

Synthesis and Properties of Blue Fluorescent Dyes Based on Diphenylamine by Introducing an Acetylene Linkage Group with Carbazole and 1,8-Naphthalimide

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The photosynthesis of all plants requires the absorption of sunlight by chlorophyll *a* and *b*, which maximally absorb at 430 and 680 nm, respectively.^{1,2} Therefore, the 400–700 nm range is generally recognized as photosynthetically active radiation (PAR).³ In this study, blue fluorescent dyes based on diphenylamine connected to either a carbazole or naphthalimide group are shown to be useful in fluorescent light-emitting films for converting UV light and thus can be used to enhance the efficiency of photosynthesis.^{4–8}

In previous studies, a series of blue fluorescent dyes based on 1,8-naphthalimide derivatives connected with an acetylene linkage group, which can readily increase the planarity of dye molecules, were synthesized through the use of the Sonogashira coupling reaction.^{9–14} The improved thermal stability of these 1,8-naphthalimidyl fluorescent dyes makes them suitable for use in light-emitting materials.^{15,16}

The structures of the synthesized fluorescent dyes were characterized by ¹H NMR and MASS (MALDI-TOF) spectroscopy. The optical and electrochemical properties of the synthesized fluorescent dyes were also calculated by time-dependent density functional theory (TD-DFT) using the Gaussian 09 program with the hybrid B3LYP exchange correlation function and the 6-31G basis set.

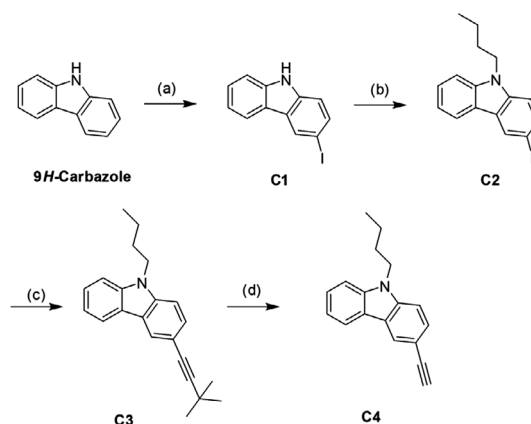
Experimental

Synthesis of Intermediates C1–C4. The synthetic process was referred by Wu *et al.* (Schemes 1 and 2).¹⁷

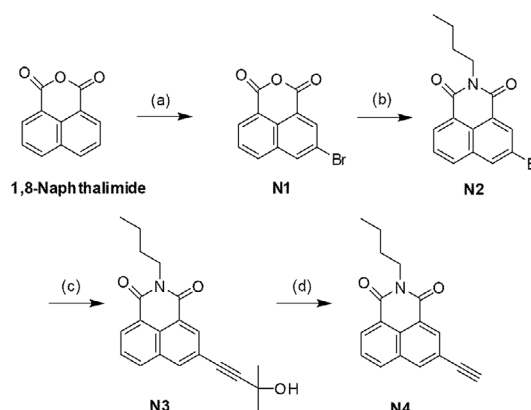
Synthesis of Intermediates N1–N4. The synthetic process was referred by Kim *et al.* (Scheme 3).⁹

Synthesis of Intermediate D1 and D2. The synthetic process was referred by Namuangruk *et al.* (Scheme 4).¹⁸

Synthesis of Fluorescent Dye 1. Anhydrous tetrahydrofuran (THF) (100 mL) was added to a solution of intermediate **D1** (16.94 mmol, 5 g), copper(I) iodide (0.07 mmol, 397.5 mg), triphenylphosphine (0.7 mmol, 327.5 mg), and bis(triphenylphosphine)palladium(II) dichloride (1.4 mmol, 1 g). The resulting mixture was stirred under nitrogen for 20 min, then triethylamine (75 mL) was added and the mixture was stirred for 30 min, then intermediate **C4**

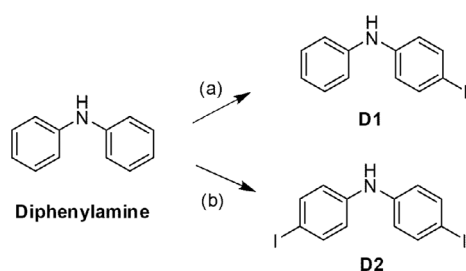


Scheme 1. Reagents and conditions¹⁷: (a) KI, KIO₃, AcOH, 110 °C, 2 h; (b) 1-bromobutane, NaH, DMF, 70 °C, 3 min; (c) 2-methyl-3-butyne-2-ol, Pd(PPh₃)₂Cl₂, Pd(II), CuI, TEA, THF under nitrogen, 80 °C, 3 h; (d) KOH, toluene, under nitrogen, reflux, 2 h.



Scheme 2. Reagents and conditions⁹: (a) Ag₂SO₄, Br₂, H₂SO₄, 70 °C, 12 h; (b) *n*-butylamine, EtOH, 60 °C, 10 h; (c) 2-methyl-3-butyne-2-ol, Pd(PPh₃)₂Cl₂, Pd(II), CuI, TEA, THF under nitrogen, 80 °C, 3 h; (d) KOH, toluene, under nitrogen, reflux, 1 h.

(16.94 mmol, 4.18 g) was added, followed by 30 min of stirring. The resulting mixture was refluxed for 2 h. The reaction mixture was cooled and added to ammonia water. Ethyl acetate was used to separate the layers and the ethyl



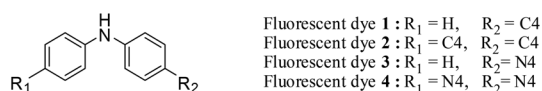
Scheme 3. Reagents and conditions¹⁸: (a) KI, KIO₃, AcOH, 10 °C, 5 h; (b) KI, KIO₃, AcOH, 80 °C, 5 h.

acetate layer was rinsed with excess water. The obtained organic layer was dried using MgSO₄·anhydrous as a drying agent and then evaporated to obtain the reaction product. The obtained reaction product was purified via column chromatography (absorbent: silica gel, eluent: ethyl acetate/*n*-hexane 1:5). Yield: 75.5%; ¹H NMR (500 MHz, DMSO-*d*₆) 0.90 (m, 3H, CH₃), 1.31 (m, 2H, CH₂), 1.74 (m, 2H, CH₂), 4.16 (m, 2H, CH₂), 6.59 (m, 2H, ArH), 6.81 (t, 1H, ArH), 7.20 (m, 2H, ArH), 7.28 (m, 3H, ArH), 7.34 (m, 2H, ArH), 7.42 (m, 2H, ArH), 7.59 (d, 2H, ArH), 7.75 (s, 1H, ArH), 8.17 (s, 1H, ArH), 8.36 (d, 1H, NH); GC-MS 414(M+1); elemental analysis found C:86.88, H:6.27, N:6.71 calculated for C₃₆H₂₆N₂ C:86.92, H:6.32, N:6.76.

Synthesis of Fluorescent Dye 2. Fluorescent dye 2 was synthesized using intermediate **D2** (11.87 mmol, 5 g) and intermediate **C4** (33.88 mmol, 8.36 g) via the method used to prepare fluorescent dye 1. Yield: 68.7%; ¹H NMR (500 MHz, DMSO-*d*₆) 0.90 (m, 6H, CH₃), 1.31 (m, 4H, CH₂), 1.74 (m, 4H, CH₂), 4.16 (m, 4H, CH₂), 6.59 (m, 4H, ArH), 7.34 (m, 8H, ArH), 7.56 (m, 4H, ArH), 7.78 (m, 4H, ArH), 8.36 (d, 2H, ArH), 8.36 (s, 1H, NH); GC-MS 659 (M + 1); elemental analysis found C:87.35, H:6.23, N:6.33 calculated for C₄₈H₄₁N₃ C:87.37, H:6.26, N:6.37.

Synthesis of Fluorescent Dye 3. Fluorescent dye 3 was synthesized using intermediate **D1** (16.94 mmol, 5 g) and intermediate **N4** (16.94 mmol, 4.69 g) via the procedure used to prepare fluorescent dye 1. Yield: 79.1%; ¹H NMR (500 MHz, DMSO-*d*₆) 0.90 (m, 3H, CH₃), 1.31 (m, 2H, CH₂), 1.56 (m, 2H, CH₂), 3.14 (t, 2H, CH₂), 6.59 (d, 2H, ArH), 6.81 (t, 1H, ArH), 7.20 (m, 2H, ArH), 7.28 (d, 2H, ArH), 7.34 (d, 2H, ArH), 7.79 (t, 1H, ArH), 8.14 (s, 1H, ArH), 8.19 (s, 1H, ArH), 8.36 (d, 1H, NH), 8.41 (m, 2H, ArH); LC-MS 444(M - 1); elemental analysis found C:81.05, H:5.43, N:5.43, O:7.16 calculated for C₃₀H₂₄N₂O₂ C:81.06, H:5.44, N:6.30, O:7.20.

Synthesis of Fluorescent Dye 4. Fluorescent dye 4 was synthesized using intermediate **D2** (11.87 mmol, 5 g) and intermediate **N4** (23.74 mmol, 6.58 g) via the procedure



Scheme 4. Reagents and conditions: (a) Pd(PPh₃)₂Cl₂, Pd(II), CuI, TEA, under nitrogen, reflux, 2 h.

used to prepare fluorescent dye 1. Yield: 64.3%; ¹H NMR (500 MHz, DMSO-*d*₆) 0.90 (m, 6H, CH₃), 1.31 (m, 4H, CH₂), 1.56 (t, 4H, CH₂), 3.14 (t, 4H, CH₂), 6.59 (m, 4H, ArH), 7.34 (m, 4H, ArH), 7.79 (t, 2H, ArH), 8.19 (d, 4H, ArH), 8.35 (s, 2H, ArH), 8.36 (s, 1H, NH), 8.41 (d, 2H, ArH); LC-MS 719(M - 1); elemental analysis found C:80.07, H:5.12, N:5.81O:8.84 calculated for C₄₈H₃₇N₂O₄ C:80.09, H:5.18, N:5.84, O:8.89.

The absorption maxima of fluorescent dyes 1–4 were observed in the range 315–346 nm so the fluorescent color by these dyes will be in the blue region, as shown in Table 1. In particular, the absorption maxima of fluorescent dyes 2 and 4 were bathochromically shifted relative to those of analogue dyes 1 and 3. The absorption maximum of fluorescent dye 2 exhibited a bathochromic shift of 6 nm compared with that of dye 1, which could be caused by increased π -conjugation (Figure 1). The bigger shift was observed for dye 4 in comparison to analogue 3, where the introduction of a further electron-withdrawing group in the form of a naphthalimidyl moiety caused a red shift of 19 nm. In terms of the Stokes shift, it was found that the dyes substituted with two acetylene linkage groups tended to shift more, thus dye 4 exerted the greatest shift. The quantum yields ranged from 0.61 to 0.78, with higher fluorescent efficiency with more extended π -conjugation by an acetylene group (Figure 1).

As shown in Figure 2 and Table 2, for fluorescent dyes 1–2, the electrons of the HOMO and LUMO levels are delocalized, whereas in the case of dyes 3–4, the electrons are localized at the HOMO and LUMO levels, respectively. Fluorescent dyes 1–2 feature higher energy levels and can more readily donate electrons, leading to an increase in their HOMO energy levels. As a result, fluorescent dyes 1 and 2 have higher HOMO energy levels (–4.77 to –4.57 eV) than analogue dyes 3 and 4 (–5.88 to –5.83 eV). In contrast, for dyes 3 and 4, in which an acetylene group is linked

Table 1. Photochemical properties of fluorescent dyes 1–4.

Fluorescent dye	$\lambda_{\max}^{a,b,*}$	$\lambda_{\max}^{\text{em}*}$	Stokes shift (nm)	ϵ_{\max}	ϕ^a
1	340	406	66	31 000	0.61
2	346	428	82	33 000	0.71
3	315	403	88	32 000	0.64
4	328	422	94	34 000	0.78

^a Reference: Anthracene.

^b Determined in methylene chloride.

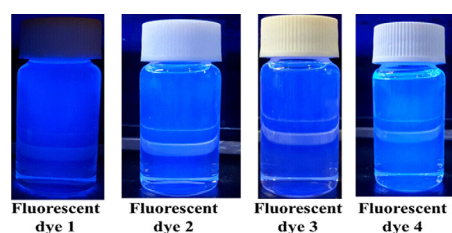


Figure 1. Fluorescence emissions of fluorescent dyes 1–4 in methylene chloride (10 ppm) under UV light ($\lambda_{\max} = 365$ nm).

Table 2. HOMO–LUMO energies and energy bandgaps for fluorescent dyes 1–4 based on TD-DFT calculations (B3LYP/6-31G).

Fluorescent dye	Electrochemical properties		
	HOMO (eV)	LUMO (eV)	Band gap (eV)
1	−4.77	−1.03	3.74
2	−4.57	−0.99	3.58
3	−5.83	−2.56	3.27
4	−5.88	−2.74	3.14

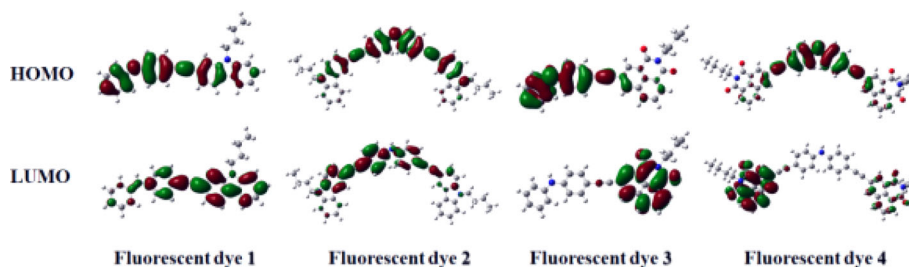
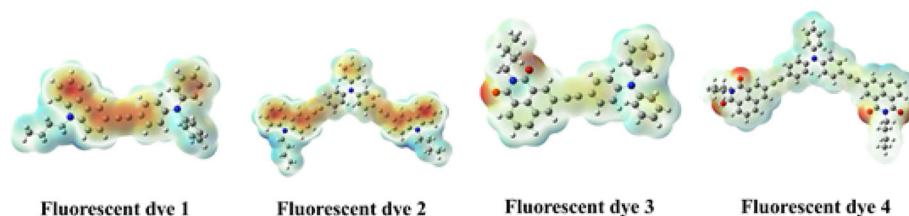
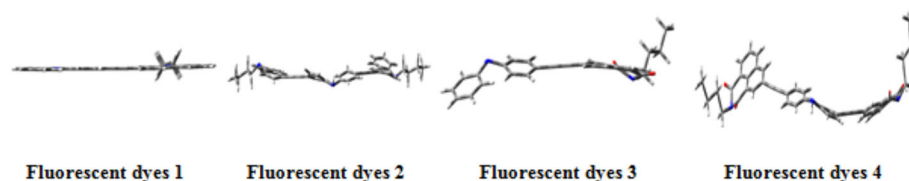
to a naphthalimidyl group, the electron-donating effect exerted by an amino group onto an electron-accepting moiety (the naphthalimidyl group) can be readily enhanced. Therefore, the LUMO energy levels (−2.74 to −2.56 eV) of dyes 3 and 4 were calculated and found to be lower than those of the corresponding dyes 1 and 2 (−1.03 to −0.99 eV). The optical band gaps of dyes 1–4 were in the range 3.14–3.74 eV. In particular, a small bandgap was calculated for dyes 3 and 4. The trend of the band gaps is consistent with the results of the DFT calculations. The electron density of synthesized dyes 1–4 is illustrated in Figure 3.

Geometry. Judging from the structural properties, dyes 1–4 have a plane structure of π – π interactions centered on an acetylene linkage. Fluorescent dye 1 has dihedral angles of 0.41°, 0.77°, and 0.38°, whereas dye 2 has dihedral angles of 0.63°, 0.91°, and 0.48°. In addition, fluorescent dye 4 has larger dihedral angles (0.83°, 1.36°, and 0.86°) compared with those of

corresponding dye 3 (0.56°, 0.61°, and 0.42°). These results indicate that fluorescent dyes 2 and 4, substituted by two acetylene groups, have relatively large steric hindrance, however, both substituents maintain planarity owing to the presence of the acetylene linkage, as shown in Figures 4 and 5.

Thermogravimetric analysis (TGA) indicated that dyes 2 and 4 were comparatively more stable than the corresponding dyes 1 and 3, as shown in Figure 6. The resultant % weight loss exerted by dyes 2 and 4 those substituted by two acetylene groups was less than that observed by dyes 1 and 3, particularly over 300 °C, which can be attributed to the increased molecular weight and the increased presence of planar acetylene groups. As it is well-known, the increased s-character of sp-hybridized orbitals for acetylene groups is one of the main parameters to enhance the stability of dye molecules compared that to sp² or sp³ analogues. In case of these four dyes 1–4, the difference in percentage weight loss was apparent at high temperatures over 280 °C.

In addition, the contribution of the naphthalimidyl group to the reduced decomposition, particularly in the range of 200–250 °C, was observed by comparison of dyes 1 and 2 substituted by a carbazole moiety with corresponding dyes 3 and 4. It can be assumed that the naphthalimidyl system may increase the π orbital conjugation throughout the dye molecule in comparison to that of the corresponding carbazole analogue, however the effect was smaller from temperatures of 260°C up to 350 °C.

**Figure 2.** Molecular orbital plots of fluorescent dyes 1–4 (B3LYP/6-31G).**Figure 3.** Electron density of synthesized fluorescent dyes 1–4 (B3LYP/6-31G).**Figure 4.** Geometry-optimized structures of the synthesized fluorescent dyes 1–4.

Dyes No.	R ₁	R ₂	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$
1	C4	H	0.41	0.77	0.38
2	C4	C4	0.63	0.91	0.48
3	D4	H	0.56	0.61	0.42
4	D4	D4	0.83	1.36	0.86

$\alpha(^{\circ})$ =Diphenylamine - Acetylene linkage dihedral angles
 $\beta(^{\circ})$ =Acetylene linkage - Carbazole or Naphthalimide dihedral angles
 $\gamma(^{\circ})$ =Carbazole or Naphthalimide - *n*-butyl substituent dihedral angles

Figure 5. Theoretically calculated dihedral angles of fluorescent dyes 1–4.

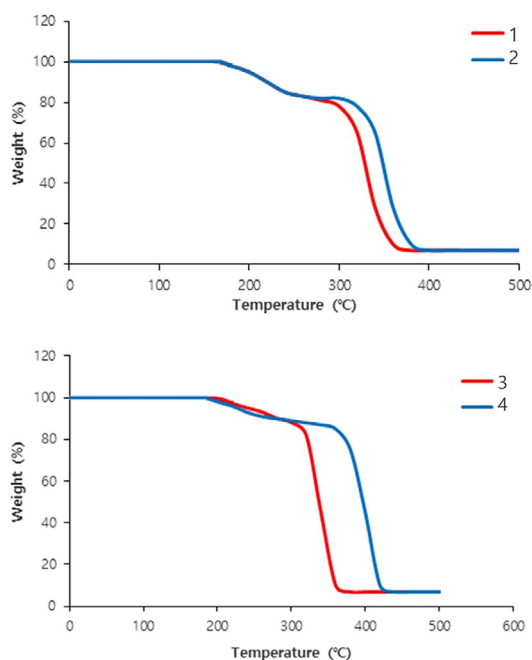


Figure 6. TGA analysis of fluorescent dyes 1–4.

Judging from these results, it can be concluded that the introduction of two acetylene linkage groups between diphenylamine and either carbazole or naphthalimidyl groups enhances the thermal stability and quantum yield of the dye molecules whilst retaining their blue fluorescent emission properties.

There is an increase in the demand for facilities in the horticultural industry to improve agricultural productivity by using light-emitting diodes (LEDs). However, as the energy costs exceed the economic value, the use of LEDs

in industry is extremely limited, hence light conversion film containing a fluorescent emitting dye can replace the LEDs. In this research, the prepared blue-emitting dyes will be coated onto polyethylene film to integrate favorable wavelengths for photosynthesis from sunlight. Such films are expected to increase the efficiency of photosynthesis.

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References

1. K. R. Cope, M. C. Snowden, B. Bugbgg, *Photochem. Photobiol.* **2014**, *90*, 574.
2. D. R. Whang, D. H. Apaydin, *ChemPhotoChem* **2018**, *2*, 149.
3. K. Hidaka, K. Yoshida, K. Shimasski, D. Yasutake, M. Kitano, *J. Faculty Agri.* **2008**, *53*, 549.
4. K. H. Lin, M. Y. Huang, M. H. Hsu, Z. W. Yang, C. M. Yang, *Sci. Hortic.* **2013**, *150*, 86.
5. A. Dieleman, *Int. Soc. Hortic. Sci.* **2005**, *691*, 225.
6. S. Pearson, A. E. Wheldon, P. Hadley, *J. Agric. Eng. Res.* **1995**, *62*, 61.
7. Y. Nishimura, Y. Fukumoto, H. Aruga, Y. Sshimoi, *Hortic. Environ. Biotechnol.* **2009**, *50*, 416.
8. H. Jang, J. W. Namgoong, M. G. Sung, Y. Chang, J. P. Kim, *Dyes Pigments* **2018**, *158*, 142.
9. K. W. Kim, G. H. Kim, S. H. Kwon, H. I. Yoon, J. E. Son, J. H. Choi, *Dyes Pigments* **2018**, *158*, 353.
10. R. El-Berjawi, P. Hudhomme, *Dyes Pigments* **2018**, *159*, 551.
11. K. W. Kim, G. H. Kim, C. E. Park, J. H. Choi, *Bull. Kor. Chem. Soc.* **2017**, *38*, 956.
12. X. Zhang, Y. Song, M. Liu, H. Li, H. Sun, M. Sun, H. Yu, *Dyes Pigments* **2019**, *160*, 799.
13. S. Kotowicza, M. Korzeca, M. S. Golbac, E. S. Balcerzaka, *Dyes Pigments* **2018**, *158*, 65.
14. T. S. Reddy, J. Hwang, M. S. Choi, *Dyes Pigments* **2018**, *158*, 412.
15. L. Guo, *Mol. Biomol. Spectrosc.* **2018**, *201*, 376.
16. G. Saulius, *Mater. Chem. Phys.* **2001**, *72*(3), 395.
17. Y. Wu, H. Guo, T. D. James, J. Zhao, *J. Org. Chem.* **2011**, *76*, 5685.
18. S. Namuangruk, R. Fukuda, M. Ehara, J. Meeprasert, T. Khanasa, S. Morada, T. Kaewin, S. Jungsuttiwong, T. Sudyoadsuk, V. Promarak, *J. Phys. Chem.* **2012**, *116*, 25623.