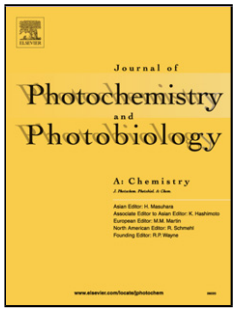

Title: A spectroscopic exploration of the influence of charge donor group on ESIPT process and its consequences in a salicylimine

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A spectroscopic exploration of the influence of charge donor group on ESIPT process and its consequences in a salicylimine

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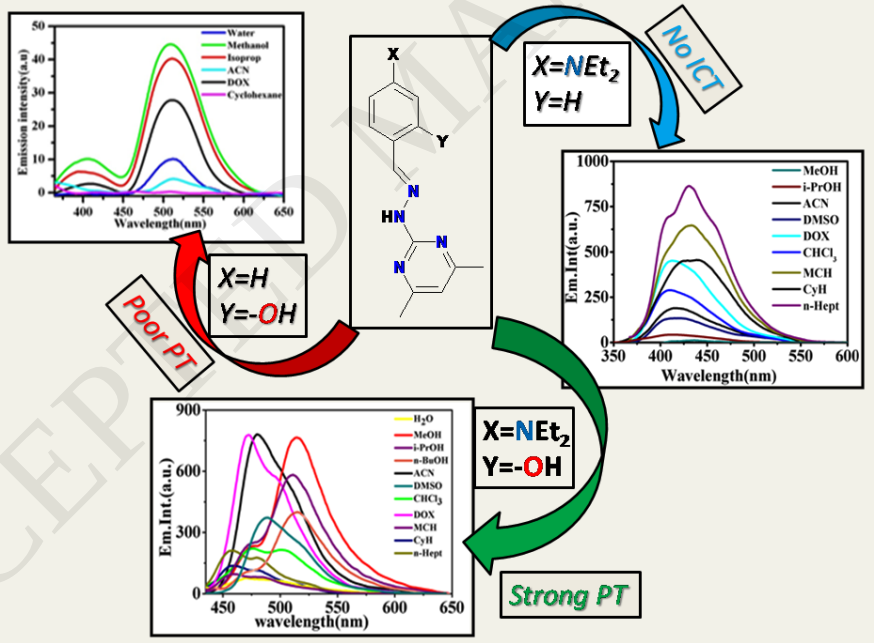
Graphical Abstract



Research highlights

- Newly designed Schiff bases capable for excited state proton donor and charge donor reaction
- Hydrogen bonding interaction from single crystal analysis
- Study the influence of charge donor on Keto-enol tautomerisation using spectroscopically
- Study the effect of the nature of solvents on ESIPT reaction
- Theoretical DFT calculations on ESIPT process corroborates experimental results

Abstract

Photophysical properties of a newly designed synthetic compound DYMDAP have been investigated in combination with computational calculations. DYMDAP shows a solvent dependent emissive behavior which in non-polar solvents shows two distinct peaks along with a shoulder but with increasing polarity as also proticity of the solvents the intensity of each band varies significantly. Along with the two bands, a new band is observed in polar protic solvent due to the proton transfer (PT) in the excited state of the compound. Only in polar protic solvents, intensity of the PT band increases significantly whereas in non-polar or polar aprotic medium intensity is sparse. By comparing the spectral observations of DYMDAP with two control compounds DYMP and DYMDAB the proton transfer process is assigned to be due to solvent mediated and the proton transfer process is enhanced by the presence of charge transfer moiety.

Keywords: 1-[1-(4,6-dimethylpyrimidine-2-yl)-hydrazonomethyl]-4-diethylamino-2-phenol (DYMDAP), ESIPT, Fluorescence spectroscopy, DFT

1. Introduction

Since the epoch making report by Weller in 1956 [1], the phenomenon of excited state intramolecular proton transfer (ESIPT) process still fascinates physicists and chemists alike. With each passing year, researchers are trying to device molecular entities to tune the rate of proton transfer process as well as to get a better insight about the ESIPT process compared to reports available in literature [2-3]. Similarly fascinating, if not more, is the phenomenon of excited state charge transfer (CT) which was first reported by Grabowski et al [4] in the celebrated molecule dimethyl aminobenzonitrile (DMABN). The charge transfer phenomenon is assisted in polar solvents, unlike ESIPT processes where increment in polarity/hydrogen bonding ability of the medium damps the aptitude of ESIPT probes to display dual emission bands barring a few exceptions. Thus, charge transfer probes are better candidates to probe bio-molecular assemblies under physiological conditions. But, due to their dual emission behavior, proton transfer probes are more likely to show ratiometric type of interaction with analytes, thereby decreasing the chance of measurement error, compared to single emission type probes, where monitoring the same band leads to considerable measurement errors. Taking all these facts in mind, chemists are engaged in developing probes which show intramolecular charge transfer (ICT) coupled ESIPT or vice versa [5]. The numbers of complex molecular entities where both charge transfer and proton transfer processes occur in the excited state are plentiful. However, reports where the sole effect of a potential ICT group is to only enhance the ESIPT process in the same molecular framework are sparse. Our group has been involved in exploring the various types of interplay possible between ESIPT and ICT processes in purposefully designed

molecules (Scheme 1). We reported the charge transfer suppressed proton transfer in the excited state for 4-diethylamino salicylaldehyde [6]. In another report, we also reported proton transfer assisted charge transfer in an azine linked hetero anil Schiff base, which also involved 4-diethylamino salicylaldehyde at one end of the azine linkage [7]. Thus, it is obvious that compounds constituting 4-diethylamino salicylaldehyde are likely to exhibit exciting correlation between ICT and ESIPT processes. Apart from our reports, various reports dealing with the interplay of ICT and ESIPT are well documented in literature [8-11].Taking queue of the above discussed facts, we devised a simple molecule - [1-(4, 6-dimethylpyrimidine-2-yl)-hydrazonomethyl]-4-diethylamino-2-phenol (DYMDAP) obtained by condensing 3, 5-dimethyl 2-hydrazino pyrimidine with 4-Diethylamino salicylaldehyde. Our rationale in choosing this molecule is as follows: i) we are interested to check whether introduction of a weak acceptor of charge in the form of the electron rich pyrimidine moiety on one end of the azine linkage would damp the charge transfer process due to the presence of diethylamino group and drive the system towards ESIPT exclusively. ii) As it contains the biologically interesting pyrimidine moiety, application of DYMDAP in biological systems would be justified after the photophysical investigation of the same. DYMDAP has been thoroughly investigated by means of monitoring its absorption, steady state as also time resolved emission profiles in various solvents as also by observing the effect of acid/base on the same. We also obtained single crystals of DYMDAP to understand its absolute structure and extended our analysis by conducting Density Functional Theory (DFT) level optimization of DYMDAP in the ground state as well as in the excited state. We have concluded that DYMDAP favours proton transfer in the excited state due to the presence of charge donor. In addition to this, another remarkable property exhibited by DYMDAP is that it shows a rarely encountered proton transfer in polar protic solvent, which

undoubtedly enhances its potential to be a useful tool to probe biomimetic assemblies. Thus, rather than being yet another entry to our already existing reports [12,13] on interesting photophysical phenomena in self-designed molecules, the current report deserves its own merit on grounds of novelty, structural simplicity and exciting photophysical properties.

2. Experimental details

2.1. Chemicals

4-diethylamino salicylaldehyde, acetyl acetone and hydrazine hydrate have been purchased from Merck. All solvents were of spectroscopic grade and purchased from Spectrochem India Pvt Limited. The solvents are abbreviated as n-Hept: n-Heptane; CyH: Cyclohexane; MCH: Methylcyclohexane; DCM: Dichloromethane; $CHCl_3$: Chloroform; ACN: Acetonitrile; n-BuOH: n-butanol; i-PrOH: isopropanol; MeOH: Methanol; DMSO: dimethylsulfoxide; TFA: Trifluoroacetic acid. Triple distilled water was used wherever needed.

2.2. Steady state absorption and emission measurements

All the absorption and emission measurements were carried out using very dilute solution of DYMDAP ($\sim 10^{-6}$ (M)) to avoid the aggregation of the compound and the reabsorption effect which can be responsible for the deviation from the Lambert-Beers law in case of absorption spectra and for self quenching effect for the emission measurements. All the measurements were done at room temperature using freshly prepared solutions of DYMDAP. The absorption measurement was done using Hitachi UV-Vis U-3501 spectrometer and the emission spectra were obtained using Perkin Elmer LS55 luminescence spectrophotometer.

Following equation has been used to measure fluorescence quantum yield of the compound relative to the Coumarin-153 whose quantum yield is known (Φ=0.38) in ethanol medium.

$$\Phi_S = \Phi_R \times \frac{A_S}{A_R} \times \frac{(Abs)_R}{(Abs)_S} \times \frac{\eta_S^2}{\eta_R^2}$$

Where 'A' denotes for area under the curve of the fluorescence spectra, '(abs)' and 'η' denotes the absorbance and the refractive index of the solvents respectively.Φ' refers to the fluorescence quantum yield of the corresponding compounds. Subscripts 'R' and 'S' denote reference and sample respectively.

2.3. Time resolved emission spectra measurements

Fluorescence lifetime of the compound was measured by the method of time correlated single photon counting (TCSPC) technique using HORIBA Jobin Yvon Fluorocube-01-NL fluorescence lifetime spectrometer. The sample was excited using a picosecond diode laser of 404 nm and the fluorescence signal was recorded keeping the emission polariser at the magic angle (54.7^0) with respect to the excitation polariser to eliminate the loss of signal for the contribution of anisotropy decay and fluorescence decays were deconvoluted using DAS6 software. The goodness of the fits was judged by χ^2 criteria. The relative contributions (α_n) to the fluorescence decay of the multi exponential decay were obtained using the following relation:

$$a_n = \frac{B_n}{\sum_{i=1}^{N} B_i}$$

B_i is the pre-exponential factor of a single exponential decay. The average lifetime of the compound was calculated using the following relation:

$$\langle t \rangle = \frac{\sum a_i t_i^2}{\sum a_i t_i}$$

2.4. Computational details

Theoretical calculations were performed using Gaussian 09W suite program [14]. The optimized structure of the compound at the global minima was obtained using 6-311G++ (d,p) basis set at Density functional theory (DFT) level using B3LYP (which is Backe's three parameter hybrid exchange functional in conjunction with nonlocal correlation function of Lee, Yong and Parr) hybrid orbital. 6-311G++(d,p) basis set was used because it is based on the triple-ζ function for valence electron with diffusion function which is very useful for the calculation of anionic structures or for the compounds containing lone pair electrons. To get optimized structure of the compound in solvents of different polarity, Polarisable Continuum Model (PCM) was used. In this method the target compound is surrounded by the solvent molecules, which treated quantum mechanically, and solvents are characterized by its bulk properties like dielectric constant or polarity.

2.5. Syntheses

The short description of synthetic procedures for synthesis (Scheme 2) of the title compound DYMDAP and two other relevant compounds- [1-(4, 6-dimethylpyrimidine-2-yl)-hydrazonomethyl]-4-diethylamino-2-benzene (DYMDAB) and o-[1-(4, 6-dimethylpyrimidine-2-yl)-hydrazonomethyl]-phenol (DYMP) is as follows:

I) The title compound DYMDAP was synthesized as follows (Scheme 2):

a) Synthesis of 3, 5-dimethyl 2-hydrazino pyrimidine

It was prepared by the condensation of acetyl acetone with urea followed by sequential treatment with $POCl_3$ and Hydrazine hydrate as per literature report [15].

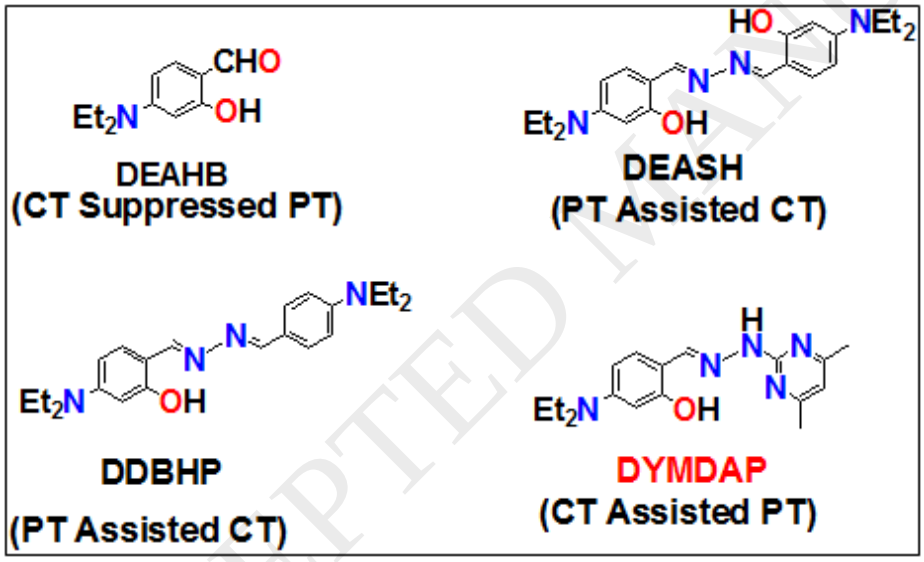
b) Synthesis of DYMDAP

1.0 mM of 4-diethylamino salicylaldehyde was dissolved in methanol (5 mL) and a hot solution of 1.0 mM 3, 5-dimethyl 2-hydrazino pyrimidine in 2 mL methanol was added drop wise

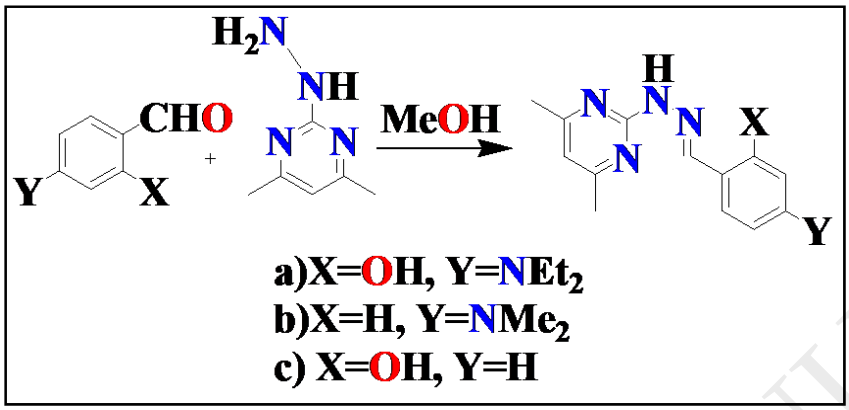
to it. After stirring overnight and then reducing the volume to ~3 mL, deep yellow crystals were obtained. It was washed with cold methanol and dried in vacuum overnight. Yield: 68%.

II) The control compound DYMDAB was obtained by refluxing an equimolar mixture of 4-dimethylaminobenzaldehyde with 3, 5-dimethyl 2-hydrazino pyrimidine (Scheme 2) in 10 mL methanol for 6 hours, leading to light yellow shiny particles, which were filtered, washed with methanol and dried in vacuum.

III) The control compound DYMP was synthesized (Scheme 2) by report available in the literature [16].



Scheme 1: List of previously reported compounds with the current one. DDBHP**:** 5-diethylamino-2-[(4-diethylamino-benzylidene)-hydrazonomethyl]-phenol**,** DEASH**:** N, N′-bis(4-N,Ndiethylaminosalisalidene)hydrazine, DDEAHB: 4-(diethylamino)-2-hydroxybenzaldehyde



Scheme 2: Synthetic scheme of a) **DYMDAP**, b) **DYMDAB**, c) **DYMP**.

3. Results and discussion

The compounds DYMDAP, DYMDAB and DYMP have been synthesized following simple condensation reaction between hydrazono pyrimidine and substituted benzaldehyde (Scheme 2). All compounds have been characterized by ^{1}H, ^{13}C NMR, IR and mass (Fig. S1-S8) spectroscopic methods. The main purpose of synthesizing DYMDAB and DYMP was to ascertain the influence of each of the dialkylamino and –OH group present in DYMDAP upon comparison. The crystals of DYMDAP were obtained by slow evaporation of a saturated solution of the same in a 1:1 (V: V) binary solvent system comprising of methanol and water. Single crystal X-ray diffraction studies indicate that compound DYMDAP crystallizes in $P2_{/c}$ space group (Table S1). The ORTEP diagram of DYMDAP with 30% atomic probability has been shown in ESI (Fig. S9). The crystal structure of DYMDAP shows that two aromatic rings are not in same plane, tiled by

an angle ~ 24^{o} where an intramolecular H-bonding is present between the phenolic –OH (O12) and imine nitrogen (N7) having distance 2.563 Å (Fig. 1, Table S2). Beside this intramolecular H-bond, an intermolecular H-bonded network is formed based on water molecule. It has been found that one water molecule is H-bonded with three DYMDAP molecules through intermolecular H-bond where two DYMDAP molecules act as H-bond acceptor (O13….N113, 2.85 Å and O13….N113, 2.855 Å) and one molecule acts as H-bond donor (O13….N113, 2.867 Å, (Fig. 2) to form an one dimensional layer (Fig. S10, Table S2). This 1D layer is connected with another almost perpendicular 1D layer via CH….π interaction (distance 3.157 Å, Fig. S11, Table S3) to form a 3D polymeric structure.

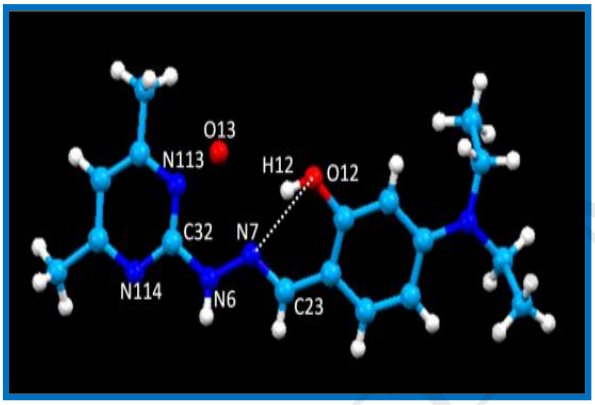


Fig. 1: Molecular structure of DYMDAP.

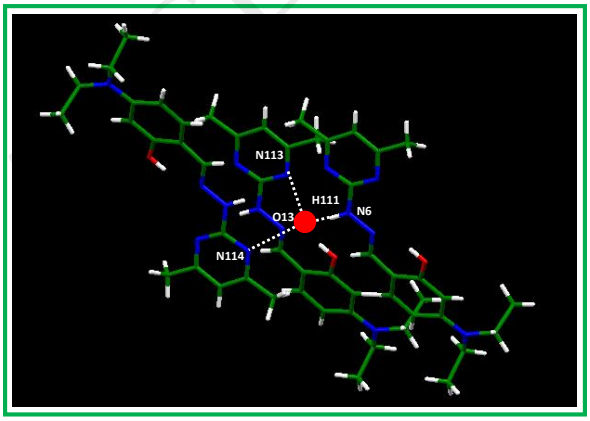


Fig. 2: H-bonding interactions via water molecule.

3.1. Absorption spectra

The absorption spectra of DYMDAP were measured in different solvents and the corresponding absorption maxima are listed in Table 1. From Fig. 3a and 3b it is clear that the absorption spectra of DYMDAP show two bands at ~365nm (strong, ε_{365} = 4.3 $LMol^{-1}$ cm^{-1}) and ~425nm (weak, ε_{425} = 0.1253 $LMol^{-1}$ cm^{-1}) and the band structures are to some extent solvent polarity dependent. In case of non-polar solvent there is a clear bifurcation in both the bands, but with increasing polarity of solvent the same gets disappeared as shown in Fig. 3a and 3a. As per the structure of the compound the absorption bands have been assigned to the π-π* transitions of the compound [17]. These bifurcated bands in solution could be due to existence of two conformers with respect to the orientation of OH group (i.e. open form and intramolecularly hydrogen bonded close form (Scheme 3). To fortify our assumptions, the absorption spectra of the two other similar compounds DYMDAB and DYMP were then recorded. In case of DYMP, which contains only –OH group shows two distinct bands (Fig. 4a), one at ~296nm and other at ~330nm. In case of DYMDAB which contains only $–NMe_2$ group shows a strong band with a shoulder at the higher energy side (Fig. 4b) unlike DYMDAP and DYMP, which may support the existence of open and closed form with respect to –OH group of DYMDAP. Therefore bifurcated bands at ~407nm and at~428nm are assigned to $S_0 \rightarrow S_1$ transitions the open and closed form of DYMDAP and bands at ~355nm and at ~370nm are assigned their higher energy states ($S_0 \rightarrow S_2$ transitions). Structurally the ground state stability difference between the open and closed forms (difference in the orientation of OH group) should be small and hence the expected π-π* transitions energies should also be small.

The disappearance of the structured bands in DYMDAP upon increasing the solvent polarity can be explained from the point of view of the effect of solvent polarity and hydrogen bonding effect. With increasing polarity and hydrogen bonding effect of solvent, a solvated form may be generated for both the forms, thereby leading to the aforesaid observation.

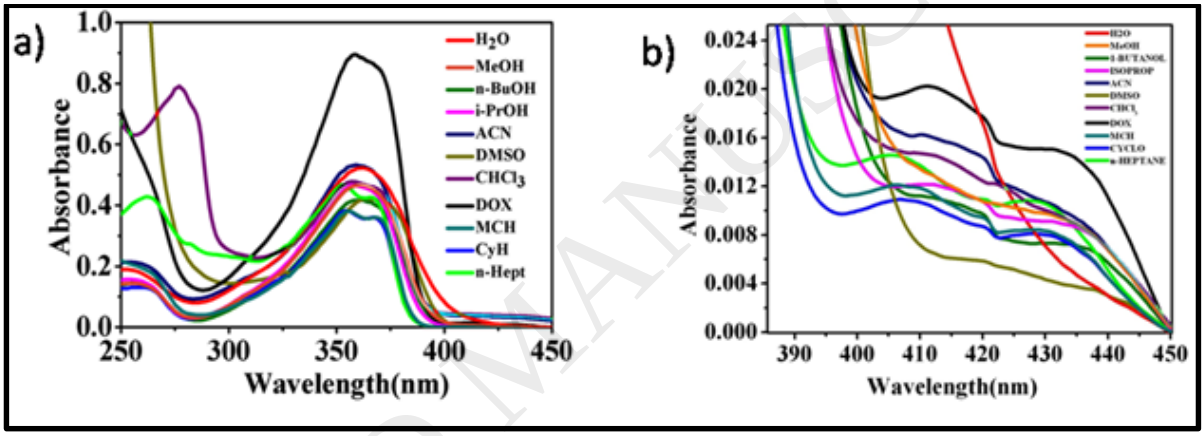
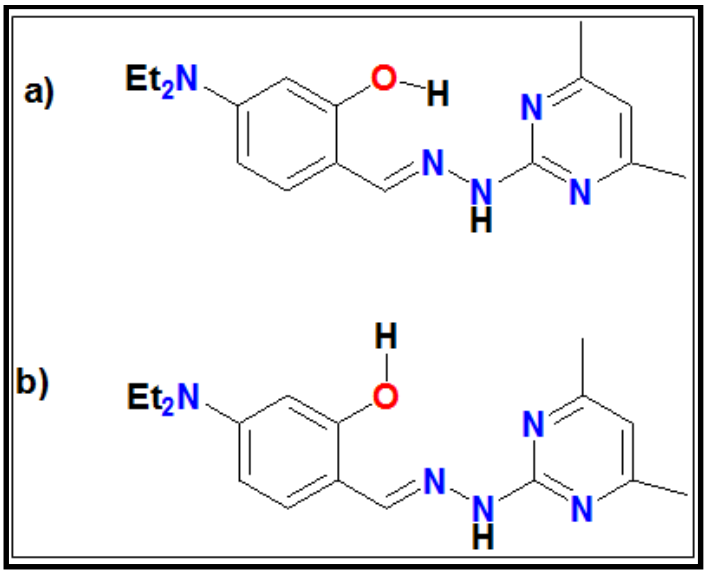


Fig. 3: Absorption spectra of DYMDAP (~10^{-6}M) in solvents of varying polarity.



Scheme 3: (a) Closed and (b) Open form of DYMDAP.

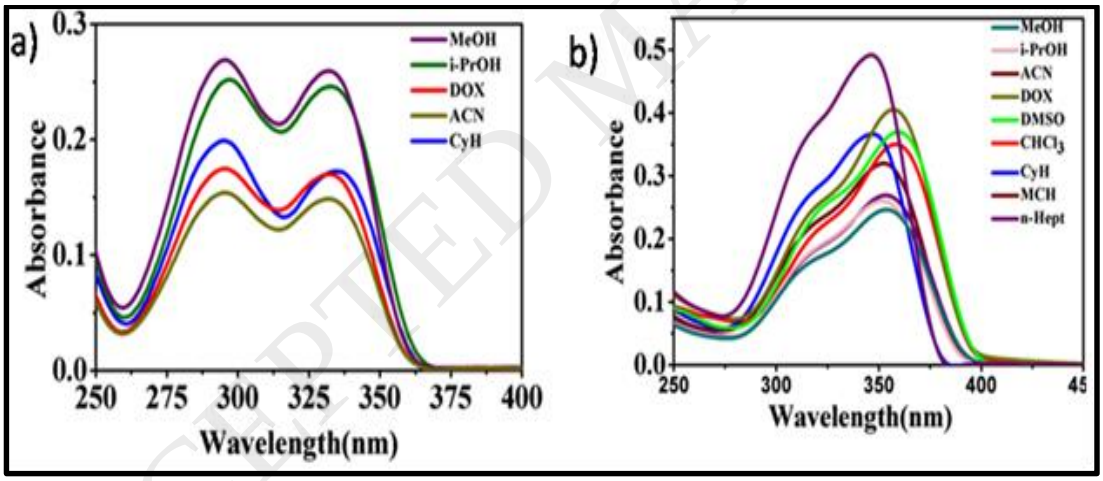


Fig. 4: Absorption spectra of a) DYMP (~10^{-6}M) and in b) DYMDAB (~10^{-6}M) solvents of varying polarity.

Table1. Spectroscopic parameters obtained from absorption and emission spectral bands of **DYMDAP**, **DYMP** and **DYMDAB** in different solvents.

Solvents	DYMDAP			DYMP			DYMDAB	
	λ_{abs}(nm)	λ_{em} (nm)	Φ_f	λ_{abs}(nm)	λ_{em}(nm)	Φ_f	λ_{abs}(nm)	λ_{em}(nm)
n-Hept	365,425	458,481, 515	0.033	--	--		313, 345	431
MCH	365,425	458,481, 515	0.034	--	--		318, 345	431
CyH	365,425	459,482, 515	0.050	295, 334	--	0.000	321, 346	431
DOX	365,425	460,487,515	0.098	295, 332	509	0.003	320, 350	433
$CHCl_3$	365,425	458,480, 520	0.092	--	--		323, 358	433
DMSO	365,425	447,485, 520	0.0614	--	--		322, 359	433
ACN	365,425	456,480, 516	0.088	295, 332	509	0.0023	317, 351	
n-BuOH	365,425	458, 483,514	0.126				--	--
i-PrOH	365,425	458,482, 514	0.094	295, 332	406, 509	0.001	318, 351	421
MeOH	363,428	458,482, 514	0.170	295, 332	406, 509	0.006	318, 352	--
Water	361	452,483,515	0.002	295, 332	406, 509	0.0003		

3.2. Steady state emission and excitation spectra

Due to a rather complex absorption profile and its dependence on the nature of the solvents, we have chosen to excite DYMDAP at all the wavelengths at which prominent or considerable absorption was found according to the solvents instead of exciting at a common wavelength. Upon low energy excitation (~425nm) the emission profiles in non-polar solvents clearly show two distinct emission bands at ~460nm, ~485nm along with a shoulder at ~515nm (Fig. 5a). Emission spectra in non-polar solvents show the band gap between two bands at~460nm and ~485nm is almost same as the band gap in the absorption spectra (407nm and

428nm) of DYMDAP. This hinted to the fact that these two bands contribute to the local emission and indirectly shows the existence of open and closed forms of DYMDAP in the excited state, but these facts demanded verification. For this purpose, we recorded the excitation spectra (Fig. 6) of DYMDAP in various solvents which furnished results closer to those obtained from UV-Vis absorption studies (Fig. 3b). Thus, the humps at ~460nm and ~485nm could be attributed to be due to local emission, which indirectly supports the existence of open and closed forms of DYMDAP in the excited state also. Thus, the peak at 515nm could be due to some excited state photophysical phenomenon. DYMDAP has both proton transfer site (i.e. a probability of transfer of proton from –OH group to –CH=N- group) along with a charge transfer moiety (i.e. probability of transfer of electron density from $–NEt_2$ group to –CH=N- group). So there is a probability of ESIPT or excited state ICT process or both. Table 1 show that the Stokes' Shift (~90nm) between the lowest energetic band and the excitation wavelength is unchanged upon solvent variation. Thus, such a large value of Stoke's Shift could be due to some photophysical processes operative in DYMDAP in the excited state. It is to point out here that excitation at the high energy band at ~365nm did not show any emission. The excited molecules dissipated energy through some non-radiative processes for higher energy excitation. This also supports the fact that 365nm absorption band is not the $S_0 \rightarrow S_1$ transitions for the open form but a transition to the higher energy excited state.

Herein, our judicially synthetic compounds DYMP (only proton transfer possible) and DYMDAB (exclusively a charge transfer group present) proved useful information about this. Compound having only –OH group shows two emission peaks one at 408nm (weak) and other at ~512nm (strong) only in polar protic and aprotic medium, but in nonpolar medium there was no fluorescence as shown in Fig. 5b. The observed weak high energy emission band may be due to

local emission and the reddest shifted emission is nothing but the ESIPT band which is dominated in polar protic solvents [19, 20]. DYMDAB group shows only one broad band at ~430nm as shown in Fig. 5c and there is less solvent dependence and hence this band is assigned to the local emission (no CT emission is observed) of DYMDAB. From all the above observations extracted from the control compounds it becomes apparent that the presence of both –OH and -NEt_2 groups lead to the emission profile of DYMDAP. Having ascertained so, further experiments were carried out to unravel the excited state photophysical phenomenon which is supposed to be occurring in DYMDAP.

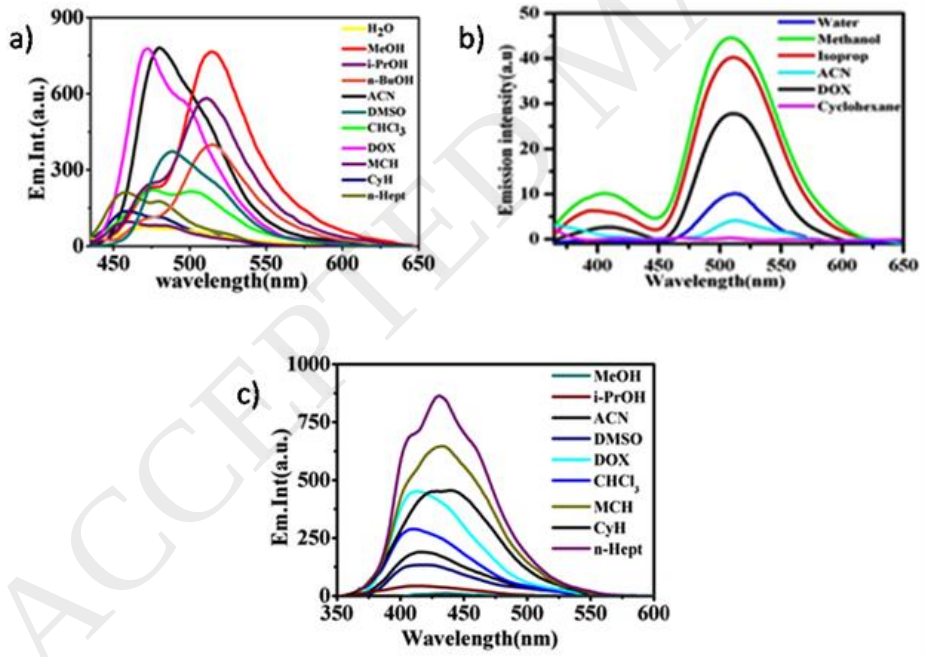


Fig. 5: Emission of a) DYMDAP (λ_{ex}=430nm), b) DYMP (λ_{ex}= 330nm) and c) DYMDAB (λ_{ex}=350 nm) in various solvents.

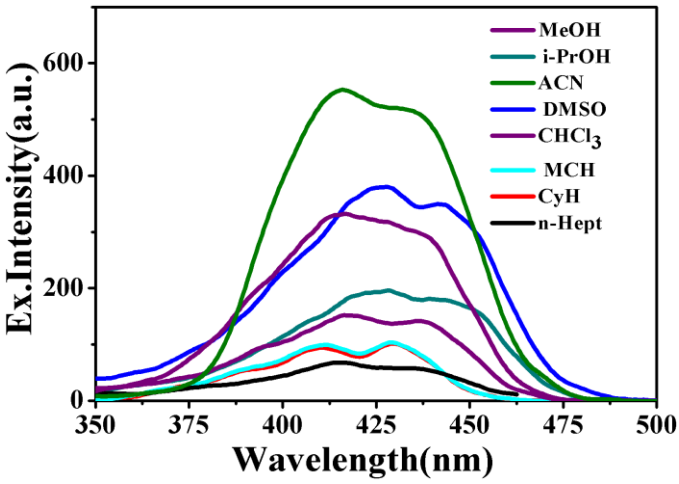


Fig. 6: Fluorescence excitation spectra of DYMDAP (λ_{em}=515nm).

3.3. Analysis of fluorescence quantum yield

The observed fluorescence quantum yield of DYMDAP was measured at room temperature with variation of polarity and hydrogen bonding ability of the solvents and the result is presented in Table 1. DYMDAP shows high quantum yield in polar protic solvents compared to that of polar aprotic and non-polar solvents. The comparative study of quantum yield with DYMP (Table 1) strongly suggests that incorporation of a charge donor group to DYMP increases the proton transfer ability of the compound, which supports our conclusion that there is a significant effect of charge donor group to the excited state proton transfer process. In case of polar aprotic solvents observed fluorescence quantum yield is higher than that of non-polar solvents, this due to the stabilisation of excited state dipole by means of solvent-dipole interaction [21]. High quantum yield in polar protic solvents reveals the effect of H-bonding on

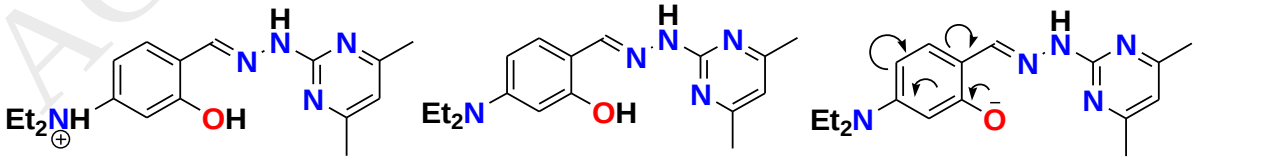
the fluorescence spectra which is also evident from the generation of a new band in fluorescence spectra only in polar protic solvents.

3.4. Effect of Acid and base on Absorption and emission spectra

As the special characteristics in the emission profile of DYMDAP is solely due to the presence of -NEt_2 and –OH groups, acid and base effects were observed as rendering the –NEt_2 and –OH groups ineffective would be useful to understand the photophysical process operative in DYMDAP. Absorbance at ~420nm increases with addition of trifluoroacetic acid (TFA) in the neat solution of DYMDAP in methanolic medium as shown in Fig. 7. There is similar observation for adding base (Fig. 7). Isosbestic points at 378 (acid addition) and 382 nm (base addition) indicate that acid effect and base effect are equilibrium driven [22]. Addition of acid results in protonation of –NEt_2 group leading to the formation of cationic species which has absorption peak different from the neutral species leading to arrest of charge transfer from diethyl amino (-NEt_2) group to imine (-CH=N-) moiety. However, concerted participation from the secondary amine functionality to the imine moiety results in attainment of a partially double bond character along the azine linkage (-N-NH-), thereby imparting planarity to the otherwise non-planar structure of DYMDAP, as evident from its crystal structure.

In case of fluorescence spectra, intensity of emission decreases with addition of both acid and bases. In both cases, intensity of the band at 515nm decreases uniformly. However, the decrease in intensity of the band at 460nm was differentially affected by addition of acid and base. Upon adding base, the intensity of the band at 515nm decreases to a much greater extent compared to the same in 460nm (Fig. 8a). However, upon acid addition the intensity of both bands at 460nm and 515nm decreased uniformly (Fig. 8b). As diethyl amino group of DYMDAP

was protonated with addition of acid, thereby local emission of the neutral species decrease. A schematic representation of effect of acid and base on DYMDAP has been provided in Scheme 5. At this stage it was assumed that a proton transfer process could be operative in DYMDAP as decrease in fluorescence intensity upon loss of phenol –OH (addition of base) strongly indicates an ESIPT process in accordance to literature report [23]. As far as acid effect is concerned, protonation of the donor in DYMDAP causes immediate protonation of the NEt_2 group, thereby causing a loss in charge transfer. This also resulted in quenching of fluorescence. Thus, it was now evident that presence of NEt_2 group in its neutral form is indispensable for DYMDAP to exhibit its dual emission in polar solvents. But the main concern in assigning an ESIPT process operative in DYMDAP was that it was observed only in polar protic solvents, in contrast to a fair number of literature reports [21-24] where ESIPT occurs only in non-polar/polar aprotic solvents having similar cavity designed for proton transfer. Thus, even if ESIPT occurs in DYMDAP it was assisted by the diethyl amino group (charge transfer moiety) which lead to assuming DYMDAP shows the very rare phenomenon of charge transfer assisted proton transfer in polar protic medium, which is a merit in itself. Steady state spectral measurements could thus far indicate the aforementioned photophysical phenomenon which needed even further analysis. With this aim in mind, TCSPC measurements were next done.



protonated form, donation from 2^0-amine operative

DYMDAP

anionic form, resonance stablised

Scheme 5: Acid and Base effect on DYMDAP

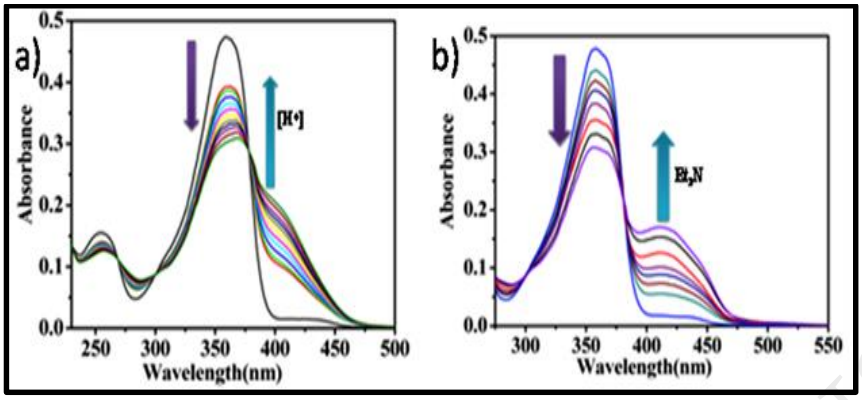


Fig. 7: Absorption spectral changes on addition of a) TFA and b) Et_3N to DYMDAP in methanol medium.

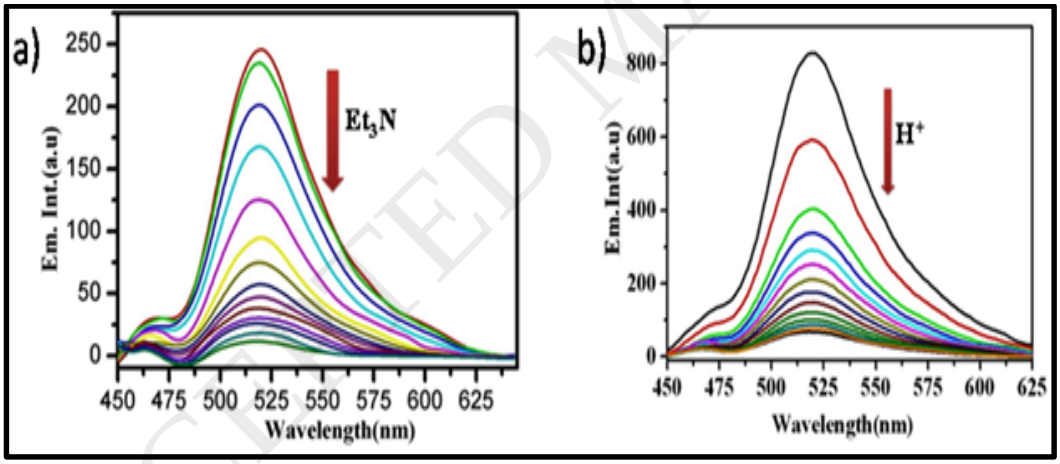


Fig. 8: Effect of a) addition of base to DYMDAP and b) addition of TFA to DYMDAP on the emission spectra in methanol.

3.5. Analysis of Fluorescence lifetime

To ascertain the various species present in the excited state, fluorescence lifetime of DYMDAP in different solvents were measured (Fig 10) and the corresponding residuals

regarding to the goodness of the exponential fitting have been given in S9. Irrespective of solvent polarity or proticity, all decay profiles well fitted into triexponential decay and the time resolved data are given in Table 2 (λ_{ex}=404nm, λ_{em}=465nm, 515nm). Decay analysis suggested the open and closed forms collectively contributed to the local emission and the proton transfer form was responsible for the third component in the excited state. Corroborating to results of steady state emission, the three components undergo alteration in their relative contribution upon varying the H-bonding ability of the solvents. As the open form of the molecule cannot take part in proton transfer process so there should be at least one component whose lifetime and contribution to average life time would be almost unperturbed. Since τ_2 and α_2 do not change with changing the solvent polarity, species corresponding to life time τ_2 is nothing but the open form of DYMDAP in the excited state. Decay component corresponding to life time τ_1 suffers decrease in lifetime as well as in α_1 upon solvent variation whereas the third component (with life time τ_3) picks up in both τ_3 and α_3. At this juncture, it was possible to assign components lifetimes τ_2, τ_1 and τ_3 to be open, closed and proton transferred forms of DYMDAP respectively. Switching of average contribution between second and third form resulted upon varying the polarity as well as proticity of the solvent. However, the values of lifetime of the proton transferred form in various solvents were way below that observed in literature [14], which needed to be rationalized. This could be explained by considering the proton transferred form of DYMDAP, where the unrestricted bond rotation about the hydrazine linkage affects the excited state lifetime of the keto form in DYMDAP (Fig. 9). Apart from the primary effect of diethylamino group in assisting the ESIPT phenomenon in DYMDAP the auxiliary effect of polarity as well as proticity of the medium, if any, still needed to be analyzed. The participation of protic solvent to relay the proton transfer process was also analyzed by lifetime

measurements. This was achieved by plotting relative contribution to the fluorescence decay to the emission wavelength profiles in two extreme environments- one in n-hexane and in methanol (Fig. 10 and Fig. 11). The plots clearly reflected that undergoing ESIPT is an innate property of DYMDAP; otherwise there would have been no contribution of the third component to the overall profile in n-heptane. However, the contributions from each component barely converged in n-heptane. However, excellent convergence followed by crossover of emissive species was observed in methanol medium. However, component with lifetime τ_2 did not show any convergence or crossover, irrespective of any medium. Thus, the role of solvent is a key factor apart from the essential condition of -NEt_2 group to be present in DYMDAP to obtain observable ESIPT. Lifetime data of DYMDAP in n-Heptane and methanol medium have been represented in Table S4 and Table S5 respectively.

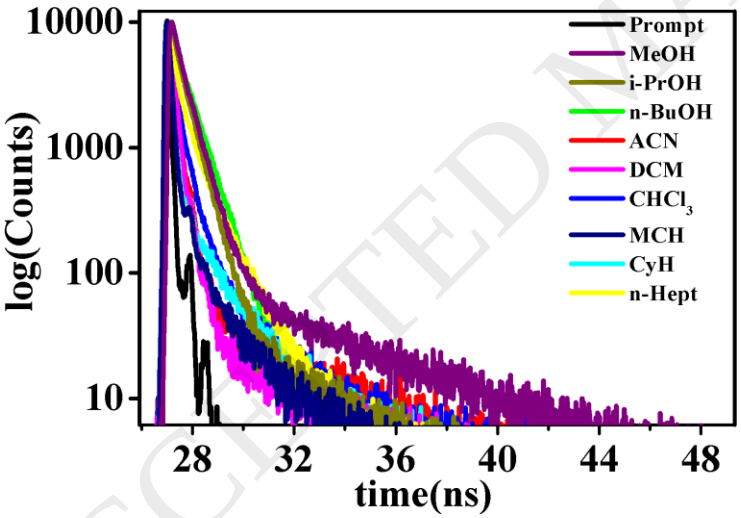


Fig. 9: Fluorescence lifetime decay pattern in different solvents .

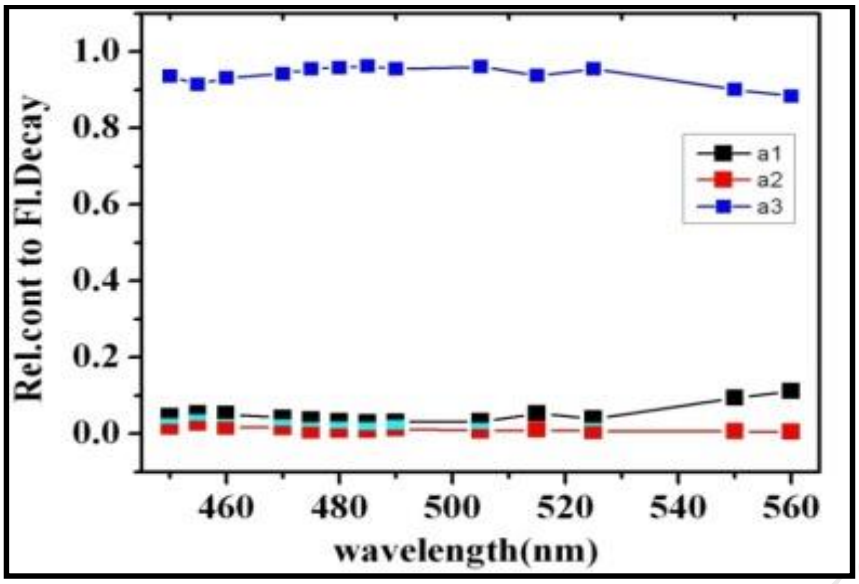


Fig. 10: Plot of rel. contribution to the fluorescence decay (Fl. Decay) to the emission wavelength in n-Heptane medium ('a' in the figure legend denotes 'α'; having usual meaning)**.**

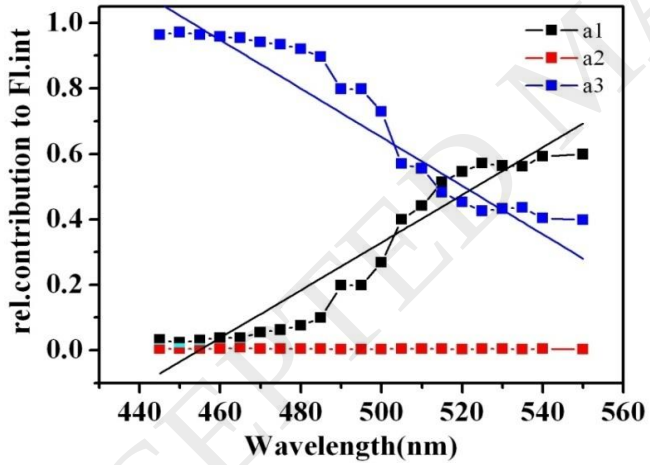


Fig. 11: Plot of rel. contribution to the fluorescence decay to the emission wavelength in methanol medium ('a' in the figure legend denotes 'α'; having usual meaning).

Table 2: Time resolved data of DYMDAP in different solvents.

Solvents	**Emission at 460nm**

	τ1(ns)	τ2(ns)	τ3(ns)	α1	α2	α3	<τ>(ns)	χ^2
n-Hept	0.062	0.525	0.020	0.621	0.021	0.358	0.416	1.12
CyH	0.102	0.578	0.036	0.582	0.033	0.385	0.324	0.98
MCH	0.092	0.750	0.035	0.501	0.054	0.445	0.410	1.02
DCM	0.043	0.869	0.046	0.485	0.005	0.510	0.196	1.25
$CHCl_3$	0.066	0.584	0.049	0.201	0.118	0.681	0.181	1.08
ACN	0.021	0.498	0.071	0.057	0.012	0.931	0.717	1.06
n-BuOH	0.003	0.685	0.069	0.042	0.056	0.902	0.687	0.89
i-PrOH	0.005	0.569	0.089	0.035	0.025	0.940	0.895	0.98
MeOH	0.002	0.457	0.092	0.023	0.016	0.961	0.925	1.01
Emission at 515nm								
Solvents	τ1(ns)	τ2 (ns)	τ3(ns)	α1	α2	α3	<τ>(ns)	χ^2
n-Hept	0.070	1.337	0.054	0.765	0.042	0.193	0.067	0.98
CyH	0.095	2.433	0.094	0.980	0.005	0.015	0.095	1.08
MCH	0.135	2.338	0.072	0.453	0.094	0.453	0.110	0.87
DCM	0.054	3.062	0.036	0.901	0.003	0.096	0.053	0.99
$CHCl_3$	0.076	2.862	0.049	0.792	0.006	0.202	0.073	0.96
ACN	0.086	4.123	0.035	0.783	0.003	0.214	0.081	1.01
n-BuOH	0.008	1.749	0.063	0.520	0.009	0.471	0.560	1.02
i-PrOH	0.008	2.852	0.048	0.358	0.005	0.637	0.415	1.02
MeOH	0.007	5.471	0.055	0.446	0.006	0.548	0.592	1.12

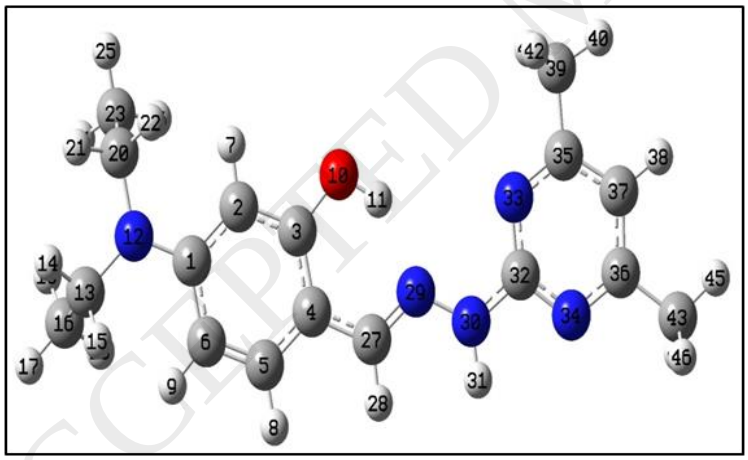
3.6. Computational Details

The first insight into the electronic structure reorganization during the proton transfer processes has been achieved by the aid of theoretical calculations. The intramolecular proton transfer is achieved by determination of structure calculation both in ground state as well as in excited state. The ground state structure (Scheme 4) was calculated by using DFT method and the structural data are given in Table 3. The excited state geometry was calculated by TDDFT method. Although this method does not lead to optimized structure in the excited state, the data obtained from this calculation is good enough to support our experimental findings.

Evaluation of the GSIPT curve for intrinsic intramolecular proton transfer was done by optimizing the geometry at B3LYP/6-311++G** level in Polarisable Continuum (PCM) Model for a number of structures of DYMDAP generated with O_{10}–H_{11} distance varying in the range 0.98–1.48Å. The ESIPT curves are obtained by adding the vertical excitation energy to the GSIPT curve. Fig. 12 shows the plot of variation of potential energy of DYMDAP with increasing the O-H bond length. It is found that energy of DYMDAP in the S_0 state increases with increasing the O-H bond length and it is also found that enol form is the global minima and keto form is the local minima in potential energy surface of S_0 state. It is found that enol form is more stable than the keto form by 18kcal/mole and the energy barrier is 28kcal/mole in the ground state. But in the excited state the case is reversed, the keto form is energetically stable than the enol form with a significant decrease in the potential energy barrier height. Here in the excited state the keto the stabilized structure than that of enol form by an amount of >10kcal/mole and it is in plain sight observation that the energy barrier is ~10 kcal/mole which quite smaller that of the ground state structure so this theoretical results prove that there is a certain role of solvent proticity on the ESIPT process.

Table 3. Ground state optimized geometrical parameters of closed form of DYMDAP at DFT level with B3LYP functional and 6-311++G (d, p) basis set.

Bond	**Calculated values**	**Bond angles/Dihedral angles**	**calculated values**
$\mathbf{R}_{C1\text{-}C2}$	1.409	$\angle C_{30}O_{10}H_{11}$	109.15
$\mathbf{R}_{C4\text{-}C27}$	1.444	$\angle C_4C_{27}N_{29}$	121.68
$\mathbf{R}_{C27\text{-}C29}$	1.291	$\angle C_3C_4C_{27}$	122.55
$\mathbf{R}_{N29\text{-}N30}$	1.353	$\angle N_{30}C_{32}N_{33}$	118.84
$\mathbf{R}_{O\text{-}H}$	0.985	$\angle C_4C_3C_{27}N_{29}$	0.1210
$\mathbf{R}_{N30\text{-}C32}$	1.375	$\angle C_{27}N_{29}N_{30}C_{32}$	0.5500



Scheme 4: Optimized ground state structure of the closed form of DYMDAP (DFT/ B3LYP/6-311++G**).

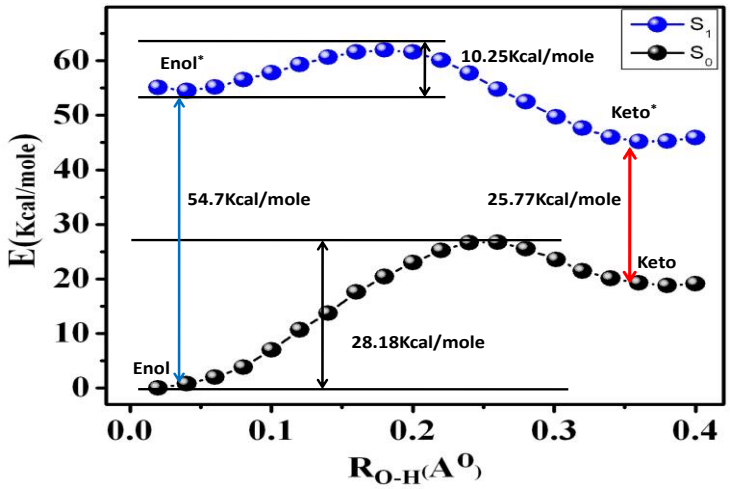


Fig.12. Potential energy curves for the ground (S_0) and first excited state (S_1) of DYMDAP with variation of O_{10}–H_{11} distance using B3LYP functional and 6-311++G** basis set.

4. Conclusion

In this present work, an asymmetric Schiff base DYMDAP has been synthesized by simple condensation reaction between 4-diethylamino salicylaldehyde and 5-dimethyl 2-hydrazino pyrimidine and characterized by NMR, IR and single crystal XRD analysis. The photophysical properties of DYMDAP have been investigated thoroughly in different solvents. The spectroscopic data furnished by UV, fluorescence and TCSPC experiments reveal that DYMDAP exhibits charge transfer assisted excited state proton transfer phenomenon in polar protic solvents, which is a novelty in itself.

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