

N-2-Aryl-1,2,3-Triazoles: A Novel Class of Blue Emitting Fluorophores-Synthesis, Photophysical Properties Study and DFT Computations

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Received: 9 March 2015 / Accepted: 4 May 2015 / Published online: 15 May 2015
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Abstract Novel fluorescent 2-[4-(4,5-diphenyl-1*H*-imidazol-2-yl) phenyl]-2*H*-naphtho [1,2-*d*] [1,2,3] triazolyl derivatives were synthesized from 4-(4,5-diphenyl-1*H*-imidazol-2-yl) aniline and substituted naphthalen-2-amine. The photophysical properties of the three new fluorophores were evaluated in acetonitrile, methanol, dimethylsulfoxide and *N,N*-dimethylformamide solvents and were compared with the reported analogs. The compounds show the absorption in the ultraviolet region and the emission in the blue region. The thermal stabilities of these compounds was evaluated by thermogravimetric analysis. The solvatochromism data are used for ground and excited state dipole moment determination of the synthesized triazoles using Bakhshiev and Bilot-Kawski correlations. The experimental absorption and emission were compared with the theoretical data obtained by DFT and TD-DFT computations and they are well in agreement with each other.

Keywords Triazole · Fluorescence · Photophysics · Imidazole · Thermal stability · DFT · TD-DFT

Electronic supplementary material The online version of this article (doi:10.1007/s10895-015-1580-7) contains supplementary material, which is available to authorized users.

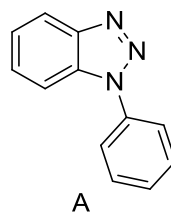
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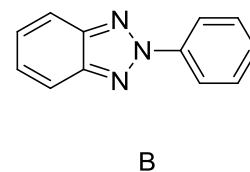
Introduction

1,2,3-Triazole and 1,2,4-triazole are important classes of heterocyclic compounds due to their wide applications in the biology [1, 2] and as functional materials [1, 2]. 1,2,3-Triazoles are commercially used as ultraviolet absorbers [3], fluorescent brightening agents and finishing agents [4, 5]. Since last two decades triazoles are used as metal sensors [6], in optoelectronic devices [6], chemosensors [7], anion sensor [8] and donor-acceptor chromophores [9]. More recently triazole derivatives are reported as sensor for nitric oxide [10], Cu (II) sensor [11], Hg (II) sensor [11], Pd (II) sensor [11], live cell sensor [12], organic light emitting diodes [13], Zn (II) sensor [14], and in the sensing of DNA in human cells [15].

N-1-Substituted 1,2,3-triazoles are explored more and they have been widely applied in materials chemistry [16–19]. *N*-2 Aryl analogues have more desirable photophysical properties as compared *N*-1-aryl substituted triazoles [22]. *N*-1-Aryl triazole **A** gave almost no emission, while *N*-2- aryl-triazole **B** showed good emission [22]. Better properties are expected based on literature and structural consideration [22]. However, *N*-2-aryl analogs of 1,2,3-triazole have received very less attention [20–22] and hence we have studied photophysics of 2-aryl substituted triazoles.



Quantum yield: 0.009



Quantum yield: 0.154

The synthesis methods for *N*-2-aryl triazoles are difficult [23]. The most of the *N*-2-aryl-1,2,3-triazoles have been synthesized through reactions involving S_NAr mechanism [23]. The substitution effect of *N*-aryl-1,2,3-triazole is not discussed much more till date [23]. The fluorescence properties of the triazoles depend on the substitution pattern [22].

This literature results suggested that the *N*-2-aryl-triazoles may adopt effective co-planar conformation between the triazole ring and the *N*-2- aryl ring even with the presence of a “free” rotatable N-C bond [22]. This unique characteristic suggested that *N*-2-aryl-triazole might be applied as new building blocks to reach effective UV/blue-emitting compounds by overcoming the challenges associated with the other small molecule systems.

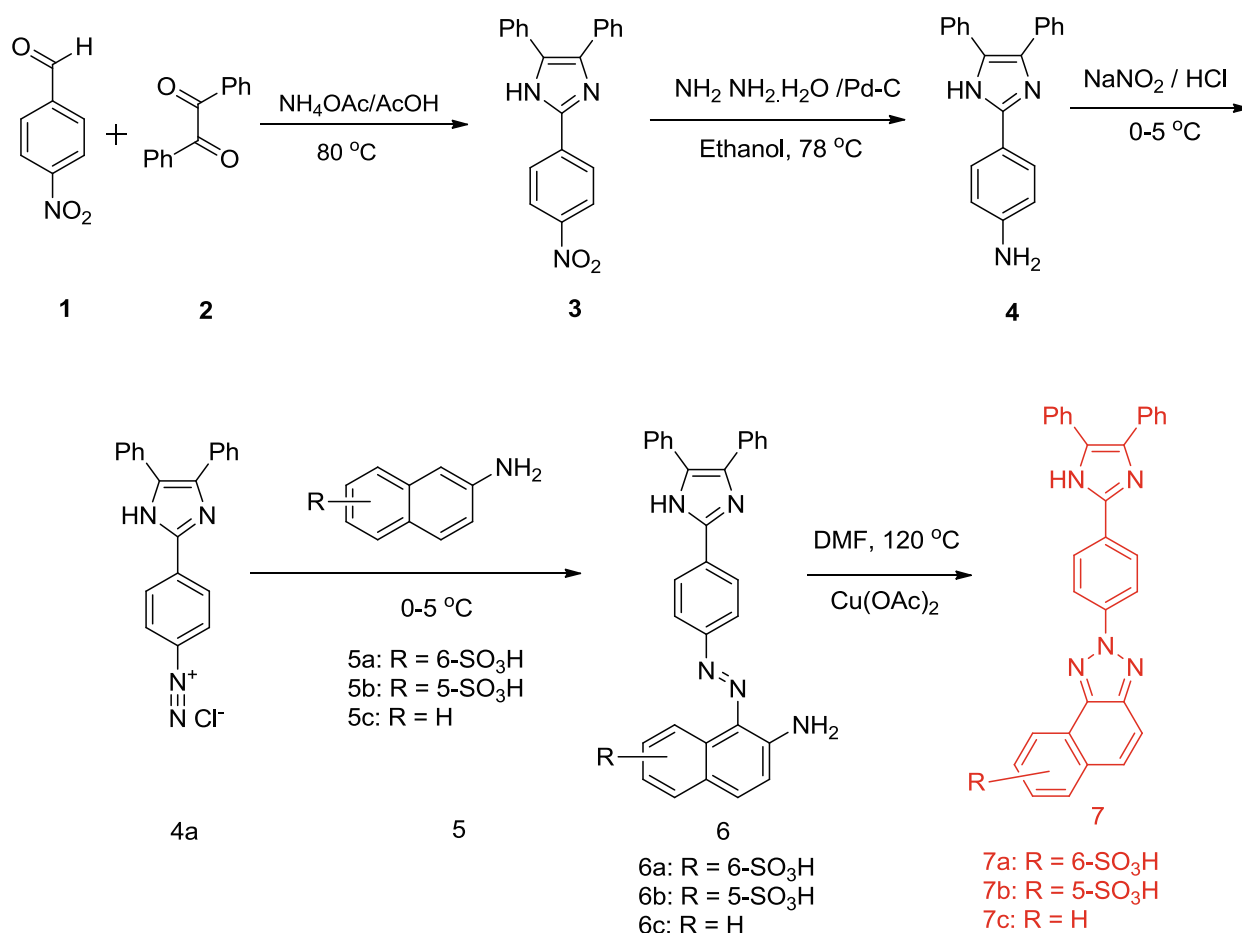
Blue emitting compounds are commercially used as fluorescent brightening agents. Coumarins are well known fluorescent brighteners, but have less photostability and their synthesis methods are tedious [24]. These limitations were overcome by triazole fluorescent brighteners. In

triazole family *N*-1-substituted 1,2,3-triazoles and *N*-2-substituted 1,2,3-triazoles emit in blue region by varying substitution on benzene ring attached to triazole ring [25–31]. Considering all these factors in this paper, three novel 2-aryl-1,2,3-triazoles were synthesized as shown in Scheme 1. The optical properties of these compounds were investigated in methanol, acetonitrile, DMF and DMSO. The photophysical properties of these fluorophores were compared with that of the reported triazole analogs [25–31]. The experimental photophysical properties were compared with theoretical data obtained by DFT and TD-DFT computations.

Experimental

Experimental Methods

Reagents and Analysis Methods *p*-Nitrobenzaldehyde, benzil, ammonium acetate, Pd-C (10 %), hydrazinehydrate



Scheme 1 Synthesis of *N*-2-aryl triazoles **7a–7c**

(99 %), 2-aminonaphthyl-substituted sulphonic acid and solvents were purchased from Spectrochem Pvt. Ltd. The FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR Spectrometer. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on VXR 300 MHz instrument using TMS (trimethylsilane) as the internal standard. Mass spectra were recorded on Finnigan mass spectrometer.

UV Absorption Spectra Absorption spectra were recorded on a Perkin-Elmer Lambda-25 spectrophotometer in 1 cm-length quartz cell with resolution of 0.1 nm. All the samples were measured from 1×10^{-6} mol L^{-1} solution of N-2-aryl-1,2,3-triazole in methanol, acetonitrile, DMF and DMSO with the wavelength range between 300 and 700 nm.

Fluorescence Emission Spectra Fluorescence emission spectra were measured on Varian Cary Eclipse fluorescence spectrophotometer with slit width of 2.5 nm. The emission spectra were obtained from 1×10^{-6} mol L^{-1} solution. The excitation wavelength was absorption maxima of the corresponding compound.

Quantum Yield The quantum yields of the compounds **7a-7c** were evaluated in methanol, acetonitrile, DMF and DMSO. The comparative method [32, 33] was used for quantum yield determination. Anthracene (ϕ : 0.27 in ethanol) was used as the standard.

Thermal Stability The thermogravimetric studies have been carried out in the temperature range 50–600°C under nitrogen gas at a heating rate of 10°C min^{-1} on Water India TGA instrument.

Synthesis of 2-(4-nitrophenyl)-4,5-diphenyl-1H-imidazole 3

A mixture of benzil (2.1 g, 10 mmol) and ammonium acetate (7.7 g, 0.01 mol) in glacial acetic acid (20 mL) was stirred at 80°C for 1 h under nitrogen atmosphere. *p*-Nitro benzaldehyde (1.5 g, 0.01 mol) in glacial acetic acid (10 mL) was added drop wise over a period of 15 min at the same temperature and stirred for another 3 h. The resulting homogenous solution was poured over crushed ice (100 g). The yellow precipitate was collected by filtration and washed with cold water, then dried under vacuum. The crude product was recrystallized from acetone to afford the pure **3**.

Yield 2.83 g, 83 %. m.p.: 209–210°C.
 FT-IR (KBr) 1443, 1518, 1600, 3394 cm^{-1} .
 $^1\text{H NMR}$ (300 MHz CDCl_3) (δ : ppm) 7.26 (s, 1H, $J=6.0\text{Hz}$, Ar-H), 7.34–7.36 (d, 6H, $J=6.0\text{Hz}$), 7.54 (s, 4H,

Ar-H), 8.02–8.04 (d, 2H, $J=2.2$, 6.0 Hz, Ar-H), 8.26–8.29 (dd, 2H, $J=2.2$, 6.0 Hz, Ar-H).

Synthesis of 4-(4,5-diphenyl-1H-imidazol-2-yl) aniline 4

Palladium-carbon catalyst (10 %) was added portion wise over a period of 5–10 min lot wise to a hot solution of **3** (1.0 g, 0.0032 mol) in ethanol (60 mL) containing hydrazine hydrate (1.12 g, 0.022 mol). The mixture was heated at reflux temperature for 1 h. The hot solution was filtered through a Whatman paper No 41 to remove Pd and further filtrate was filtered through silica gel (10 g) and solvent was evaporated. Pure product was obtained and used without purification.

Yield 0.69 g, 76 %. m.p.: 243°C
 Decomposes.
 FT-IR (KBr) 1465, 1610, 2930, 3205, 3430 cm^{-1} .
 $^1\text{H NMR}$ (300 MHz CDCl_3) (δ : ppm) 3.84 (s, 2H, $-\text{NH}_2$), 6.62–6.65 (dd, 2H, $J=1.5$, 6.0 Hz, Ar-H), 6.81–6.83 (dd, 2H, $J=1.5$, 6.0 Hz, Ar-H), 7.02–7.04 (dd, 4H, $J=1.5$, 6.0 Hz, Ar-H), 7.11–7.14 (dd, 2H, $J=1.5$, 9.0 Hz, Ar-H) 7.62–7.65 (dd, 2H $J=9.0\text{Hz}$, Ar-H), 8.97–8.99 (d, 2H).

General Procedure for Preparation of *o*-Amino azo Compounds 6

4-(4,5-Diphenyl-1H-imidazol-2-yl) aniline **4** (2 g, 0.008 mol) was dissolved in HCl (2 mL) with stirring and cooled to 0–5 °C. It was diazotized with sodium nitrite (0.69 g, 0.010 mol). The excess of nitrous acid was destroyed by the addition of urea. 2-Aminonaphthyl-substituted sulphonic acid **5** (1.78 g, 0.008 mol) was neutralized with 10 % aqueous sodium carbonate and the diazo compound was added to it slowly maintaining the pH 6 of the solution 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 compound **6** was filtered, washed with dilute sodium carbonate solution and dried. Yield: 72–84 %

General Procedure for the Formation of Triazols 7

The *o*-amino azo compounds **6** (0.01 mol) was dissolved in DMF (5 mL) and basic cupric acetate

(0.012 mol) solution was added. The mixture was heated at 120 °C and air was rapidly bubbled into it. After 15–30 min, the red color was discharged and the mixture was poured to ice cold water (10 mL). The separated solid was filtered, washed well with water and dried in oven at 60 °C for 10 h to yield the crude triazolyl compounds, which were further recrystallized from DMF. Yield: 79–87 %

2-[4-(4,5-Diphenyl-1H-imidazole-2-yl) phenyl]-2H-naphtho [1,2-d] [1,2,3] triazole-7-sulphonic acid (7a)

Yield	79 %
m.p.	> 300°C
FT-IR (KBr)	3439, 3115, 1612, 1570, 1488, 1453, 1181, 1028, 988, 833, 775, 699 cm ⁻¹ .
¹ H NMR (300 MHz DMSO)	7.28 (d, 1H, <i>J</i> =7.5 Hz, Ar-H), 7.33–7.37 (t, 2H, <i>J</i> =1.8, 7.5 Hz, Ar-H), 7.39–7.47 (m, 8H, <i>J</i> =1.8, 7.5 Hz, Ar-H), 7.53–7.56 (dd, 4H, <i>J</i> =1.8, 7.5 Hz, Ar-H), 7.94–7.97 (d, 2H, <i>J</i> =7.5 Hz, Ar-H), 8.08–8.10 (d, 2H, <i>J</i> =1.8, 7.5 Hz, Ar-H), 8.98 (s, 1H), 12.5 (s, 1H).
¹³ C NMR (100 MHz DMSO)	112.2, 124.0, 126.0, 126.7(s), 127.0, 127.3, 127.6 (s), 128.1, 128.4 (s), 129.0, 129.2 (s), 129.7, 130.3, 132.4, 134.8, 138.2(s), 139.0, 141.2, 179.4.
Mass (m/z)	543.34 (M+123 %) 542.40 (100 %), 356.52 (12 %), 260.34 (46 %)

Synthesis of 2-[4-(4,5-diphenyl-1H-imidazol-2-yl) phenyl]-2H-naphtho [1,2-d] [1,2,3] triazole-6-sulphonic acid (7b)

Yield	83 %
m.p.	> 300°C
FT-IR (KBr)	3432, 3106, 1618, 1573, 1492, 1458, 1179, 1031, 991, 778 cm ⁻¹ .
¹ H NMR (300 MHz DMSO)	7.31 (d, 1H, <i>J</i> =8.0 Hz, Ar-H), 7.34 (t, 2H, <i>J</i> =1.6, 8.0 Hz, Ar-H), 7.43–7.46 (m, 8H, <i>J</i> =1.6, 8.0 Hz, Ar-H), 7.50–7.53 (dd, 4H, <i>J</i> =1.6, 8.0 Hz, Ar-H), 7.91–7.94 (d, 2H, <i>J</i> =8.0 Hz, Ar-H), 8.06–8.08 (d, 2H, <i>J</i> =1.6, 8.0 Hz, Ar-H), 8.87 (s, 1H), 12.7 (s, 1H).
¹³ C NMR (100 MHz DMSO)	112.0, 123.7, 125.9, 126.0 (s), 127.4, 127.7, 127.9 (s), 128.0, 128.3 (s), 129.2, 129.6 (s), 130.0, 130.7, 132.6, 134.9, 138.4 (s), 139.7, 141.9, 181.3.
Mass (m/z)	543.30 (M+148 %) 542.36 (100 %), 355.12 (29 %), 260.00 (39 %)

Synthesis of 2-[4-(4,5-diphenyl-1H-imidazole-2-yl) phenyl]-2H-naphtho [1,2-d] [1,2,3] triazole (7c)

Yield	87 %
m.p.	> 300°C
FT-IR (KBr)	3441, 3119, 1581, 1489, 1449, 1184, 1032, 991, 836, 701.
¹ H NMR (300 MHz DMSO)	7.23 (d, 1H, <i>J</i> =7.8 Hz, Ar-H), 7.29–7.31 (t, 2H, <i>J</i> =1.6, 7.8 Hz, Ar-H), 7.34–7.37 (m, 8H, <i>J</i> =1.6, 7.8 Hz, Ar-H), 7.47–7.51 (dd, 5H, <i>J</i> =1.8, 7.8 Hz, Ar-H), 7.87–7.89 (d, 2H, <i>J</i> =7.8 Hz, Ar-H), 8.04–8.07 (d, 2H, <i>J</i> =1.6, 7.8 Hz, Ar-H), 8.77 (s, 1H).
¹³ C NMR (100 MHz DMSO)	109.3, 119.0, 123.3, 124.7 (s), 125.9, 126.1, 127.0 (s), 127.4, 127.9 (s), 128.4, 128.9 (s), 129.0, 129.3, 129.8, 131.8, 134.8 (s), 136.1, 137.2, 168.0.
Mass (m/z)	464.33 (M+163 %) 465.30 (100 %), 332.78 (47 %), 268.79 (12 %).

Results and Discussion

Chemistry

Three new triazoles were prepared by the cyclisation, reduction, diazotization and oxidation reactions Scheme 1. The reaction of 4-nitrobenzaldehyde with benzil in the presence of ammonium acetate in acetic acid at 80°C to afford the compound **3** in good yield. The compound **3** on Pd-C/ hydrazine hydrate reduction in ethanol at reflux temperature gave the amine **4**, which on further diazotization using sodium nitrite gave the corresponding diazonium salt. The diazonium salt **4a** was coupled with different substituted naphthalen-2-amine at low temperature to give the diazo compounds **6**. The triazoles **7a–7c** was obtained by air oxidation of the compound **6** in basic cupric acetate solution at 120°C in DMF. The structures of the compounds were confirmed by spectral analysis.

Photophysical Properties

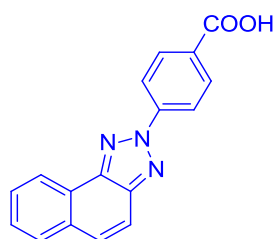
N-2-Aryl-1,2,3-triazoles are good fluorescent fluorophores compared to the *N*-1-Aryl-1,2,3-triazoles [22]. The photophysical properties of the *N*-2-Aryl-1,2,3-triazoles are not studied intensively. In the literature, very few reports are available which describe the photophysical properties of the *N*-2-aryl-1,2,3-triazoles [22]. In the present paper, we discuss the photophysical properties of the novel *N*-2-aryl-1,2,3-triazoles **7a–7c**. The photophysical properties are compared with the reported analogs [25–31]. The effect of the substituents on the

photophysical properties are highlighted in the comparison study. The DFT and TD-DFT computation were performed to estimate theoretical absorption and emission. The experimental results were compared with computed data and experimental results are in good agreements with theoretical data.

Substituent's Effect on Photophysical Properties

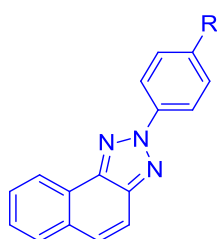
The electron donor and the acceptor groups tune the absorption and the emission properties [29]. The substit-

uents attached to the para position with respect to the triazole ring show significant change in the absorption and the emission. The different electron donor, acceptor and extended conjugated groups are considered for the comparison **8–11**. Electron donor and extended conjugation groups show the red shifted absorption as well as the emission as compared to the electron acceptor group attached to 2-aryl position. The compound **8** shows a blue shifted absorption and emission compared to the compounds **9** and **11**.



Absorption: 340 and 360 nm
Emission: 370 and 380 nm

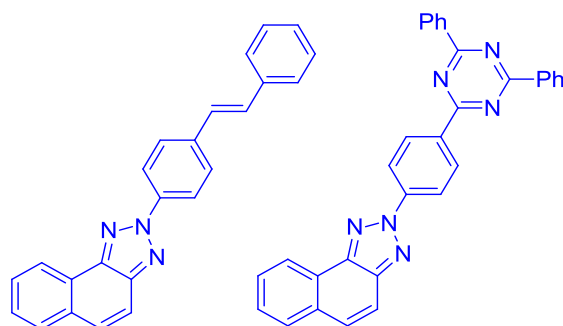
8



Absorption: 335 - 354 nm
Emission: 415 - 447 nm

9

R: -NH₂, -CH₃, -F, -Ph, -CH₂OH



Absorption: 373 nm
Emission: 425 nm

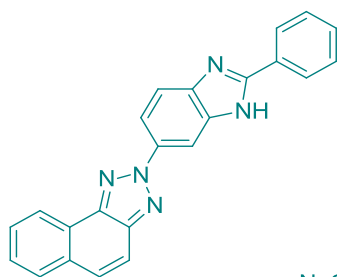
10

Absorption: 360 nm
Emission: 430 nm

11

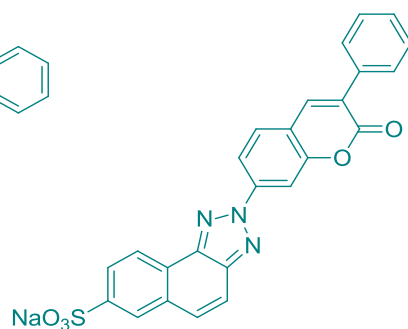
The planarity and extended conjugation or push-pull-type of chromophores gives bathochromic shift because of the effective aromatic conjugation, usually these compounds possess a low energy gap between the excited and the ground states, thus, giving emission at a longer wavelength [22].

The effect of the fused groups on optical properties attached to *p*-position with respect to the triazole ring is also considered in the present study. Three different fused triazoles **12–14** were compared. The compounds **12–14** show red shifted absorption and the emission compared to compounds **8–11**.



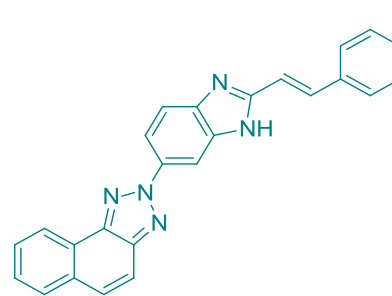
Absorption: 364 nm
Emission: 428 nm

12



Absorption: 375 nm
Emission: 432 nm

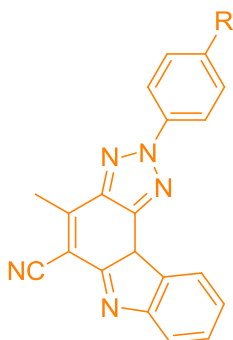
13



Absorption: 373 nm
Emission: 425 nm

14

The electron donor or fused system on the naphthalene ring shows red shifted absorption and emission compared to the other substituents on the triazoles. The triazole **15** contains electron donor carbazole type of ring fused with triazole ring, which helps in a better delocalization and hence red shifted absorption and emissions are observed.



R: -CH₃, -OCH₃, -NO₂, -NH₂, NHCOCH₃

Absorption: 398–421 nm

Emission: 448–530 nm

15

Novel triazoles **7a–7c** contains sulphonic acid on the naphthalene ring and phenyl groups on the imidazole ring. These compounds are novel class of blue emitting compounds which emits at wavelengths similar to the reported analogs **8–15**. The compounds **7a–7c** show absorption peaks around 350 nm in ultraviolet region. The absorption wavelengths were used as excitation wavelength for the fluorescence measurements. The compounds show emission in blue region between 400 and 430 nm with considerable Stokes shift and quantum efficiency. It is seen that the absorption-emission characteristics of the compounds **7a–7c** are nearly same. The absorption and emission spectra of the compounds **7a–7c** are shown in Figs. 1, 2 and 3 and photophysical data are summarized in Table 1. The compound **7a** absorbs between 353 and 360 nm in acetonitrile, methanol, DMF and DMSO. In DMF and DMSO compound **7a** shows red shifted absorption as compared to methanol and acetonitrile. The absorption

properties of the compound **7b** are similar to the compound **7a**. The compound **7c** shows absorption between 353 and 361 nm. The compounds **7a–7c** show red shifted absorption in DMSO and DMF. The compounds **7a–7c** are fluorescent in solution. The compounds show emission in the visible region in between 401 and 431 nm. The emission properties of the compounds depend on solvent polarity. In polar solvents (DMF and DMSO) the compounds show red shift as compared to the other solvents, methanol and acetonitrile. The quantum efficiency of the compounds **7a–7c** are between 13 and 19 % in the studied solvents.

Computational Methodology

DFT method was used for the ground state optimization, while for the excited state optimization, TD-DFT and Configuration Interaction Singles (CIS) methods were employed. The hybrid functionals namely B3LYP (Becke3-Lee-Yang-Parr hybrid functional) [34–37] was used. The 6-31G(d) basis set was used for all the atoms and later was ascertained in the literature [38]. The Polarizable Continuum Model (PCM) [39] was used to optimize the ground and excited state geometries in solvents. On the basis of the optimized ground state structures absorption characteristics, oscillator strengths and configuration were systematically evaluated using TD-DFT with polarizable continuum model PCM model. The solvents used were methanol (MeOH), acetonitrile (ACN), *N,N*-dimethyl formamide (DMF), dimethylsulfoxide (DMSO). All computations were performed with the Gaussian 09 package [40].

The calculated excitation spectra using B3LYP functional at 6-31G(d) levels in solvents of varying polarity, oscillator strength, and their orbital contribution are shown in Table 2. The vertical excitation computed by TD-DFT is compared with the experimental absorption maxima. The chromophore **7a** has absorption at 353 nm in MeOH, its calculated vertical excitation at 6-31G(d) level is 353 nm and it is well in agreement with the experimental value. The experimental absorption maxima for **7a** is 354 nm in acetonitrile, 360 nm in DMF and 354 nm in DMSO, while the computed vertical excitations are 350 nm in acetonitrile and 349 nm in DMF and

Fig. 1 Absorption and emission spectra of compound **7a**, **a** Absorption spectra **b** Emission spectra

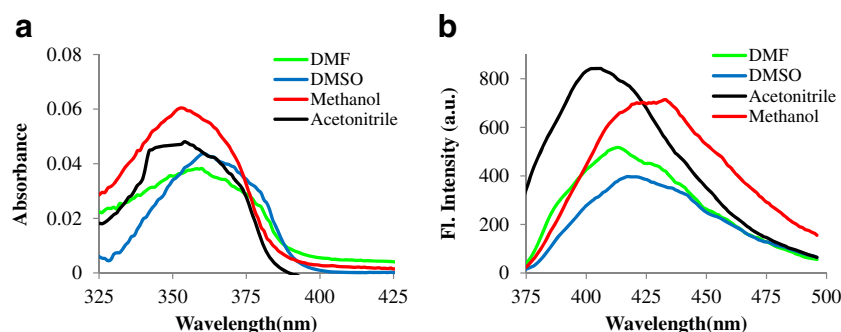
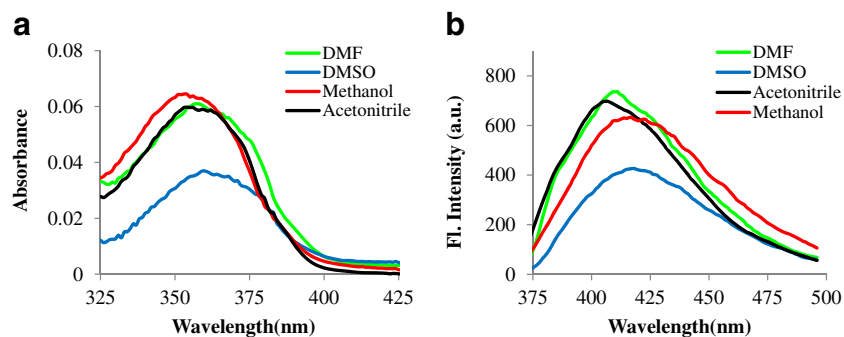


Fig. 2 Absorption and emission spectra of compound **7b**, **a** Absorption spectra **b** Emission spectra



DMSO. It is observed that the chromophore **7a** shows less deviation of 3 nm in methanol while more deviation of 14 nm is observed in DMSO. The chromophore **7b** shows more deviation of 14 nm in methanol while less deviation of 11 nm in DMSO. The chromophore **7c** shows highest deviation as compared to chromophore **7a** and **7c** which is in the range of 18–25 nm, in methanol solvent it is 18 nm, and 25 nm in DMSO. In the case of emission a large difference was observed between experimental emission and TD-DFT emission. The compounds **7a** and **7b** show more deviation as compared to the compound **7c**. A large difference was observed for the compound **7a** in acetonitrile (87 nm). The major orbital contribution for the charge transfer transition arises from HOMO to LUMO+1 for the compounds **7a** and **7b** and it is 98 % while for the compound **7c** the major orbital contribution is HOMO-1 to LUMO and it is 94 %. The frontier molecular orbital diagrams for the compounds **7a–7c** in acetonitrile solvent are shown in Table 3. In the case of HOMO-1 the electron density is distributed over the complete structure, while in the case of HOMO the electron density is distributed over the diphenyl and the imidazole core. In the case of LUMO the electron density is distributed over the triazole and the naphthalene units, while the electron density is on the diphenyl and the naphthalene units for LUMO+1 orbitals. Thus, the absorption leading to the electronic excitation from the HOMO or HOMO-1 to the LUMO+1 or LUMO orbital can constitute to the charge transfer from the triazole unit to the imidazole containing two phenyl units.

The optimized bond angles and dihedral angles at B3LYP/6–31 g (d) level are summarized in SI Table 1. The compound **7a** shows bond angle N(17)-N(16)-C(8), 121.8° at the ground state but at the excited state it is slightly higher (122.7°) but significant change is observed for the dihedral angle C(12)-C(13)-C(33)-N(36) between the central benzene ring and the imidazole segment. The dihedral angle of **7a** in acetonitrile at the ground state is 173.3° while in the excited state it is 175.68° which indicates that imidazole core attached with benzene segment is more planar in the singlet excited state as compared to the ground state. But there is very small change observed for the central benzene core and the triazole segment which indicates that a small change is observed for planarity between central benzene core and triazole segment. A similar trend is observed for the compound **7a** in the other solvents like DMF, DMSO and MeOH. The dihedral angle, N(37)-C(34)-C(49)-C(50) show 2° change in the excited state. This indicates a slight twisting occurring when the molecule is excited; the two phenyl rings attached to the imidazole core become twisted. The trend is similar in all the other solvents. An interesting result was observed for the compound **7b** - the dihedral angle, N(17)-N(16)-C(8)-C(9) between the triazole and benzene ring at the ground state is 174.7° but in the singlet excited state it is changed by 5° . The dihedral angle, N(17)-N(16)-C(8)-C(10) at the ground state is 5.2° and in the excited state it is change to 0.6° which confirms that, the triazole core attached to the central benzene segment is more planar in the excited state as compared to the ground state. The compound

Fig. 3 Absorption and emission spectra of compound **7c**, **a** Absorption spectra **b** Emission spectra

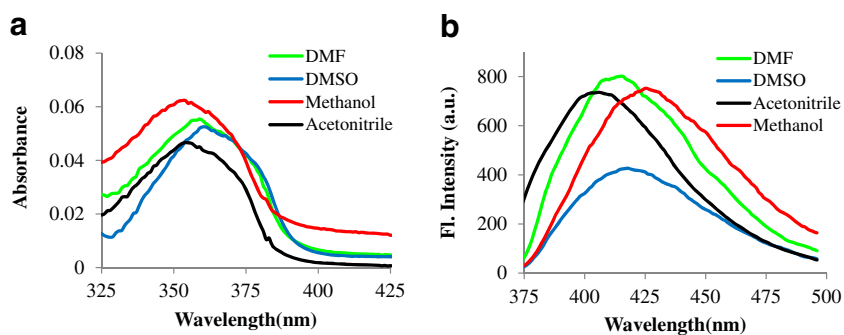


Table 1 Photophysical properties of compounds **7a–7c**

Compounds	Solvents	Absorption (nm)	Emission (nm)	Stokes Shift (nm)	Stokes Shift (cm ⁻¹)	^a Quantum Yields (%)	TD-DFT Emission (nm)
7a	Methanol	353	431	78	5200	16	494
	Acetonitrile	354	403	49	3400	17	490
	DMF	360	413	53	3500	14	494
	DMSO	363	418	55	3600	17	493
7b	Methanol	353	416	63	4300	19	490
	Acetonitrile	355	406	51	3500	18	490
	DMF	358	410	52	3500	17	490
	DMSO	359	418	59	3500	13	490
7c	Methanol	353	426	73	3900	17	467
	Acetonitrile	354	401	47	4800	19	467
	DMF	359	415	56	3300	18	467
	DMSO	361	418	57	3800	19	467

λ_{max} and λ_{em} were measured in nm and solvent used are methanol, acetonitrile, dimethylsulfoxide, and dimethylformamide, Measurements were carried out at room temperature

^a Anthracene is used as standard

7b in acetonitrile shows dihedral angle, C(12)-C(13)-C(32)-N(35) 178.5° in the ground state and it is reduced to 3° in the excited state. Similarly the dihedral angle, C(12)-C(13)-C(32)-N(36) at the ground state is 1.9° increased to 4° in the excited state. It clearly shows that the central benzene core attached to the imidazole segment is more planar in the ground state as compared to the excited state. But the two imidazole containing phenyl rings exhibit little change 1 or 2° in the excited state. A similar trend was observed in the other polar solvents like MeOH, DMF and DMSO. The compound **7c**

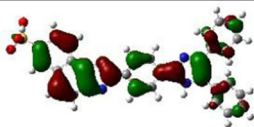
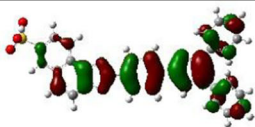
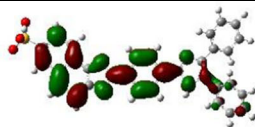
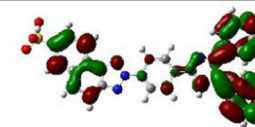
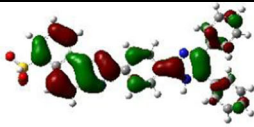
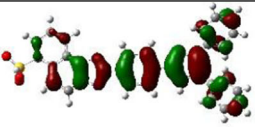
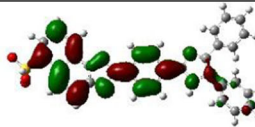
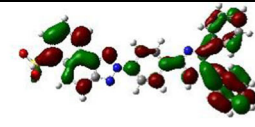
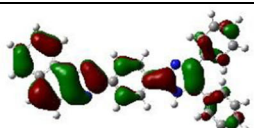
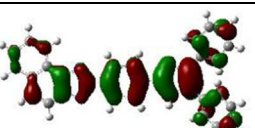
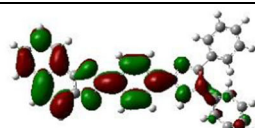
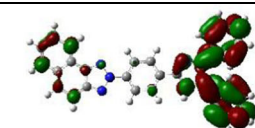
shows the dihedral angle, N(17)-N(16)-C(8)-C(9) at the ground state 178.9° but in the excited state it is changed by 1°. The dihedral angle, N(17)-N(16)-C(8)-C(10) at the ground state is 1.1° and in the excited state it is changed to 0.5° which confirms that the triazole core attached to the central benzene segment is closer to planarity in the excited state as compared to the ground state. But it is noteworthy that the compound **7c** in acetonitrile shows a dihedral angle, C(12)-C(13)-C(32)-N(30) 169.4° in the ground state and it is increased up to 6° in the excited state. While the dihedral angle, C(12)-C(13)-

Table 2 Observed absorption and computed vertical excitation for compounds **7a–7c** in various solvent

Structure	Solvent	^a Exp. λ_{max}	TD-B3LYP/6-31G(d)			
			Vertical excitation		Oscillator strength (<i>f</i>)	^c Orbital contribution
			^b λ_{nm}	eV		
7a	Methanol	353	350	3.5462	0.0162	H→L+1 (95 %)
	Acetonitrile	354	350	3.5465	0.0165	H→L+1 (95 %)
	DMF	360	350	3.5465	0.0173	H→L+1 (95 %)
	DMSO	363	349	3.5473	0.0175	H→L+1 (95 %)
7b	Methanol	353	367	3.3740	0.0929	H→L+1 (98 %)
	Acetonitrile	355	367	3.3741	0.0928	H→L+1 (98 %)
	DMF	358	367	3.3730	0.0920	H→L+1 (98 %)
	DMSO	359	368	3.3737	0.0923	H→L+1 (98 %)
7c	Methanol	353	335	3.7011	0.2457	H-1→L (94 %)
	Acetonitrile	354	335	3.7001	0.2457	H-1→L (94 %)
	DMF	359	336	3.6949	0.2468	H-1→L (94 %)
	DMSO	361	336	3.6954	0.2461	H-1→L (94 %)

^a Experimental absorption in nm; ^b Vertical excitation (theoretical absorption in nm); ^c Electronic transitions

Table 3 Electronic distribution in the selected molecular orbitals of compound **7a–7c** in acetonitrile solvent

Comp.	HOMO-1	HOMO	LUMO	LUMO+1
7a				
7b				
7c				

C(32)–N(31) at the ground state is 10.9° it is reduced to 6° in the excited state. This clearly indicates that the central benzene core attached to the imidazole segment is more planar in the excited state as compared to the ground state. But the imidazole attached to two phenyl ring shows little change up to 1° in the excited state. All the compounds show a similar behavior in all the other solvents. The optimized structures of the compounds **7a–7c** are summarized in SI Fig. 1.

Dipole Moment Determination by Solvatochromic Method

The properties of solvents such as dielectric constant, refractive index and permittivity are very important for study the physicochemical process of the molecules. These properties of solvent induce changes in the electronic transitions of solutes (solvatochromism) depending on the nature and the degree of interaction between the solute solvent in ground and first excited states of solutes (developed locally in the immediate vicinity) [41, 42]. In short we can say that change in the dipole moment of short-lived species (excited state) is considerably affected by properties of solvent and can be clearly indicated by solvatochromism and solvatofluorism. The dipole moment of electronically excited species is of great importance in revelation of the nature of excited state, designing non linear optical material and parameterization of semi-empirical quantum chemical procedures of these states [43]. A most accepted technique for dipole moment calculation is based on Lippert–Mataga equation [44–47]. This technique is based on the absorption and emission maxima with polarity functions of solvents, expressed by the relative permittivity (ϵ) and refractive index (η) of the

solvent medium [48, 49]. Hence solvatochromism and solvatofluorism are found to be excellent tools to evaluate the ground state and excited state dipole moments of the short-lived species [50–59].

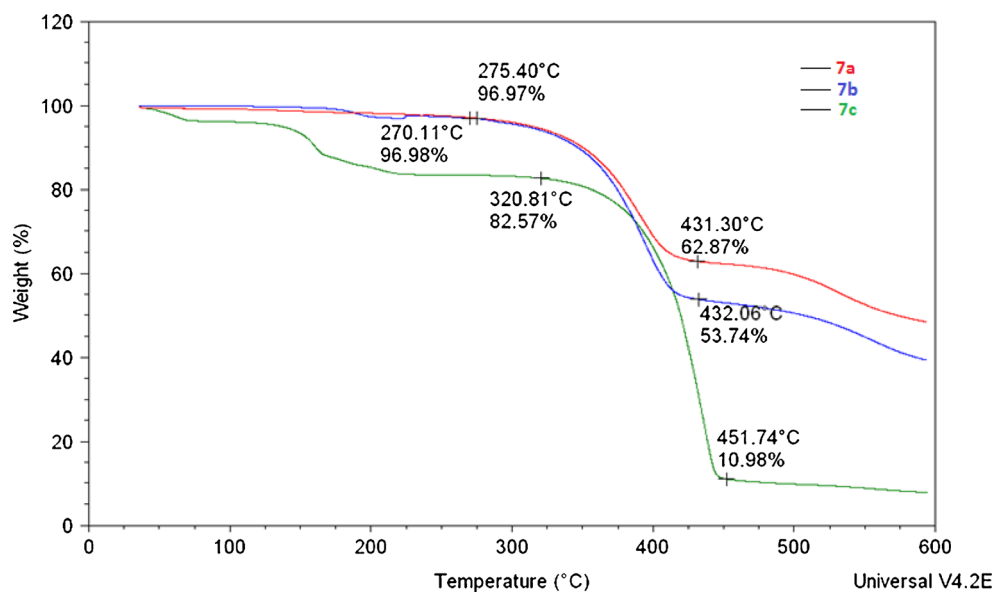
In this paper, we evaluated the ratio of ground to excited state dipole moment of the synthesized triazoles using Bakhshiev [60] and Bilot-Kawski correlations [61, 62]. The detailed theory for the calculation of dipole moment is described in SI (Supporting Information).

Calculations of Dipole Moment The solvent polarity functions $f_1(\epsilon, \eta)$ and $f_2(\epsilon, \eta)$ for each solvent were calculated by substituting the respective values for dielectric constant and refractive index in equations 4 and 7 (SI) the values obtained are tabulated in SI Table 2. Graph of $f_1(\epsilon, \eta)$ verses Stokes shift in cm^{-1} is plotted and calculated m_1 as slope 1, as well as graph of $f_2(\epsilon, \eta)$ verses $(\sqrt{\nu_a + \nu_r})/2$ in cm^{-1} were plotted to get values of function m_2 as slope 2, the obtained values are tabulated in SI Table 3. Further the ratio of the excited state dipole moment to the ground state dipole moment is calculated from equation 12 by substituting the values

Table 4 Excited state and ground state dipole moment (in Debye) ratio value for dyes **7a–7c**

Compound	$ m^1 + m^2 $	$ m^1 - m^2 $	$\frac{\mu_e}{\mu_g}$
7a	2695	85	0.031
7b	3515	1091	0.310
7c	6948	2655	0.382

Fig. 4 Thermogravimetric curve of compounds **7a–7c**



of m_1 and m_2 and summarized in Table 4. The calculated values demonstrate that the compounds **7a–7c** has more polar ground state than the excited state indicating that the charge transfer processes occurs in the ground state rather than in the excited state.

Thermal Stability Study

In addition to a large Stokes shift and quantum efficiency thermal stability is also an important parameter for the compounds which are applicable in high-technology. The TGA curves of the compounds are shown in Fig. 4. The TG results indicate that the framework of the synthesized compounds are stable up to 300°C. Above 300°C the TG curves of the synthesized compounds show a loss in weight. The compound **7c** shows complete weight loss around 451°C, while the compounds **7a** and **7b** show 50 % weight loss around 450°C. The compounds **7a** and **7b** does not show complete weight loss even up to 600°C. The comparisons of the T_d (decomposition temperature) showed that the thermal stability of **7a–7c** decreases in the order **7a**>**7b**>**7c**. Thermal stability and their plausible degradation scheme are presented in Fig. 4.

Conclusion

In summary, first time the *N*-2-aryl-1,2,3-triazoles absorbing in UV region and emitting in the blue region have been studied. The compounds show good quantum efficiency (14–19 %) and large Stokes shift. The compounds emit at wavelength in which similar reported analogs emits. The dipole moments at the ground state and the excited state were calculated from absorption and emission data. The ground states of the compounds are more polar as compared to the excited

states which were confirmed by the structure optimization by DFT and TD-DFT. The experimental photophysical properties were correlated with the theoretical data and they are in good agreements. The maximum deviation between experimental absorption and vertical excitation is 25 nm. The compounds are thermally stable up to 300°C.

Acknowledgments Vikas Padalkar and Santosh Chemate are thankful to the Institute of Chemical Technology, Mumbai, India for the encouragement. Sandip Lanke is thankful to UGC-CSIR for Senior Research Fellowship.

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