Synthesis of Novel Fluorescent 2-{4-[1-(Pyridine-2-yl)-1*H*-pyrazol-3-yl] phenyl}-2*H*-naphtho [1,2-*d*] [1,2,3] triazolyl Derivatives and Evaluation of Their Thermal and Photophysical Properties

Vikas S. Padalkar, Kiran R. Phatangare, and N. Sekar*

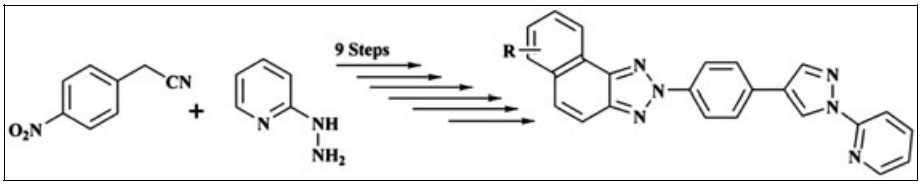
Tinctorial Chemistry Group, Intermediate and Dyestuff Technology Department, Institute of Chemical Technology, N. P. Marg, Matunga, Mumbai 400019, Maharashtra, India

*E-mail: n.sekar@ictmumbai.edu.in

Received February 8, 2012

DOI 10.1002/jhet.1697

Published online in Wiley Online Library (wileyonlinelibrary.com).



Novel 2-{4-[1-(pyridine-2-yl)-1*H*-pyrazol-3-yl] phenyl}-2*H*-naphtho [1,2-*d*] [1,2,3] triazolyl fluorescent derivatives were synthesized from *p*-nitrophenylacetic acid and 2-hydrazino pyridine through Vilsmeier–Haack and diazotization reactions. Photophysical properties were evaluated, and results show that compounds have good fluorescence quantum yields. Thermal analysis showed that they are reasonably stable. The structures of the compounds were confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR, and mass spectral and elemental analysis.

J. Hetercyclic Chem., **00,** 00 (2013).

INTRODUCTION

1,2,3-Triazole and its derivatives are used as fluorescent brightening agents, UV absorbers to retard the photodegradation of wool [1–3]. Synthesis of heterocyclic systems for use as fluorescent whiteners has two approaches: the first one in which the same or different heterocyclic systems are linked together so as to increase the overall conjugation in the resulting molecule, and another is incorporation of a fused system to provide planarity to increase the conjugation and rigidity in the molecule [4]. Over the last two decades, a variety of triazole derivatives have been synthesized and studied for their optical brightening properties [5,6].

Moreover, pyrazole is one of the classes of heterocyclic compounds and also an important intermediate for the synthesis of biologically active benzofuran and coumarin systems. Although various pyrazole derivatives are reported in literature [7–10], fluorescent derivatives of pyrazole heterocycle have received little attention. Synthesis and applications of fluorescent 1,2,3 or 1,3,4-triazole containing different heterocyclic ring systems are known in literature as sensors [11–13]. However, there are only few reports available that describe synthesis and photophysical properties of triazole with pyrazole heterocycles in a single moiety [14].

It is our interest to synthesize a triazole, which would exhibit higher fluorescence quantum yield and also absorption in the UV region and emission in the visible region of the spectrum, which is a basic requirement for compounds that function as fluorescent brightening agent. As a part of ongoing research on synthesis of fluorescent compounds for high-technology applications [15–20], here we report the synthesis and photophysical properties of novel fluorescent triazole derivatives.

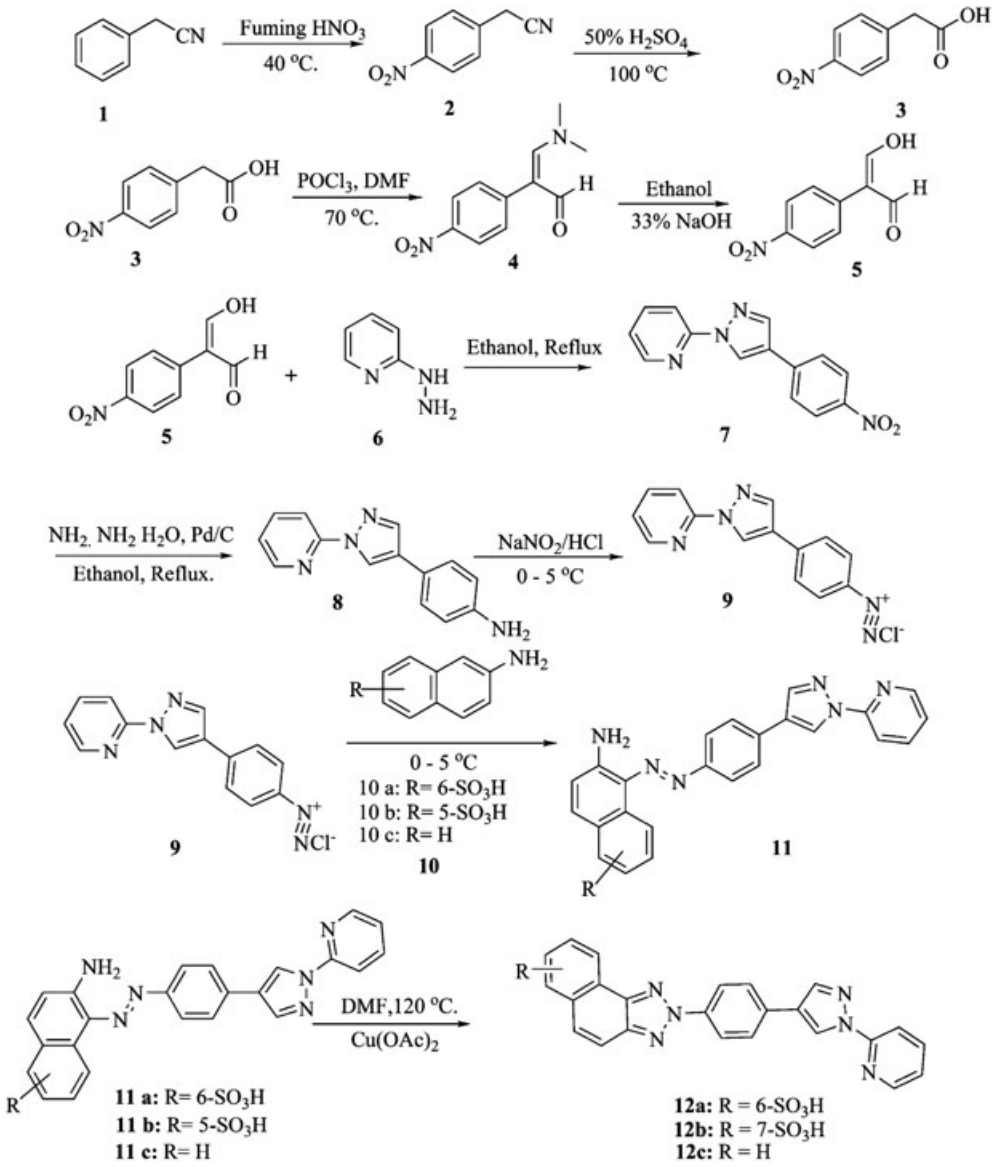
RESULTS AND DISCUSSION

Vilsmeier–Haack reaction for the synthesis of various heterocyclic ring systems has been exploited. It was envisaged that the Vilsmeier–Haack reaction on *p*-nitrophenylacetic acid would yield malondialdehyde, which would serve as useful synthon for the construction of various heterocycles. As a continuation of work on Vilsmeier–Haack reaction and heterocyclic compounds synthesis for high-technology application [21], we develop novel triazoles that contain pyrazole moiety from phenyl acetonitrile and 2-hydrazino pyridine.

p-Nitrophenylmalondialdehyde **5** was obtained by Vilsmeier–Haack formylation of *p*-nitrophenylacetic acid **3**, which in turn was prepared from phenyl acetonitrile **1** by nitration followed by hydrolysis reaction. Compound **5** on reaction with 2-hydrazinopyridine **6** yielded the nitropyazoles **7**. The nitro group of **7** was reduced to give the corresponding amino compound **8**, which was diazotized and coupled with sulfonic acid substituted 2-naphthylamine to yield the corresponding *o*-amino azo compounds **11**. These *o*-amino azo compounds were air oxidized in basic cupric acetate in dimethyl formamide to give their corresponding triazoles **12a–12c** (Scheme 1), which were evaluated for their thermal and photophysical properties.

Thermal stability. To examine the thermal stability of triazoles **12a–12c**, thermogravimetric analyses (TGA) were carried out between 40 and 600°C under nitrogen

Scheme 1. Synthesis of triazoles **12a–12c**.



atmosphere. The TG curves of the compounds are shown in Figure 1. The TG results indicate that the synthesized compounds are stable up to 270°C. Above 270°C, the TG curves of the synthesized compounds show a loss in weight. TGA curves for **12a–12c** are as shown in Figure 1.

Photophysical properties. An effective fluorescent fluorophore for biological application has to present a good fluorescent intensity and high quantum yield with high photostability. The quantum yields of the fluorescence of compounds **12a–12c** were determined by using anthracene as a standard. Absorption and emission characteristics of standard as well as synthesized compounds were measured at different concentrations of synthesized compounds and

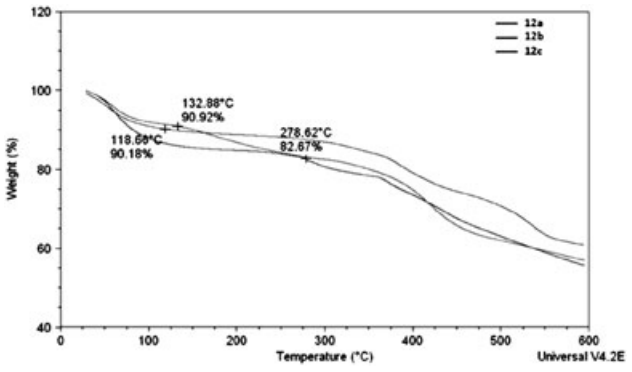


Figure 1. Thermogravimetric analysis overlay graph of compounds **12a–12c**.

standard (2, 4, 6, 8, and 10 ppm levels). Absorbance intensity values were plotted against emission intensity values. A linear plot was obtained. Gradients were calculated for each compound and for standard. All the measurements were carried out keeping the parameters constant, namely, solvent and slit width. Relative quantum yield of all synthesized triazole derivatives **12a–12c** were calculated using a formula reported in literature [22,23].

The fluorescence quantum yields of **12a–12c** were recorded in ethanol at room temperature. It is observed that the quantum yield of **12a** and **12b** are much higher than those recorded for **12c**. The higher quantum yields of **12a** and **12b** are presumably due to the presence of sulfonic acid groups on triazole ring of fluorophore **12a** and **12b**. Sulfonic acid may enhance the strength of acceptor; as a consequence, fluorophore acts as good donor-π system–acceptor type of chromogen, which may enhance the fluorescence properties. Furthermore, it was observed that the absorption–emission characteristics of compounds **12a–12c** are nearly the same except that the intensities of absorption and emission showed some difference. The compound **12c** absorbs and emits with lower intensity as compared with compounds **12a** and **12b**. The details of absorption, emission intensity, Stoke's shift, and quantum yield are summarized in Table 1.

EXPERIMENTAL

Materials and methods. All commercial reagents and solvents were purchased from S.D. Fine Chemicals (India) and were used without purification. The reaction was monitored by thin layer chromatography on 0.25 mm silica gel 60 F_{254} precoated plates (Merck KGaA, 64271, Darmstadt, Germany), which were visualized under UV light. The FT-IR spectra were recorded on PerkinElmer (USA) 257 spectrometer using KBr discs. ^{1}H NMR and ^{13}C NMR spectra were recorded on a VXR 300-MHz and VXR 75-MHz instrument, respectively, using timethylsilane as an internal standard (Varian, Palo Alto, CA). Mass spectra were recorded on Finnigan mass spectrometer (Mediagrafix Art: Technology, Australia) (EI). The visible absorption spectra of the compounds were recorded on a Spectronic Genesys 2 UV–vis spectrometer. TGA measurements were performed on SDT Q 600 v8.2 Build 100 model of TA instruments Waters (India) Pvt. Ltd. Elemental analysis was carried out using FLASH EA 1112 series instrument of Thermo Finnigan.

Synthesis of triazoles 12a–12c

4-Nitrophenyl acetonitrile 2. Concentrated nitric acid (specific gravity 1.42) (138 mL, 2.15 mol) was cooled to 0–10°C and, phenylacetonitrile **1** (50 g, 0.425 mol) was added to it at such a rate that the temperature remained at about 10°C and did not exceed 20°C during addition. After the addition of phenyl acetonitrile, the ice-cold bath was removed, and the reaction mixture warmed at 40°C for 2 h. From the reaction mass poured on crushed ice (500 g), a yellow solid was separated. The solid was filtered, washed separately with ice-cold water to remove trace of acid, and dried to yield **2**. Yield: 55 g, 79%; mp 114°C (115–116°C, lit [22]).

4-Nitrophenylacetic acid 3. Concentrated sulfuric acid (150 mL, 2.75 mol) was added to water (150 mL), and 4-nitrophenylacetonitrile **2** (50 g, 0.31 mol) was added to this mixture. The reaction mixture was refluxed for 30 min, diluted with 150 mL of water, and cooled to 0°C when colorless crystalline solid separated. The solid was filtered off, washed with ice-cold water to remove trace of acid, and dried to yield **3**. Yield: 53 g, 95%; mp 150°C (151–152°C, lit [22]).

Z-2-(4′-Nitrophenyl)-3-N,N-dimethylaminopropenal 4. To a vigorously stirred solution of DMF (2.9 mL) at 0°C, $POCl_3$ (2.8 mL) was added dropwise. After 5 min, the 4-nitrophenylacetic acid **3** (1.81 g, 0.01 mol) was carefully added in solution of DMF (5 mL). The reaction mixture was warmed to 70°C for 12 h and then poured on ice. After neutralization by K_2CO_3, a solution of NaOH 50% (12 mL) was added, and a precipitate was obtained upon cooling at 0°C. The precipitate was dissolved in dichloromethane and recrystallized from diethyl ether to give yellow powder **4**. Yield: 1.43 g, 65%, mp 131°C (131°C, lit [22]), (recrystallized from diethyl ether). ^{1}H NMR (DMSO-d_6, δ, ppm): 9.12 (s, 1H, CHO), 8.19–8.22 (d, 2H, J = 8.7 Hz, Ar–H), 7.35–7.38 (d, 2H, J = 8.7 Hz, Ar–H), 6.97 (s, 1H), 2.87 (s, 6H, HN $(CH_3)_2$).

Z-2-(4′-Nitrophenyl)-3-hydroxypropenals 5. 33% NaOH (20 mL) was added to a solution of *Z*-2-(4′-nitrophenyl)-3-*N*,*N*-dimethylaminopropenal **4** (2.2 g, 0.01 mol) in ethanol (20 mL), and the reaction mixture was stirred at reflux for 3 h. Ethanol was removed under reduced pressure, and the residue was cooled down with ice to give a powder, which was filtered and washed with CH_2Cl_2, then taken up in water and acidified by 6*N* HCl to give a precipitate. The solid was dissolved in acetone and recrystallized from ether to give **5** as a light brown powder. Yield: 1.37 g, 71%, mp 220°C (223°C, lit [22]), (recrystallized

Table 1

Absorption, emission, Stoke's shift, and quantum yield of compounds **12a–12c**.

Compound	Absorption λ_{max} (nm) (Extinction coefficient)	Emission λ_{em} (nm)	Stoke's shift (nm)	Quantum yield[a] (Φ)
12a	376 (25766)	515	139	0.51
12b	364 (24829)	501	137	0.45
12c	367 (13983)	521	154	0.24

λ_{max} and λ_{em} were measured in nm, and solvent used is DMF,
Samples conc. 1×10^{-6} μL
Measurements were carried out at room temperature.
[a]Solvent used for quantum yield measurement: ethyl alcohol; reference standard used for quantum yields calculation: anthracene.

from diethyl ether). ^{1}H NMR (DMSO-d_6, δ, ppm): 14.45 (s, 1H, OH), 8.64 (s, 2H, CHO), 8.18–8.23 (d, 2H, J = 8.8 Hz, Ar–H), 7.82–7.85 (d, 2H, J = 8.8 Hz, Ar–H).

Synthesis of 2-[3-(4-Nitrophenyl)-1H-pyrazol-1-yl] pyridine 7. A mixture of *p*-nitrophenylmalondialdehyde **5** (2.0 g, 0.01 mol), 2-hydrazinopyridine **6** (1.10 g, 0.01 mol), and ethanol (40 mL) was refluxed for 5 h, cooled, and poured into ice water (100 mL) to yield **7**. Yield: 1.56 g, 89%. (Recrystallized from ethyl alcohol). mp 198–200°C. FT-IR (KBr): 1610, 1578, 1559, 1355, 1340 cm^{-1}. ^{1}H NMR (DMSO-d_6, δ, ppm): 8.45 (d, 1H, J = 9.0, 1.8 Hz), 8.29 (s, 1H), 8.27(s, 1H), 8.09 (d, 2H, J = 8.0, 1.8 Hz), 8.01 (d, 2H, J = 8.0, 1.8 Hz), 7.87 (d, 1H, J = 8.6, 2.4 Hz), 7.72 (d, 1H, J = 8.0, 2.4 Hz) 7.70 (d, 1H, J = 8.0, 2.4 Hz). *Anal*. Calcd for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04. Found: C, 63.27; H, 3.64; N, 21.00.

Synthesis of 4-[1-(Pyridin-2-yl)-1H-pyrazol-3-yl] aniline 8. Palladium-carbon catalyst (10%, 0.05 g) was added portionwise for 5–10 min to a hot solution of **7** (2.0 g, 0.007 mol) in ethanol (mL) containing hydrazine hydrate (2.61 g, 0.052 mol). The mixture was refluxed for 1 h. The hot solution was filtered through a Whatman paper (Swastik Scientific Company, Mumbai,India) to remove Pd, and further the filtrate was filtered through silica gel (10.0 g), and the solvent was evaporated. A pure product was obtained, which was further used without purification. Yield: 1.62 g, 89%, mp 174°C. FT-IR (KBr): 3540, 3230, 1605 cm^{-1}. ^{1}H NMR (DMSO-d_6, δ, ppm): 8.56 (s, 1H), 8.42 (s, 1H), 7.97 (d, 1H, J = 11.0, 2.8 Hz), 7.80 (d, 1H, J = 8.2, 2.2 Hz), 7.41(d, 1H, J = 8.6, 2.8 Hz), 7.18 (d, 1H, J = 8.6, 2.6 Hz), 6.75 (d, 2H, J = 5.5, 2.4 Hz), 6.68 (d, 2H, J = 5.5, 2.4 Hz), 5.88 (s, 2H, –NH_2). *Anal*. Calcd for $C_{14}H_{12}N_4$: C, 71.17; H, 5.12; N, 23.71. Found: C, 71.21; H, 5.08; N, 23.68.

General procedure for preparation of *o*-amino azo compounds 11a–11c. 4-[1-(Pyridin-2-yl)-1*H*-pyrazol-3-yl] aniline **8** (2 g, 0.008 mol) was dissolved in 5*N* HCl (4 mL) with stirring and was cooled to 0–5°C, and sodium nitrite (0.69 g, 0.010 mol) was added in portions. 2-Aminonaphthyl substituted sulfonic acid **10a–10c** (1.78 g, 0.008 mol) was neutralized with 10% aqueous sodium carbonate, and the diazo compound **9** was added to it while carefully maintaining the pH of the solution at pH 6 by adding sodium acetate. The solution was stirred at 10°C for 2 h and then at 30°C for 1 h. It was finally heated at 70°C for 3 h. The red *o*-amino azo compounds **11a–11c** were filtered and washed with dilute sodium carbonate solution. Wet cake of *o*-amino azo was directly used for the next step, that is, formation of triazoles **12a–12c**.

General procedure for the formation of triazole 12a–12c. The *o*-amino azo compounds **11a–11c** (0.01 mol) were dissolved in DMF (5 mL), and basic cupric acetate (0.012 mol) solution was added to it. The reaction mixture was heated at 120°C, and air was rapidly bubbled through it. After 15–30 min, the red color disappeared, and the mixture was poured in ice-cold water (10 mL). The solid that separated was filtered, washed well with water, and dried in oven at 60°C for 12 h to yield the crude triazolyl compounds, which were further recrystallized from DMF.

Spectral data

2-{4-[1-(Pyridin-2-yl)-1H-pyrazol-4-yl]phenyl}-2H-naphtho [1,2-d][1,2,3]triazole-6-sulfonic acid (12a). Purified yield: 73%. Yellowish brown solid, mp >300°C (crystallized from ethanol). FT-IR (KBr): 3643, 3085, 1612, 1487,1317,1180,1028, 966,773, 701, 655 cm^{-1}. ^{1}H NMR (DMSO-d_6, δ, ppm): 9.25 (d, 1H, J = 8.8, 2.4 Hz), 8.45 (s, 1H), 8.43 (s, 1H), 8.18 (d, 1H, J = 6.6, 2.4 Hz), 7.94–7.97 (d, 2H, J = 7.7, 2.0 Hz), 7.75–7.78 (d, 1H, J = 8.8, 2.0 Hz), 7.57–7.61 (m, 3H, J = 2.5, 4.0 Hz), 7.42–7.44 (t, 2H, J = 7.4, 6.8,1.8 Hz), 7.30 (t, 1H, J = 8.0, 6.2, 1.0 Hz), 6.96–6.98 (t, 1H, J = 7.3, 1.4, 0.8 Hz), 6.87–6.89 (d, 1H, J = 8.0, 1.2 Hz), 4.62 (s, 1H). ^{13}C NMR (DMSO-d_6, δ, ppm): 152.42, 151.02, 140.12, 139.03, 138.43, 135.80, 135.21, 133.67, 132.0, 131.39, 130.99, 130.24, 129.45(s), 127.89, 127.00, 126.98(s), 126.56, 126.45, 126.30, 125.98, 124.67. Mass: m/z = 469.27 (M + 1). *Anal*. Calcd for $C_{24}H_{16}N_6O_3S$: C, 61.53; H, 3.44; N, 17.94; S, 6.84. Found: C, 61.62; H, 3.54; N, 17.87; S, 6. 75.

2-{4-[1-(Pyridin-2-yl)-1H-pyrazol-4-yl]phenyl}-2H-naphtho [1,2-d][1,2,3]triazole-7-sulfonic acid (12b). Purified yield: 79%. Brown solid, mp >300°C (crystallized from ethanol). FT-IR (KBr): 3558, 3121, 1453, 1181, 1031, 765, 717c cm^{-1}. ^{1}H NMR (DMSO-d_6, δ, ppm): 9.28 (d, 1H J = 9.0, 2.4 Hz), 8.46–8.45 (d, 1H, J = 8.0, 4.0 Hz), 8.20–8.21 (d, 1H, J = 6.0, 2.0 Hz), 7.98–8.00 (d, 3H, J = 7.7, 1.8 Hz), 7.81 (d, 1H, J = 8.8, 2.4 Hz), 7.64–7.70 (t, 3H, J = 8.0, 6.8, 2.4 Hz), 7.41–7.44 (t, 2H, J = 11.0, 7.3, 1.4 Hz), 7.30 (t, 1H, J = 8.0, 6.2, 1.0 Hz), 6.97–6.99 (t, 2H, J = 8.0, 6.8, 1.4 Hz), 6.58 (s, 1H). ^{13}C NMR (DMSO-d_6, δ, ppm): 152.21, 150.67, 139.12, 139.00, 137.12, 135.23, 134.09, 133.10, 132.67, 130.43, 129.46, 128.67 (s), 128.12, 127.00, 126.46 (s), 125.98, 124.45, 123.70, 122.93, 122.47, 121.67. Mass: m/z = 469.23 (M + 1). *Anal.* Calcd for $C_{24}H_{16}N_6O_3S$: C, 61.53; H, 3.44; N, 17.94; S, 6.84. Found: C, 61.59; H, 3.49; N, 17.86; S, 6.84.

2-{4-[1-(Pyridin-2-yl)-1H-pyrazol-4-yl]phenyl}-2H-naphtho [1,2-d][1,2,3]triazole (12c). Purified yield: 69%. Yellowish brown solid, mp >300°C (crystallized from ethanol). FT-IR (KBr): 3493, 3155, 1612, 1488, 1181, 1028, 699 cm^{-1}. ^{1}H NMR (DMSO-d_6, δ, ppm): 9.21 (d, 1H, J = 8.6, 2.2 Hz), 9.10 (d, 2H, J = 6.6, 2.5 Hz), 8.45–8.47 (d, 1H, J = 8.0, 2.2 Hz), 8.24–8.27 (d, 3H, J = 8.0, 2.2 Hz), 8.00–8.02 (d, 2H, J = 7.7, 4.0 Hz), 7.71 (d, 1H, J = 7.3, 2.4 Hz), 7.05 (d, 2H, J = 8.0, 1.0 Hz), 6.84–6.99 (t, 3H, J = 7.3, 6.8,1.4 Hz), 6.78 (d, 1H, J = 8.0,1.4 Hz). ^{13}C NMR (DMSO-d_6, δ, ppm): 149.67, 149.00, 138.29, 138.12, 136.76, 134.93, 134.34, 133.67, 132.54, 130.07, 128.99, 128.23, 127.92 (s), 126.56, 126.02, 125.45(s), 123.95, 123.21, 122.19, 120.43, 119.54. Mass: m/z = 389.20 (M + 1). *Anal*. Calcd for $C_{24}H_{16}N_6$: C, 74.21; H, 4.15; N, 21.64. Found: C, 74.26; H, 4.12; N, 21.62.

CONCLUSION

In summary, three novel fluorescent 2-{4-[1-(pyridine-2-yl)-1*H*-pyrazol-3-yl] phenyl}-2*H*-naphtho [1, 2-*d*] [1,2,3] triazolyl derivatives were successfully synthesized from phenyl acetonitrile, 2-hydrazinopyridine, and sulfonic acid substituted 2-naphthylamine. The position effect of the sulfonic group on absorption and emission properties of compounds was investigated. Photophysical properties study reveals that synthesized triazoles have good quantum yields, absorption ability in UV region, and emission in visible region of the spectrum. The three triazoles are thermally stable up to 270°C, and they can be good candidates as fluorescent brightening agents.

Acknowledgment. The authors are thankful to the Indian Institute of Technology, Mumbai, for providing analytical support.

REFERENCES AND NOTES

[1] Waters, P. J.; Evans, N. A. Text Res J 1978, 48, 251.

[2] Leaver, I. H.; Waters, P. J.; Evans, N. A. Polym Degrad Stab 1983, 5, 339.

[3] Evans, N. A. Aust J Chem 1981, 34, 691.

[4] Bernard, V. Molecular Fluorescence: Principles and Application. Wiley-VCH: Verlag GmbH, 2002.

[5] Godivikora, T. I.; Galova, S. P.; Vozchikova, S. A.; Ignateva, S. L.; Povarin, M. R.; Khmelnitskii, L. I. Chem Heterocycl Compd 1996, 32, 580.

[6] Wang, X.; Li, W.; Zhang, X.; Liu, D.; Zhou, X. Dyes Pigm 2005, 64, 141.

[7] Reddy, G. J.; Latha, D.; Thirupathaiah, C.; Rao, K. Heterocycl Commun 2004, 10, 359.

[8] Karale, B. K.; Gadakh, A. M.; Pandit, C.; Rindhe, S. S. Bioorg Med Chem Lett 2010, 20, 5572.

[9] Boyer, F. E.; Vara Prasad, J. V. N.; Choy, A. L.; Chupak, L.; Dermyer, M. R.; Ding, Q.; Huband, M. D.; Jiao, W.; Kaneko, T.; Khlebnikov, V.; Kim, J. Y.; Romero, K.; Wu, X. J Bioorg Med Chem Lett 2007, 17, 4694.

[10] Tanitame, A.; Oyamada, Y.; Ofuji, K.; Terauchi, H.; Kawasaki, M.; Wachi, M.; Yamagishi, J. Bioorg Med Chem Lett 2005, 15, 4299.

[11] Ruan, Y.; Maisonneuve, S.; Xie, J. Dyes Pigm 2011, 90, 239.

[12] Kim, H.; Lee, S.; Lee, J.; Tae, J. Org Lett 2010, 12, 5342.

[13] Liu, X.; Yang, X.; Peng, H.; Zhu, C.; Cheng, Y. Tetrahedron Lett 2011, 52, 2295.

[14] Huang, X.; Meng, J.; Dong, Y.; Cheng, Y.; Zhu, C. Polymer 2010, 51, 3064.

[15] Gupta, V.; Padalkar, V.; Phtangare, K.; Patil, V.; Umape, P.; Sekar, N. Dyes Pigm 2011, 88, 378.

[16] Patil, V.; Padalkar, V.; Gupta, V.; Phtangare, K.; Umape, P.; Sekar, N. J Phys Chem A 2012, 116, 536.

[17] Padalkar, V.; Patil, V.; Sekar, N. Chem Cent J 2011, 5, 72.

[18] Sekar, N.; Padalkar, V.; Tathe A.; Gupta, A.; Phatangare, K.; Patil, V. J Fluoresc 2012, 22, 311.

[19] Sekar, N.; Padalkar, V.; Patil, V.; Phtangare, K.; Gupta, V.; Umape, P. Mat Sci Eng B 2011, 170, 77.

[20] Sekar, N.; Raut, R.; Umape, P. Mat Sci Eng B 2010, 168, 259.

[21] Padalkar, V.; Borse, B.; Patil, V. J. Heterocycl Chem 2013, published ahead to print (Accepted).

[22] Padalkar, V.; Sekar, N. CCLett 2012, 1, 1.

[23] Williams, A.; Winfield, S.; Miller, J. Analyst 1983, 108, 1067.