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ORIGINAL PAPER

Synthesis and Photo-Physical Characteristics of ESIPT Inspired 2-Substituted Benzimidazole, Benzoxazole and Benzothiazole Fluorescent Derivatives

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Abstract Novel 2-(1*H*-benzimidazol-2-yl)-5-(*N,N*-diethylamino) phenol, 2-(1,3-benzoxazol-2-yl)-5-(*N,N*-diethylamino) phenol, 2-(1,3-benzothiazol-2-yl)-5-(*N,N*-diethylamino) phenol and their derivatives have been synthesized from *p-N,N*-diethyl amino salicylaldehyde with different substituted *o*-phenylenediamine or *o*-aminophenol or *o*-aminothiophenol and their photo-physical properties were studied. Effects of solvent polarity in the absorption-emission properties of synthesized compounds were investigated. All these compounds shows excited state intra-molecular proton transfer pathway having single absorption and dual emission characteristics. The fluorescent compounds were characterised by FT-IR, ^{1}HNMR, ^{13}C NMR and Mass spectral analysis. TGA analysis showed these compounds are thermally stable up to 200 °C.

Keywords Dual emission · ESIPT · Solvatochromism · Fluorescence · Photo-physics · Benzimidazole · Benzoxazole · Benzothiazole

Introduction

Stimuli-sensitive materials have wide applications in bio-sensing and biomedical diagnostics. In particular, the direct visualisations of general biochemical events, specific molecular targets or defined biochemical processes are indispensible for both in vitro [1–4] and increasingly in vivo applications [3–6]. In recent years, advances in imaging technique have made these applications very encouraging particularly in the use of an array of different labels, probes and channels in multi-channel multiple studies [7–9] and the real time analysis of cells and whole organism [10–13].

Fluorescent molecules which can be incorporated into probes with defined optical and chemical properties having compatibility in bio-materials are becoming increasingly important. Fluorescent molecules exhibiting dual emission find applications in ratiometric sensing since two band ratiometric detection can provide self calibration of fluorescence signal which allows compensation of all fluorescence quenching effect [14, 15].

Study of photophysical properties of molecules exhibiting excited state intra-molecular proton transfer reactions has received much attention in recent years [16–25]. This is not only because of their importance in understanding the ultrafast reactions at the molecular level [26], but also because of the fact that these molecules undergoing the ESIPT process find applications ranging from polymer UV stabiliser [27, 28], laser dyes [29–31] to photo-chromic materials [32].

The fundamental requirements of ESIPT process are the presence of intra-molecular hydrogen bonding between the acidic proton, basic moiety and the suitable geometry of molecular system. The acidic proton mostly used are -OH, -NH_2 etc. and basic centres are =N-, carbonyl oxygen (=C=O). A large number of potential molecules [33–36] which show ESIPT are reported in literature and their absorption-emission properties are also studied as a function of their environment.

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It has been observed that Stokes shifts are higher when molecules contain benzimidazole, benzothiazole, benzoxazole and benzotriazole units. The high intensity of fluorescence emission and large Stokes shift are due to the excited state intramolecular proton transfer phenomenon [37–52] which allows these molecules to have many interesting applications [53].

In this paper, we report the synthesis and characterization of novel hydroxy benzimidazole, benzoxazole and benzothiazole derivatives. These compounds have interesting absorption-emission characteristics and solvatochromism properties.

Experimental Section

Materials and Equipments

All commercial reagents and solvents were procured from s.d.fine chemicals (India) and were used without purification. The reactions were monitored by TLC using on 0.25 mm E-Merck silica gel 60 F_{254} precoated plates, which were visualized with UV light. Melting points were measured on standard melting point apparatus from Sunder industrial product Mumbai and are uncorrected. The FT- IR spectra were recorded on a Perkins-Elmer 257 spectrometer using KBr discs. ^{1}H NMR spectra were recorded on VXR 300-MHz instrument using TMS as an internal standard. LC-MS were recorded on FINNIGAN LCQ ADVANTAGE MAX instrument from Thermo Electron Corporation (USA). The absorption spectra of the compounds were recorded on a Spectronic Genesys 2 UV-Visible spectrophotometer; UV-Visible emission spectra were recorded on JASCO – FP 1520. Simultaneous DSC-TGA measurements were performed on simultaneous DSC-TGA Waters (India) Pvt Ltd. DFT calculations were performed on a HP workstation XW 8600 with Xeon processor, 4 GB RAM and Windows Vista as operating system. The software package used was Guassian 03 W. The ground state geometry was optimized at B3LYP level of theory and 6–31 G (d) as basis set and excited state geometry was optimized by TD-DFT with B3LYP/6–31 G (d) basis set 3 [54].

Photo-Physical Properties

An effective fluorescent dye for biological application should have good fluorescence intensity, high quantum yield and high photostability. Quantum yield of compounds **4a–4i** were determined by using anthracene as standard. Absorption and emission characteristics of standard as well as unknown samples were measured at different concentration of unknown samples and standard at (2, 4, 6, 8 and 10 ppm level). Absorbance intensity values were plotted against emission intensity values. A linear plot was obtained. Gradients were calculated for each unknown compound and for standard. All the measurements were done by keeping the parameters such as solvent and slit width constant. Relative quantum yield of all synthesized compounds **4a–4i** were calculated by using the **Formula 1** [55].

Formula 1: **Relative fluorescence quantum yield**

$$\Phi x = \Phi_{ST}(\mathrm{Gradx}/\mathrm{Grad}_{ST})\left(\eta^2_x/\eta^2_{ST}\right)$$

Where:

Φ_X	Quantum yield of unknown sample
Φ_{ST}	Quantum yield of standard used
Grad_X	Gradient of unknown sample
Grad_X	Gradient of standard used
η^2_{ST}	Refractive index of solvent for standard sample
η^2_X	Refractive index of solvent for sample

The fluorescence quantum yields of **4a–4i** were recorded in ethanol as well as acetonitrile at room temperature. The compounds **4a–4i** showed similar fluorescence behaviour with respect to fluorescence quantum yield in both the solvents, the details are given in the Table 1.

Synthesis and Characterisation

Synthesis of 4-(N,N-diethyl amino)-2-hydroxybenzaldehyde **(2)**

Phosphorous oxychloride ($POCl_3$) (2.75 ml, 0.03 mol) was slowely added to dimethylformamide (DMF) (3.65 ml, 0.05 mol) at 5–10 °C under the stirring. To this cooled reagent 3-(*N,N*-diethyl amino) phenol (0.01 mole) was added by dissolving it in to DMF (6 ml) under the stirring and the resulting mixture was heated at 75 °C for 4 h. The reaction mixture was cooled to room temperature and then poured into ice cold water (60 ml). Reaction mass was

Table 1 Quantum yield of compounds **4a - 4i** in ethanol and acetonitrile

Compounds	Quantum yield ethanol	Quantum yield acetonitrile
4a	0.105	0.094
4b	0.188	0.209
4c	0.122	0.139
4d	0.158	0.168
4e	0.121	0.121
4f	0.139	0.130
4g	0.124	0.131
4h	0.118	0.098
4i	0.136	0.132

λmax and λem were measured in nm

Samples were prepared in ethanol and acetonitrile

Analyses were carried out at room temperature

neutralised with sodium carbonate, brown colored solid separated out. Separated product was filtered and washed with cold water, dried and crystallised from ethanol to afford the pure product **2** (m.p. 62 °C) (lit. 62–64 °C [56])

General Procedure for Synthesis of 2-substituted Benzimidazole, Benzoxazole and Benzothiazole **(3)**

Phosphorus trichloride (0.33 mol) was added dropwise to a solution of the *p-N,N*-diethyl salicylaldehyde (0.33 mol) and substituted 1,2-phenylenediamine or *o*-aminophenol and *o*-aminothiophenol (0.33 mol) in ethanol (50 ml). During addition of PCl_3 maintained the temperature 40–45 °C. The mixture was heated at 60 °C for 4 h, reaction was monitored by thin layer chromatography. The reaction mass was cooled to room temperature and made alkaline to pH 8 with aqueous 20% sodium bicarbonate solution. Reaction mass was concentrated under vacuum and the solid obtained was collected and crystallized from isopropyl alcohol.

General Procedure for Synthesis of 2-substituted Benzimidazole, Benzoxazole and Benzothiazole **(4a–4i)**

Palladium-carbon catalyst (10%) was added portion-wise over a period of 10 min to a hot solution of compound **3** (1.0 g, 0.28 mol) in ethanol (50 ml) containing hydrazine hydrate (0.007 g, 1.96 mol). The mixture was heated under reflux for 1 h. The hot solution was filtered through a Whatman paper to remove Pd-C and further filtered through silica gel (5 g) to minimise excess hydrazine hydrate. Filtrate was concentrated under reduced pressure to afford pure products **4a–4i,** and they were further analyzed without further purification.

Spectral Data of Synthesized Compounds **(4a–4i)**

2-(1H-Benzimidazol-2-yl)-5-(N,N-diethylamino) phenol **(4a)**

M.p. 192 °C

FT-IR (KBr): 2975, 1620, 1518, 1145, 817, 733 cm^{-1}.

^{1}H NMR (DMSO- d_6, 400 MHz): δ 1.13 (t, 6H), 3.32 (q, 4H), 6.17 (s, 1H), 6.30–6.52 (d, 1H, *J*=8.8 Hz, Ar-H), 6.98–7.00 (d, 2H, *J*=8.8 Hz, Ar-H), 7.57–7.59 (d, 1H, *J*= 8 Hz, Ar-H), 7.83–7.85 (d, 2H, *J*=8 Hz, Ar-H), 8.23–8.25 (d, 1H, *J*=8 Hz, Ar-H), 12.13 (s, 1H).

LC-MS: (M+1: 282.3, 97.89%).

5-(N,N-Diethylamino)-2-(5-nitro-1H-benzimidazol-2-yl) phenol **(4b)**

M.p.264 °C

FT-IR (KBr): 2991, 1620, 1520, 1338, 1149, 946, 817, 733 cm^{-1}.

^{1}H NMR (DMSO- d_6, 400 MHz): δ 1.17 (t, 6H), 3.45 (q, 4H), 6.42 (s, 1H), 6.53–6.55(d, 1H, *J*=8.8 Hz, Ar-H), 7.83–786 (d, 1H, *J*=8.8 Hz, Ar-H), 8.03–8.05 (d, 1H, *J*= 9.2 Hz, Ar-H),8.25–8.28 (d, 1H, *J*=10.8, 2.0 Hz, Ar-H), 8.50–8.55 (d, 1H, *J*=2.0 Hz, Ar-H), 13.00 (s, 1H).

LC-MS: (M+1: 327.3, 97.99%).

2-(5-Amino-1H-benzimidazol-2-yl)-5-(N,N-diethylamino) phenol **(4c)**

M.p. 272 °C

FT-IR (KBr): 3417, 3285, 2971, 1642, 1575, 1484, 1270, 1124, 1077, 784 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.12 (t, 6H), 3.35 (q, 4H), 5.30 (s, 1H), 6.17 (s, 2H), 6.18–6.33 (d, 1H, *J*=8.8, 2.4 Hz, Ar-H), 6.52–6.55 (d, 1H, *J*=8.8, 2.0 Hz, Ar-H), 6.69 (s, 1H, Ar-H), 7.22–7.24 (d, 1H, *J*=8.4 Hz, Ar-H), 7.69–7.77 (d, 1H, *J*=8.8 Hz, Ar-H), 8.16 (s, 1H, Ar-H), 12.63 (s, 1H).

LC-MS: (M+1: 297.3, 98.76%).

2-(1,3-Benzoxazol-2-yl)-5-(N,N-diethylamino)phenol **(4d)**

M.p. 268 °C

FT-IR (KBr): 3013, 1656, 1575, 1484, 1287, 1270, 1124, 1077, 784 cm^{-1}.

^{1}H-NMR (400 MHz): δ 1.16 (t, 6H), 3.41 (q, 4H), 5.61 (s, 1H), 5.87–5.89 (d, 1H, *J*=8.8 Hz, Ar-H), 6.08–6.10 (d, 1H, *J*=8.8 Hz, Ar-H), 6.42–6.44 (d, 1H, *J*=8.8 Hz, Ar-H), 6.78 (s, 1H, Ar-H), 6.89–6.91(d, 1H, *J*=8.8 Hz, Ar-H), 7.11–7.13 (d, 1H *J*=8 Hz, Ar-H), 7.23 (s, 1H, Ar-H), 7.59 (s, 1H, Ar-H), 8.19 (s, 1H, Ar-H), 8.63 (s, 1H, Ar-H), 11.23 (s, 1H).

LC-MS: (M+1: 283.3, 96.25%)

5-(N,N-Diethylamino)-2-(6-nitro-1,3-benzoxazol-2-yl) phenol **(4e)**

M.p. 218 °C

FT-IR (KBr): 2987, 1635, 1530, 1350, 1145, 1098, 847, 742 cm^{-1}.

^{1}H-NMR (400 MHz): δ 1.22 (t, 6H), 3.40 (q, 4H), 5.62 (s, 1H), 5.98–6.00 (d, 1H, *J*=8 Hz, Ar-H), 6.12–6.14 (d, 1H, *J*=8 Hz, Ar-H), 6.45–6.47 (d, 1H, *J*=8.8 Hz, Ar-H), 6.80 (s, 1H), 6.91–6.93 (d, 1H, *J*=8.8 Hz, Ar-H), 7.14–7.16 (d, 1H *J*=8 Hz, Ar-H), 7.26 (s, 1H, Ar-H), 7.60 (s, 1H, Ar-H), 8.16 (s, 1H, Ar-H), 8.65 (s, 1H), 11.37 (s, 1H).

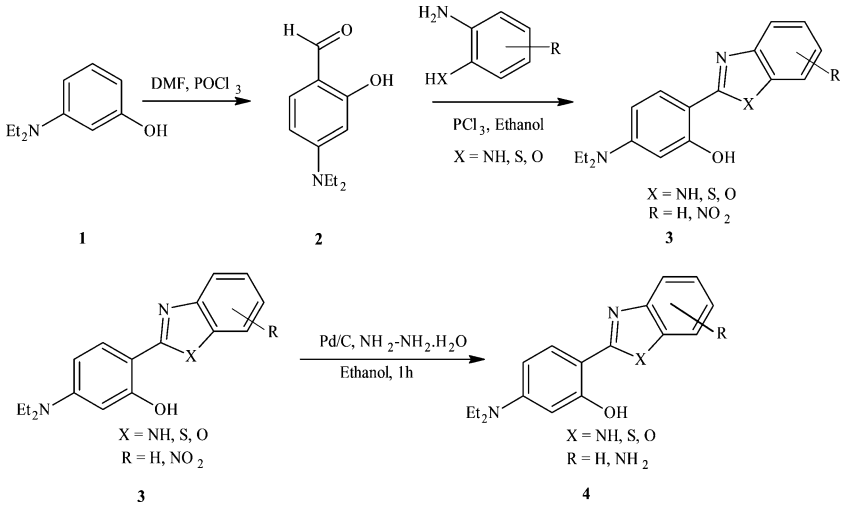
LC-MS: (M+1: 328.3, 97.12%)

5-(N,N-Diethylamino)-2-(5-nitro-1,3-benzoxazol-2-yl) phenol **(4f)**

M.p. 240 °C Decomposes

FT-IR (KBr): 2987, 1632, 1535, 1347, 1147, 1100, 845, 740 cm^{-1}.

Scheme 1 Synthesis of 2-substituted benzimidazole, benzoxazole and benzothiazole compounds **4a–4i**



1 **2** **3** **3** **4**

^{1}H-NMR (400 MHz): δ 1.23 (t, 6H), 3.42 (q, 4H), 5.59 (s, 1H), 5.88–5.90 (d, 1H, *J*=8 Hz, Ar-H), 5.98–6.00 (d, 1H, *J*=8 Hz, Ar-H), 6.16–6.18 (d, 1H, *J*=8.8 Hz, Ar-H), 6.95 (s, 1H), 7.06–7.08 (d, 1H, *J*=8.8 Hz, Ar-H), 7.12–7.14 (d, 1H *J*=8 Hz, Ar-H), 7.44 (s, 1H), 8.63 (s, 1H), 9.16 (s, 1H), 11.03 (s, 1H), 11.77 (s, 1H).

LC-MS: (M+1: 328.3, 98.62%).

2-(6-Amino-1,3-benzoxazol-2-yl)-5-(N,N-diethylamino) phenol **(4g)**

M.p.269 °C Decomposes

FT-IR (KBr): 3427, 3281, 2967, 1643, 1560, 1487, 1267, 1124, 1067, 774 cm^{-1}.

^{1}H-NMR (400 MHz): δ 1.10 (t, 6H), 3.31 (q, 4H), 5.90 (s, 1H), 6.14 (s, 2H), 6.24–6.26 (d, 1H, *J*=8.8, 2.4 Hz, Ar-H), 6.59–6.61 (d, 1H, *J*=8.8, 2.0 Hz, Ar-H), 6.74 (s, 1H), 7.27–7.29 (d, 1H, *J*=8.4 Hz, Ar-H), 7.71–7.73 (d, 1H, *J*=8.8 Hz, Ar-H), 8.23 (s, 1H), 12.13 (s, 1H).

LC-MS: (M+1: 298.3, 96.62%).

2-(5-Amino-1,3-benzoxazol-2-yl)-5-(N,N-diethylamino) phenol **(4h)**

M.p. 250 °C Decomposes.

FT-IR (KBr): 3431, 3290, 3013, 1656, 1567, 1484, 1276, 1260, 1227, 1068, 780 cm^{-1}.

^{1}H-NMR (400 MHz): δ 1.09 (t, 6H), 3.32 (q, 4H), 5.93 (s, 1H), 6.21 (s, 2H), 6.23–6.25 (d, 1H, *J*=8.8, 2.4 Hz, Ar-H), 6.61–6.63 (d, 1H, *J*= 8.8, 2.0 Hz, Ar-H), 6.74 (s, 1H), 7.29–7.31 (d, 1H, *J*=8.4 Hz, Ar-H), 7.69–7.71 (d, 1H, *J*=8.8 Hz, Ar-H), 8.16 (s, 1H), 12.09 (s, 1H).

LC-MS: (M+1: 298.3, 95.62%).

2-(1,3-Benzothiazol-2-yl)-5-(N,N-diethylamino)phenol **(4i)**

M.p. 168 °C.

FT-IR (KBr): 2875, 1630, 1618, 1456, 1342, 1135, 812, 743 cm^{-1}.

^{1}H-NMR (400 MHz): δ 1.21 (t, 6H), 3.41 (q, 4H), 6.27 (s, 1H), 7.26–7.28 (d, 1H, *J*=8.0 Hz, Ar-H), 7.29–7.31 (d, 1H, *J*=8.8, 2.0 Hz, Ar-H), 7.44–7.46 (d, 1H, *J*=8.8, 2.0 Hz, Ar-H), 7.80–7.86 (d, 2H, *J*=8.0, 2.0 Hz, Ar-H), 12.56 (s, 1H).

LC-MS: (M+1: 299.4, 98.67%).

Results and Discussion

2-Substituted benzimidazole, benzoxazole and benzothiazole fluorescent derivatives **4** were prepared by the reaction of 4-(*N,N*-diethyl amino)-2-hydroxybenzaldehyde **2** with substituted 1,2-phenylenediamines or *o*-aminophenol or *o*-aminothiophenol in the presences of phosphorus trichloride

Table 2 Synthesized benzimidazole, benzoxazole and benzothiazole derivatives

Compound	X	R
4a	-NH	H
4b	-NH	3-NO_2
4c	-NH	3-NH_2
4d	O	H
4e	O	4-NO_2
4f	O	5-NO_2
4g	O	4-NH_2
4h	O	5-NH_2
4i	S	H

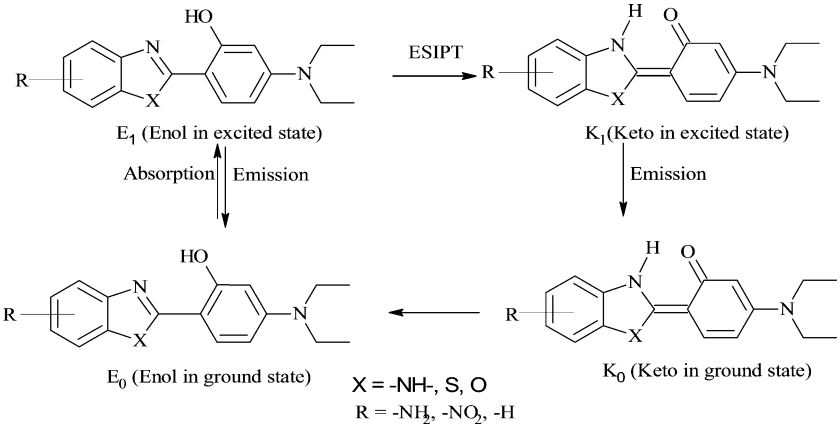


Fig. 1 Excited state proton transfer reaction pathways

in ethanol as shown in Scheme 1 and preparative details are presented in Table 2.

Synthesized benzimidazole, benzothiazole and benzoxazole molecules which contain acidic hydroxy group at 2′-position and *N,N′*- diethyl group at 4′-position with respect to basic –N=moiety. The location of these groups is such that there is existence of intra-molecular hydrogen bonding in the ground state. On excitation, the –N=moiety become strongly basic and -OH as well as p-*N N′*-diethyl group becomes strongly acidic. This leads to the excited state intra-molecular proton transfer (ESIPT) and thus the formation of keto isomer (k_1).

The ESIPT reactions of *o*-hydroxy and *o*-amino benzazoles (benzimidazole, benzoxazole and benzothiazole) have been studied extensively and it has been reported that *o*-amino benzazoles have lower fluorescent quantum yield accompanied by shorter Stokes shift as compared to the respective *o*-hydroxy benzazoles [57]. This observation has been explained in the light of the fact that NH_2 group is low acidic compared to the -OH group. In addition improving the basicity of = N- on the azole ring will also help in accepting proton from the -OH or -NH_2 facilitating the ESIPT phenomenon. In this paper we report ESIPT molecules where the basicity of = N- group on the azole ring is enhanced by the presence of *N,N*-diethyl amino group on the phenyl ring containing -OH group. Quantum yield of *2-(1H*-benzimidazol-2-yl)-5-(*N,N*-diethylamino) phenol **4a** is (0.105) high compared to the compound where -NH_2 group is present in place of hydroxyl group (0.027) in ethanol. Synthesized compounds **4a–4i** show single absorption and dual emission with large Stokes shift. Single absorption and dual emission are due to ESIPT phenomenon as shown in Fig. 1.

UV–Vis Absorption-Emission Analysis

Synthesised novel benzimidazole, benzoxazole and benzothiazole **4a–4i** compounds are fluorescent in solution as well as in the solid state when irradiated with UV light. Compounds **4e** and **4i** show solid state fluorescence and the other compounds show fluorescence in solution. As against the known compounds devoid of N,N-diethylamino group [58] the synthesized new compounds **4a–4i** show high fluorescence emission intensity with high Stokes shift value. This property attributed due to the intra-molecular proton

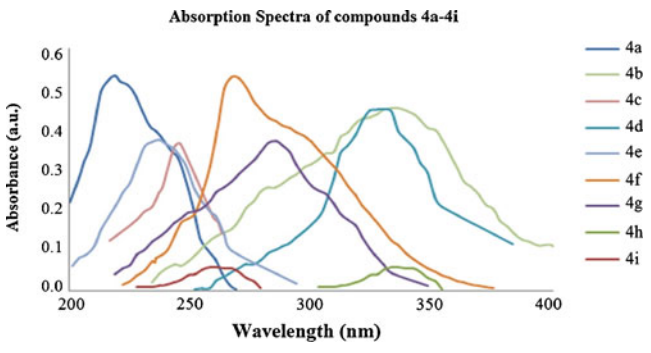


Fig. 2 Absorption spectra of compounds **4a–4i** in acetonitrile

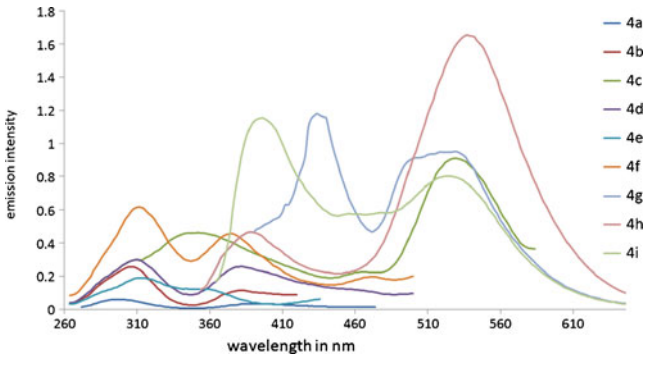


Fig. 3 Emission spectra of compound **4a–4i** in acetonitrile

Table 3 Absorption-Emission with molar extinction coefficient at 1×10^{-6} M concentration of compounds **4a–4i** in acetonitrile

Compound	λ_{max} absorbance in nm (intensity)	λ_{max} emission in nm (intensity)	Stokes shift
4a	218 (0.531)	296(0.597)	078
		396(0.032)	178
4b	333(0.452)	404(0.189)	071
		480(0.113)	147
4c	246(0.364)	352(0.461)	106
		526(0.903)	280
4d	324(0.444)	412(0.298)	088
		482(0.257)	158
4e	234(0.368)	310(0.298)	076
		482(0.257)	248
4f	264(0.550)	316(0.189)	052
		374(0.461)	110
4g	282(0.366)	434(1.180)	152
		532(0.946)	250
4h	333(0.056)	388(0.455)	055
		542(1.643)	209
4i	264(0.056)	398(1.146)	134
		526(0.800)	262

λmax and λem were measured in nm

Samples were prepared in acetonitrile

Analyses were carried out at room temperature

transfer reaction as well as basic *p-N,N′*-diethyl group present in the system. The quantum yield of compound **4a** which contains a *N,N*-diethylamino group has been compared with a parallel compound devoid of *N,N*-diethylamino group, which has been synthesized by our group [59]. Quantum yield of *2-(1H*-benzimidazol-2-yl)-5-(*N,N*-diethylamino) phenol

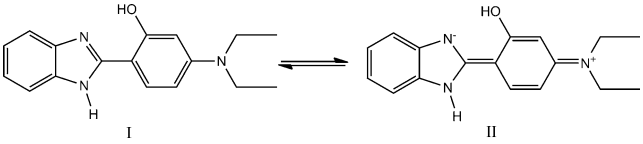


Fig. 4 Resonating effect of p-*N,N*-diethyl group which extend the conjugation

4a is (0.105) higher compared to the parallel compound devoid of *N,N*-diethylamino group (0.005) in ethanol.

The absorption and fluorescence emission spectra of these compounds are shown in the Figs. 2 and 3 respectively. All analyses were performed at room temperature in acetonitrile as a solvent and the compounds concentration are 1×10^{-6} M. Table 3 shows the absorption and emission values and the corresponding Stokes shifts for the compound **4a–4i**. The Stokes shift values of new compounds **4a–4i** are relatively higher than the reported hydroxy benzimidazole, benzoxazole and benzothiazole derivatives. The Stokes shift for molecules that do not show structural change in the excited state is generally found between 50 and 70 nm [60]. In contrast, novel compounds **4a–4i** that exhibit ESIPT phenomenon with Stokes shift in between 50 and 280 nm. The occurrence of the dual emission of synthesised compound is clearly reflected in emission spectrum. The spectrum consists of two emission maxima ranging from 302 to 546 nm.

UV-Visible Absorption and Fluorescence Emission of Compound **4a** and 2-(1H-benzimidazol-2-yl) phenol in Different Solvent (Solvatochromism)

To evaluate the effect of solvent polarity on absorption-emission properties of synthesized compounds absorption,

Table 4 Effect of solvent polarity on photo-physical properties of compound **4a**

Solvent	λabs nm (Intensity)	λem nm (Intensity)	Stokes Shift	Quantum Yield
DCM	213(1.324)	282 (0.657) 370 (0.093)	69 157	0.1009
1,4 – Dioxane	215(1.287)	287 (0.445) 378 (0.234)	72 163	0.0930
Acetonitrile	218(1.531)	296 (0.597) 396 (0.032)	78 178	0.094
Ethyl acetate	218(1.439)	310 (0.632) 405 (0.043)	108 187	0.122
Ethanol	222(0.989)	312 (0.567) 417 (0.012)	90 195	0.1050
Methanol	224(1.568)	321(1.214) 423 (0.037)	97 199	0.1164
DMF	229(1.893)	328 (0.098) 429 (0.056)	99 200	0.0789
DMSO	232(2,173)	333 (0.076) 435 (0.087)	101 203	0.1323

DCM Dichloromethane, *DMF* Dimethyforamide, *DMSO* Dimethyl sulphoxide

Table 5 Effect of solvent polarity on photo-physical properties of 2-(1*H*-benzimidazol-2-yl) phenol

Solvent	λabs nm (intensity)	λem nm (intensity)	Stokes shift
DCM	237 (0.087)	272 (0.145)	35
		320 (0.10)	73
1,4 – Dioxane	243 (0.543)	287 (0.149)	44
		312 (0.094)	69
Acetonitrile	243 (0.091)	301 (0.323)	58
		318 (0.037)	75
Ethyl acetate	246 (0.212)	279 (0.152)	33
		328 (0.056)	82
Ethanol	246 (0.431)	278 (0.097)	42
		322 (0.034)	76
Methanol	243 (0.068)	290 (0.114)	47
		330 (0.032)	87
DMF	246 (0.302)	296 (0.078)	50
		321 (0.034)	75
DMSO	249 (0.503)	301 (0.260)	52
		333 (0.100)	84

DCM Dichloromethane, *DMF* Dimethyforamide, *DMSO* Dimethyl sulphoxide

emission properties of compound **4a** is studied in eight different solvents of varying polarity and hydrogen bonding capability as shown in Table 4. The absorption-emission spectrum of **4a** is affected by a change in polarity and hydrogen bonding capacity of the solvent. The absorption-emission spectrum of compound **4a** is slightly red shifted in polar solvents relative to that of non-polar solvent. Red shift increases as the polarity of the solvent increases. In dichloromethane and 1,4-dioxane the absorption—emission shifted towards the blue region and in DMF and DMSO red shift is observed as compared to acetonitrile. Effect of solvent polarity on quantum yield of **4a** was also studied in different solvent. Quantum yield results show that quantum yield is sensitive towords the polarities of solvent and results are summarized in Table 4. A previous investigation of unsubstituted benzimidazole, benzoxazole and benzothiazole derivatives has suggested that the long wavelength

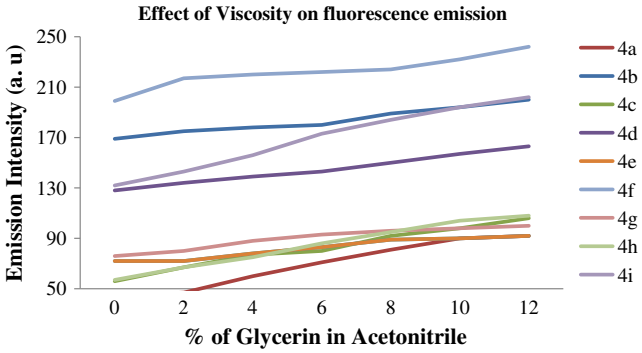


Fig. 6 Effect of viscosity on fluorescence emission of compound **4a–4i**

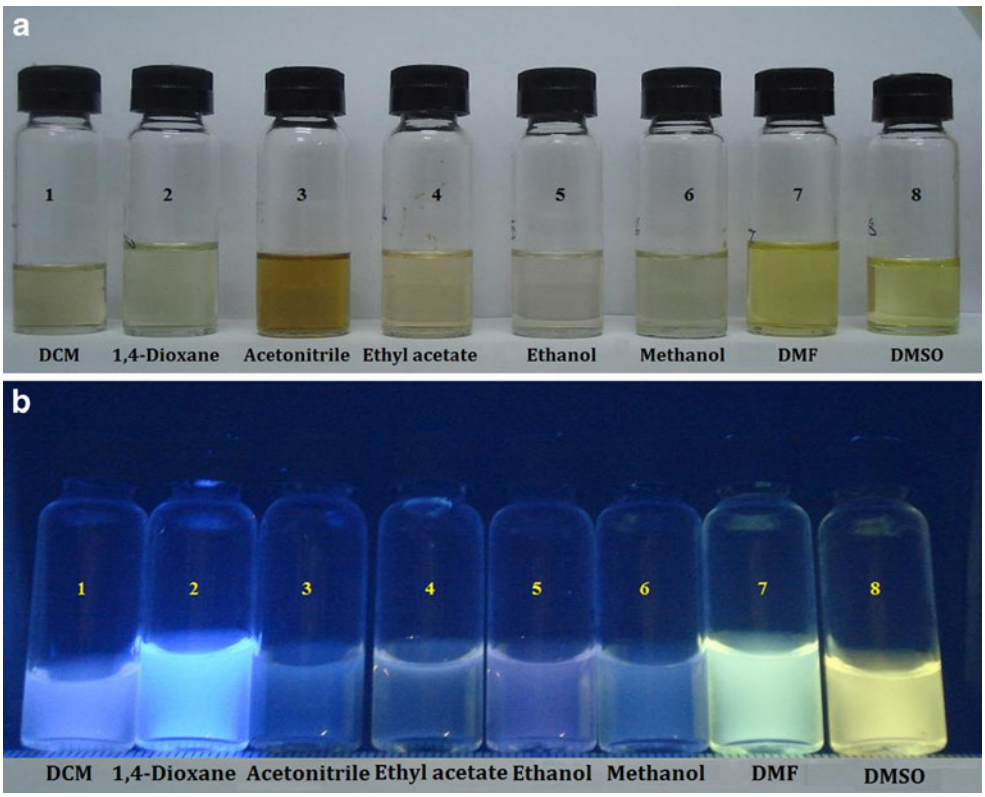


Fig. 5 **a** Effect of different solvent polarity on absorption of compound **4a** (Day light). **b** Effect of different solvent polarity on emission of compound **4a** (UV- light)

Table 6 Thermal Gravimetric Analysis of Compound **4a–4i**

Compound	TGA
4a	158 (95.97%)
4b	155 (98.94%)
4c	149 (99.22%)
4d	195 (100.0%)
4e	208 (99.11%)
4f	226 (99.98%)
4g	273 (98.41%)
4h	186 (95.04%)
4i	226 (99.59%)

[a] TGA measured in °C

transition is localised on the phenyl ring and is π-π* in nature. The moment corresponding to this transition is polarised along the axis, since band shape for compound **4a** are almost similar to those of unsubstituted benzimidazole, benzoxazole and benzothiazole except for the red shift. The red shift in the absorption-emission characteristic of novel compound **4a** is explained by the resonance effect of the *p-N,N′*-diethyl group which extends the conjugation leading to structure **II** (Fig. 4).

Structure **II** is more rigid than structure **I** and being polar is more stable in polar solvent, As a result the fluorescence emission spectrum of compound **4a** shows red shift in polar solvents, and this is due to conjugation of electron donor *N, N*-diethyl group with electron acceptor imidazole ring Table 4. In case of 2-(1*H*-benzimidazol-2-yl) phenol devoid of *N,N*-diethylamino group at para position, absorption and emission characteristics as a function of polarity of solvent were also studied in different nonpolar and polar solvents. 2-(1*H*-Benzimidazol-2-yl) phenol shows single absorption and dual emission due to acidic -OH group at 2-position with respect imidazole ring. Observed stokes shift of this compound is far less than compound **4a,** this clearly indicates that *p-N,N*-diethyl group plays an important role to enhance the fluorescence properties due to the delocalisation of lone pair of electrons present on nitrogen. Absorption and emission properties of 2-(1*H*-benzimidazol-2-yl) phenol are not sensitive towards the polarity of solvents as shown in Table 5, which may be due to absence of electron donating group on phenyl ring.

In polar solvent observed Stokes shift of **4a** is higher as compared to non polar solvent, the difference in Stokes shift between polar and nonpolar solvent is significant. But in case of 2-(1*H*-benzimidazol-2-yl) phenol devoid of *N,N*-diethylamino group such a definite trend was not observed from nonpolar to polar solvent. The absorption and emission maxima with Stokes shift of the compound **4a** in different solvents are summarised in Table 4 and for 2-(1*H*-benzimidazol-2-yl) phenol in Table 5. The changes in fluorescence intensity with change in solvent polarity of compound **4a** is as shown in Fig. 5a and b.

Effect of Viscosity on Fluorescence Emission

In order to understand the sensitivity of fluorescence of compounds **4a–4i** to the microenvironment, particularly viscosity fluorescence measurements were carried out under varying viscous environments with added glycerin. Fluorescence emission of compound **4a–4i** before and after addition of glycerine were recorded at different concentration of glycerine (2, 4, 6, 8, and 10%), results reveals that the compounds **4a–4i** are sensitive towards the viscosity. Fluorescence intensity of compounds **4a–4i** increases with increase in percentage of glycerine. Emission intensity against% of glycerine in acetonitrile is shown in Fig. 6.

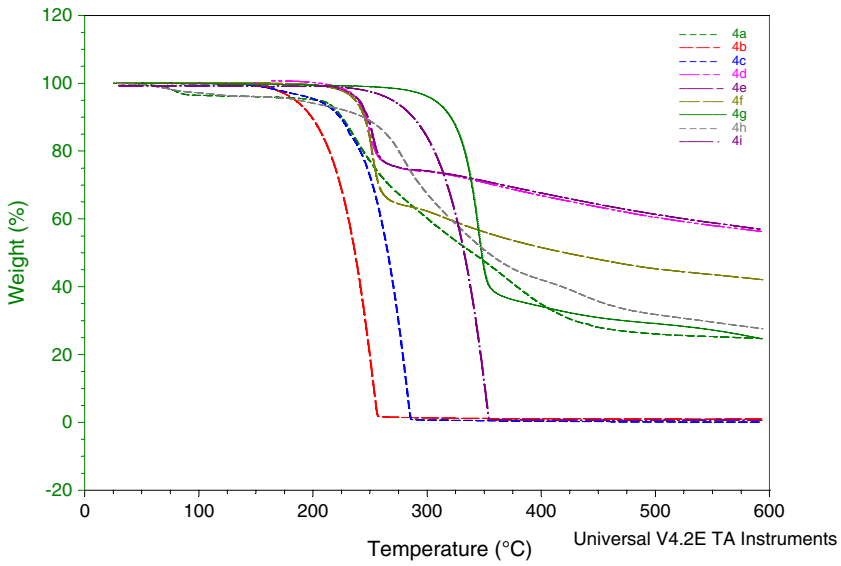


Fig. 7 TGA Plots of compounds **4a–4i**

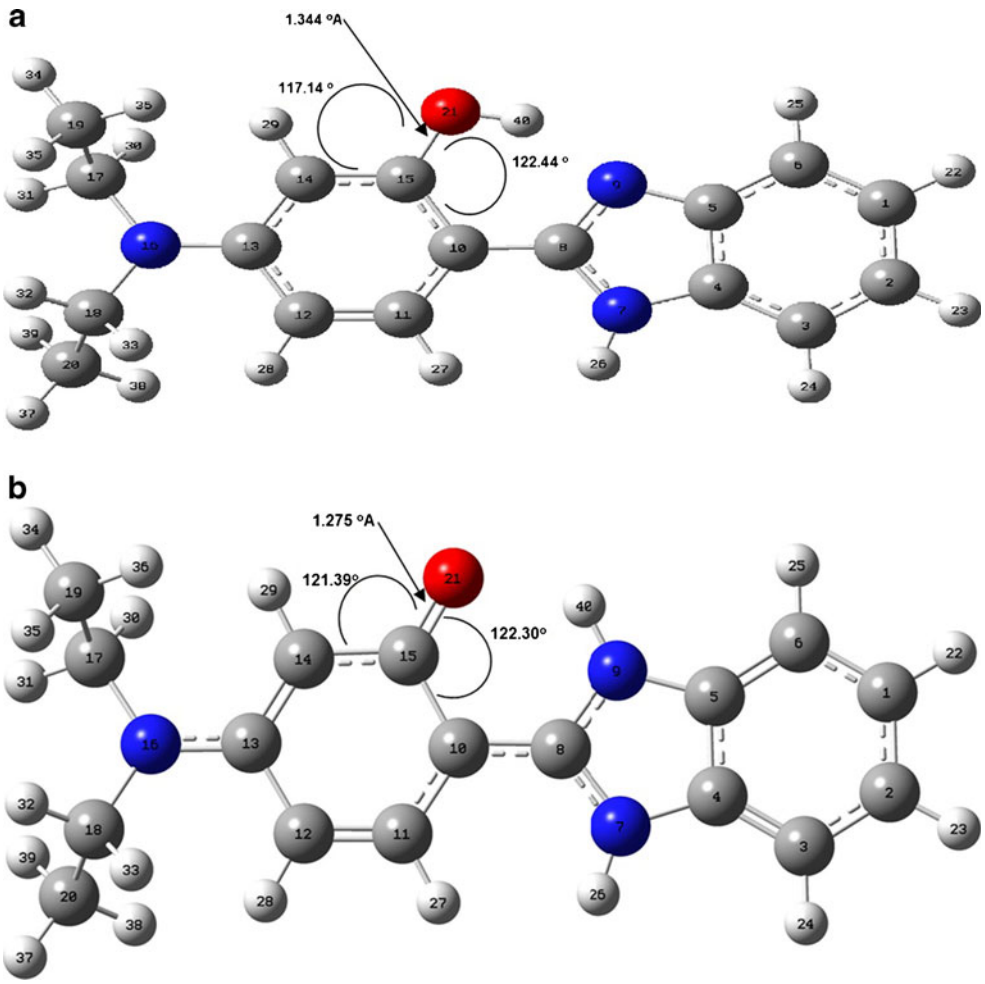


Fig. 8 **a** Optimized structural model of compound **4a** (Enol form). **b** Optimized structural model of compound **4a** (Keto form)

Thermal Stability

In order to give more insight into the compounds **4a–4i** the thermal studies have been carried out using thermogravimetric techniques (TGA). The thermogravimetric analyses have been carried out in the temperature range 50–600 °C under nitrogen. The TGA results in Table 6 indicates that the frame work of the synthesized compound is stable up to 149 °C. Above 149 °C the thermo gravimetric curve of the synthesized compounds show a major loss in weight. The comparisons of the T_d (decomposition temperature) showed that the thermal stability of the **4a–4i** decreases in the order **4g>4f>4i>4e>4d>4h>4a>4b>4c** Table 6. Above 149 °C, the thermo gravimetric curve of **4a–4i** shows continuous significant weight loss. TGA analysis curves of compound **4a–4i** are shown in Fig. 7.

Structural Properties of Compound **4a**

The structural changes Fig. 8 (8a and 8b) due to ESIPT phenomenon in terms of bond angle, bond distances and geometry are investigated by using Gaussian 03 software

Table 7 Structural properties of compound **4a**

Properties	**4a** (Enol)		**4a** (Keto)	
Stoichiometry	$C_{17}H_{19}N_3O$		$C_{17}H_{19}N_3O$	
Framework Group	$C_1(\times(C_{17}H_{19}N_3O)$		$C_1(\times(C_{17}H_{19}N_3O)$	
Point Group	C_1		C_1	
Bond Distances	Bond	Bond Length	Bond	Bond Length
	R(15–21)	**1.3444**	**R(15–21)**	**1.2755**
Bond Angle	Angle	Bond Angle	Angle	Bond Angle
	A(10,15,21)	**122.443**	**A(10,15,21)**	**122.301**
	A(14,15,21)	**117.145**	**A(14,15,21)**	**121.390**

Bond angle in degree,
Bond length in °A Unit

package as shown in Table 7. It clearly indicates that due to the intra-molecular hydrogen bonding the molecule has a six-member ring conformation in excited state. The main feature of the molecular structures like stiochiometry, framework group, degree of freedom and point group of compound **4a** are same in both enol and keto forms which are shown in Table 7, while bond length [$\mathbf{R_{Enol}}$ **(15–21); 1.344)]** and [$\mathbf{R_{Keto}}$ **(15–21); 1.275]** and bond angle **[**$\mathbf{A_{Enol}}$ **(10-15-21); 122.443 and** $\mathbf{A_{Enol}}$ **(14-15-21);117.145]** and **[**$\mathbf{A_{Keto}}$ **(10-15-21); 122.301 and** $\mathbf{A_{Keto}}$ **(14-15-21);121.390]** differ from each other in enol and keto form respectively. Compound **4a** is roughly planar in enol form with dihedral angle 0.0139° between N_9-C_8-C_{10}-C_{15} and facilitate excited state intra-molecular hydrogen transfer. In enol form the bond C_{15}-O_{21} is a single bond having bond length 1.3442°A, while in keto form double bond character of C_{15}-O_{21} bond increases and bond length decrease bond length 1.2755°A.

Density Function Theory Calculation

Density functional theory calculations were performed to optimise the geometry of compound **4a**. Ground state geometry was optimised with B3LYP level of theory and 6–31/G (d) basic set. Excited state geometry was optimised by time dependent-DFT with B3LYP level and 6–31/G (d) basic set. It is observed that the enol form of **4a** is stabilised by 79.40 Kcal/mole than the ground state keto form and so it exists only in enol form (supported by UV-Visible spectrum with single absorption and dual emission). The dihedral angle of almost zero between two rings N_9-C_8-C_{10}-C_{15}: 0.013 and the distance between N_9-H_{40} (1.715) at ground state suggests a strong hydrogen bonding. As enol form goes to excited state the change in dipole moment has been observed from 6.975 to 6.737 and negative charge on O_{21} decreases from −0.69 to −0.68, whereas negative charge on N_9 is −0.72 to −0.71. The structure remains planar in excited state with N_9-H_{40} distance of 1.732 this distance suggests a strong H-bonding. These conditions facilitate the ESIPT phenomenon.

Conclusion

The above study proves that,

(i) Synthesized new compounds shows single absorption and dual emission due to excited state intra-molecular proton transfer.
(ii) Fluorescence properties of the synthesized compound depend on solvent polarity, in non-polar solvent it absorbs and emits in blue region and polar solvent it shows red shift.
(iii) Synthesized compounds exist in to two form keto (K) and enol (E) form. Compounds are planar in enol form and non-planar in keto form.
(iv) Synthesised compounds have good thermal properties.
(v) Existences of Excited States Intramolecular Proton Transfer (ESIPT) were confirmed by Density Function Theory (DFT).

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