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Imine-amine Tautomerismvs. Keto-enol Tautomrisation:Acceptor Basicity Dominates Over Acceptor Electronegativity in ESIPT Process through Six-member Intramolecular H-Bonded Network

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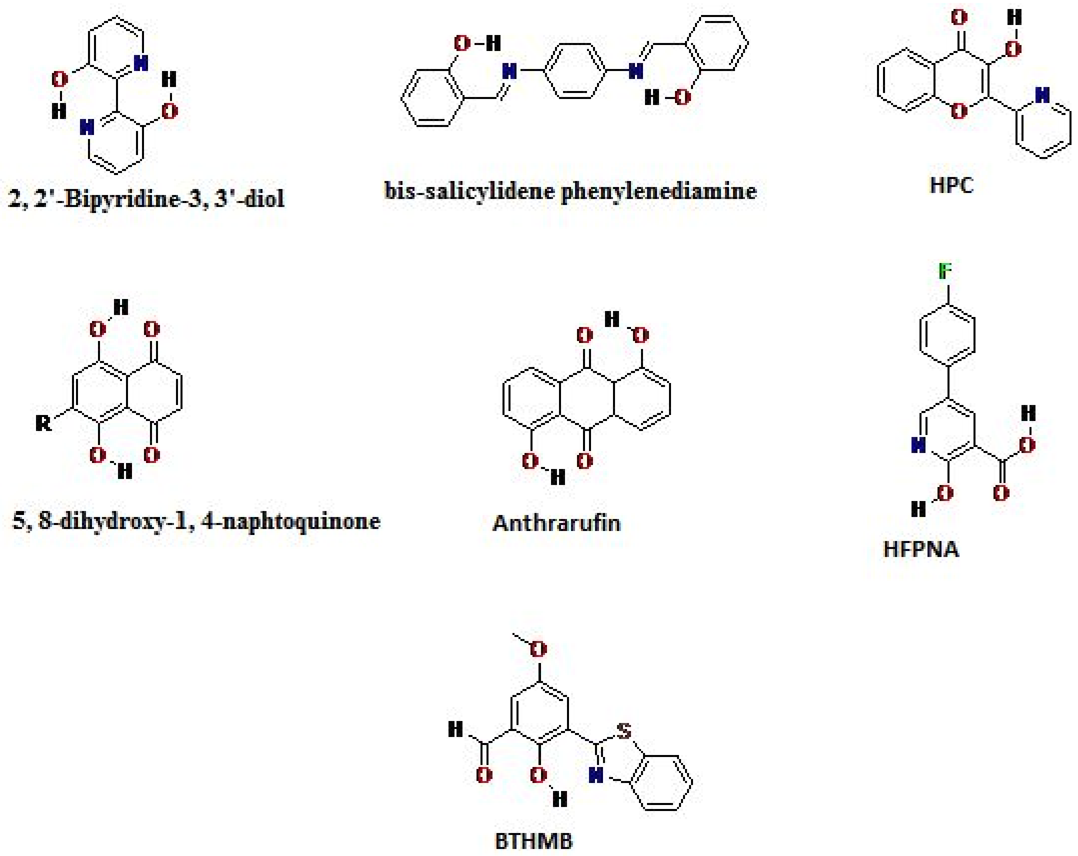
Abstract: Photophysical properties of a synthesized asymmetric two ways proton transfer molecule 3-(benzo[d]thiazol-2-yl)-2-hydroxy-5-methoxybenzaldehyde (**BTHMB**) was studied in details. **BTHMB** could undergo excited state intramolecular proton transfer (ESIPT) involving a 6-member H-bonded network towards either N as well as the O atom present in the molecule as proton acceptors. From tedious spectroscopic dissection, however, it was established that ESIPT was driven exclusively towards N centre over O center in solid state as well as in the solution phase. The aforementioned deduction was based on spectral comparison with judicially synthetic compounds 2-hydroxy-5-methoxybenzaldehyde (**HMB**) and 2-(benzo[d]thiazol-2-yl)-4-methoxyphenol (**BTMP**). In solution, the co-existence of anion and neutral form of **BTHMB** in basic solvents DMSO and DMF enables **BTHMB** to behave as a white light emitter. Thus, apart from establishment of directionality of ESIPT in double ESIPT probes, current work deserves special merit as **BTHMB** can be considered a standard in future designs involving red light and solvent specific white light emitters.

1. Introduction

Since the epoch making report by Weller et al[1]regarding excited state intramolecular proton transfer (ESIPT) in methyl salicylate, the said excited state phenomenon has been enjoying tremendous attention by chemists till date. With passage of times, several ESIPT active fluorophores have been synthesized and reported by various groups, providing deeper insight into the aforesaid excited state phenomenon[2-6]. ESIPT may involve through a 6-membered (salicylic acid), 5-membered (3-hydroxy flavones) or even a 4-membered (2-hydroxypyridine)hydrogen bonded network between the donor and acceptor groups. However, on thermodynamic grounds, 6-membered H-bonded network is more favoured over the other two. Thus, the ESIPT systems where ESIPT occurs through 6-membered hydrogen bonded site have been studied more rigorously by chemists over the years. Of late, there has been a mounting interest in the spectroscopic study of organic compounds having double proton transfer sites. For example, compounds like 2, 2'-Bipyridine-3, 3'-diol have been reported to undergo simultaneous ESIPT[7], whereas bis-Schiff bases like salicylidene phenylenediamine[8] are reported to undergo single ESIPT involving a single enol to keto photo conversion (Scheme 1). The aforementioned ESIPT probes contain N atom as acceptor(s) of proton whereas a phenolic group is present as proton donor site(s). Another important class of double ESIPT probes are those where carbonyl oxygen is present as the proton acceptor. Some noteworthy examples are 5, 8-dihydroxy-1, 4-naphtoquinones and anthrarufin[9-10], among which the former undergoes simultaneous double proton transfer whereas the latter undergoes ultrafast single ESIPT process. Some noteworthy theoretical calculations have also been carried out for some biologically as well as spectroscopically interesting molecules such as Deep Red Pigment Alkannin[11], bisflavonols[12] as well as 3-hydroxyisoquinoline[13]. From the above discussions, it is evident that the fundamental understanding of double EISPT processes is a problem which has garnered tremendous attention from experimental as well as theoretical chemists. A scrutiny of the structures of the stated compounds reveals that both the proton transfer sites are identical, i.e. the systems have exactly similar sites where ESIPT can occur. On the contrary, very little emphasis has been provided on synthesized systems where the same molecule has two different proton transfer sites. A report by Chou et al is worth mentioning at this juncture (Scheme 1) where the double ESIPT of a pyridine bearing 3-hydroxy flavone derivative, 3-Hydroxy-2-(pyridin-2-yl)-4*H*-chromen-4-one **(HPC)** were studied (Scheme 1) [14]. The study revealed that in solid state, ESIPT occurred between pyridine N and the-OH proton, with an emission band at 540 nm. However, in the solution phase an additional ESIPT process occurred between the carbonyl oxygen with the –OH group. Although the two proton transfer sites are genuinely asymmetric in nature, one site involved 5-member hydrogen bonded network whereas 6-membered hydrogen bonded network is involved for ESIPT between N atom and OH group. Our group also came up with a report where lactim-lactam tautomerism was favoured over enol-keto tautomerism in a nicotinic acid derivative2-hydroxy-5-(4-Fluorophenyl) Nicotinic Acid **(HFPNA)**[15], which had the same drawback of the differing H-bonded ground state geometries. In order to have a better model for ascertaining the directionality of ESIPT, we decided to synthesize a molecule containing two asymmetric proton transfer sites and involving 6-member H-bonded network for the two potential ESIPT processes, namely3-(benzo[d]thiazol-2-yl)-2-hydroxy-5-methoxybenzaldehyde (**BTHMB**) (Scheme 1).**BTHMB** has two ESIPT sites, one involving keto-enol tautomerism, whereas the other involves imine-amine tautomerism. Detailed steady state and time resolved studies revealed that ESIPT occurs exclusively towards the N centre than the O centre in solid state as well as in solution phase. The current report holds particular importance as we could state that the basicity of N atom in **BTHMB** dominates the ESIPT process, overruling the electronegativity of the O atom.Another impact of the current report is the influence of the methoxy substitution in **BTHMB** (Scheme 2). Goswami et al reported a structurally similar compound 5(Benzothiazol-2-yl)-4-hydroxyisophthalaldehyde (**BHI)**as an amino acid sensor[16]. **BHI**, equipped with a Formyl group para to the phenolic –OH functionalityshowed ESIPT emission at ~520 nm and yellow green color could be observed in solution. **BTHMB** containing an electron releasing methoxy functionality showed ESIPT emission at ~600 nm and orange red emission is observed. That the aforementioned band occurs due to N being the acceptor was established by spectral comparison with control compounds 2-hydroxy 5-methoxy benzaldehyde **(HMB)**and 2-(benzo[d]thiazol-2-yl)-4-methoxyphenol (**BTMP)**.As an added advantage, it was seen that **BTHMB** was a white light emitter in DMSO as the mentioned basic solvent affords the anion and neutral form of **BTHMB** in solution. The design of **BTHMB** could be treated as a simple starting point for construction of white light emitters in solution. Hence, our current report holds importance as far as designing, exploring and tuning of the properties of ESIPT active probes are concerned.



2, 2'-Bipyridine-3, 3'-diol

bis-salicylidene phenylenediamine

HPC

5, 8-dihydroxy-1, 4-naphtoquinone

Anthrarufin

HFPNA

BTHMB

Scheme 1. Earlier reported double proton transfer probes and our current report.

2. Experimental section

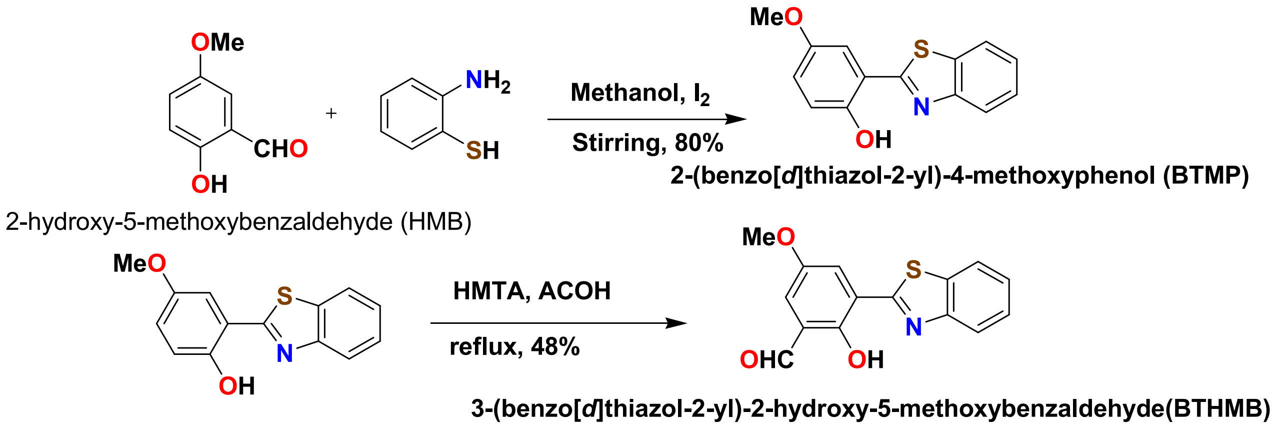
2.1.Chemicals and apparatus

All chemicals were purchased from Merck and used without any further purification. Solvents were of UV-grade and purchased from Spectrochem. NMR spectra were recorded in Bruker Advanced Supercon 300 MHz NMR spectrophotometer using TMS as internal standard. Steady State UV-Vis absorption profiles were recorded on a Shimadzu UV-1900 spectrophotometer. Steady state emission and excited state decay profiles were recorded on HORIBA Jobin Yvon Flurolog 3 (Model 3-11) and Horiba Delta Flex-01-NL time resolved fluorimeter respectively.Mass spectrometrywas carried out inWatersXevo G2-S Q TOF mass spectrometer.

During steady state absorption and emission measurements, the concentration of probe was maintained at micro molar range to avoid aggregation, re absorption or self-quenching respectively. All data were recorded at room temperature. The excited state lifetime measurements were carried out by exciting the sample using a picoseconds laser diode of 375nm and 450nm. The signals were obtained by setting the emission polarizer at magic angle (54.7º) to prevent anisotropy and the decays were deconvoluted using DAS6 software. The goodness of fitting was judged using χ^2 criteria. The average lifetime was calculated using standard procedures[17]. The quantum yield values were calculated using anthracene as standard[18].

2.2. Synthetic procedure of BTMP and BTHMB

The synthetic outline has been provided in Scheme 2. A 5 mmol methanolic solution of 2-hydroxy 5-methoxy benzaldehyde (**HMB)** was treated with equivalent amount of 2-aminothiphenol and ~2.5 mmol of molecular iodine and stirred overnight to get pure **BTMP** in 80% yield. **BTMP** was characterized using NMR and ESIMS (ESI, Figures S1-S3). **BTMP** (2 mmol) was suspended in 10mL glacial acetic acid and treated with 10 mmol hexamethylenetetramine (**HMTA**). The reaction mixture was refluxed with stirring for 16 hours, after which TLC analysis showed complete consumption of starting material. The reaction mixture was then poured onto 100 mL chilled 2 (M) HCl solution, whereupon a reddish brown precipitate appeared while being stirred. The solid was filtered, washed with ~50 mL water in portions and dried overnight in vaccum to obtain **BTHMB** in 48% yield. **BTHMB** was characterized using NMR and ESI-MS (ESI, Figures S4-S6).

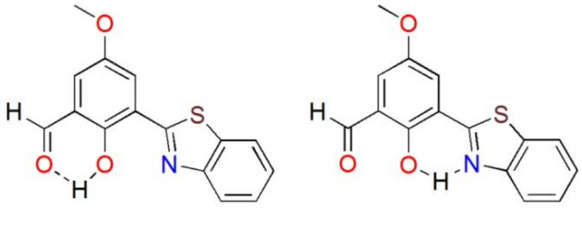


Scheme 2. Synthetic outline of **BTMP** and **BTHMB.**

3. Results and discussions

3.1. Absorption Spectral Studies. The basic photophysical survey of **BTHMB** was started by recording the absorption profiles of a 5 μM solution of **BTHMB** in various solvents. Two prominent absorption bands were obtained at ~300 nm and ~385 nm respectively. In polar solvents like DMSO, DMF and isopropanol an additional band was obtained at ~480-520 nm depending on the solvent (Figure 1, Table 1). The red sided band also appeared when triethylamine as a source of base was added to an acetonitrile solution of **BTHMB** (Figure 1). Hence, the third band was assigned to be due to the anion of the probe. The higher acidity of the phenolic –OH proton in **BTHMB** due to the presence of electron withdrawing Formyl group facilitates anion formation in basic solvents having high dielectric constants as in DMF, DMSO and isopropanol. For assigning the bands at ~300 and ~385 nm, absorption profiles of the two control compounds **HMB** and **BTMP** were recorded (Figure 2, ESI, Table S1). **HMB**, bearing an aldehyde group and an electron releasing methoxy substituent showed absorption band at

~365 nm in almost all solvents. Based on our previous report on 4-diethylamino 2-hydroxy benzaldehyde[19], the red shifted band was assigned to be due to π- π* transition. On the other hand, **BTMP** showed two bands at ~290 nm and ~360 nm (Figure 2, ESI, Table S2). The low energy band was assigned to be due to the coupling of benzothiazole moiety with the methoxy phenyl moiety, whereas the high energy band was due to that of the benzothiazole moiety, in accordance to the report by Kim et al[20]. It is noteworthy to mention that the anionic band did not appear in the absorption profiles of any of the control compounds. Thus, the presence of anion band in polar solvents for **BTHMB** was due to the higher acidity of the phenolic –OH in the same. Since the control compound **BTMP** showed two bands 70 nm apart, the spectral resemblance of **BTHMB** absorption profile prompted us to assign the high energy band to be due to coupling of the phenolic –OH proton with the aldehyde O atom, whereas the low energy band is due to the coupling with thiazole N atom (Scheme 3). However, the almost similar absorption maxima of the control compounds **HMB** and **BTMP** hinted that in solution phase, equilibrium may be prevalent between the two forms of **BTHMB** in the ground state.The red shift in absorption maxima is due to the greater chromophoric stabilization in **BTHMB** compared to either of the two control compounds.



O---H bonded form N---H bonded form

Scheme 3. Two possible conformers of **BTHMB** in the ground state.

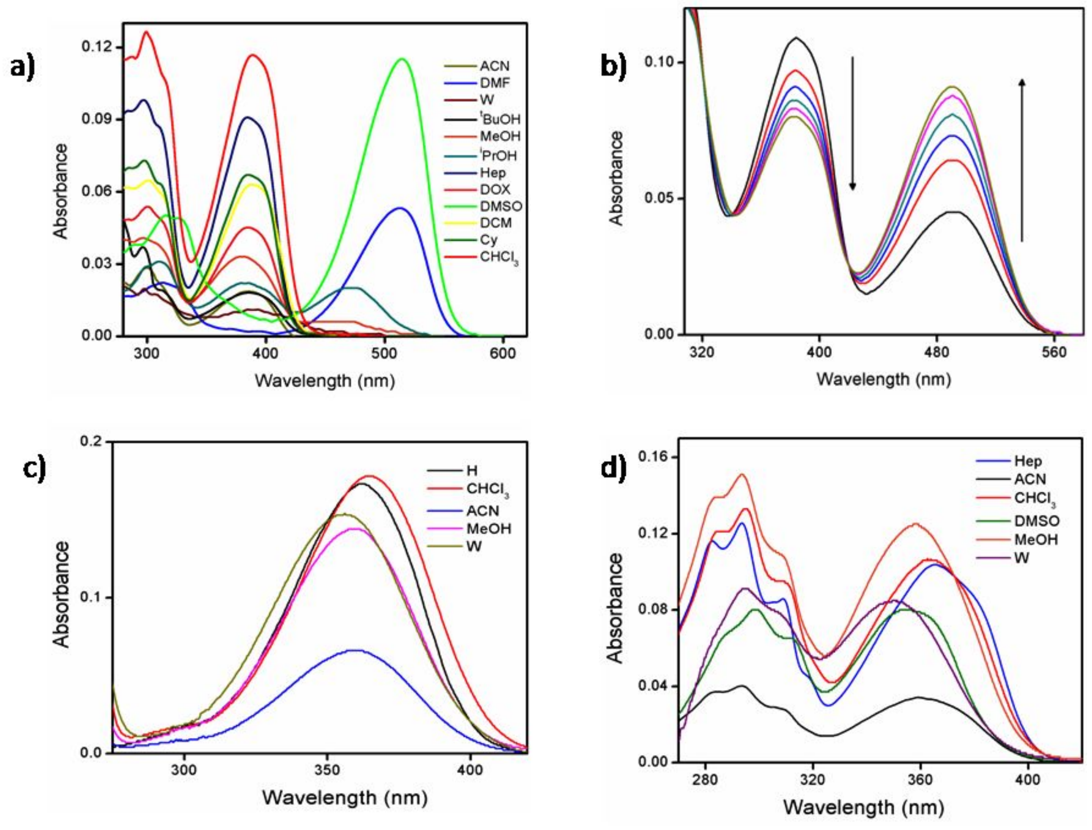


Figure 1. Absorption profiles of (a) **BTHMB** in various solvents (5 μM), (b) **BTHMB** upon addition of base in acetonitrile, (c) **HMB** (10 μM) in various solvents and (d) **BTMP** in various.

3.2. Steady State Emission spectra. Upon exciting **BTHMB** at 380 nm, a broad band with high Stokes' Shift was observed at ~600nm in non-polar heptanemedium (Table 1, Figure 2) and solvents of slightly higher polarity like chloroform and cyclohexane. In DMSO and DMF, dual emission was observed. However, bands appeared at ~420 nm and ~556 nm respectively. Upon adding base to a solution of **BTHMB** in acetonitrile, the low energy emission band at ~595 nm underwent a blue shifting to ~565 nm (Figure 2). The band at ~565 nm was also obtained when **BTHMB** was excited at their corresponding anion bands in various solvents where the anion was found to exist in the ground state along with the neutral form (Figure 2). Hence, the band observed in polar solvents between ~556-565 nm was due to the anion of **BTHMB** formed in solution. Since the anion of HBT derivatives is reported to be emitting at higher energy compared to the ESIPT emission maxima[2], our results are in accordance with literature reports. The shift in emission maxima of the anion could be an outcome of greater stabilization of the same in solution due to presence of Formyl group, which was also observed in the ground state while recording the absorption profiles. When **BTHMB** was excited at 300 nm, a single emission band was obtained between 390-420 nm, depending on the solvent (Table 1,Figure 2). The nature of these two emission bands were ascertained once again by comparing steady state emission spectra of the control compounds **HMB** and **BTMP**. **HMB** when excited at 350 nm showed emission band with very high Stokes' Shift at ~500 nm, whereas a high energy band was obtained at ~435 nm which underwent slight red shift in methanol (Figure 3, ESI, Table S1). The band at ~500 nm was assigned to be due to ESIPT from phenolic –OH to the aldehyde moiety in **HMB**, in accordance with reports regarding salicylaldehyde equipped with electron donating groups[21]. Since **BTMP** showed two prominent absorption bands, it was excited at 295 nm and 350 nm individually. Upon exciting **BTMP** at 350 nm, ESIPT band was obtained at ~570 nm, in close accordance with the report by Kim et al[17] regarding **BTMP**(Figure 3, ESI Table S2).Thelocal emission band was obtained at ~410 nm. Only the local emission band of **BTMP** was obtained when the molecule was excited at 295 nm. Thus, from spectral comparison of **BTHMB** with the other two control compounds, we assigned the ESIPT band in **BTHMB** appears due to proton transfer from phenolic –OH to thiazole N atom. Had ESIPT occurred from –OH proton to aldehyde O atom, the ESIPT band would have appeared at around 500 nm. If we revisit Scheme 3, it could thus be stated that the N---H bonded form would be the most important structure for explaining the above observations.

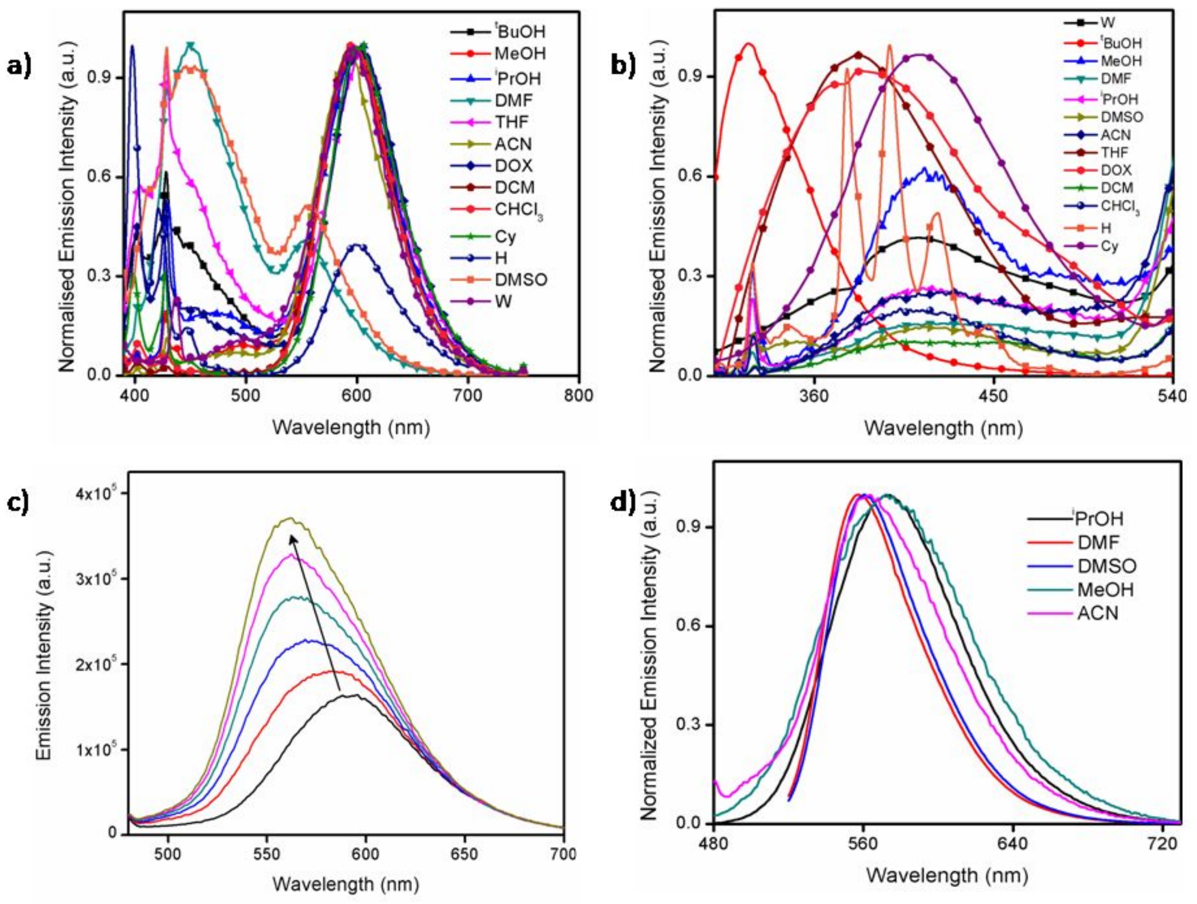


Figure 2. Emission profiles of **BTHMB** in (a) various solvents when excited at 380 nm, (b) various solvents when excited at 300 nm, (c) presence of base addition in acetonitrile and (d) various solvents when excited at their corresponding anionic absorption band (for ^{i}PrOH and MEOH, λ_{ex}=478 nm, DMF and DMSO, λ_{ex}=500 nm, ACN, λ_{ex}=420 nm).

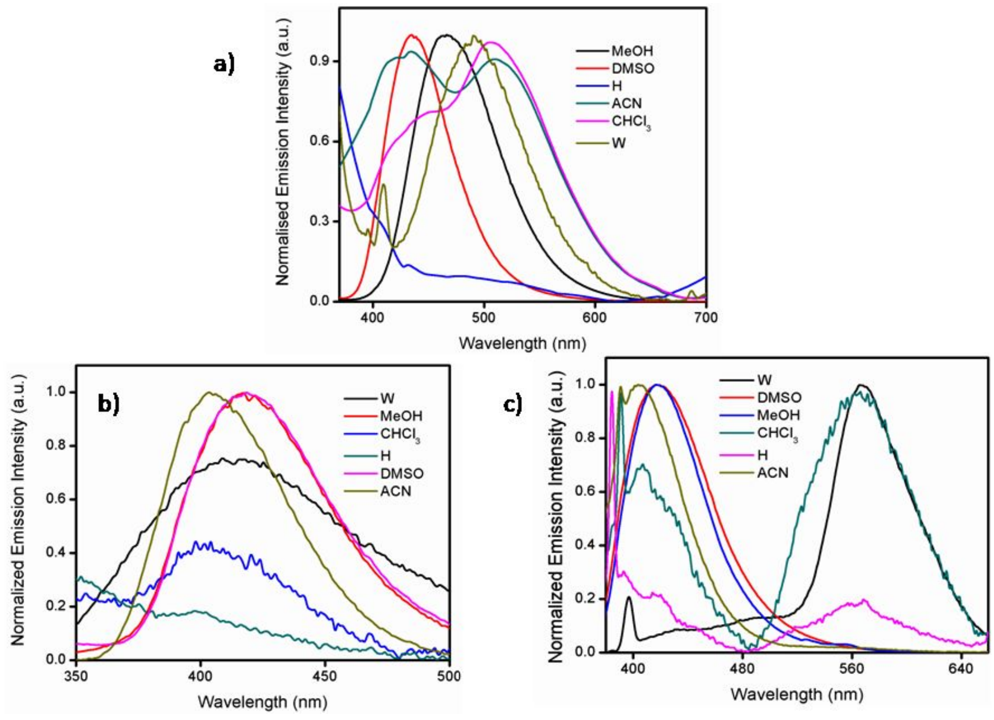


Figure 3. Emission spectrum of (a) **HMB** in various solvents (λ_{ex}=350 nm), (b) **BTMP** in various solvents (λ_{ex}=290 nm) and (c) **BTMP** in various solvents (λ_{ex}=350 nm).

Moreover, the emission bands obtained when **BTHMB** was excited at 300 nm matched reasonably well with the local emission bands of **BTMP** in various solvents. Since none of the emission profiles matched with **HMB**, it could be well stated that the ESIPT process occurring in **BTHMB** involves proton transferred from –OH group to the N atom. Hence, the Formyl group present in **BTHMB** could by no means participate in the ESIPT process. Moreover, the solid state emission spectrum of **BTHMB** matched with those obtained in solution phase as depicted in Figure 4. The current work is of particular interest as it establishes ESIPT directed towards N atom in presence of more electronegative O acceptor. This most probably is an outcome of greater availability of the lone pairs on N atom of the thiazole moiety, since the pair is not involved in any sort of conjugation with the benzothiazole moiety. An interesting optical property was revealed when solutions of **BTHMB** in various solvents were observed under UV-light (Figure 4). In several organic solvents, the color was red to orange. Interestingly, the color of **BTHMB** was white in DMSO solvent. This could be due to the fact that the dual emission bands in DMSO spanned the entire visible range; thereby the color of **BTHMB** appears to be white. Thus, this property makes **BTHMB** one of those rare examples where white light emission occurs through single molecular probe, as reported by Das et al[22]. Having probed the solid state properties of **BTHMB**, exited state lifetime measurements were carried out to gain further insight into the ESIPT process occurring in the probe (Figure 5, Table 2).

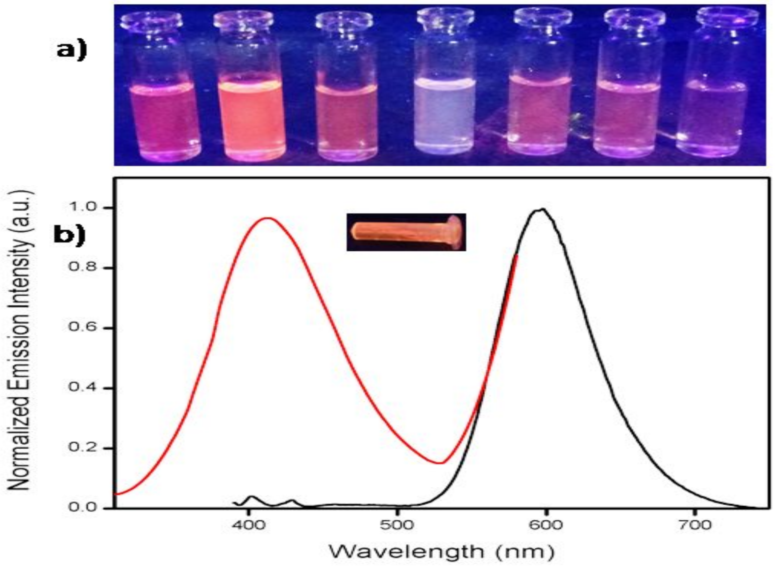


Figure 4. (a) Color of **BTHMB** in (from left) n-Heptane, Chloroform, Acetonitrile, Dimethylsulfoxide, Methanol, Isopropanol and Water and (b) Solid state emission profiles of **BTHMB** when excited at 300 nm (red profile) and 380 nm (black profile), (inset) color of **BTHMB** in solid state under UV-light.

Table 1. Steady State spectral parameters of **BTHMB**

Solvent[*]	λ_{max}^{abs}	λ_{max}^{em}	**ε(moll^{-1}cm^{-1})×10^{4}**	**Φ**
H	300,380	410[a],600[b]	1.73	0.18
Cy	300,380	410[a],600[b]	1.27	0.24
$CHCl_3$	300,390	410[a],600[b]	2.22	0.88
DCM	300,385	415[a],600[b]	1.19	0.69
DOX	300,380	400[a],420[b],600[b]	0.86	0.48
THF	300,380	400[a],420[b],524[b],600[b]	0.79	0.35
ACN	300,386	415[a], 593[b]	0.35	0.26
DMSO	310,515	415[a],420[b],560[b]	0.96	0.12
DMF	310,520	420[a],420[b],553[b]	0.23	0.12
MeOH	300,380,467	415[a],420[b],570[b]	0.77	0.14
^{i}PrOH	310,383,473	415[a],420[b],573[b]	0.37	0.59
^{t}BuOH	300,390	415[a],420[b],600[b]	0.36	0.65
W	300,380	415[a],420[b],600[b]	0.21	0.03

[*] Solvent abbreviation provided in Supplementary Information Section, [a] emission band obtained upon excitation at 300 nm, [b] emission band obtained upon excitation at 380 nm. Quantum yield were measured using anthracene as standard.

3.3. Excited State Lifetime Measurements. For TCSPC experiments, 336 nm pulsed LASER diode source was used to probe the band at 420 nm, whereas 375 nm sources was used to probe the band at 600 nm. For monitoring the anion band, 375 nm was used. When the ESIPT wavelength at ~600 nm was probed (Table 2), strictly monoexponential decay having lifetime of ~2.0 ns was observed in non-polar solvents. In more polar solvents like chloroform and dichloromethane, the lifetime component was ~3.0 ns. The higher lifetime in chloroform and DCM was in accordance with the higher quantum yield of **BTHMB** in these two solvents. This lifetime component was assigned to be due to the keto form of **BTHMB**.In 1, 4-dioxane biexponential decay was obtained with a faster component (~0.10 ns) along with a slower component matching with the lifetime of keto form (1.5 ns). The same pattern was obtained in acetonitrile. The relatively faster component was thus assigned to be due to the local emission or enol form of **BTHMB**. Starting from acetonitrile, the excited state population of the enol form started exceeding that of the keto form. This could be rationalized from the fact that ESIPT is hindered in polar solvents[23]. When the anionic band was monitored (Table 2), lifetime components of ~6.0 ns were obtained in DMF and DMSO with contributions of the anion of the enol forms. Thus, the slower lifetime values were assigned to be due to the anion of **BTHMB** in those solutions. In THF, apart from the anion and enol forms, another lifetime component faster than the instrumental resolution was obtained. This could be due to some solvent-solute interactions between the probe and solvent. Finally, when the enol form emissions were monitored (Table 2), multiexponential decays were observed in all solvents. In non-polar solvents the enol lifetime values were very fast. Lifetime of enol form underwent increment upon increasing the polarity as well as the proticity of the solvents.

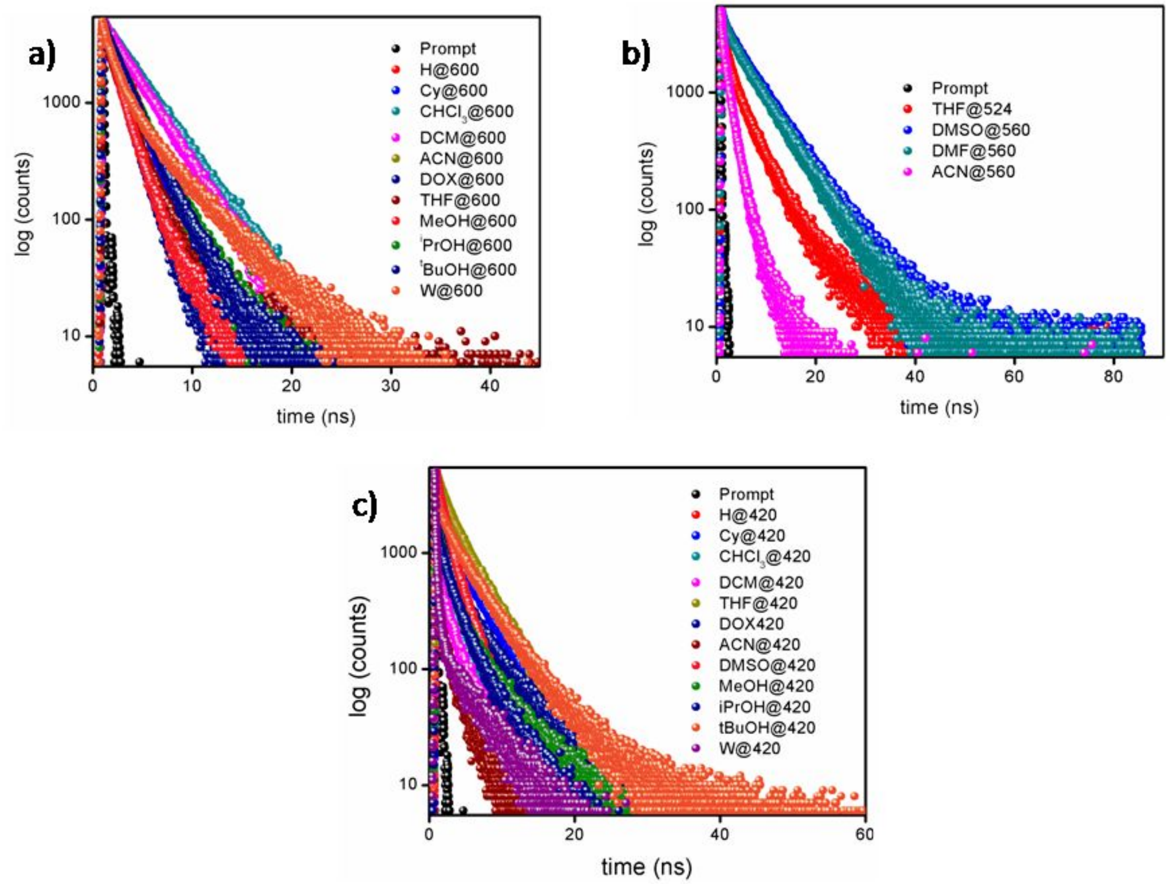


Figure 5. TCSPC decay profiles of (a) **BTHMB** when monitored at 600 nm (λ_{ex}=375 nm), (b) **BTHMB** when monitored at corresponding anion bands (λ_{ex}=375 nm) and (c) **BTHMB** when monitored at 600 nm (λ_{ex}=336 nm).

Table 2. Excited State lifetime parameters of **BTHMB** in various solvents

Solvent/Wavelength monitored(nm)	**τ_1^a(ns)/B_1**	**τ_2^b(ns)/B_2**	**τ_3^c(ns)/B_3**	**χ^2**
H/410	-/42%	3.23/58%	-	1.25
H/600	2.05/100%	-	-	1.12
Cy/410	-/18%	2.15/82%	-	1.06
Cy/600	2.39/100%	-	-	1.01
$CHCl_3$/410	0.89/42%	3.43/33%	-/25%	1.05
$CHCl_3$/600	3.49/100%	-	-	1.07
DCM/410	0.75/24%	3.27/40%	-/36%	1.10
DCM/600	3.19/100%	-	-	1.16
DOX/410	1.16/33%	5.06/55%	-/22%	1.18
DOX/600	0.10/10%	1.38/85%	3.66/5%	1.05
THF/410	1.35/19%	4.05/81%	-	1.13
THF/560	4.02/68%	13.36/14%	0.91/18%	1.30
THF/600	1.29/75%	3.98/25%	-	1.22
ACN/560	1.49/72%	4.73/12%	3.89/16%	1.25
ACN/600	1.33/77%	2.49/23%	-	1.12

DMSO/420	1.09/46%	2.61/54%	-	1.03
DMSO/560	0.95/5%	6.78/95%	-	1.20
DMF/420	1.12/30%	2.85/60%	-/10%	1.09
DMF/553	1.05/6%	6.37/94%	-	1.12
MeOH/420	1.19/4%	4.97/10%	-/86%	1.06
MeOH/570	1.23/15%	3.87/85%	-	1.20
^{i}PrOH/420	1.23/4%	3.81/6%	-/90%	1.00
^{i}PrOH/573	1.84/65%	3.65/35%	-	1.10
^{t}BuOH/420	-/7%	2.97/57%	6.91/36%	1.05
^{t}BuOH/600	1.82/69%	3.15/32%	-	1.12
W/420	0.27/16%	4.71/24%	-/60%	1.19
W/600	1.17/43%	4.75/57%	-	1.14

[a] Standard deviation=5%, [b] Standard deviation=3%, [c] Standard deviation=5%.

3.4. Theoretical Calculations

The experimental observations could be explained by considering ESIPT from –OH to N acceptor atom and overruling the possibility of ESIPT towards the Formyl O atom. The reason behind the observation has been stated to be basicity of N atom in **BTHMB** dominating the electronegativity of O atom. Although O is reported to be more electronegative than N in various scales of electronegativity like Pauling Scale, Mulliken Scale and so on[24], it was yet to be verified whether the same trend was present in case of **BTHMB** also. For this purpose, the structure of **BTHMB** was optimized using Gaussian 09 software[25] at DFT level and utilizing B3LYP functionality (ESI, Figure S7). Both conformers as shown above in Scheme 3 were constructed. A perusal of the Mulliken Charge densities on the N and O atoms in both forms (ESI, Table S3)ensured the higher electronegativity of O than N in the case of **BTHMB** as reflected from the negative values of Mulliken Charge on O atom. Hence, from the results of our theoretical calculations we could state that although O is more electronegative acceptor in our probe of interest, the basicity of N truly dominated electronegativity.

4. Conclusions

The photophysical properties of a potential two ways proton transfer molecule **BTHMB**, having asymmetric acceptors O and Nwere investigated by means of steady state and time resolved emission spectroscopic experiments. **BTHMB** shows imine-amine tautomerisminvolving the acceptor N atom present in **BTHMB**. Although more electronegative O atom is present in the system, it is not involved in ESIPT process. According to our knowledge, this is by far the first rational comparison of ESIPT between N and O donors present in the same molecule and occurring through 6-memenbered hydrogen bonded network. Furthermore, **BTHMB** is a white light emitter in DMSO and DMF, due to dual emission spanning the entire spectral region. Since **BTHMB** shows an orange-red color emission under UV solvents in some solvents, the current report also depicts how insertion of an electron donating group in ESIPT probe enables harvesting of red emission compared to previous reports where green emission was obtained from such probes containing electron withdrawing groups.

Associated Content

Supplementary Information

Contains characterization of the compounds, Spectroscopic information for **HMB** and **BTMP** and solvent abbreviation index.

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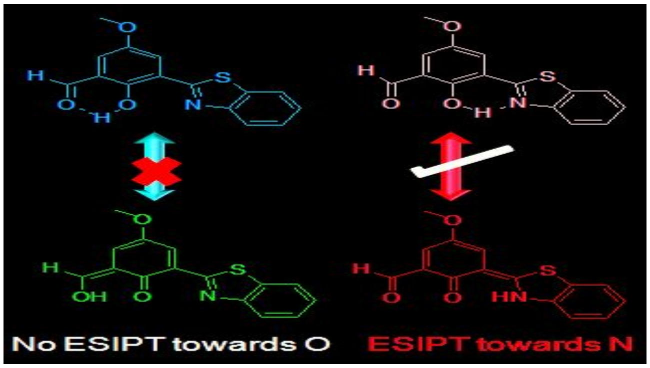
TOC Graphic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