda_{\text{Ex, dye }7} = 375$ nm and $\lambda_{\text{Ex, dye }9} = 436$ nm; THF: $\lambda_{Ex,\text{ dye }3} = 420$ nm, $\lambda_{\text{Ex, dye }4} = 375$ nm, $\lambda_{\text{Ex, dye }6} = 420$ nm, $\lambda_{\text{Ex, dye }7} = 375$ nm and $\lambda_{\text{Ex, dye }9} = 420$ nm.

Fig. 4 shows the normalised absorption and fluorescence spectra of dye 3 in DMF solution at five different concentrations of 2×10^{-5} M, 4×10^{-5} M, 6×10^{-5} M, 8×10^{-5} M and 1×10^{-4} M. In the long-wavelength area, the fluorescent spectrum is the mirror image of the absorption. This is because of the preserved planarity of the dye's molecular structure in excited state [33,34]. For all concentrations of dye 3 in DMF solution, the overlap of the absorption and fluorescent spectra is small and an aggregation effect has not been observed at the studied concentrations of the dye 3 [34].

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 all dyes were determined by Eq. (1) [35].

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

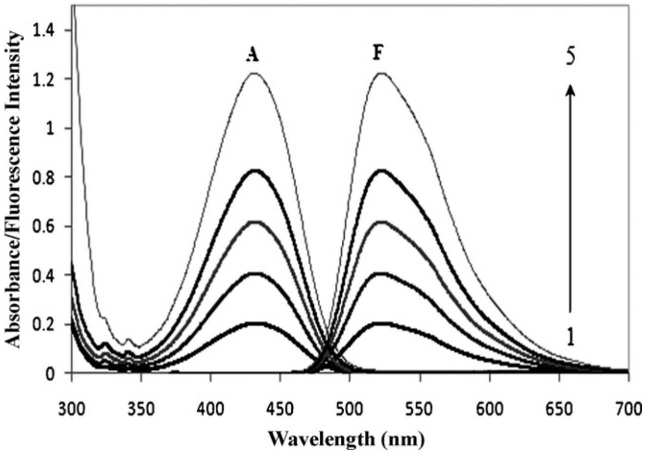

Fig. 4. Normalised absorption (A) and fluorescence spectra (F) of dye 3 in DMF solution at five different concentrations of (1) 2×10^{-5} M, (2) 4×10^{-5} M, (3) 6×10^{-5} M, (4) 8×10^{-5} M and (5) 1×10^{-4} M in DMF solution with $\lambda_{Ex,\text{ dye }3} = 435$ nm, $\lambda_{\text{Ex, dye }4} = 375$ nm, $\lambda_{\text{Ex, dye }6} = 430$ nm, $\lambda_{\text{Ex, dye }7} = 375$ nm and $\lambda_{\text{Ex, dye }9} = 436$ nm.

where $\nu_A - \nu_F$ is Stokes shift, λ_A and λ_F are absorption and fluorescence maxima, respectively.

The Stokes shift values of the acetylamino substituted 1,8-naphthalimide dyes 4 and 7 (6070 and 6600 cm^{-1}) were higher than those of the amino derivatives of 1,8-naphthalimide substituted dyes 3, 6 and 9 (4100, 4620, and 4000 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 [36]. This effect cause the red shift in the fluorescence maxima resulting in large-scale addition of the Stokes shift values for acetylamino substituted 1,8-naphthalimides [37].

The oscillator strength (f) demonstrates the effectiveness of the 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 Eq. (2) [38].

$$f = 4.32 \times 10^{-9}\,\Delta\nu_{1/2}\varepsilon_{\max} \tag{2}$$

where $\Delta\nu_{1/2}$ is the width of the absorption band at 1/2 ($\varepsilon_{\max}$).

The oscillator strengths of all dyes in DMF solution were between 0.353 and 0.525, which is according to the other 1,8-naphthalimide derivatives which are studied previously [39]. For the dyes 4 and 7 having an acetylamino group as a substituent at the C-4 position, the f values are higher. 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 fluoroscein (Φ_{ref} = 0.95) as a standard material according to Eq. (3) [40].

$$\Phi_F = \Phi_{ref}\left(\frac{S_{sample}}{S_{ref}}\right)\left(\frac{A_{ref}}{A_{sample}}\right)\left(\frac{n^2_{sample}}{n^2_{ref}}\right) \tag{3}$$

where, Φ_F is quantum yield of samples, Φ_{ref} is quantum yield of fluoroscein, 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. Comparison of the fluorescence quantum yields of the dyes containing pyridine (dyes 3, 4, 6 and 7) and ester groups (dye 9) represented that dyes containing aminomethylpyridine group have quantum yield lower than dye containing ester group in DMF solutions. On the other hand, 4-amino-N-ester-1,8-naphthalimide has higher energy yield of fluorescence. The energy yield of fluorescence obtained using Eq. (4) [41].

$$E_F = \Phi_F \frac{\lambda_A}{\lambda_F} \tag{4}$$

As can be seen from the data shown in Table 3, the quantum yield of fluorescence of dye 9, possessing N-ester group in naphthalimide ring has the most of quantum yield respect to other dyes. This finding may be related to polarity of dye 9 due to having N-ester group and primary amino substituted in C-4 position. Therefore, dye 9 could be having stronger interaction with DMF which is a polar solvent. This interaction between dye molecules and DMF can increase rigidity dye molecules and therefore, the quantum yield increases [42].

The fluorescent compounds based on C-4 position of 1,8-naphthalimide were synthesized by other researchers and reported their quantum yields in DMF solution. The comparison of quantum yields of these compounds with the synthesized dyes showed that quantum yield values of all dyes are in the range of the dyes which have been synthesized by the other researchers [39,43,44].

Also, the photophysical properties of all these dyes were evaluated in THF solution and are represented in Table 3. The results illustrated that dyes have emission wavelength ranging from 478 to 513 nm which is related to dyes 4 and 6, respectively. As seen, the fluorescent maxima of all dyes in polar solvent depicted a bathochromic shift in comparison to non-polar solvent. In this respect, the greater bathochromic shift can be ascribed to the dipole moment of the molecule which is enhanced upon excitation due to electron density redistribution. The excited molecule is better stabilized in polar solvent, because of the stronger interactions with the solvent's dipoles [45].

The Stokes shift of all dyes in THF showed that the highest and lowest values of Stokes shift are related to dyes 7 and 9, respectively. It was observed that in the less polar solutions, the values of Stokes shifts were lower than that obtain in the polar media.

4. Conclusion

A series of novel fluorescent dyes based on naphthalimide derivatives containing amino and acetylamino functional groups were synthesized using imidation, reduction and acetylation reactions. All dyes and intermediates were characterized by DSC, TLC (R_f values), FTIR, ^{1}HNMR, ^{13}CNMR and UV–visible techniques.

The spectrophotometric properties of the synthesized dyes in DMF and THF solvents were examined and absorption maxima and their intensities have also been obtained. The results showed that the dyes containing acetylamino group in C-4 position of naphthalimide ring have the lowest maximum wavelengths and dyes containing amino group in C-4 position have the highest maximum wavelengths.

The fluorescence properties of the synthesized dyes showed that dyes containing functional amino group in C-4 position of naphthalimide ring have fluorescence wavelength higher than dyes containing acetylamino group.

Comparison of the fluorescence quantum yield of the dyes containing pyridine and ester groups demonstrated that dyes containing aminomethylpyridine group have quantum yields lower than dye containing ester groups in N-substituted naphthalimide rings. Moreover, in this series, dyes incorporated with amino group in C-4 position of naphthalimide ring have quantum yields higher than those containing acetylamino groups.

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