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Spectral characteristics of 2-(3′,5′-diaminophenyl)benzothiazole: effects of solvents and acid–base concentrations

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Abstract

Spectral characteristics of 2-(3′,5′-diaminophenyl)benzothiazole (3,5-DAPBT) have been studied in different solvents and H_0/pH/H range of −10 to 16. Increase in Stokes shifts observed with increase in polarity of solvents is due to increase in dipole moment (μ) on excitation to first excited singlet (S_1) state. Polarization also plays a major role in the increase of excited-state dipole moment (μ_e). Combining the results observed in absorption, fluorescence and fluorescence excitation spectra and lifetime studies, it is found that (i) MC1 is the only monocationic (MC) species in polar aprotic and polar protic solvents, whereas MC1 and MC3 (Scheme 1) are formed in cyclohexane + trifluoroacetic acid (TFA) medium in the ground (S_0) and S_1 states; (ii) DC2 is the only dicationic species present in polar protic solvents, whereas DC1 and DC2 (Scheme 1) are dicationic species in non-polar and polar aprotic solvents; (iii) only one kind of tricationic species is present in polar and protic solvents; (iv) monoanion (MA) formed by the deprotonation of any of the $-NH_2$ group, is non-fluorescent. Semi-empirical quantum mechanical calculations (AM1) and density functional calculations (DFT) have been performed on all kinds of ionic species. The spectral characteristics have been assigned to various prototropic species combining the experimental and theoretical results.

Keywords: 2-(3′,5′-Diaminophenyl)benzothiazole; Absorption spectrum; Fluorescence spectrum; pK_a values; Theoretical calculations

1. Introduction

Study of photophysical properties of heterocyclic organic molecules has achieved a considerable importance recently because many of these molecules form an integral part of intermediates [1], fine product for drugs [2–5] and pesticides [6,7], color industries [8], redox systems for solar energy [9], organized assemblies [10], laser dyes [11] and complex-forming agents [12,13].

Although substituted 2-aryl benzothiazoles are found to be useful from industrial point of view (for e.g., fluorescence whitening agents [14], and photoconducting materials [15] and as herbicides in agriculture), have not received much attention. The molecules belonging to benzothiozole series, which have been studied extensively are 2-(2′-hydroxyphenyl)benzothiazole (2-HPBT) [16], 2-(2′-aminophenyl), 2-(3′-amino phenyl) and 2-(4′-aminopheenyl)benzothiazoles (2-APBT, 3-APBT, 4-APBT) [17]. 2-HPBT has been studied extensively as this molecule gives rise to excited-state intramolecular proton transfer (ESIPT) [16], whereas the amino derivatives were studied from the following angles: (i) being strong electron donor in the excited-state, fluorescence spectrum of amino derivatives are more sensitive to the solvent polarity than the absorption spectrum. These molecules have been used as probe to study the various structural aspects of biological systems; (ii) molecules contain both electron-donating group ($-NH_2$) and electron-accepting group (=N–) without involving intramolecular hydrogen bonding (IHB) in S_0 state. Their monocations (MC) are formed by protonating $-NH_2$ group, which becomes strong acid in S_1 state [18] and may thus donate proton to =N– moiety in S_1 by second kind of ESIPT involving solvent molecules [19,20]. These studies have shown that 3-APBT is

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polar than 2-APBT or 4-APBT in S_1 state and thus is better probe molecule. It has also been observed that dipole moment of diamino aromatic system is the maximum if two substituents are present meta to each other than at any other positions. In other words, aromatic molecules containing two amino groups meta to each other can prove to be a very good probe system.

Present study on 3,5-DAPBT is a continuation of our earlier work on aromatic diamino compounds [21–25]. In this molecule, two amino groups are present meta to each other in the phenyl ring containing benzothiazole (BT) as an electron-acceptor moiety. Based on earlier studies, this molecule should be quite polar and can lead to greater interactions with the polar aprotic and polar protic solvents. In order to confirm the above-mentioned facts, absorption, fluorescence excitation and fluorescence spectroscopy, as well as, time-dependent spectrofluorimetry have been used. Effect of acid–base concentrations on the spectral characteristics have also been investigated and pK_a values for different prototropic reactions have been determined in S_0 and S_1 states. Characterization of various ionic species has been carried out by doing electronic structural calculations using semi-empirical AM1 method and DFT procedure using Gaussian 98 program.

2. Materials and methods

3,5-DAPBT was synthesized by refluxing equivalent amounts of 1-amino phenylthiol and 3,5-diaminobenzoic acid in polyphosphoric acid, as described in Ref. [26]. 3,5-DAPBT was purified by repeated crystallization from methanol. Purity of the compound was checked by chemical analysis, single point on TLC, NMR data and resemblance of fluorescence excitation spectra recorded at different emission wavelengths (λ_{em}). All the solvents used were either of spectroscopic grade or HPLC grade from Merck and thus were used as such. Spurious emission was checked for each solvent by exciting at the same wavelength as used for each solution of 3,5-DAPBT in different solvents. Triply distilled water was used for the preparation of aqueous solutions.

Procedure used to prepare the solutions and adjustment of pH was the same as described in our recent papers [20,27]. Hammett's acidity scale [28] was used for $H_2SO_4{\cdot}H_2O$ mixtures for pH < 1 and Yagil's basicity scale [29] was used for $NaOH{\cdot}H_2O$ mixtures for pH > 13. Details of instruments used for recording absorption, fluorescence excitation and fluorescence spectra and measuring lifetimes are the same as described in our recent papers [20,27]. Fluorescence quantum yield (Φ_f) was measured from solutions having absorbance less than 0.1 using quinine sulphate in 1N H_2SO_4 as reference ($\Phi_f = 0.55$) [30]. Concentration of 3,5-DAPBT was kept at 7×10^{-6} M. Prototropic reactions were studied in aqueous medium containing 1% (v/v) methanol.

3. Theoretical calculations

Theoretical parameters (e.g. total energy, E, relative to the most stable species; dipole moment, μ, etc.) of 3,5-DAPBT in S_0 and S_1 states were obtained by optimizing the geometry in the respective state using AM1 method (QCMP137, MOPAC 6/PC) [31,32]. In S_1 state, configuration interactions (CI = 5 in MOPAC, 100 configurations) were considered to optimize the geometry. Transition energies for absorption and emission processes were obtained by carrying out single point calculations in AM1 method and employing S_0 and S_1 state geometries, respectively. The respective data are compiled in Table 1.

Dipolar solvation energies for different species in different states have been calculated using the following expression based on Onsager's theory [33]:

$$\Delta E = -\left(\frac{\mu^2}{a^3}\right) f(D)$$

where $f(D) = (D-1)/(2D+1)$, D the dielectric constant of the medium, μ the dipole moment in the respective state and a the Onsagar cavity radius. For non-spherical molecules like 3,5-DAPBT, value of a has been obtained by taking 40% of the maximum length of the molecule [34]. It is found to be 0.49 nm.

Theoretical parameters for different cationic species (three monocations, MCs and three dications DCs, Scheme 1) were also obtained using the above-mentioned theoretical procedures and the relevant data are compiled in Tables 1 and 2, respectively. The electronic structure calculations were also performed on each species, as mentioned in Scheme 1, using Gaussian 98 program [35]. The geometry optimization was performed on each species of 3,5-DAPBT in S_0 state using hybrid density functional theories (DFT) [36,37] B3LYP with 6-31 G^{**} basis set [35,38]. The geometry of these stationary points on S_1 state (π, π^*) was calculated using configurations interaction singles (CIS) [35,39] theory with 6-31G^{**} basis sets. Time-dependent (TD) [40,41] DFT B3LYP was also used to calculate the excited-state energies at calculated stationary point geometry in S_0 and S_1 states. Relevant data are complied in Tables 1 and 2, respectively.

4. Results and discussion

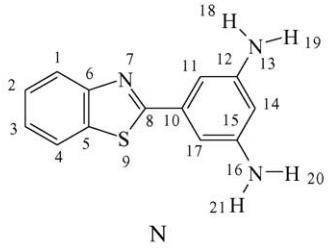
4.1. Effect of solvents

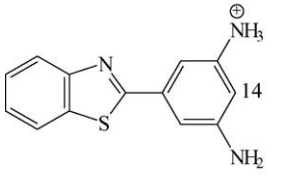
4.1.1. Absorption spectrum

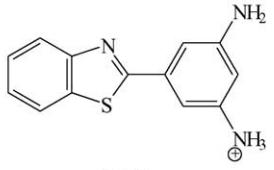
Table 3 depicts the absorption band maxima (λ_{max}^{ab}) and molecular extinction coefficient ($\log \varepsilon_{max}$) in all the solvents except cyclohexane because 3,5-DAPBT is partially soluble in this solvent. Besides a broad shoulder around ~360 nm, a structured band appears at ~313 nm with vibrational frequency of $910 \pm 60\ cm^{-1}$ in non-polar solvents. Structure is lost as polarity and hydrogen bonding capacity of the solvents increase. As compared to 1,3-diaminobenzene (1,3-

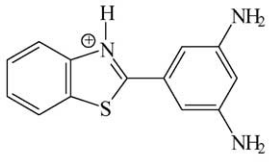
Table 1
Calculated parameters of 3,5-DAPBT (neutral and monocations) in ground and excited singlet states using AM1 and TD (DFT)

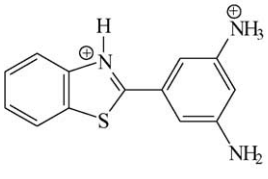
Characteristics	N	MC1	MC2	MC3
S_0 state				
AM1 method				
E (kJ mol^{-1})	−2630.3178	66.7	67.1	0.0
E_{sol} (kJ mol^{-1})	−2639.3363	1.3	0.0	20.7
μ_g (D)	2.4	16.5	17.0	2.2
DFT				
E (kJ mol^{-1})	−1064.4667	58.8	65.1	0.0
μ_g (D)	2.9	15.7	16.5	1.8
S_1 state				
AM1 method				
E (kJ mol^{-1})	−2626.2916	217.3	243.0	0.0
E_{sol} (kJ mol^{-1})	−2626.6002	250.4	254.0	0.0
μ_e (D)	9.8	7.7	11.4	12.9
Transition energies (nature of transitions)/(oscillator strength, nm)				
CNDO/S-CI method				
S_0—S_1	381 (π, π^*) (0.022)	360 (π, π^*) (0.012)	358(π, π^*) (0.013)	586(π, π^*) (0.01)
S_0—S_2	323 (π, π^*) (0.339)	339 (π, π^*) (0.5128)	339(π, π^*) (0.452)	461(π, π^*) (0.164)
Single point AM1 method				
S_0—S_1	327	361	334	567
TD (DFT)				
S_0—S_1	381	360	358	586

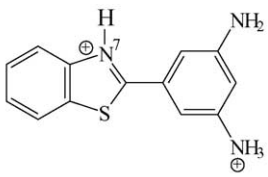


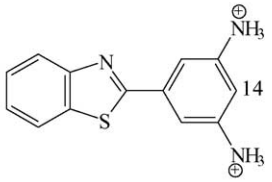












Scheme 1.

Table 2
Calculated parameters of dications of 3,5-DAPBT in the ground and excited singlet states

Characteristics	DC1	DC2	DC3
S_0 state			
AM1 method			
E (kJ mol^{-1})	1.0	0.0	118.0
E_{sol} (kJ mo^{-1})	65.0	68.0	0.0
μ_g (D)	13.7	12.7	27.6
DFT			
E (kJ mol^{-1})	3.9	0.0	113.4
μ_g (D)	14.0	13.0	25.3
S_1 state			
AM1 method			
E (kJ mol^{-1})	0.0	9.7	20.7
E_{sol} (kJ mol^{-1})	5.4	0.0	53.2
μ_e (D)	10.5	17.5	13.0

DAB) [21] or 3-APBT [17], shoulder at 360 nm and main band at 313 nm are red shifted in 3,5-DAPBT. Similar to 1,3-DAB [21], main λ^{ab}_{max} is red shifted with increase in polarity of the solvents and blue shifted in protic ones. Blue shift observed in water is quite large such that λ^{ab}_{max} (water pH = 7 < λ^{ab}_{max} (cyclohexane)). This behavior suggests an interaction between solute–solvent, which is supported by the increase in full-width at half-maximum height (FWHM) in going from cyclohexane (5320 cm^{-1}) to water (5840 cm^{-1}).

Spectral studies of 2-aryl benzoxazoles and corresponding benzothiazoles by Passarini [42] have suggested that the aryl group acts as the main parent moiety and benzazole moiety perturbs the electronic transition of aryl group. Our experimental observations and DFT calculations have confirmed the earlier results and have shown that both HOMO and LUMO are localized mostly on the phenyl ring and partly on the benzothiazole ring. Thus 3,5-DAPBT can be considered as substituted diamino benzene. Similar results were also obtained by CNDO/S-CI and PPP calculations for 2-phenyl benzoxazole (2-PBO) and 2-(3′-aminophenyl)benzoxazole (3-APBO) molecules [43,44]. The electronic spectra of aromatic amines have been studied extensively [45] and red shift observed in absorption spectrum of aromatic moiety is due to the resonance interaction of the π-cloud of aromatic ring and lone pair on the amino group [45]. This interaction increases if the lone pair of electrons and π-cloud is parallel to each other. In 3,5-DAPBT, dihedral angles φ_1 (C_{11}–C_{10}–C_8–N_7), φ_2 (H_{18}–N_{13}–C_{12}–C_{11}) and φ_3 (H_{21}–N_{16}–C_{15}–C_{17}) are only 26°, −24° and 22°, respectively and one would expect a strong interaction between the π-cloud of phenyl ring and those of BT with lone pairs of amino groups. Large red shift observed as compared to 2-PBT and 3-APBT in the absorption spectrum supports the above arguments. Red shift observed in polar aprotic solvents is due to dispersive interactions and blue shift in polar protic solvents is due to hydrogen bonding interactions with the lone pairs of amino groups and thus inhibiting them from resonance interactions with π-cloud of phenyl group. Increase in FWHM in polar protic solvents supports this.

4.1.2. Fluorescence spectrum

Fluorescence spectral data of 3,5-DAPBT in different solvents are compiled in Table 4. Unlike absorption spectrum, fluorescence spectrum is a broad band and more sensitive to solvents. This is in agreement with the fact that greater charge transfer takes place from amino group to aromatic ring in S_1 state than S_0 state. This is depicted by the decrease in the dihedral angles φ_1, φ_2 and φ_3 from 26° to 9°, −24° to −19° and 22° to 3°, respectively, as well as, the reduction in bond distances of C_8–C_{10} and C_{15}–N_{16} from 1.46 to 1.39 and 1.399 to 1.361 Å, respectively on excitation from S_0 to S_1 state. A regular red shift is observed with increase in polarity and hydrogen bonding nature of solvents. This suggests an increase in delocalization of lone pair of electrons of the amino group throughout the aromatic ring in S_1 state. The value of Φ_f of 3,5-DAPBT is small than that of 3-APBT [17] but larger than that of 1,3-DAB [21] in any given solvent. Similar to 1,3-DAB and 3-APBT [21,17], Φ_f of 3,5-DAPBT decreases in going from cyclohexane to water. λ^{f}_{max} and Φ_f of 3,5-DAPBT is independent of excitation wavelength (λ_{exc}) in all the solvents. This indicates that emission in all the solvents is occurring

Table 3
Absorption band maxima (λ^{ab}_{max}, nm) and log ε_{max} of 3,5-DAPBT in different solvents [3,5-DAPBT] = 6.09 × 10^{-6} M and ionic species [3,5-DAPBT] = 7.38 × 10^{-6} M

Solvents	λ^{ab}_{max} (log ε_{max})			
Cylcohexane	244	258 sh	313	360
Ether	246, 4.298	258 sh	316, 4.186	360, 3.361
Dioxane	247, 4.326	258 sh	317, 4.190	360, 3.419
Ethyl acetate	–	254, 4.287	317, 4.206	360, 3.419
Acetonitrile	246, 4.361	–	317, 4.205	360, 3.419
Isopropanol	244, 4.326	–	316, 4.200	360, 3.495
Methanol	243, 4.376	–	313, 4.213	360, 3.494
Water				
pH = 7.0	240 sh	–	310, 4.259	360, 3.278
pH = 3.0	246 sh	–	300, 4.245	–
H_0 = −0.50	254, 4.035	–	315, 4.265	–
H_0 = −10	254, 4.132	–	328, 4.287	–
H = 16.0	263, 4.078	–	343 (broad), 4.114	–

Table 4
Fluorescence band maxima (λ^{f}_{max}, nm), fluorescence quantum yield (Φ_f), excited-state lifetimes (τ, ns), radiative (k_r, $10^7\ s^{-1}$) and non-radiative (k_{nr}, $10^7\ s^{-1}$) rate constants of 3,5-DAPBT in different solvents

Solvents	λ_{exc} = 315 nm λ^{f}_{max}, (Φ_f)	τ/χ^2	k_r	k_{nr}
Cyclohexane	410.5 (0.102)	4.63 (1.13)	2.2	19.39
Ether	457 (0.061)	3.20 (1.08)	1.9	29.35
Dioxane	458 (0.060)	4.09 (1.09)	1.47	22.98
Ethyl-acetate	468 (0.053)	3.84 (1.13)	1.38	24.66
Acetonitrile	482 (0.05)	4.14 (1.07)	1.2	22.95
Isopropanol	513 (0.055)	6.40 (1.08)	0.86	14.76
Methanol	519 (0.015)	2.07 (1.01)	0.72	47.58
Water				
pH = 7.0	541 (0.0091)	1.32 (0.95)	0.69	75.06
pH = 3.0	493.5 (0.064)	3.87 (1.12)	1.65	24.18
pH = 0.50	402 (0.011)	0.59 (0.97)	1.86	167.63
$H_0 = -10$	460 (0.008)	0.52 (1.09)	1.54	190.76
H = 16.0	484 (0.002)	3.98 (1.20)	0.05	25.07

from the most relaxed excited-state and also agreeing with the fact that solvent relaxation times of the solvents used are smaller than that of fluorophore. FWHM of the fluorescence band increases from 3540 cm^{-1} in cyclohexane to 4420 cm^{-1} in water, suggesting an increase in solvent interactions, but FWHM of the fluorescence band is smaller than that noticed in the absorption band of 3,5-DAPBT in any given solvent. This may be due to loss in flexibility of 3,5-DAPBT upon excitation to S_1 state, as mentioned above.

Fluorescence excitation spectrum of 3,5-DAPBT was recorded in each solvent by monitoring at different emission wavelengths (λ_{em}) in the range of 390–600 nm, depending upon the solvent. Fluorescence excitation spectra so obtained in each solvent resembled with each other in all aspects and also with respective absorption spectrum. This suggests that there is only one species in S_0 state and emission is occurring from the same state which is excited.

Excited-state lifetimes 3,5-DAPBT were measured by exciting at 311 and 337 nm and monitoring at λ^{f}_{max} in different solvents. Fluorescence decay in each case followed a single exponential with $\chi^2 = 1 \pm 0.1$ and good autocorrelation functions. Relevant data are compiled in Table 4. Values of radiative (k_r) and non-radiative (k_{nr}) decay constants were calculated from the following relations and are compiled in Table 4.

$$k_r = \frac{\Phi_f}{\tau}, \qquad k_{nr} = \left(\frac{1}{\tau}\right) - k_r \tag{1}$$

Although amino groups in 3,5-DAPBT are not conjugated with the electron withdrawing BT moiety, λ^{f}_{max} of 3,5-DAPBT is large red shifted in comparison to 2-PBT or 3-APBT [17] with increase in solvent polarity. This could be due to large increase in dipole moment of the given molecule upon excitation to S_1 state (see Section 4.1.3). Anomalously large red shift observed in protic solvents could be due to formation of 1:1 solute–solvent complex in S_1 state. This is supported by the fact that red shift observed in the fluorescence spectrum of 3,5-DAPBT by the addition of 1% (v/v) methanol to cyclohexane (does not suppose to change the overall characteristics of cyclohexane but can cause 1:1 specific interactions) is 2503 cm^{-1}, whereas in 100% methanol it is only 5060 cm^{-1}. Similarly presence of 5% (v/v) water to acetonitrile cause a red shift of 984 cm^{-1} in emission spectrum as compared to pure acetonitrile and only 2260 cm^{-1} in 100% water. Similar behavior has also been observed in 5-aminoindazole and other aromatic amines [46]. This solute–solvent interaction enhances the stability of singlet state and thereby decreasing the S_1–T_1 energy gap, which in turn increases the probability of intersystem crossing [47]. This fact explains the decrease of Φ_f and increase in k_{nr} of 3,5-DAPBT with increase in solvent polarity and hydrogen-bond-forming tendency in going from cyclohexane to water. Further it is also well known that decrease in flexibility of the molecule decreases the non-radiative decay constants in their excited-state [48]. As mentioned earlier, BT moiety and amino groups become planar to phenyl ring and their bond distances decrease. All these factors introduce higher bond order and thus loss of flexibility of the amino groups and BT moiety in S_1 state. In other words, there should be a decrease in the value of k_{nr}, whereas results of Table 4 suggest other way around. It may thus be concluded that increase in non-radiative rate constants observed in solvents with increasing polarity and hydrogen bonding tendency could be due to solvent-induced fluorescence quenching. Similar results have been observed in other molecules also [19,47–52].

4.1.3. Dipole moment

Values of μ_g obtained by using AM1 and TD (DFT) methods after optimizing the geometry of 3,5-DAPBT are 2.4 D and 2.9 D, respectively. Many equations are available in literature to calculate μ_e from the absorption and fluorescence data. We shall use Bilot–Kawaski (BK) [53] equation (2) to calculate μ_e. BK parameter for polarizability, $\alpha = 0$ and 1 have been taken from Ref. [53].

$$\bar{\nu}_{ss} = \bar{\nu}_{ab} - \bar{\nu}_{fl} = mf(D, N) + \text{constant} \tag{2}$$

$$m = \frac{(\mu_e - \mu_g)^2}{\beta a^3} \tag{3}$$

where $\beta = 2\pi\varepsilon_0 hc = 1.105 \times 10^{-35}\ C^2$, h the Planck's constant, c the velocity of light and a the Onsagar's cavity radius. In case of isotropic polarizability of molecules, the condition $2\alpha/4\pi\varepsilon_0 a^3 = 1$, is frequently satisfied and Eq. (2) will represent BK equation. When the polarizability of the fluorophore is neglected, Eq. (2) is reduced to Eq. (4) known as Lippert–Mataga [54,55] equation.

$$\bar{\nu}_{ss} = \bar{\nu}_{ab} - \bar{\nu}_{fl} = m_1 \left[\frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1}\right] + \text{constant} \tag{4}$$

where D is the dielectric constant and n the refractive index. Fig. 1 represents the plot between $\bar{\nu}_{ss}$ and BK parameters for $\alpha = 0$ and 1. A plot of $\bar{\nu}_{ss}$ versus $E_T(30)$ parameters is

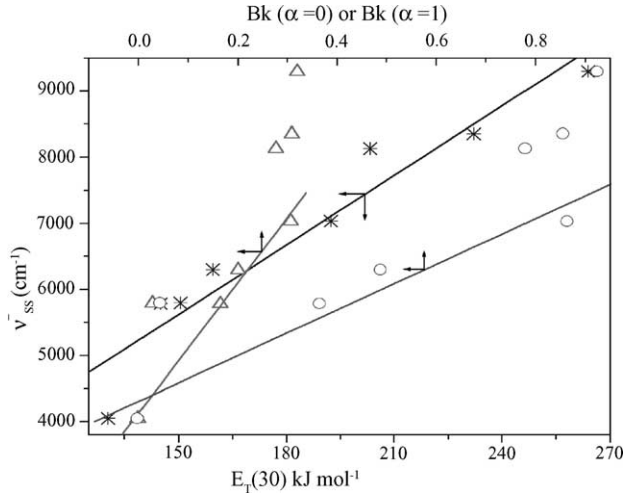


Fig. 1. Plot of Stoke's shifts vs. BK parameters: △ ; $\alpha = 0$, ◯; $\alpha = 1$, *; $E_T(30)$.

also given in Fig. 1. It is clear from Fig. 1 that a linear relation is obtained for the non-polar and polar aprotic solvents, whereas departure from linearity is quite large for polar protic solvents and dioxane. As explained in literature for other aromatic amines [56] large deviation from linearity shown by protic solvents is due to the fact that hydrogen bond between protic solvent and lone pair of amino group in S_0 state is broken on excitation and a hydrogen bond is formed between the amino proton and lone pair of solvent molecule. Because of this a large red shift is observed in the emission spectra of aromatic amines. This is reflected by a linear plot observed in case of $E_T(30)$ parameters, as these parameters include both the dispersive and specific interactions. Peculiar properties of dioxane as a solvent are well known and large deviation from linearity observed can be explained on the same lines as done by Ledger and Supan [57]. If dioxane and protic solvents are omitted, the regression coefficients obtained from BK ($\alpha = 0$ and 1) parameters are found to be 0.99 and 0.97, respectively. Based on these values of regression coefficients, it is not possible to draw any conclusion about whether polarizability of the molecule plays a role or not in calculating the values of μ_e.

The value μ_e was determined from the slope of linear part of the plots of Fig. 1 using μ_g (2.4 D) and Onsager's cavity radius (0.49 nm), obtained from AM1 calculations. These values are 12.0 and 8.1 D at $\alpha = 0$ and 1, respectively. This clearly suggests that polarizability of the fluorophore plays a major role in determining μ_e. In order to solve this problem, we have calculated μ_e by fully optimizing the geometry of 3,5-DAPBT in S_1 state by taking into account the configurations interaction (CI = 5 in MOPAC, 100 configurations) and using AM1 method. Similar to experimental results, theory also predict that $\mu_e > \mu_g$. Comparing the experimental and theoretical results it is clear that better agreement is achieved if BK parameters are used involving polarizability of the fluorophore. Small discrepancy between the two μ_e values could be due to the assumption that polarizability is isotropic. Similar behaviour is also observed for some other aromatic amines [49,51].

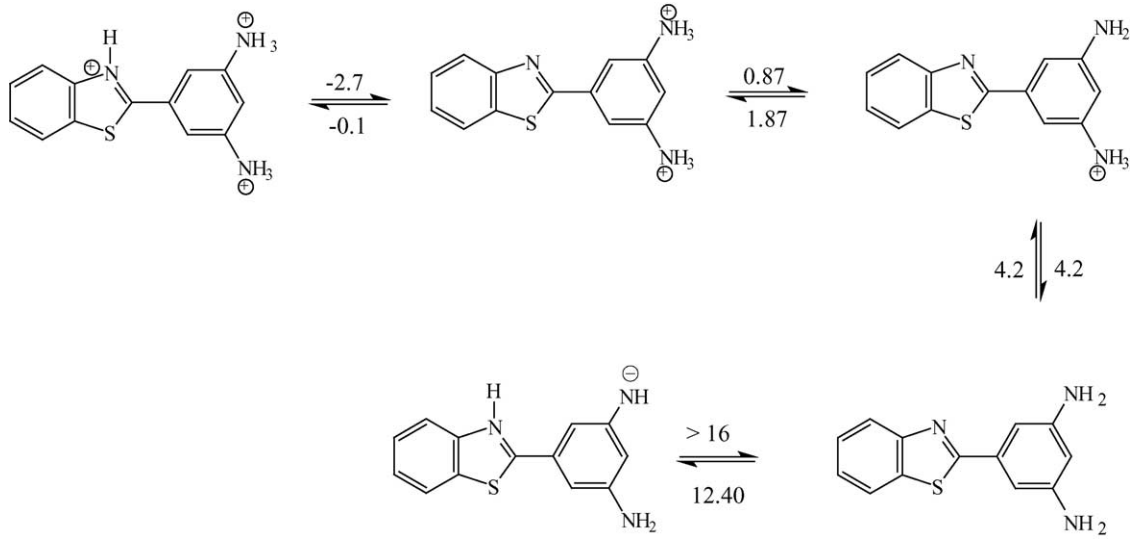
4.2. Effect of acid–base concentration

4.2.1. Aqueous medium

3,5-DAPBT is neutral in the pH range of 6.5–14 with λ^{ab}_{max} at 310 nm and shoulder at ∼360 nm. The value of λ^{ab}_{max} of neutral species is red shifted with increase of base concentration and at $H_- = 16.0$, the highest base concentration used, λ^{ab}_{max} is at 343 nm. Formation of this species is not complete even at this base concentration and this pK_a value for deprotonation cannot be determined. Similar behaviour is also observed in other aromatic amines [18]. With decrease of pH, λ^{ab}_{max} is blue shifted to 300 nm with decrease of absorbance, having an isosbestic point at 302 nm, suggesting equilibrium between MC and neutral (N) species. 3,5-DAPBT is present as MC in the pH range 3.0–2.0. With further decrease of pH, absorption spectrum of MC is red shifted to 316 nm slowly up to $H_0 = -0.5$ without isosbestic point, but slight increase in absorbance is noticed. With further increase of acid strength, λ^{ab}_{max} is red shifted from 315 to 328 nm with an isosbestic point at 320 nm. No further change in absorption spectrum is obtained at $H_0 < -5.50$.

The pK_a values for the various prototropic equilibria were determined using absorption data and are listed on top of the arrows of Scheme 2. Absorption spectra of various prototropic species are shown in Fig. 2 and relevant data are compiled in Table 3.

Fluorescence spectrum of 3,5-DAPBT was also studied in the acid–base concentration range of (H_0/pH/H_-) −10 to 16. Fluorescence spectra of various ionic species are given in Fig. 3 and relevant data are compiled in Table 4. Fluorescence spectrum of 3,5-DAPBT is invariant in the pH range of 6–11 and 541 nm band maximum is assigned to neutral species. Fluorescence intensity of 541 nm band decreases without any change in λ^{f}_{max} and FWHM. The former reduces to zero at $H_- = 14.5$. With further increase of basic strength, a blue shifted emission band appears at 488 nm and its fluorescence intensity keeps on increasing even up to $H_- = 16$. The value λ^{f}_{max} is red shifted with increase of λ_{exc} and this could be due to the presence of neutral species even at this base strength. This is supported by the fact that fluorescence excitation spectrum is red shifted from 326 to 336 nm with increase of λ_{em} from 450 to 500 nm, agreeing with the absorption spectrum at $H_- = 16$. Single exponential observed in the fluorescence decay at short wavelength emission (4.0 ns) at $H_- = 16$ suggests the presence of single species. The value λ^{f}_{max} of neutral species (541 nm) of 3,5-DAPBT is blue shifted to 494 nm with increase of fluorescence intensity up to pH = 3, suggesting the formation of MC. Fluorescence characteristics of MC at pH = 3 is invariant to λ_{exc} and fluorescence excitation spectrum is invariant to λ_{em}, agreeing with the absorption spectrum. This suggests the presence of only one species (MC) and supported by sin-



Scheme 2.

gle exponential fluorescence decay of lifetime 3.87 ns. With increase of acid concentration, λ^{f}_{max} is further blue shifted to 402 nm, reaching its maximum fluorescence intensity at pH = 0.5 and possessing an isoemissive point at ~430 nm. With further increase of acid concentration, 402 nm emission band is red shifted to 460 nm with isoemissive point at ~450 nm upto $H_0 = -2$. At $H_0 < -2$, λ^{f}_{max} and fluorescence intensity does not change even up to $H_0 = -10$. The values λ^{f}_{max} and λ^{exc}_{max} are invariant to λ_{exc} and λ_{em}, respectively at pH = 0.5 and $H_0 = -2$. Agreement of fluorescence excitation spectra with the absorption spectra at these acid concentration and single exponential fluorescence decay confirm the presence of only one ionic species (Table 4). The pK_a values for the various prototropic equilibrium in S_1 state (pK_a^+) were determined with the help of fluorimetric titrations by exciting at the respective isosbestic points. These values are listed below the arrows in Scheme 2.

4.2.2. Non-aqueous medium

Spectral characteristics of cationic species of 3,5-DAPBT have been studied in cyclohaxane + TFA (up to 0.1 M), acetonitrile and methanol + H_2SO_4 (up to 1 M). Spectral characteristics of the ionic species formed in methanol + H_2SO_4 are similar to those observed in aqueous medium except that (i) 1 M H_2SO_4 concentration is too small to form trication and, (ii) λ^{f}_{max} of MC up to 10^{-2} M H_2SO_4 (465 nm) and DC > 10^{-2} M H_2SO_4 (394 nm) are largely blue shifted in comparison to those observed in water (494 and 402 nm, respectively). In acetonitrile as medium, λ^{ab}_{max} and λ^{f}_{max} are blue shifted up to 10^{-4} M, as observed in protic solvents. Both the absorption bands are red shifted, specially the long wavelength one and becomes broad, in the range of 10^{-4} M < H_2SO_4 < 10^{-1} M and finally blue shifted to 325 nm at [H_2SO_4] > 10^{-1} M. On other hand, fluorescence intensity

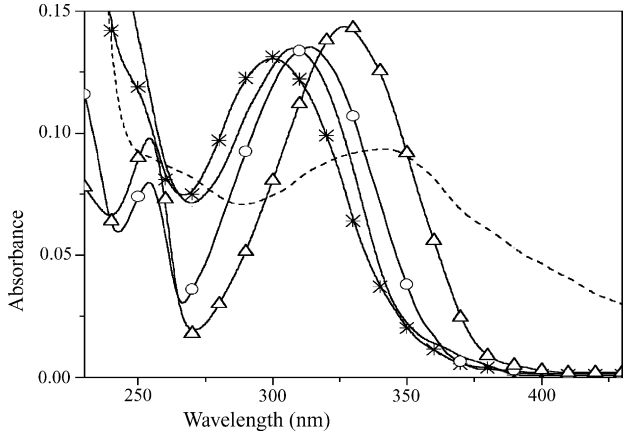


Fig. 2. Absorption spectra of the prototropic species of 3,5-DAPBT in aqueous medium. (△) $H_0 = -10$, TC; (◯) $H_0 = -0.5$, DC; (*) pH = 3.0, MC; (——) pH = 7.0, *N*; (- - - -) $H_- = 16$, MA. [3,5-DAPBT] = 7.38×10^{-6} M.

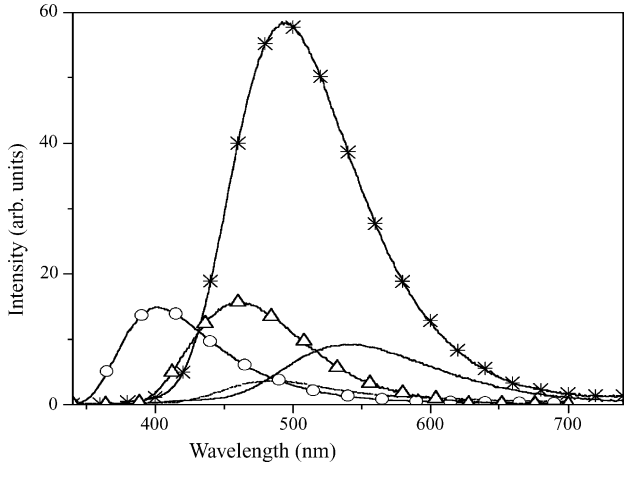


Fig. 3. Fluorescence spectra of the prototropic species of 3,5-DAPBT in aqueous medium. (△) $H_0 = -10$, TC; (◯) $H_0 = 0.5$, DC; (*) pH = 3.0, MC; (——), pH = 7.0, *N*; (- - - -), $H_- = 16$, MA. [3,5-DAPBT] = 7.38×10^{-6} M.

of 438 nm emission band decreases with increase in H_2SO_4 concentration from 10^{-4} M onward and is nearly zero at 10^{-2} M H_2SO_4, except a very broad band is there in the range of 400–600 nm. Unlike in protic solvents, a new red shifted emission band appears at 478 nm at $[H_2SO_4] > 10^{-1}$ M. Spectral characteristics of 3,5-DAPBT in cyclohexane + TFA are very different from those observed in other two solvents containing H_2SO_4 up to 10^{-3} M TFA. Absorbance of 310 nm band decreases drastically, followed by a red shifted λ_{max}^{ab} (330 nm), as well as, increase in absorbance of 350 nm band. With further increase in TFA concentration, λ_{max}^{ab} is blue shifted to 320 nm. With increase of TFA in cyclohexane containing 3,5-DAPBT, 411 nm emission band develops into a weak dual emission at 384 and 525 nm at 10^{-3} M concentration and 443 and 558 nm at 0.1 M concentration using λ_{exc} = 310 nm. At λ_{exc} = 360, 384 nm emission band is absent and dual emission develops at 443 and 560 nm, with increase of TFA. Whereas at λ_{exc} = 420 nm, neutral emission is absent and a single emission band develops at 566 nm. Fluorescence intensity of all the dual bands is too weak to measure lifetimes in S_1 state. Figs. 4–7 represent the absorption and fluorescence spectra of 3,5-DAPBT in cyclohexane + TFA and acetonitrile + H_2SO_4, respectively. Relevant data are compiled in Table 5.

4.2.2.1. Monocations. The 3,5-DAPBT has three basic centers, i.e., two $-NH_2$ groups and one BT=N-atom. Thus three MCs can be obtained on protonation (Scheme 1). From the geometry of the molecule, MC1 and MC2 are structurally similar. This is supported by: (i) similar total energy of MC1 and MC2 under isolated conditions obtained by AM1 and DFT calculations and when dipolar solvation energies are included in AM1 calculations and (ii) similar absorption transition energies predicted by single point calculations of AM1 and TD (DFT) calculations. On other hand, in S_1 state MC1 is more stable than MC2 by 25.7 and 3.6 kJ mol^{-1} under isolated conditions and when dipolar solvation energies are included.

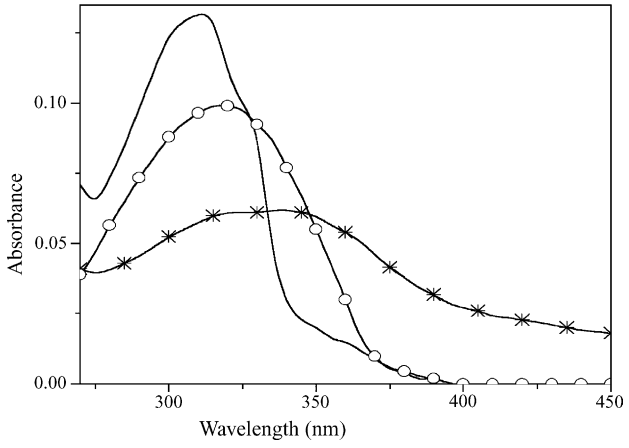


Fig. 4. Absorption spectra of 3,5-DAPBT in cyclohexane containing TFA: (——) 0 M TFA; (*) 10^{-3} M TFA; (◯) 0.1 M TFA.

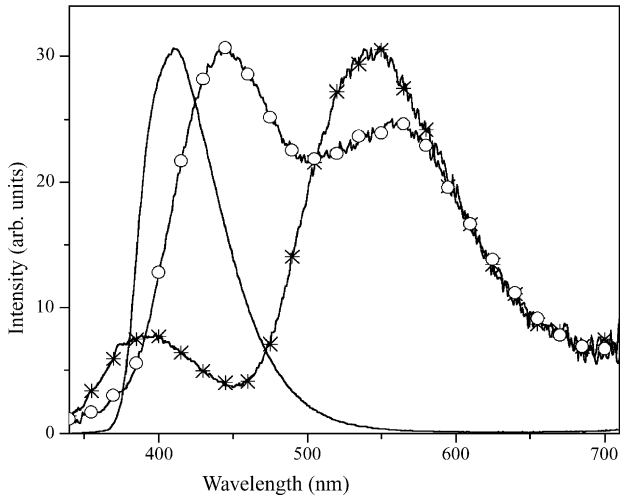


Fig. 5. Normalized fluorescence spectra of 3,5-DAPBT in cyclohexane containing TFA: (——) 0 M TFA; (*) 10^{-3} M TFA; (◯) 0.1 M TFA.

Thus it may be concluded that both experimental and theoretical calculations cannot differentiate between MC1 and MC2 in both the states (S_0 and S_1) in polar protic solvents. Similar behaviour is also observed in the first protonation of aromatic diamines [21–25]. Between MC1 and MC3, MC3 is stable than MC1 by 66.7 kJ mol^{-1} in AM1 calculations and 58.8 kJ mol^{-1} in DFT calculations under isolated conditions, whereas MC2 is stable than MC3 by 20.7 kJ mol^{-1} when dipolar solvation energy is taken into account in AM1 method. This is because the dipole moment of MC2 in S_0 state (17.0 D) is very large as compared to that of MC3 (2.2 D). In other words, MC3 can be present in non-polar solvents and MC1 in polar solvents.

Based on above discussion and earlier results [17,19,44,58], protonation of amino group and BT=N–

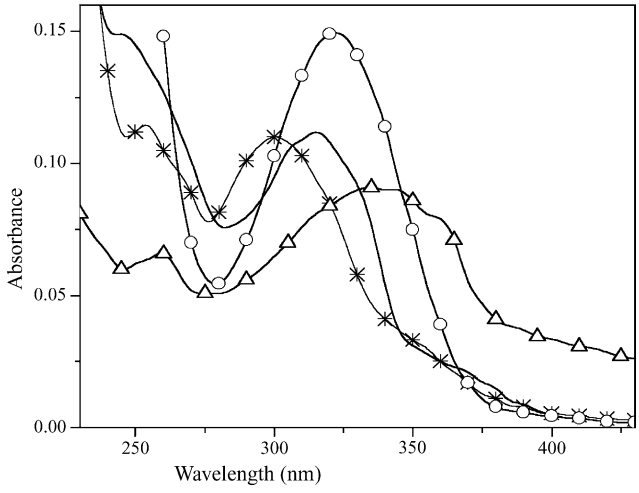


Fig. 6. Absorption spectra of 3,5-DAPBT in acetonitrile containing H_2SO_4: (——) 0 M H_2SO_4; (*) 10^{-5} M H_2SO_4; (△) 10^{-2} M H_2SO_4; (◯) 1 M H_2SO_4. [3,5-DAPBT] = 7.02×10^{-6} M.

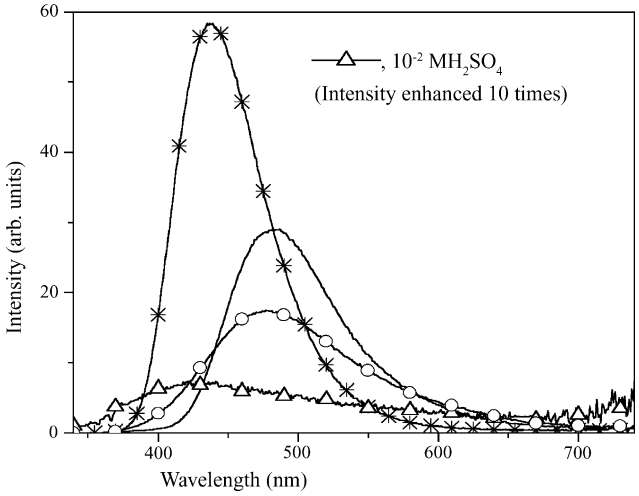


Fig. 7. Fluorescence spectra of 3,5-DAPBT in acetonitrile containing H_2SO_4: (——) 0 M H_2SO_4; (*) 10^{-5} M H_2SO_4; (△) 10^{-2} M H_2SO_4; (◯) 1 M H_2SO_4. [3,5-DAPBT] = 7.02×10^{-6} M.

atom lead to blue shift and red shift, respectively, in the spectral characteristics of the molecule if π and π^* is the lowest energy transition. Protonation constant of =N– atom of 2-PBT is 0.7 [17], those of $-NH_2$ group in 1,3-DAB and 3-APBT are 4.86 [21] and 3.4 [17], respectively. These results suggest that first protonation occurs at the amino group of 3-APBT. Results of Table 4 (blue shifts in the absorption and fluorescence spectra of neutral 3,5-DAPBT) and the first protonation constant of 4.2 clearly establishes that MC1 is the positively charged species formed in S_0 and S_1 states in aqueous medium, methanol and acetonitrile. Red shift observed in the fluorescence band maxima of MC1 with increase in protic nature of the solvents suggests that MC1 is stabilized by the hydrogen bonding of the solvents. Red shift observed in the absorption and fluorescence spectra of 3,5-DAPBT in cyclohexane containing up to 10^{-3} M TFA is also consistent with the presence of MC3, i.e. monocation formed by protonating BT=N– atom, predicted by both AM1 and DFT calculations in non-polar solvents. Presence of short wavelength emission and its red shift with increase in λ_{exc} suggests the presence of MC1, solvated to different extent in cyclohexane containing 10^{-3} M TFA or presence of MC1, which is stabilized to different extent in comparison to MC3 in S_1 state. Since fluorescence intensity of SW emission is so small that the fluorescence excitation spectra recorded at different emission wavelengths do not give any meaningful results and lifetimes could not be recorded. Very broad absorption band at ∼335 nm does suggest some information about the presence of multi-species in this medium. It may be concluded that MC1 is the only species in polar solvents and MC3 in non-polar solvents. Small amount of MC1 may be present in cyclohexane + TFA, due to increase in the polarity of cyclohexane by the addition of TFA.

Fluorimetric titration method gives the ground state pK_a value, suggesting that protonation equilibrium is not achieved in the excited-state. This could be due to shorter lifetime of the conjugate acid–base pair of 3,5-DAPBT and smaller acid concentration. Similar behaviour is also observed in the first protonation of aromatic diamines [25,26] and 4-(9′-anthryl)-*N*,*N*-dimethylaniline [58].

4.2.2.2. Dications. Similar to MCs, there can also be three DCs, DC1, DC2, DC3 (Scheme 1) and DC1 and DC2 will be similar to each other. This has also been shown by AM1 and DFT calculations. DC1 (DC2) are more stable than DC3 by 118 kJ mol^{-1} (AM1 method) and 113.4 kJ mol^{-1} (DFT calculations) under isolated conditions and DC3 is more stable than DC1 (DC2) by 65 ± 3 kJ mol^{-1} when dipolar solvation energy is included. This is because μ_g for DC3 (27.6 D) is large as compared to that of DC1 (13.7 D).

Based on earlier experimental results [21–24], further protonation of MC1 (MC2) at second amino group or of MC3

Table 5
Absorption band maxima (λ^{ab}_{max}, nm) and fluorescence band maxima (λ^{f}_{max}, nm) of 3,5-DAPBT in cyclohexane, acetonitrile, methanol containing different amount of acid

Solvents	λ^{ab}_{max}					λ^{f}_{max}	
Cyclohexane	258	313	328	360	411		
Cyclohexane + 10^{-3} M TFA	–	–	340 (broad)	–	384[a], 417[c]	394[b], 508[d]	543 ± 2
Cyclohexane + 10^{-1} M TFA	–	–	320	–	443		559 ± 1
Acetonitrile	246	317	–	360	482		
Acetonitrile + 10^{-4} M H_2SO_4	255	300	–	350	438		
Acetonitrile + 10^{-2} M H_2SO_4	259	342	364	388	–		
Acetonitrile + 1 M H_2SO_4	–	323	–	–	478		
Methanol	243	313	–	360	518		
Methanol + 10^{-3} M H_2SO_4	253	300	–	355	465		
Methanol + 1M H_2SO_4	257	310	–	–	394		

Cyclohexane + 10^{-3} M TFA, λ_{exc}.
[a] 310 nm.
[b] 330 nm.
[c] 360 nm.
[d] 420 nm.

at any amino group will lead to the blue shifts in the absorption and emission spectra of MCs. DCs obtained will be DC3 or DC1 (DC2), respectively, whereas the protonation at the BT=N– atom will shift the spectra towards red and DC will be DC1 (DC2). Further, second protonation constants of 1,3-DAB and 3-APBT are 1.89 [21] and 0.07 [17], respectively. In other words, in aqueous medium or polar medium and based on pK_a values of the respective basic centers, DC3 should be formed, leading to the blue shifts in the spectral characteristics. On the contrary, absorption spectrum of MC of 3,5-DAPBT is red shifted in polar solvents on further acidification, whereas the fluorescence spectrum is blue shifted. In cyclohexane, both the absorption and fluorescence spectra are blue shifted. Thus in non-polar solvents, DC is either DC1 or DC2 and consistent with the results of Table 2. Whereas in protic solvents, dication formed is DC3. This is also in agreement with the data of Table 2 when dipolar solvation energy is included. Small red shift observed in the MC of 3,5-DAPBT could be due to the planarity of the diamino phenyl ring with the BT moiety of DC as compared to MC. Similar fluorescence excitation spectra at different λ_{em} and single lifetime confirms only one kind of DC in polar medium. Thus it may be concluded that DC1 (DC2) is formed in cyclohexane + TFA combination and DC3 is formed in other solvents.

4.2.2.3. Anionic species. Spectral characteristics of 3,5-DAPBT in basic medium is in agreement with earlier results [16,18,21–25] and MA1 is formed by deprotonating the $-NH_2$ group. Non-fluorescent nature of MA1 also agrees with the earlier results with few exceptions [59,60] and it has been shown [61,62] that non-fluorescence nature of MA so formed is due to solvent-induced fluorescence quenching. The value pK_a^* (12.40) obtained from fluorimetric titration also supports this. Though we do not have any proof, but based on earlier results [59,60], it can be speculated that blue shifted emission band (484 nm) is formed by deprotonation of any $>$C–H bond.

5. Conclusions

Following conclusions can be obtained from the above experimental and theoretical results. (i) Large Stoke's shift observed in neutral 3,5-DAPBT in different solvents is due to large increase in μ_e in S_1 state. Polarization plays an important role in increase in μ_e. Decrease in Φ_f is due to solvent-induced fluorescence quenching. (ii) MC1 is the only monocation in polar aprotic and protic solvents, whereas MC1 and MC3 are the monocationic species in cyclohexane + 10^{-3} M TFA. (iii) DC2 is the main species in polar protic solvents, whereas DC1 is the main species in non-polar and polar aprotic solvents. Unusual red shift observed in DC2 in comparison to MC1 could be due to planar configuration of both the moieties. (iii) Only one kind of TC is formed. (iv) Monoanion formed by deprotonation of $-NH_2$ group is non-fluorescent, whereas that formed by $>$C–H moiety is fluorescent.

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