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# Photophysical properties of ESIPT inspired fluorescent 2-(2-hydroxyphenyl)-6-methylimidazo[4,5-*f*]isoindole-5,7(1H,6H)dione and its derivative: Experimental and DFT based approach



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# HIGHLIGHTS

- Synthesis of phthalimide based ESIPT molecules.
- Spectroscopic investigations of a series of new benzimidazole.
- Existence of ESIPT has been experimentally and is computationally supported.
- Good thermal stability.

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## ABSTRACT

The excited-state intramolecular proton transfer chromophores 2-(2-hydroxyphenyl)-6-methylimidazo[4,5-f]isoindole-5,7(1H,6H)-dione and 2-(4-(diethylamino)-2-hydroxyphenyl)-6-methylimidazo[4,5-f]isoindole-5,7(1H,6H)-dione are synthesized from 4,5-diamino-*N*-methylphthalimide. The photophysical behavior of the synthesized chromophores was studied using UV-visible and fluorescence spectroscopy in the polar and non-polar solvents. The synthesized *o*-hydroxyphenyl benzimidazole derivatives are fluorescent and very sensitive to the solvent polarity. These dyes are thermally stable up to 317 °C. Density Functional Theory computations have been used to understand the structural, molecular, electronic and photophysical properties of the chromophores. The experimental absorption and emission wavelengths are in good agreement with the computed vertical excitation and theoretical emission obtained by Density Functional Theory and Time Dependant Density Functional Theory.

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#### Introduction

# Excited state intramolecular proton transfer (ESIPT) is of prime importance in molecular probes [1], luminescent materials [2,3], metal ion sensors [4–6], organic light emitting devices (OLEDs)

[7–10] and molecular logic gates [11]. The most significant photophysical property of the ESIPT chromophores is the large Stokes shift, compared to the normal fluorophores such as fluorescein, boron-dipyrromethene (BODIPY) or rhodamine [12,13]. The large Stokes shift is a distinct characteristic for fluorophores because the self-absorption, or the inner filter effect, can be avoided and the fluorescence can be improved with this kind of fluorophores. It is difficult to increase the Stokes shift of the conventional fluorophores by chemical modification [14].

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Upon photoexcitation to the first excited state, the acidity of the acidic center and the basicity of the basic center increase simultaneously because of the redistribution of the charge density of the chromophore realized in the first singlet excited state. This leads to the migration of the acidic proton of the acidic center to the basic nitrogen unit via the already existing hydrogen bond coordinate to give the phototautomer. The ESIPT process is a very fast process occurring within subpicosecond time scale, and on excitation the molecule passes to the potential well and then relaxes vibrationally [15,16]. Generally the ESIPT chromophores show dual emission, one being to the normal emission from the local excitation and the second which is largely Stokes shifted (up to 10,000 cm<sup>-1</sup>), due to the tautomer formed by proton transfer [14].

Therefore, taking into consideration the wide applications and importance of ESIPT inspired molecules and in continuation of our research work on ESIPT materials [17–19] herein, we report the synthesis, photophysical properties and the computational study of novel *o*-hydroxyphenyl benzimidazole (**HPBI**) derivatives, wherein the phthalimide–imidazole fused heterocycle. It may possess good electron-accepting ability. So the substitution by amine leads to push–pull dipolar compounds. Prominent red-shifted absorption of **6a** is due to the ICT present in this compound. Phthalimide and naphthalimide-based dyes are interesting due to their excellent electron accepting properties [20].

# **Experimental section**

#### Materials and equipments

All the commercial reagents and the solvents were purchased from S. D. Fine Chemicals Pvt. Ltd. Mumbai and were used without purification. The reaction was monitored by TLC using 0.25 mm 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. FT-IR spectra were recorded on Jasco 4100 using ATR accessory. <sup>1</sup>H NMR spectra were recorded on VARIAN 400/500-MHz

instrument (USA) using TMS as an internal standard. Mass spectra were recorded on Finnigan mass spectrometer. The visible absorption spectra of the compounds were recorded on a Perkin Elmer Lambda 25 spectrometer; fluorescence emission spectra and fluorescence quantum yields were recorded by using quinine sulfate (0.54 in 0.1 M  $H_2SO_4$ ) as reference [21] on Varian Cary Eclipse fluorescence spectrophotometer. Simultaneous DSC–TGA measurements were performed on SDT Q 600 v8.2 Build 100 model of TA instruments Waters (India) Pvt. Ltd.

#### Computational methods

The compounds **6a–6b** and their tautomers involved are illustrated in Fig. 1. The ground state (S0) geometry of the tautomers of compounds **6a** and **6b** in their Cs symmetry was optimized using the tight criteria in the vacuum phase using Density Functional Theory (DFT) [22]. The functional used was B3LYP. The B3LYP method combines Becke's three parameter exchange functional (B3) [23] with the nonlocal correlation functional by Lee, Yang, and Parr (LYP) [24]. The basis set used for all atoms was 6-31G(d), the latter has been justified in the literature [25-27] for the current investigation. The vibrational frequencies at the optimized structures were computed using the same method to verify that the optimized structures correspond to local minima on the energy surface [28]. The vertical excitation energy and oscillator strengths at the ground state equilibrium geometries were calculated using TD-DFT with the same hybrid functional and basis set [29-31]. The low-lying first singlet excited state (S1) of the dves was relaxed using TD-DFT to obtain its minimum energy geometry. The difference between the energies of the optimized geometries at the first singlet excited state and the ground state was used in computing the emissions [32,33]. Frequency computations were also carried out on the optimized geometry of the low-lying vibronically relaxed first excited state of the conformers. All the computations in solvents of different polarities were carried out using the Polarizable Continuum Model (PCM) [34]. All the electronic structure computations were carried out using the Gaussian 09 program [35].



Fig. 1. Excited state intramolecular proton transfer (ESIPT) pathway.



**Reaction and Condition: (i)** NaNO<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>, CuCl/HCl; (ii) HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>, 0-5 °C to RT; (iii) Urea, 150 °C; (iv) H2, Pd/C, MeOH; (v) PCl3/EtOH, 80 °C.

Scheme 1. Synthesis of ortho-hydroxybenzimidazole (HPBI) derivatives (6a-6b).

#### Synthetic strategy

They were synthesized by the conventional condensation of 5,6-diamino-2-methylisoindoline-1,3-dione **5** with the aromatic hydroxy aldehydes **a** and **b** as shown in scheme 1. In the first step, *N*-methyl-4-chlorophthalimide **2** was synthesized using Sandmeyer reaction on 4-amino-*N*-methylphthalimide **1**. Nitration of the compound **2** with fuming HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> gave the compound **3**, which on fusion with urea gave **4**. The reduction of the compound **4** using H<sub>2</sub>-10% Pd/C to gave **5**. Finally, diamino **5** and aromatic hydroxy aldehydes **a** or **b** were refluxed in absolute ethanol containing a catalytic amount of PCl<sub>3</sub> to yield the desired compounds **6a** and **6b**.

The structures of the compounds were confirmed by FTIR, <sup>1</sup>H NMR, and Mass spectral analysis. In <sup>1</sup>H NMR spectra of the compound **6a**, the –OH and –NH protons are not observed, it is because of the exchange of proton with the deuterated solvent. But the structure is confirmed by mass spectral analysis. The M+1 peak was found to be at 365.13. In the case of the compound **6b** the proton exchange with the solvent was not observed during <sup>1</sup>H NMR scanning. Their –OH, –NH proton signal was observed at 13.588 ppm, 12.222 ppm and its (M) peak was found to be at 293.13, which is in good agreement with the molecular weight. To find out the effect of solvent polarities on the absorption–emission properties, photophysical properties were studied in solvents of different polarity.

## Synthesis and characterization

The synthetic scheme for the preparation of the *o*-hydroxybenzimidazole derivatives are shown in Scheme 1. *N*-Methyl-4-chloro-5-nitrophthalimide (**3**) was prepared by the reported procedure from 4-amino-*N*-methylphthalimide (**1**) [36,37].

# *N-Methyl-4-amino-5-nitrophthalimide* (4)

A mixture of *N*-methyl-4-chloro-5-nitrophthalimide (**3**) 2.4 g (10 mmol) and urea 0.9 g (15 mmol) was fused at 135 °C for 2 h. Then, decrease the temperature up to 60 °C and water was added, stirred for 1 h. The product obtained was filtered and recrystallized from ethanol to give (**4**).

Yield: 1.8 g (80%), m.p.: 254–256 °C.

*FT-IR*: 3115 (—NH), 1711, 1697 (—C=O), 1612, 1517 (C=C ring stretching), 1545, 1352 (N=O) cm<sup>-1</sup>.

<sup>1</sup>*H* NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 2.99 (s, 3H, -CH<sub>3</sub>), 7.43 (s, 1H, -Ar), 8.23 (s, 1H, -Ar), 8.36 (brs, 2H, -NH<sub>2</sub>).

## 4,5-Diamino-N-methylphthalimide (5)

A solution of *N*-methyl-4-amino-5-nitrophthalimide (**4**) 1.8 g, (8 mmol) in methanol (10 mL) was hydrogenated in presence of 10% Pd–C (20 mg) for 4 h at room temperature; the catalyst was removed by filtration. The filtrate was concentrated under reduced pressure to obtain the crude product, which was further recrystalized from methanol to give **5**.

Yield: 1.3 g (84%), m.p.: 258-260 °C (decomposed).

Mass m/z: 214.06 (M+Na)<sup>+</sup>.

*FT-IR*: 3121 (—NH), 1702, 1695 (—C=O), 1607, 1527 (C=C ring stretching) cm<sup>-1</sup>.

<sup>1</sup>*H* NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 2.88 (s, 3H, –CH<sub>3</sub>), 5.51 (s, 4H, –NH<sub>2</sub>), 6.84 (s, 2H, –Ar).

*General procedure for the preparation of benzimidazole.* Phosphorus trichloride 0.22 mL (2.6 mmol) was added drop wise to a solution of 4,5-diamino-*N*-methylphthalimide **5** 0.5 g (2.6 mmol), and substituted *o*-hydroxybenzaldehyde (**a** or **b**) (2.6 mmol) in ethanol (5 mL), maintaining the temperature at 40–45 °C. The mixture was refluxed for 6 h. On completion of the reaction (checked by TLC) the product obtained was filtered, dried and recrystallized from ethanol to give the desired product **6a** and **6b**. On completion of the reaction or room temperature to obtained **6a–6b**. The separated product was recrystallized from ethanol.

2-(4-(Diethylamino)-2-hydroxyphenyl)-6-methylimidazo[4,5-

f]isoindole-5,7(1H,6H)-dione **6a** 

*Yield:* 0.60 g (63%), *m.p.:* 178–180 °C. *Mass m/z:* 365.13 (M+1).

*FT-IR*: 3312 (–OH), 2977 (–NH), 1769, 1706 (–C=O), 1607, 1509 (C=C, C=N ring stretching), 1412, 1372 (C–N amide stretching) cm<sup>-1</sup>.

<sup>1</sup>*H* NMR (400MHz, DMSO-d<sub>6</sub>): δ 1.17 (t, 6H, -CH<sub>3</sub>), 3.07 (s, 3H, -NCH<sub>3</sub>), 3.507 (q, 4H, -NCH<sub>2</sub>), 6.31 (s, 1H, -ArH), 6.51 (d, 1H, -ArH, *J* = 6.4 Hz), 7.92 (d, 1H, -ArH, *J* = 6.8 Hz), 7.97 (s, 2H, -ArH).

#### Table 1

Observed UV-visible absor	ption and the compute	d absorption of the co	mpound 6a in d	lifferent solvents <sup>a</sup>
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Solvent	Experimental <sup>b</sup>		TD-DFT <sup>c</sup>	TD-DFT <sup>⊂</sup>					
	$\lambda_{\max}^{a}(nm)$	Molar absorptivity, $\varepsilon$ (L mol <sup><math>-1</math></sup> cm <sup><math>-1</math></sup> )	Vertical excitation (nm)	<i>f</i> <sup>h</sup>	Orbital contribution <sup>f</sup>				
THF	371 <sup>d</sup>	17,108	366	1.107	$H \rightarrow L + 1 (98\%)$	1.37			
	308 <sup>e</sup>	6443	295	0.351	$H - 3 \rightarrow L (52\%)$	4.29			
Acetone	371 <sup>d</sup>	49,431	367	1.101	$H \rightarrow L + 1 (98\%)$	1.21			
	302 <sup>e</sup>	21,076	296	0.356	$H - 3 \rightarrow L (54\%)$	2.11			
DCM	371 <sup>d</sup>	21,403	367	1.114	$H \rightarrow L + 1 (98\%)$	1.20			
	308 <sup>e</sup>	8044	295	0.354	$H - 3 \rightarrow L (54\%)$	4.18			
Ethanol	375 <sup>d</sup>	44,954	367	1.075	$H \rightarrow L + 1 (98\%)$	2.13			
	309 <sup>e</sup>	18,236	295	0.352	$H - 3 \rightarrow L (54\%)$	4.53			
Methanol	396 <sup>d</sup>	30,066	366	1.093	$H \rightarrow L + 1 (98\%)$	7.51			
	306 <sup>e</sup>	6042	296	0.360	$H - 3 \rightarrow L (54\%)$	3.35			
Acetonitrile	372 <sup>d</sup>	6443	367	1.098	$H \rightarrow L + 1 (98\%)$	1.45			
	280 <sup>e</sup>	22,495	296	0.356	$H - 3 \rightarrow L (54\%)$	5.65			
DMF	374 <sup>d</sup>	47,356	368	1.123	$H \rightarrow L + 1 (98\%)$	1.61			
	332 <sup>e</sup>	28,465	296	0.359	$H - 3 \rightarrow L (54\%)$	10.81			
DMSO	377 <sup>d</sup>	41,059	368	1.120	$H \rightarrow L + 1 (98\%)$	2.42			
	305 <sup>e</sup>	15,543	296	0.358	$H - 3 \rightarrow L (54\%)$	2.90			

 $^{\rm a}$  Analyses were carried out at room temperature (25 °C).

<sup>b</sup> Experimentally observed  $\lambda_{max}$ .

<sup>c</sup> TD-DFT computations were carried out with the use of optimized structures at B3LYP method with 6-31G(d) basis set.

 $\lambda_{max}$ .

e Shoulder peak.

<sup>f</sup> Only major contributions are presented.

<sup>g</sup> % Deviation between experimental absorption and the vertical excitation computed by DFT.

<sup>h</sup> Oscillator strength.

# 2-(2-Hydroxyphenyl)-6-methylimidazo[4,5-f]isoindole-5,7(1H,6H)dione **6b**

Yield: 0.55 g (65%), m.p.: 172–174 °C.

Mass m/z: 293.13 (M).

*FT-IR*: 3332 (–OH), 2982 (–NH), 1760, 1687 (–C=O), 1618, 1535 (C=C, C=N ring stretching), 1426, 1374 (C–N amide stretching) cm<sup>-1</sup>.

<sup>1</sup>*H* NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  3.07 (s, 3H, --NCH<sub>3</sub>), 7.08 (t, 1H, --ArH, *J* = 6 Hz), 7.12 (d, 1H, --ArH, *J* = 6.8 Hz), 7.45 (d, 1H, --ArH, *J* = 6.4 Hz), 8.07 (brs, --ArH, 2H,), 8.18 (d, 1H, --ArH, *J* = 6.4 Hz), 12.22 (brs, 1H, --NH), 13.59 (brs, 1H, --OH).

# **Result and discussion**

#### ESIPT phenomenon

The synthesized compounds **6a** and **6b** contain an acidic –OH group at the *o*-position with respect to the benzimidazole ring. The location of the acidic proton of the -OH group and the benzimidazole =N- groups is such that there exists an intramolecular hydrogen bonding in the ground state. On excitation, the =Nmoiety of the benzimidazole ring becomes strongly basic and the proton of the -OH group becomes strongly acidic as shown by the changes in the Mulliken charge distribution in the ground and the excited states. Absorption of the radiation leads to the excitation of the ground state enol (E-Enol) to the excited enol (E-Enol<sup>\*</sup>). This E-Enol<sup>\*</sup> form undergoes a fast proton transfer (ESIPT) to form the excited state keto (K-Keto<sup>\*</sup>) form, the tautomer in a subpicosecond time scale or emits a radiation and returns to the ground state enol form (E-Enol). The excited state keto form (K-Keto<sup>\*</sup>) emits radiation and comes to the ground state keto form (K-Keto). A schematic diagram for ESIPT is shown in Fig. 1.

# Rotamers and conformers and their ground state energy

The compounds **6a** and **6b** have a fused imidazole ring (at 4- and 5-position of the *N*-methylphthalimide ring), which is rigid

and a free phenyl group having the ortho-hydroxyl group participating in the proton transfer at the excited state [38]. In the ground state the molecule can exist in equilibrium with the different conformers arising from rotamerism and their tautomers are summarized in Fig. S1. The usually planar syn form (E-Enol) allows an intramolecular hydrogen bond between the acidic --OH group and the basic nitrogen atom of the N-methylphthalimide ring. The enol (E) conformer undergoes proton transfer to form keto (K) tautomer. The conformer enol (E) can undergo rotamerization around the single bond of ortho-hydroxyphenyl group generating the anti enol (E1) conformer, where the probability of proton transfer happens to be very remote. The compounds **6a** and **6b** can coexist in various conformers with their tautomers in solution. DFT computations showed that in all the solvents, the syn enol form is more stable than the keto and anti enol form, which is preferred in the ground state (Tables S1 and S2). The keto forms are prohibitively higher in energy such that they do not exist in the ground state. The absence of the long wavelength absorption in the absorptive species is also indicative of the non-existence of the keto form.

#### Photophysical properties

The UV–Vis absorption and fluorescence emission spectra of the benzimidazole derivatives (**6a** and **6b**) in the solvents of varying polarities are reported in Tables 1 and 2. The absorption spectra of the compounds in all the studied solvents are almost nearly the same; their absorption property is independent of the solvent polarity except for the compound **6a** in methanol (Fig. S2). However, the absorption intensity is very sensitive toward the solvent polarity. The intensity of transition in the compounds **6a** and **6b** (both computed and observed) of the short wavelength absorption is always nearly twice and half the intensity of long wavelength absorption respectively. The decreasing order of the absorption intensity in the short wavelength region is DMF > ACN > Acetone > EtOH > DMSO > DCM > THF > MeOH for the compound **6a** and THF > MeOH > EtOH > DMF > ACN > Acetone > DMSO for the

Table 2					
Observed UV-visible absor	ption and comp	outed absorpti	ion of the com	pound <b>6b</b> in (	different solvents. <sup>a</sup>

Solvent Experiment			TD-DFT <sup>c</sup>			D% <sup>g</sup>
	$\lambda_{\max}^{a}(nm)$	Molar absorptivity, $\varepsilon$ (L mol <sup>-1</sup> cm <sup>-1</sup> )	Vertical excitation (nm)	f <sup>h</sup>	Orbital contribution <sup>f</sup>	
THF	337 <sup>d</sup>	27,073	329	0.457	$H \rightarrow L + 1 (90\%)$	2.37
	271 <sup>e</sup>	59,655	277	0.852	$H - 1 \rightarrow L + 1 (57\%)$	2.23
Acetone	343 <sup>d</sup>	18,869	328	0.455	$H \rightarrow L + 1 (90\%)$	4.26
	268 <sup>e</sup>	42,632	277	0.861	$H - 1 \rightarrow L + 1 (58\%)$	3.37
DCM	340 <sup>d</sup>	28,978	329	0.463	$H \rightarrow L + 1 \ (90\%)$	3.20
Ethanol	340 <sup>d</sup>	24,846	328	0.453	$H \rightarrow L + 1 (90\%)$	3.47
	271 <sup>e</sup>	52,330	277	0.859	$H - 1 \rightarrow L + 1 (58\%)$	2.21
Methanol	338 <sup>d</sup>	26,253	328	0.449	$H \rightarrow L + 1 (90\%)$	2.94
	272 <sup>e</sup>	55,055	277	0.861	$H - 1 \rightarrow L + 1 (58\%)$	1.78
Acetonitrile	340 <sup>d</sup>	22,883	328	0.453	$H \rightarrow L + 1 (90\%)$	3.47
	271 <sup>e</sup>	47,554	277	0.863	$H - 1 \rightarrow L + 1 (58\%)$	2.21
DMF	343 <sup>d</sup>	25,403	329	0.474	$H \rightarrow L + 1 (90\%)$	4.11
	274 <sup>e</sup>	48,433	278	0.869	$H - 1 \rightarrow L + 1 (58\%)$	1.34
DMSO	334 <sup>d</sup>	23,821	329	0.472	$H \rightarrow L + 1 (90\%)$	1.56
	277 <sup>e</sup>	39,877	278	0.869	$H - 1 \rightarrow L + 1 (58\%)$	0.22

 $^{\rm a}$  Analyses were carried out at room temperature (25  $^{\circ}\text{C}).$ 

<sup>b</sup> Experimentally observed  $\lambda_{max}$ .

<sup>c</sup> TD-DFT computations were carried out with the use of optimized structures at B3LYP method with 6-31G(d) basis set.

<sup>d</sup> More intense peak.

e Less intense peak.

<sup>f</sup> Only major contributions are presented.

<sup>g</sup> % Deviation between experimental absorption and the vertical excitation computed by DFT.

<sup>h</sup> Oscillator strength.

compound **6b**. In the case of the long wavelength transition the order is acetone > DMF > EtOH > DMSO > ACN > MeOH > DCM > THF and DCM > THF > MeOH > DMF > EtOH > DMSO > ACN > acetone for the compounds **6a** and **6b** respectively (Tables 1 and 2, Fig. S2a and b). The compounds **6a** and **6b** have two absorption maxima. Among these two transitions, first one is higher energy absorptions between 268 nm and 332 nm probably due to the aryl core and  $\pi$ - $\pi$ <sup>\*</sup> transition while the lower energy band between 334 nm and 396 nm attributed to the intramolecular charge transfer transition (ICT) between the donor group and the acceptor moiety. The excitation spectra illustrated in Figs. S3 and S4 were obtained by using shorter (439–510 nm) and longer wavelength (538–588 nm) emissions of the respective solvents.

The red shifted absorption maxima indicates that the o-hydroxy and N,N-diethylamino moiety present in 6a (396 nm) has a stronger electron donating effect than the compound **6b** (343 nm) devoid of N,N-diethylamino group. These results also showed that the compound **6a** exhibited strong solvatochromic properties in emission as compared to the compound 6b. The introduction of electron donor group in the positions induced intramolecular charge transfer and mesomeric dipole moment. When compared with unsubstituted analogues [19] of the molecules **6a** and **6b** later have shown a red shifted absorption. The electron withdrawing effect of cyclic amide group has induced efficient donor to acceptor charge transfer. The molecule 6a absorbs at 396 nm and 6b at 338 nm in methanol as compared to blue shifted absorption of their unsubstituted analogue at 224 nm and 243 nm respectively. It is also observed that molecule **6a** absorbs at longer wavelength than the nitro substituted analogue. Nitro group being strong electron withdrawer than amide was expected to show a red shift in absorption [19]; however, the cyclic amide group gives rigidity and planarity to the molecules and proved to be a efficient electron withdrawer.

The fluorescence emission study of the compound **6a** reveals that a dual emission is observed in non-polar as well as highly polar solvents (THF, dichloromethane, acetonitrile, DMF and DMSO) and in the polar protic solvents (methanol, ethanol, acetone) a single emission (Table 3, Fig. S5a), while the compound

6b shows dual emission only in ethanol, DMF (Table 4, Fig. S5b). The emission property of the compound **6a** is red shifted in polar solvent like DMF (588 nm) and DMSO (583 nm) as compared to the other solvents, while compound 6b red shifted in DMF (538 nm), ethanol (543 nm) and acetonitrile (448 nm) than the other solvents. It is well known that in the ESIPT molecules, the long wavelength emission is attributed to the excited state keto tautomer originating from the excited state enol tautomer [14.25]. The driving force after the proton transfer is associated with an intrinsic extra stabilization of the keto tautomer at the excited state. This aspect is confirmed by the TD-DFT computations that the excited state keto form has lower energy in non-polar as well as high polar solvents (Table 5) and this reveals that the stabilization is exclusively intrinsic and not due to the solvent (non polar or polar) environment. The TD-DFT calculation at the excited state reveals that there is hardly any difference between the energy of the optimized enol and keto tautomers. The difference between the energies of the optimized geometries at the first singlet excited state and the ground state are used to calculate the emissions in all the solvents are summarized in Tables S3-S6.

In highly polar solvent the emissive S1 state of intramolecular charge transfer (ICT) character is strongly solvated and its energy is hence significantly lowered. As a consequence, the energy gap  $\Delta E$  (S1, S2) is enlarged so that the coupling of the S1 state directly to the ground state stays opened and the intersystem crossing from S1 to T state is enhanced. The high electron-donating character of *N*,*N*-diethylamino moiety leads to a red shift (lower energy) of the emission relative to the absorption is caused by the energy losses due to the dissipation of vibrational energy during the decay and is influenced by the interaction between the fluorophore and the solvent molecules around the excited dipole, hydrogen bonding and formation of charge complexes.

# Relative quantum yield of compounds

The fluorescence quantum yields of the synthesized compounds **6a** and **6b** were determined in different solvents and tabulated in Tables 3 and 4. The fluorescence quantum yield mostly depends

#### Table 3

Observed and the compu-	ed emission of the com	ipound <b>6a</b> in various s	solvents along with its	quantum vield. <sup>a</sup>
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Solvent	Experimental (short emission)			TD-DFT	Experimental (lo	Experimental (long emission)			Excitation	Total
	Emission (nm)	$\Delta\lambda$ (nm)	$arPhi^{\mathrm{b}}$	(short emission) <sup>c</sup> (nm)	Emission (nm)	$\Delta\lambda$ (nm)	$\Phi^{d}$	emission) <sup>c</sup> (nm)	(nm)	quantum yield <sup>e</sup>
THF	436	65	0.06	479	553	182	0.09	570	376	0.15
Acetone	429	58	0.03	486	570	199	0.04	570	377	0.07
DCM	436	65	0.04	481	553	182	0.07	568	382	0.11
Ethanol	510	135	0.06	487	-	-	-	-	276, 369	0.06
Methanol	507	111	0.06	488	-	-	-	-	282, 372	0.06
Acetonitrile	435	63	0.03	488	539	167	0.04	561	280, 346	0.07
DMF	436	62	0.04	488	588	214	0.06	560	282, 380	0.10
DMSO	429	52	0.02	489	583	206	0.03	560	282, 381	0.05

 $^{\rm a}$  Analyses were carried out at room temperature (25  $^{\circ}\text{C}\textsc{)}.$ 

<sup>b</sup> Quantum yield for short wavelength emission, quinine sulfate was used as reference standard.

<sup>c</sup> Computed using TD-DFT method with the B3LYP/6-31G(d).

<sup>d</sup> Quantum yield for long wavelength, quinine sulfate was used as reference standard.

<sup>e</sup> Summation of short wavelength and long wavelength quantum yield.

Table 4
Observed and computed emission of compound <b>6b</b> in various solvents along with its quantum yield.

Solvent	Experimental (short emission)		TD-DFT	Experimental (long emission)			TD-DFT	Excitation	Total quantum	
	Emission (nm)	$\Delta\lambda$ (nm)	$arPhi^{b}$	(short emission) <sup>c</sup> (nm)	Emission (nm)	$\Delta\lambda$ (nm)	$arPsi^{ m d}$	(long emission) <sup>c</sup> (nm)	(nm)	yield <sup>e</sup>
THF	436	97	0.10	395	-	-	-	-	352	0.10
Acetone	434	91	0.06	398	-	-	-	-	348	0.06
DCM	435	95	0.08	396	-	-	-	-	336	0.08
Ethanol	431	91	0.04	398	543	203	0.04	545	357	0.08
Methanol	445	107	0.06	397	-	-	-	-	372	0.06
Acetonitrile	448	108	0.07	399	-	-	-	-	350	0.07
DMF	440	100	0.05	399	538	198	0.04	546	377	0.09
DMSO	431	97	0.06	399	-	-	-	-	335	0.06

<sup>a</sup> Analyses were carried out at room temperature (25 °C).

<sup>b</sup> Quantum yield for short wavelength emission, quinine sulfate was used as reference standard.

<sup>c</sup> Computed using TD-DFT method with the B3LYP/6-31G(d).

<sup>d</sup> Quantum yield for long wavelength, quinine sulfate was used as reference standard.

<sup>e</sup> Summation of short wavelength and long wavelength quantum yield.

on both the nature of the substituent and the solvent polarity. Here, it has been observed that the quantum yield is higher in the non-polar solvents than in the polar solvents and this can be attributed to the contribution coming from the long wavelength emission. The quantum efficiency of the compounds 6a and 6b was much higher in the DMF ( $\Phi$  = 0.10 and 0.09) as compared to the other polar solvents. The short wavelength emission of the compound **6a** occurs in all cases with a narrow range of Stokes shift (72-76 nm) except in acetonitrile (106 nm). It is observed that the short wavelength emission is much red shifted in acetonitrile. In the case of the compound **6a**, the solvent polarity effect on the fluorescence emission is significant; it shows a red shifted emission from non polar to polar solvents for both the shorter and the longer wavelength regions (Fig. S6). However, for the compound **6b**, the long wavelength emission is independent of the solvent polarity but the short wavelength emission is dependent on the solvent polarity (Fig. S7).

#### Thermal stability

Intramolecular interaction from compact aggregates enhances the thermal stability of the compounds [39]. Thermal stability studies have been carried out using thermo gravimetric analysis (TGA) in the temperature range 40–600 °C under nitrogen gas at a heating rate of 10 °C min<sup>-1</sup>. The TGA results indicated that the synthesized compounds are thermally stable up to 317 °C. TGA revealed the onset decomposition temperature ( $T_d$ ) of **6a** and **6b** are 317 °C (95%) and 375 °C (91%), respectively. In general the backbones of these compounds are stable up to 317 °C, above 317 °C and 375 °C for compound **6a** and **6b**, the thermogravimetric curve showed a major loss in the weight respectively. The comparisons of the  $T_d$  (decomposition temperature) show that the thermal stability of the compound **6b** is more than that of the compound **6a**. The compound **6b** showed a sharp decomposition after a temperature of 317 °C and completely decomposed beyond 450 °C. However, the compound **6b** showed sluggish decomposition nature and it does not decompose completely up to 600 °C (Fig. S8).

#### Electronic vertical excitations (TD-DFT)

The electronic vertical excitations were calculated using TD-B3LYP/6-31G(d) method. The experimental absorption wavelengths and the computed vertical excitation spectra associated with their oscillator strengths, orbital composition, and their

#### Table 5

Excited state energy difference between K1-Enol\* and K1-Keto\* in kcal mol-1.ª

Solvents	THF	Acetone	DCM	Ethanol	Methanol	Acetonitrile	DMF	DMSO
<b>6a</b> -E <sup>*</sup> -K <sup>*</sup> (kcal mol <sup>-1</sup> )	1.23	0.13	0.94	0.03	0.09	0.13	0.14	0.21
<b>6b-</b> E <sup>*</sup> -K <sup>*</sup> (kcal mol <sup>-1</sup> )	12.52	11.71	12.31	11.63	11.76	11.5	11.49	11.44

<sup>a</sup> Excited state energy were computed using TD-DFT with B3LYP method and 6-31G(d) basis set.

corresponding assignments for the compounds **6a** and **6b** are summarized in Tables 1 and 2. The absorption band occurring at the lower energy with higher oscillator strength is due to the intramolecular charge transfer (ICT) and it is the characteristic of the donor–acceptor chromophore. These ICT bands of the compounds **6a** and **6b** were mainly due to the electronic transition from the highest occupied molecular orbital HOMO and HOMO – 1 to the lowest unoccupied molecular orbital (LUMO + 1) respectively. The experimental absorption and the computed vertical excitation of the compounds **6a** and **6b** are independent of the solvent polarity.

The percent deviation between the experimental and the computed absorption at the shorter and longer wavelength of the compound 6a is 10.8% in DMF and 7.5% in methanol while compound **6b** in acetone is 3.27% and 4.26% respectively. As an example of the compound **6a**, in the case of non polar solvent like acetone HOMO to LUMO + 1 (98%) transition is responsible for the vertical excitation located at 367 nm with oscillator strength (f) 1.1007, which corresponds to the experimentally observed prominent absorption peak at 371 nm. The HOMO - 3 to LUMO (54%) (Table 1) transition is responsible for the vertical excitation at 296 nm with oscillator strength (f) 0.3561, which corresponds to the experimentally observed absorption (shoulder peak) at 302 nm. For polar solvents like DMF, HOMO to LUMO + 1 (98%) transition is responsible for the vertical excitation located at 368 nm with oscillator strength (f) 1.1232, which corresponds to the experimentally observed prominent absorption peak at 374 nm. The HOMO - 3 to LUMO (54%) transition is responsible for the vertical excitation at 296 nm with oscillator strength (f) 0.3586, which corresponds to the experimentally observed absorption (shoulder peak) at 332 nm (Table 1). For the compound **6b** in non-polar solvent like acetone HOMO to LUMO + 1 (90%) transition is responsible for the vertical excitation located at 328 nm with oscillator strength (f) 0.4548, which corresponds to the experimentally observed absorption (shoulder peak) at 343 nm. The HOMO - 1 to LUMO + 1 (58%) (Table 2) transition is responsible for the vertical excitation at 277 nm with oscillator strength (f) 0.8607, which corresponds to the experimentally observed prominent absorption peak 268 nm. For the polar solvents like DMF, HOMO to LUMO + 1 (90%) transition is responsible for the vertical excitation located at 329 nm with oscillator strength (f) 0.4741, which corresponds to the experimentally observed absorption (shoulder peak) at 343 nm. The HOMO - 1 to LUMO + 1 (58%) transition is responsible for the vertical excitation at 278 nm with oscillator strength (f) 0.8685, which corresponds to the experimentally observed prominent absorption peak at 274 nm (Table 2).

# Frontier molecular orbital

The different frontier molecular orbitals were studied to understand the electronic transition and the charge delocalization within the molecules. The comparative increase and decrease in the energy of the HOMO's and LUMO's gives a qualitative idea of the excitation properties and the ability of the hole or electron injection [40]. The first allowed and the strongest electron transitions usually correspond almost exclusively to the ICT of an electron from HOMO  $\rightarrow$  LUMO + 1 energies of different molecular orbitals involved in the electronic transitions of these compounds in different solvents are illustrated in Tables S7 and S8. In the case of the entire solvents energy gap between the HOMO  $\rightarrow$  LUMO + 1 orbital nearly same as the solvent polarity was increased or decreased (Figs. S9 and S10). The HOMO and LUMO energy level of the compounds 6a and 6b in DMF remains same, and it may be due to the very similar reduction potential (Fig. S11). This is understandable because of these structural isomer having same reduction site [41].

#### Table 6

Frontier molecular orbital's of the compounds 6a and 6b in DMF.



Molecular orbital diagrams of the compounds **6a** and **6b** are shown in Table 6. From the pictorial diagram the compounds **6a** and **6b** were found that HOMO  $\rightarrow$  LUMO + 1 orbitals fully delocalized throughout the molecule. The electron densities of the compounds **6a** and **6b** in the HOMO were slightly more located on the donor core and the electron densities on the LUMOs were shifted toward the acceptor end (imidazole core). The cyclic four level photophysical process involving the excited state proton transfer of the compounds **6a** and **6b** (E-Enol/E-Enol\*/K-Keto\*/K-Keto) is exemplified in Figs. S12 and S13.

#### Structural properties of the compounds

During the photoexcitation of the enol form the first excited singlet state undergoes redistribution of charge densities leading to a different geometry in terms of bond angles and bond distances favoring a proton transfer and ultimately the excited state keto form, which becomes an emissive species. In the excited state, the hydrogen attached to oxygen approaches near to the basic nitrogen of imidazole unit via six member hydrogen bonding for transfer of proton. Molecular planarity is also the most important factor for ESIPT facilitating the proton transfer in the excited state. This ESIPT aspect is evident from the TD-DFT computation. The differences between the ground state and excited state of the optimized geometries of the enol as well as the keto form (bond angles, bond lengths, Mulliken charges) are explained with the help of TD-DFT. This aspect is evident from the TD-DFT computations.

As a representative example, the structural aspects of the compounds **6a** and **6b** in the ground and the excited state of the enol as well as the keto form in acetone using Gauss View 5.0 software [42] are summarized in Figs. S14 and S15. The bond distances N<sub>13</sub>—H<sub>37</sub>, O<sub>23</sub>—H<sub>37</sub>, O<sub>23</sub>—C<sub>17</sub>, C<sub>14</sub>—C<sub>16</sub> and Mulliken charges on N<sub>13</sub>, H<sub>37</sub>, and O<sub>23</sub> of the ground and the excited state of the optimized geometries of the enol form as well as the excited state geometry of keto form are summarized in Tables S9–S11. The compound **6a** in acetone, the N<sub>13</sub>—H<sub>37</sub> hydrogen bonding distance decreases by 0.049 Å from the ground state enol (1.732 Å) to the excited state enol (1.683 Å) while the Mulliken charges on H<sub>37</sub> and O<sub>23</sub> were decreased by 0.001|e| and 0.005|e| from the ground state enol (E) to the excited state enol (E<sup>\*</sup>), respectively. The distance between O<sub>23</sub>–H<sub>37</sub> bond increases by 0.009 Å from the E-enol (0.997 Å) to the E<sup>\*</sup>-enol (1.006 Å), which means that in the excited state (E-Enol) the H<sub>37</sub> approaches near the N<sub>13</sub> via hydrogen bonding for the proton transfer. The distance between  $O_{23}$ - $C_{17}$  bond decreases by 0.015 Å from the ground state enol (1.351 Å) to the excited state enol (1.336 Å), which is further decreased by 0.071 Å in the excited state keto form (1.265 Å). In addition to this, the bond angle  $H_{37}$ – $O_{23}$ – $C_{17}$  increases by  $0.28^{\circ}$ from the ground state enol (107.96°) to the excited state enol  $(108.24^{\circ})$  (Table S12). In this pathway, H<sub>37</sub> approaches closer to N<sub>13</sub> of the imidazole unit in the excited state enol form and further transfer to N leads to the excited state keto (K<sup>\*</sup>) form with N-H bond distance of 1.021 Å and H<sub>37</sub>-O<sub>23</sub> bond distance of 1.901 Å. The excited state keto returns to the ground state keto (K) conformer with N—H bond distance of 1.046 Å and H<sub>37</sub>—O<sub>23</sub> hydrogen bonding distance of 1.690 Å. As H<sub>37</sub> approaches to O<sub>23</sub>, the excited state keto (K<sup>\*</sup>) hydrogen bonding distance decreases by 0.211 Å from 1.901 to 1.690 Å and it is immediately converted to the ground state keto (K) conformer followed by the ground state enol (E) form. Similar structural behavior is observed for the compound 6b (Tables S13-S16, Fig. S15).

In the case of the excited state enol ( $E^*$ ) of the compound **Ga**, as the solvent polarity increases the O<sub>23</sub>—C<sub>17</sub> and N<sub>13</sub>—H<sub>37</sub> bond distance increases from 1.335 to 1.337 and 1.679 to 1.684 Å, while O<sub>23</sub>—H<sub>37</sub> and C<sub>14</sub>—C<sub>16</sub> bond length decreases from 1.008 to 1.006 Å and from 1.448 to 1.445 Å, respectively (Fig. S16, Tables S9–S10). The Mulliken charges on N<sub>13</sub> and H<sub>37</sub> in all the solvents increase from the ground state enol (E) to the excited state enol ( $E^*$ ) (Fig. S17, Table S11) while at the same time decrease for O<sub>23</sub> atom indicating that in the excited state enol ( $E^*$ ) form, H<sub>37</sub> is in close proximity of N<sub>13</sub> atom, which is favorable for ESIPT. From the excited state (K<sup>\*</sup>-Keto) to the ground state (K-Keto) Mulliken charges for O<sub>23</sub>, H<sub>37</sub> and N<sub>13</sub> atom increases (Fig. S18, Table S11), which supports the ESIPT process. Similar observation is observed in the compound **6b** (Figs. S19–S21).

# Effect of solvent polarity on the ground and the excited state dipole moments

The polarity of the solvents affects the fluorescence properties due to their solvation or hydrogen bonding with heteroatom present in the compounds. The dipole moment also depends on the polarity as well as the groups present in the molecule. The geometry of the compound at the ground and the excited state decide their electronic behavior. The effect of the solvent on the absorption and the emission spectra clearly indicates the change in the dipolar characteristics of the compounds in the excited state, which means that the solvatochromic data gives an efficient tool to understand the change in the dipole moment in the first excited state.

Table 7	
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Dipole moment ( $\mu$  in Debye) of the compounds **6a** and **6b**.

Here, we report the ground and excited state dipole moments of the compounds **6a–6b** using Bakhshiev [43] and Kawski–Chamma–Viallet correlations [44,45]. This method is based on a linear relation between the absorption, emission maxima and solvent polarity functions ( $E_T^N$ ) [46–48] which is dependent on both the relative permittivity ( $\varepsilon$ ) and refractive index ( $\eta$ ) of the solvent. The polarity function of solvent has been taken from literature [49].

By using the solvatochromic data and polarity function of solvents, we calculated the dipole moment ratio of the excited state to the ground state of the compounds **6a** and **6b**. The experimental dipole moments were compared with the dipole moments in the vacuum phase computed by DFT and TD-DFT computation (Table 7). The dipole moment obtained from short wavelength emission data compared with the ratio of the dipole moment of excited state enol and ground state enol form in vacuum phase. However, the long wavelength emission data is compared with ratio of dipole moment of the excited state keto and the ground state keto form in vacuum phase. These results clearly indicate that a large difference is observed between the dipole moment.

Dipole moments of the compounds **6a–6b** were computed in the different solvents by DFT and TD-DFT to investigate the electronic behavior from the ground state to the excited state in different solvents. We observed that the dipole moments of the compounds **6a** and **6b** are higher for the excited state enol and the ground state keto forms and lower for the ground state enol and the excited state keto; this is due to the excited state of the enol form and the ground state of the keto form stabilized by solvation or hydrogen bonding with different solvents. The plots of the dipole moment ( $\mu$ ) versus solvent polarity function ( $E_T^N$ ) of compounds **6a–6b** enol and keto form in the ground and the excited state is shown in Tables S17–S18; Figs. S22–S23.

# Conclusion

To conclude, this paper reports the synthesis of the fluorescent 2-(2-hydroxyphenyl)-6-methylimidazo[4,5-f]isoindole-

5,7(1*H*,6*H*)-dione and its derivative. This compound is well characterized by FTIR, <sup>1</sup>H NMR and mass spectroscopy. The thermal stability was determined by TGA analysis and it was found that the compounds are thermally stable. The compounds **6a** and **6b** shows a single prominent absorption peak but in the case of emission of compound **6a** dual in non-polar, polar aprotic and single emission in polar protic solvent. While in compound **6b** dual emission observed only in ethanol and DMF. The photophysical properties of the compounds are sensitive toward the solvent environment. The highest quantum efficiency was observed in THF (**6a** = 0.15, **6b** = 0.10). Photophysical properties of the synthesized compounds were supported by DFT and it was observed that computational results are good agreement with the theoretical observations.

Compounds	<sup>a</sup> Enol $\mu_{\rm g}$	<sup>b</sup> Enol $\mu_{e}$	<sup>b</sup> Enol μ <sub>e</sub> ªEnol μ <sub>g</sub>	<sup>a</sup> Keto $\mu_{g}$	<sup>b</sup> Keto $\mu_{e}$	<sup>b</sup> Keto $\mu_{e}$ <sup>a</sup> Keto $\mu_{g}$	<sup>c</sup> Experimental Dipole moment	% D
6a	6.082	6.731	1.107	5.819	5.612	0.964	0.44 <sup>d</sup> 0.12 <sup>e</sup>	60 <sup>f</sup> 88 <sup>g</sup>
6b	4.7002	4.921	1.047	4.139	3.812	0.921	2.54 <sup>d</sup> 3.8 <sup>e</sup>	59 <sup>f</sup> 76 <sup>g</sup>

<sup>a</sup> Dipole moment of the compound in ground state.

<sup>b</sup> Dipole moment of the compound in excited state.

<sup>c</sup> Experimental dipole moment obtained from solvatochromism data using Bakhshiev and Kawski-Chamma-Viallet correlations.

<sup>d</sup> Dipole moment at the short wavelength emission obtained from the solvatochromism data using Bakhshiev and Kawski-Chamma-Viallet correlations.

<sup>e</sup> Dipole moment at the longer wavelength emission obtained from solvatochromism data using Bakhshiev and Kawski-Chamma-Viallet correlations.

<sup>f</sup> (% D)% Deviation between the experimental and the computed dipole moment for short wavelength emission.

<sup>g</sup> (% D)% Deviation between the experimental and computed dipole moment for long wavelength emission.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.07.021.

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