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Excited State Charge Transfer reaction with dual emission from 5-(4-dimethylamino-phenyl)-penta-2,4-dienenitrile: Spectral measurement and theoretical density functional theory calculation

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ABSTRACT

The excited state intramolecular charge transfer process in donor-chromophore-acceptor system 5-(4dimethylamino-phenyl)-penta-2,4-dienenitrile (DMAPPDN) has been investigated by steady state absorption and emission spectroscopy in combination with Density Functional Theory (DFT) calculations. This flexible donor acceptor molecule DMAPPDN shows dual fluorescence corresponding to emission from locally excited and charge transfer state in polar solvent. Large solvatochromic emission shift, effect of variation of pH and HOMO-LUMO molecular orbital pictures support excited state intramolecular charge transfer process. The experimental findings have been correlated with the calculated structure and potential energy surfaces based on the Twisted Intramolecular Charge Transfer (TICT) model obtained at DFT level using B3LYP functional and 6-31+G(d,p) basis set. The theoretical potential energy surfaces for the excited states have been generated in vacuo and acetonitrile solvent using Time Dependent Density Functional Theory (TDDFT) and Time Dependent Density Functional Theory Polarized Continuum Model (TDDFT-PCM) method, respectively. All the theoretical results show well agreement with the experimental observations.

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1. Introduction

Photoinduced intramolecular charge transfer (ICT) processes and subsequent dual fluorescence in molecules with acceptor and donor groups find importance in various applications such as electro-optical switches, pH and ion detectors, creation of new optoelectronic devices such as electroluminescence devices, solar cells and thin film transistor [1-3], chemical sensors for free volume measurement in polymers, probes for the study of micro-heterogeneous environments [4,5], degree of water penetration into the surfactant aggregates and sensing the local polarity of the microenvironment at binding sites on proteins [6]. These charge transfer molecules also have a crucial role in biological light harvesting processes such as photosynthesis [7]. The phenomenon of dual fluorescence was first reported by Lippert et al. [8] in 4-(N,N-dimethylaminobenzonitrile) (DMABN). Various models have been proposed so far for explaining the dual fluorescence in DMABN and in similar types of molecules with donor acceptor moiety attached to the chromophore group. The Twisted Intramolecular Charge Transfer (TICT) model [7,9,10], the Rehybridized

Intramolecular Charge Transfer (RICT) model [11], the Planarized Intramolecular Charge Transfer (PICT) model [12,13], and the Wagging Intramolecular Charge Transfer (WICT) model [14] are some of the most discussed among them. Twisted Intra-molecular Charge Transfer (TICT) model, proposed by Grabowski et al. [15,16] is the most acceptable one for explaining dual fluorescence in DMABN and its analogous molecules [17]. According to TICT model, after absorption, the molecule from the promoted state transforms to the twisted structure which is a local minimum on the excited state potential energy surface. This transformation is performed through a radiationless process. In the final conformation, the donor group is typically perpendicular to the rest of the molecular frame, thus generates a complete electronic decoupling state. The lower energy emission band is then thought to arise from this charge transfer (CT) state and higher energy emission arises from a locally excited (LE) state.

Till date, many compounds have been synthesized and reported which are capable for charge transfer reaction with varying donor such as primary, secondary and tertiary amino groups and acceptor such as nitrile [18,19], acid [20,21], aldehyde [22], ester [23,24], etc. attached to the chromophoric benzene [23–25] and naphthalene [26,27] rings. Recently, we have reported some new donor acceptor systems having flexible ethylenic double bond between the acceptor and chromophore [28,29] and it is found that this type





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of extra flexibility favors CT reaction [30]. To this end we are interested to follow how addition of additional ethylenic double bond effects the CT reaction. Therefore, in this work, we have synthe-5-(4-dimethylamino-phenyl)-penta-2,4-dienenitrile sized (DMAPPDN) where two ethylenic double bonds are tagged between the acceptor and chromophore and investigated its excited state ICT process using steady state absorption, fluorescence spectroscopy, and theoretical calculations. Theoretical calculations have been performed at Density Functional Theory (DFT) level using B3LYP hybrid functional and 6-31+G(d,p) basis set. The ground and excited states potential energy curves (PECs) along the donor and acceptor twisted coordinates in vacuo have been evaluated using Density Functional Theory (DFT) and Time Dependent Density Functional Theory (TDDFT) methods, respectively. On the other hand. Time Dependent Density Functional Theory Polarized Continuum Model (TDDFT-PCM) methods have been used to construct the PECs when solvent was included for both the donor and acceptor twisted path.

2. Experimental details

2.1. Materials

4-N,N-dimethylaminocinnamaldehyde was purchased from Aldrich Chemicals, USA and used as received. Spectroscopic grade solvents were purchased from Spectrochem and were used after proper distillation. Ethanol and sulfuric acid from E. Merck were used as received. Triple distilled water was used for the preparation of all aqueous solutions.

2.2. Synthesis of DMAPPDN

4-N,N-dimethylaminocinnamaldehyde (A) and triphenylphosphanylideneacetonitrile (B) in dry dichloromethane were stirred at room temperature for 24 h (Scheme 1). After the solvent was removed over vacuum, the crude product was purified by silica gel column chromatography and repeated crystallization with minimum amount of methanol to get pure nitrile compound DMAPPDN (C). The compound DMAPPDN contains mixture of E and Z isomer. After repeated column chromatography we obtained the ratio of E:Z as 2.65:1. Further separation is not possible due to their almost similar R_f values. M.P. 155 °C. ¹H NMR: δ (CDCl₃, 300 MHz) (E:Z 2.65:1) 3.03(6H, s, Me₂N); 5.01(d, JZ, 10.2 Hz, 1H); 5.21(d, JE, 15.9 Hz, 1H); 6.56–7.88(m, 7H, ArH). ¹³C NMR: δ (CDCl₃, 75 MHz) 40.05, 92.44, 94.25, 111.89, 117.50, 119.22, 119.69, 120.72, 123.10, 128.92, 129.12, 130.75, 141.97, 142.29, 150.16, 151.20, 162.22. IR ν (cm⁻¹) 989, 1371, 1600, 2206, and 2920.

Scheme 1. Synthetic scheme of DMAPPDN.

2.3. Steady state spectral measurements

All the spectral measurements were done at $\sim 10^{-5}$ – 10^{-6} M concentration of solute in order to avoid aggregation and self quenching. All absorption and emission spectra of DMAPPDN were recorded by Hitachi UV–Vis U-3501 spectrophotometer and Perkin Elmer LS55 fluorescence spectrophotometer, respectively.

The fluorescence quantum yield for the CT and LE state of DMAPPDN in solvents of different polarity were measured relative to quinine sulfate in 0.1 M sulfuric acid (Φ_f = 0.57) as secondary standard and calculated on the basis of the following equation:

$$\Phi_f = \Phi_f^0 \frac{n^2 A^0 \int I_f(\lambda_f) d\lambda_f}{n_0^2 A \int I_f^0(\lambda_f) d\lambda_f}$$
(1)

Where n_0 and n are the refractive index of the solvents, A^0 and A are the absorbances, Φ_f^0 and Φ_f are the quantum yields, and the integrals denote the area of the fluorescence band for the standard and the sample, respectively.

2.4. Computational details

All theoretical calculations were performed using Gaussian 03 W software [31]. Global minimum structure of DMAPPDN was obtained by optimizing the geometry at DFT level using B3LYP functional and 6-31+G(d,p) basis set. The ground state, first and second excited singlet state potential energy curves (PECs) have been calculated following TICT model [32-34]. Potential energy surfaces were calculated by varying the twisting angle θ_1 for donor group ($-NMe_2$) and θ_2 for acceptor group ($-(CH=CH)_2-CN$) (Scheme 2) independently. The PECs of the first and second excited singlet states were obtained using TDDFT method with same functional and basis set. The TDDFT-PCM model was used for the construction of PECs in acetonitrile solvent. We have used DFT, TDDFT and TDDFT-PCM methods because the result obtain in these methods correlate well with the experimental data of the ICT processes and also these methods have been applied in several systems in recent times [35-39]. One limitation of our study is that the potential energy surface is computed only along the twisting angle without geometry optimization for various excited states. The validity of such an approach that uses the ground state optimized geometry as a basis of representation of the excited structure has been already successfully established in many recent scientific publications [35-39]. The difference in energy between the S₀ and S₁ or S₂ states of the calculated PECs without optimization of the excited states at the twisted geometry is considered to be the emission energy. This emission energy value is just an estimation of emission energy, but not the theoretical estimate of vertical emission from the excited state, since the excited state optimization has not been considered. HOMO, LUMO diagrams were also constructed from the optimized structure and twisted form of DMAPPDN in vacuo and acetonitrile solvent.



Scheme 2. Optimized structure of 5-(4-dimethylamino-phenyl)-penta-2,4-dienenitrile (DMAPPDN) with numbering of atoms. θ_1 and θ_2 are the torsional angles at the donor and acceptor sides, respectively.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of DMAPPDN ($\sim 10^{-6}$ M) in nonpolar, polar protic and polar aprotic solvents are shown in Fig. 1a and the spectral band maxima are presented in Table 1. From the absorption spectra, it is clear that DMAPPDN shows band at ~ 390 nm in polar protic and polar aprotic solvents, except for water and acetonitrile, and in nonpolar solvents at ~ 380 nm. These absorption bands arise from the $S_0 \rightarrow S_1$ transition of benzene chromophore. Compared to our previous reported similar type of substituted benzene chromophoric systems [27,39], the absorption band maxima is found to be red shifted due to the presence of two conjugated double bond on the acceptor side and tertiary amine group as donor. The absorption band maxima is slightly blue shifted in case of



Fig. 1. (a) Absorption (b) fluorescence emission and (c) excitation spectra (monitored at corresponding emission maxima given in parenthesis) of DMAPPDN in different solvents at room temperature.

Table 1

Spectroscopic parameters and quantum yield of 5-(4-dimethylamino-phenyl)-penta-2,4-dienenitrile (DMAPPDN) in different solvents at room temperature.

Solvent	λ_{abs} (nm)	λ _{flu} (nm)	Stokes shift Δv (cm ⁻¹)	$\Phi imes 10^3$
n-hept	378	435, 415	3466	7.59
CY	381	439, 418	3433	6.55
MCH	380	441, 420	3605	9.6
n-hex	377	435, 413	3536	7.72
CCl ₄	387	448	3485	7.36
DCM	394	488	4856	11.43
THF	389	482, 415	4927	12.84
DMF	393	507	5689	28.58
DOX	386	462	4228	10.57
DMSO	398	514, 420	5670	21.33
CHCl ₃	395	476	4276	10.09
ACN	387	503	5925	16.13
BuOH	392	477	4545	8.67
ⁱ PrOH	389	478	4753	9.13
MeOH	388	504	5898	10.31
EtOH	390	490	5232	8.42
H ₂ O	372	533, 425	8083	13.01

hydrogen bonding solvents probably due to the formation of hydrogen bonded solvated clusters [40,41] in the ground state and it is prominent in water, where \sim 15 nm blue shift was observed. Moderate solvent dependency of absorption band maxima may be due to relatively high ground state dipole moment (10.8 D calculated) of DMAPPDN.

3.2. Emission spectra

The steady state fluorescence spectra of DMAPPDN were recorded in various solvents by exciting at the respective absorption maxima and shown in Fig 1b. The spectral band maxima are provided in Table 1. Interestingly, in non polar alkane type solvents, emission spectra show structured emissions with two peak heads at ~415 and ~435 nm. Compared to other commonly reported donor acceptor systems the emission band in the present case is found to be broad in nature in nonpolar solvents. In general reported similar benzene derivative shows single, sharp local emission in non polar alkane type of solvent [42,43]. In the present case, the observed structured emissions at \sim 415 and \sim 435 nm may arise due to incorporation of extra flexibility by introducing an extra double bond in DMAPPDN molecule. In polar solvents like water, DMSO and THF the emission spectra show dual emission bands. The higher energy emission at ~420 nm corresponds to LE band and lower energy solvent dependent bands to the CT band [39,44]. From emission spectra it is clear that the position of the short wavelength emission band depends slightly on the polarity of the solvent but the long wavelength emission band exhibits solvatochromic shift with increasing solvent polarity. As shown in Fig. 1c, the excitation spectra in all solvents monitored at both the high and low wavelength emission band matches with the corresponding absorption spectrum. This indicates that the molecule exists as a single species in the ground state and excited state photoinduced process is responsible for dual emission.

The high dipolar character of the emissive species can be rationalized by solvatochromic shift of the CT band and by the large change in the dipole moment of DMPPDN from ground state to the excited state. With increasing solvent polarity, the CT band shifted more to the red because the solvent dipoles orient themselves around the fluorophore to attain an energetically favorable arrangement, thereby stabilizing the polar CT state. The excited state dipole moment has been calculated from the slope of the well known Lippert–Mataga plot (Fig. 2a), i.e. Stokes shift (Δv) vs. solvent parameter $\Delta f(\varepsilon_r, n)$. According to the following Lippert–Mataga relation [45]



Fig. 2. Plot of (a) Stokes' shift (Δv) against solvent parameter (Δf) , (b) emission band maxima against hydrogen bonding parameter (α), and (c) Stokes' shift (Δv) against Reichardt solvent polarity parameter $E_T(30)$.

$$v_a - v_f = \frac{(\mu^* - \mu)^2}{2\pi\varepsilon_0 hc\rho^3} \times f(\varepsilon_r, n)$$

where
$$f(\varepsilon_r, n) = \left[\frac{\varepsilon_r - 1}{2\varepsilon_r + 1}\right] - \left[\frac{n^2 - 1}{2n^2 + 1}\right]$$

 v_a and v_f are the corresponding absorption and emission band position in cm⁻¹, respectively, ε_r is dielectric constant and n is refractive index of the medium. The terms h, ε_0 , c, ρ in the above equation are Planck's constant (6.626×10^{-34} J s), permittivity of vacuum (8.85×10^{-34} V C⁻¹ m⁻¹), velocity of light (3×10^8 m s⁻¹) and Onsagar cavity radius, respectively. The terms μ^* and μ are the ground and excited state dipole moments. It is found that

Lippert–Mataga plot shows linearity for nonpolar and polar aprotic solvents. The value of Onsagar cavity radius (ρ) was calculated to be 5.05 Å by volume test of the optimized structure of DMAPPDN at DFT level using B3LYP functional and 6-31+G(d,p) basis set. From the ratio of the slope of the Lippert plot and calculated values of ρ and μ , the excited state dipole moment was calculated to be 23.2 D. This large difference in the dipole moment ($\mu\Delta = 12.4$ D) from ground state ($\mu = 10.8$ D) to the excited state ($\mu^* = 23.2$ D) could only be possible by redistribution of charge in the excited state surface by intramolecular charge transfer process from the electron rich tertiary amino donor to the nitrile acceptor group upon photoexcitation. However, a deviation from linearity was observed in the Lippert–Mataga plot in case of the protic solvents, which indicates that hydrogen-bonding solvents have a different type of influence on the nature of the charge transfer state [46].

We have plotted the position of the emission band ($v_f \text{ cm}^{-1}$) vs hydrogen bonding parameter α [17,18,39,47] for protic solvents (Fig. 2b). The linear nature of the plot again supports that the red shifted CT band in protic solvents is influenced by the hydrogen bonding interaction. As seen in Fig. 2c, the plot of Stokes' shift vs. solvent polarity parameter $E_T(30)$ [48] generates two separate straight lines with different slope, one for the non-polar, polar aprotic solvents and the other for the polar protic solvents. This observation clearly infers that two types of interaction are present. Only dipolar interaction is effective in aprotic solvents, where both dipolar and hydrogen-bonding interactions are present in the protic solvents.

3.3. Effect of binary solvent mixture

To know the origin of CT state, we have measured the emission spectra of DMAPPDN in the binary solvent mixture of MCH and ethanol and are shown in Fig. 3a. With gradual addition of ethanol to MCH solution of DMAPPDA the emission maxima show a red shift from ~435 nm to ~485 nm (λ_{em}^{max} of DMAPPDN in EtOH 490 nm) with initial decreasing and then increasing of intensity after 30% of added ethanol. This observation indicates that the red shifted emission (CT) band originates from the LE state [19]. The emission intensity in both these solvents is almost equal due to comparable fluorescence quantum yield of DMAPPDN in both ethanol and MCH solvents (Table 1).

3.4. Effect of acid on steady state spectra of DMAPPDA

To support the phenomenon of intramolecular charge transfer reaction [18,20,25,44,47], the absorption and emission spectra were recorded in presence of acid. Addition of dilute sulfuric acid to the aqueous solution of DMAPPDN produces a blue shifted absorption band at ~302 nm with simultaneous decrease in intensity of the original absorption band at ~372 nm through an isosbestic point at ~332 nm (Fig. 3b). The blue shifted band at \sim 302 nm is generated from the protonated species of DMAPPDN. The emission spectral profile (Fig. 3c) with increasing sulfuric acid concentration produces a blue shifted emission band at ${\sim}425$ nm with progressive decrease in intensity of the original CT band and generates an isoemissive point at ${\sim}450$ nm. The emission band at 425 nm is thus assigned to the local emission of the protonated species of DMAPPDN. When acid was added, H⁺ ion prefers to bind to the lone pair of nitrogen of -NMe₂ group, which is then no longer available for charge transfer process in the excited state. As a result the intensity of the CT band decreases. However, even with high concentration of acid there is some intensity of the CT band. This may be due to the excited state deprotonation of the protonated DMAPPDN and generation of CT state in the excited state surface which can show normal red shifted CT emission. These observations support that the CT emission band is mainly due to



Fig. 3. (a) Emission spectra (λ_{ex} = 380 nm) of DMAPPDN in MCH + ethanol mixed solvent, (1 \rightarrow 9, % of EtOH = 0, 10, 15, 30, 40, 60, 70, 80, 90 respectively), Effect of dilute sulfuric acid on the (b) absorption spectra (inset shows absorbance vs pH plot) and (c) emission spectra (inset shows emission intensity vs pH plot) (λ_{ex} = 372 nm) of DMAPPDN in water at room temperature.

 $n \rightarrow \pi^*$ type of electronic transition. We have measured the absorption and emission spectra by using H₃PO₄—NaOH mixture at different pH and the spectral behavior was found to be similar to that of the effect of acid to DMAPPDN in aqueous solvent. Both the absorption and emission spectra were found to be invariant after pH 6.91, which indicates that base has no effect on the ICT process in this molecule. The variation of absorbance and emission intensity vs. pH are shown in inset of Fig. 3b and c, respectively. From both the graphs, it is clear that in acidic medium the absorbance and emission intensity increases linearly with the increase of pH of the medium. This infers that this molecule can be used as pH sensor in the acidic range.

3.5. Fluorescence quantum yield measurement

The observed fluorescence quantum yields of DMAPPDA at room temperature with variation of solvent polarity are presented in Table 1. The quantum yields for the CT emission in polar aprotic solvents are found to be higher than in the polar protic solvents. This observation indicates the existence of nonradiative decay channels by intermolecular hydrogen bonding interaction with protic solvents. We have also measured the fluorescence life time of the emissive species in different solvents by picosecond TCSPC instrument. It is found that the fluorescence decay times in different pure solvents are found to be too short to be measured with the picosecond TCSPC instrument. Extra flexibility may be the reason for so fast decay of the excited state.

3.6. Theoretical calculations

Theoretical computations have been performed at DFT level using B3LYP hybrid functional and 6-31+G(*d*,*p*) basis set to get the global minimum structure of the molecules. The optimized global minimum structure of DMAPPDN is shown in Scheme 2. In the ground state global minimum structure of DMAPPDN, the donor $-NMe_2$ [C_{13} - N_7 - C_1 - C_2 = -1.0893 (θ_1)] and acceptor $-(HC=CH)_2$ -CN [C_{21} - C_{10} - C_4 - C_3 = -0.0410 (θ_2)] are coplanar with that of the benzene ring. As a result there occurs an extensive resonance delocalization in the ground state. High ground state dipole moment (10.8 D) of the optimized structure suggests the unsymmetrical charge distribution in the ground state of DMAPPDN.

The molecules having twisted geometry of the amino donor group in their ground states prefer intense charge transfer emission [19]. The calculated geometry for DMAPPDN is found to be planer in the ground state. The angular dependency of the ground and two excited states energies can be obtained by the rotation of the donor and acceptor groups around the benzene plane. The ground state, first and second excited states potential energy curves along the twisted angle at the donor (θ_1) and acceptor (θ_2) groups both in vacuo and in ACN solvent are given in Figs. 4 and 5. The first two excited singlet states potential energy curves (PECs) were constructed using TDDFT and TDDFT-PCM model with B3LYP functional and 6-31+G(d,p) basis set in vacuo and ACN solvent, respectively. As seen in Fig. 4, the potential energy of the singlet ground state (S_0) in vacuo both for donor (Fig. 4a) and acceptor twisting (Fig. 4b) increase with increasing twist angle and reach a maxima at $\theta_1 \sim 90^\circ$. This is due to loss of delocalization of nitrogen lone pair through the benzene ring in the twist conformer. As seen in Fig. 4a, for donor twisting in vacuo, the nature of the S₁ and S₂ state surface are such that after excitation, the molecule easily transform from locally excited state to lowest energy charge transfer state through small barrier of 2.74 kcal/mol for S₁ and 6.68 kcal/mol for S₂ surface. Similarly, for acceptor twisting in vacuo, the potential energies barrier for transformation from LE to CT states are 0.83 kcal/mol and 14.17 kcal/mol for S₁ and S₂ states, respectively (Fig. 4b). In vacuo, for the conversion of LE to CT state, the acceptor twisting in the S₁ state is more favorable than donor twisting, due to less energy barrier for acceptor twisting in vacuo (0.83 kcal/mol) for S₁ state compared to the donor twisting in vacuo (2.74 kcal/mol) (Table 2). PECs has also been constructed in ACN solvent (Fig. 5) using the TDDFT-PCM model with same basis set and functional as mention before. The nature of PECs for the ground and excited states are similar with that of the vacuo except there is some difference in the energy barrier. All the absorption and emission energy and oscillator strength for experimental and theoretical calculations are presented in Table 3. For acceptor twist in vacuo, the computed absorption and emission energy [λ_{abs} = 378.7, λ_{em} = 449.4 nm] are well matched with that of the experimental values in MCH solvent [λ_{abs} = 380,



Fig. 4. Potential energy surface for the ground state, first and second excited singlet states of DMAPPDN with variation of twist angle (a) θ_1 for donor group rotation (b) θ_2 for acceptor rotation in vacuo. Inset shows the plot of variation of oscillator strength along twist coordinates.

 $\lambda_{\rm em}$ = 441 nm] (considered to be same as vacuo) as shown in Table 3. From the data presented in Table 3, it is clear that for ACN solvent acceptor twisting is more favorable compared to donor twisting motion. Theoretically, the more red shifted emission band in ACN solvent (490.3 nm for acceptor (Fig. 5b) and 533.2 nm for donor twist (Fig. 5a)) compared to the emission band in vacuo (449.4 nm for acceptor and 495.8 nm for donor twist) also supports that the emission band depends upon the solvent polarity which was also observed experimentally.

The HOMO-LUMO diagrams of DMAPPDN for optimized structure (normal form) and different twisted geometries in vacuo and ACN solvent are shown in Fig 6. In the global minima structure of DMAPPDN, the lone pair on the nitrogen atom of --NMe₂ group is more or less uniformly distributed over the entire π -system of the benzene chromophore for both the HOMO (π) as well as LUMO (π^*) . Therefore the HOMO to LUMO electronic transition is mainly $\pi \rightarrow \pi^*$ type and it is allowed transition with high oscillator strength (1.1909) (Table 3). On the other hand, for the donor twisted state (90° configuration) in vacuo, the electron density is mainly on the nitrogen atom and the HOMO (n) is a nonbonding orbital. On the other hand, in the twisted configuration, the electron density is located over acceptor group for the LUMO (π^*) orbital of DMAPPDN. Therefore, this is a $n \rightarrow \pi^*$ type forbidden transition with 0.000 oscillator strength. Due to twisting of the donor -NMe₂ group in vacuo, the nitrogen lone pair accumulated on the nitrogen atom due to non-conjugation with the benzene chromophore, and is available for transfer to the acceptor group. In the MO diagram for acceptor twisted form in vacuo, the HOMO is same



Fig. 5. Potential energy surface for the ground state, first and second excited singlet states of DMAPPDN with variation of twist angle (a) θ_1 for donor group rotation (b) θ_2 for acceptor rotation in ACN solvent. Inset shows the plot of variation of oscillator strength along twist coordinates.

Table 2													
Potential ene	rgy barrier	for	the	transformation	from	LE	to	СТ	state	on	S ₀ ,	S ₁ ,	S_2
surfaces in kc	al/mol.												

	Medium	S ₀ surface	S ₁ surface	S ₂ surface
Donor rotation	Vacuo	13.27	2.74	6.69
	ACN	15.06	4.56	5.27
Acceptor rotation	Vacuo	8.73	0.83	14.17
	ACN	10.60	2.03	13.95

as that of the optimized structure (Fig. 6a), but LUMO is different. Here HOMO to LUMO transition is $\pi_{\text{benzene}} \rightarrow \pi_{\text{acceptor}}$ type and it is a forbidden transition with oscillator strength 0.000. For donor twist geometry in vacuo and normal form in ACN solvent, the nitrogen lone pair is more localized (HOMO orbital) compared to localized HOMO orbital for the optimized normal structure and acceptor twisted structure in vacuo. In the donor twisted geometry in vacuo, the localized lone pair favors the CT process in the twisted decoupled state. In spite of symmetry forbidden nature of an $n \rightarrow \pi^*$ type transition, it is energetically generated through Frank Condon excitation, where as the CT state is generated from LE state through the crossing of a small potential energy barrier on the S₁ surface.

3.7. Effect of donor acceptor chain length on ICT process

Here the photophysical properties of DMAPPDN were compared with its analogous earlier reported without ethylene double

Table 3

Comparison of experimental spectral data with theoretical values of vertical transition energies (kcal/mol) of DMAPPDN in vacuo and ACN solvent using B3LYP hybrid functional and 6-31+G(d,p) basis set (ways of calculation are given in the experimental section).

Medium States		Absorption(kcal/mol))	Emission(kcal/mol)	Emission(kcal/mol)			
		$E_{ m th}$	Eexp	$E_{\rm th}^{\rm a}$	$E_{\rm th}{}^{\rm b}$	E_{exp}^{c}		
Vacuo	S ₁	75.50(1.191) [378.7] ^d	75.24 [380]	57.66(0.000) [495.8]	63.62(0.000) [449.4]	64.83 [441]		
	S_2	94.93(0.023) [302.9]	[]	86.05(1.356) [332.2]	100.35(0.044)			
ACN	S ₁	68.71(1.390) [416.1]	73.88 [387]	53.62(0.000) [533.2]	[284.9] 58.31(0.000)	56.84 [503]		
	S ₂	94.35(0.017) [303.0]		80.04(1.505) [357.2]	[490.3] 97.70(0.006) [292.6]			

Values in parenthesis are calculated oscillator strength.

 E_{th} is the calculated energy ($E_{\text{excited}} - E_{\text{ground}}$) at DFT level [B3LYP/6-31+G(d,p)].

 $E_{\rm exp}$ the experimental value.

^a Emission energy due to twisting of $-NMe_2$ group.

^b Emission energy due to twisting of –(CH=CH)₂–CN group.

 c E_{exp} , the experimental value in methylcyclohexane solvent.

^d Data with third bracket are absorption and emission energy in wavelength (nm).



Fig. 6. Molecular orbital pictures (HOMO and LUMO) of DMAPPDN for the (a) normal, (b) donor twisted, (c) acceptor twisted geometry in vacuo and (d) normal form in ACN solvent.

bond molecules 4-(N,N-dimethylaminobenzonitrile) (DMABN) [49-53] and with a single ethylene double bond molecules 4-(N,N-dimethylaminocinnamic acid) (DMACA) [21,54]. Till date there are no reports about the photophysical properties of 3-(4dimethylamino-phenyl)-acrylonitrile (DMAPAN). Therefore we have compared the ICT process in DMAPPDN with DMACA molecule instead of DMAPAN. In general with increasing distance between donor-acceptor group the absorption and emission bands become more red shifted from DMABN to DMAPPDN with one exception for emission spectra of DMACA in ACN solvents (Table. 4). Also the quantum yield and fluorescence life time decrease. This decrease in quantum yield and life time may be due to increase of nonradiative decay channel with increasing flexibility with in the molecule. The difference in dipole moment between the ground and excited state increases which mainly depends on the donor acceptor distance. As a result of more solvatochromic

Table 4

Spectroscopic parameters, quantum yield, dipole moment and life time of DMABN, DMACA and DMAPPDN in different solvents at room temperature for comparison of the ICT process with increasing donor acceptor chain length.

	Solvent	DMABN	DMACA	DMAPPDN
$\Delta \mu$ (Debye)		9.00 [49]	9.23 [54]	12.4
λ_{abs} (nm)	n-hept	320 [50]	353 [54]	378
	THF	320 [50]	363 [54]	389
	ACN	320 [50]	364 [21]	387
$\lambda_{\rm em} (\rm nm)$	n-hept	345 [50]	391 [54]	435
	THF	423 [50]	435 [54]	482
	ACN	469 [53]	460 [54]	503
Φ	n-hept	0.130 [50]	0.065 [54]	0.007
	THF	0.046 [50]	0.026 [54]	0.013
	ACN	0.022 [50]	0.020 [21]	0.016
$\tau(ps)$	H ₂ O	280 [51]	100 [54]	<100
	ACN	329 [52]	110 [54]	<100

 $\Delta\mu = \mu^* - \mu$, where μ^* and μ are ground and excited state dipole moments, respectively.

 Φ is the fluorescence quantum yield and τ is the fluorescence life time. References are given in parenthesis of each data.

shift and favorable ICT process was observed for DMAPPDN than its lower analogs.

4. Conclusion

In this work, the molecule DMAPPDN was synthesized, characterized and its photophysical behavior have been investigated by steady state spectroscopy in combination with quantum chemical calculations. The molecule DMAPPDN shows dual fluorescence corresponding to local and solvent polarity dependent CT emission. Additional flexibility favors Excited State Charge Transfer reaction and extremely fast excited state decay process. The high dipole moment of the excited state calculated by solvatochromic plot supports the charge transfer process in the excited state. The LE state relaxes to the twisted CT state, from which red-shifted emission band was generated and it is sensitive towards polarity and pH of the medium, hydrogen bonding ability of solvents. The large Stokes shift (\sim 8083 cm⁻¹), and large change in dipole moment from ground to excited states and highly favorable photoinduced intramolecular charge transfer process in DMAPPDA make a way for its use as pH sensor, electroluminescence devices, solar cells, chemical sensor and electro optical switches. The potential energy surfaces in vacuo and solvent along both the donor and acceptor twist coordinates have been constructed using DFT methods. Theoretical calculations also predict well the polarity dependence of the red shifted emission band.

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References

- [1] R.Y. Lai, E.F. Fabrizio, L. Lu, S.A. Jenekhe, A.J. Bard, J. Am. Chem. Soc. 123 (2001) 9112.
- [2] X.B. Sun, Y.Q. Liu, X.J. Xu, C.H. Yang, G. Yu, S.Y. Chen, H.Z. Zhao, F.W. Qiu, Y.F. Li, D.B. Zhu, J. Phys. Chem. B 109 (2005) 10786.
- [3] C. He, Q. He, Y. He, Y. Li, F. Bai, C. Yang, Y. Ding, L. Wang, J. Ye, Solar Energy Mater. Solar Cells 90 (2006) 1815.
- [4] Y.H. Kim, D.W. Cho, M. Yoon, D. Kim, J. Phys. Chem. 100 (1996) 15670.
- [5] R. Hayashi, S. Tazuke, C.W. Frank, Macromolecules 20 (1987) 983.
- [6] S. Ghosh, N. Guchhait, ChemPhysChem. 10 (2009) 1664.
- [7] C. Rulliere, Z.R. Grabowski, J. Dobkowski, Chem. Phys. Lett. 137 (1987) 408.
- [8] E. Lippert, W. Luder, F. Moll, H. Nagele, H. Boos, H. Prigge, I. Siebold-Blankenstein, Angew. Chem. 73 (1961) 695.
- [9] Z.R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, J. Lumin. 18 (1979) 420.
- [10] J. Catalan, C. Diaz, V. Lopez, P. Perez, R.M. Claramunt, J. Phys. Chem. 100 (1996) 18392.
- [11] W. Schuddeboom, S.A. Jonker, J.M. Warman, U. Leinhos, W. Kuhnle, K.A. Zachariasse, J. Phys. Chem. 96 (1992) 10809.
- [12] K.A. Zachariasse, M. Grobys, Th. Von der Haar, A. Hebecker, Yu.V. Il'ichev, Y.B. Ziang, O. Morawski, W. Kuhnle, J. Photochem. Photobiol. A: Chem. 102 (1996) 59.
- [13] K.A. Zachariasse, M. Grobys, Th. Von der Haar, A. Hebecker, Yu.V. Il'ichev, O. Morawski, I. Ruckert, W. Kuhnle, J. Photochem. Photobiol. A: Chem. 105 (1997) 373.
- [14] A.L. Sobolcwski, W. Domcke, Chem. Phys. Lett. 259 (1996) 119.
- [15] K. Rotkiewicz, K.H. Grellmann, Z.R. Grabowski, Chem. Phys. Lett. 19 (1973) 315.
- [16] Z.R. Grabowski, K. Rotkiewicz, A. Siemiarezuk, D.J. Cowley, W. Baumann, Nouv. J. Chim. 3 (1979) 443.
- [17] A.B.J. Parusel, W. Rettig, W. Sudholt, J. Phys. Chem. A 106 (2002) 804.
- [18] A. Chakraborty, S. Kar, N. Guchhait, Chem. Phys. 324 (2006) 733.
- [19] Z.R. Grabowski, K. Rotkiewicz, W. Rettig, Chem. Rev. 103 (2003) 3899.
- [20] A. Chakraborty, S. Kar, N. Guchhait, J. Photochem. Photobiol. A 181 (2006) 246.
- [21] T.S. Singh, N.S. Moyon, S. Mitra, Spectrochem. Acta Part A 73 (2009) 630.
- [22] P.R. Bangal, S. Panja, S. Chakravorti, J. Photochem. Photobiol. A: Chem. 139 (2001) 5.

- [23] A. Chakraborty, S. Ghosh, S. Kar, D.N. Nath, N. Guchhait, J. Mol. Struct. 917 (2009) 148.
- [24] T.S. Singh, S. Mitra, J. Lumin. 127 (2007) 508.
- [25] A. Chakraborty, S. Kar, N. Guchhait, Chem. Phys. 320 (2006) 75.
- [26] R.B. Singh, S. Mahanta, S. Kar, N. Guchhait, J. Lumin. 128 (2008) 1421.
- [27] S. Ghosh, A. Chakraborty, S. Kar, N. Guchhait, J. Lumin. 129 (2009) 482.
- [28] S. Jana, S. Ghosh, S. Dalapati, N. Guchhait, Spectrochem. Acta Part A 78 (2011) 463.
- [29] B.K. Paul, A. Samanta, S. Kar, N. Guchhait, J. Lumin. 130 (2010) 1258.
- [30] S. Jana, S. Dalapati, N. Guchhait, in: H. Pal, H.P. Upadhyaya, S. Nath, A.K. Pathak, et al. (Eds.), Proc. of 3rd Asia Pacific Symposium on Radiation Chemistry and DAE-BRNS 10th Biennial Trombay Symposium on Radiation and Photochemistry, India, 2010, p. 169.
- [31] M.J. Frisch, et al., Gaussian 03, Revision B.03, Gaussian, Inc., Pittsburgh, PA, 2003.
- [32] C.J. Jodicke, H.P. Luthi, J. Am. Chem. Soc. 125 (2003) 252.
- [33] A. Morimoto, L. Biczok, T. Yatsushasi, T. Shimada, S. Baba, H. Tachibana, D.A. Tryk, H. Inoue, J. Phys. Chem. A 106 (2002) 10089.
- [34] G. Kohler, K. Rechthaler, K. Rotkiewicz, W. Retting, Chem. Phys. 207 (1996) 85.
- [35] C.J. Jamorskia, H.P. Luthi, J. Chem. Phys. 119 (2003) 12852.
- [36] C.J. Jamorski, M.E. Casida, J. Phys. Chem. B 108 (2004) 7132.
- [37] S. Dhar, S. Singha Roy, D.K. Rana, S. Bhattacharya, S. Bhattacharya, S.C. Bhattacharya, J. Phys. Chem. A 115 (2011) 2216.
- [38] E.A. Perpete, V. Wathelet, J. Preat, C. Lambert, D. Jacquemin, J. Chem. Theory Comput. 2 (2006) 434.
- [39] A. Chakraborty, S. Kar, D.N. Nath, N. Guchhait, J. Phys. Chem. A 110 (2006) 12089.
- [40] C.C. Dubroca, S.A. Lyazidi, P. Cambou, A. Peirigua, Ph. Cazeau, M. Pesquer, J. Phys. Chem. 93 (1989) 2347.
- [41] Y. Kim, M. Yoon, Bull. Korean Chem. Soc. 19 (1998) 980.
- [42] C.C. Gude, W. Rettig, J. Phys. Chem. A 102 (1998) 7754.
- [43] S. Kapelle, W. Rettig, R. Lapouyade, Photochem. Photobiol. Sci. 1 (2002) 492.
- [44] S. Mahanta, R.B. Singh, S. Kar, N. Guchhait, J. Photochem. Photobiol. A: Chem. 194 (2008) 318.
- [45] N. Mataga, H. Chosrowjan, S. Taniguchi, J. Photochem. Photobiol. C: Photochem. Rev. 6 (2005) 37.
- [46] R.W. Taft, M.J. Kamlet, J. Am. Chem. Soc. 98 (1976) 2886.
- 47] S. Sumalekshmy, K.R. Gopidas, J. Phys. Chem. B 108 (2004) 3705.
- [48] C. Reichardt, Chem. Rev. 94 (1994) 2319.
- [49] E. Lippert, Z. Naturforsch. 10A (1955) 541.
- [50] N. Chattopadhyay, J. Rommens, M.V. der Auweraer, F.C. De Schryver, Chem. Phys. Lett. 264 (1997) 265.
- [51] Khader A. Al-Hassan, Uwe K.A. Klein, A. Suwaiyan, Chem. Phys. Lett. 212 (1993) 591.
- [52] K.A. Zachariasse, Th. Von der Haar, A. Hebecker, W. Kuhnle, U. Leinhos, Pure Appl. Chem. 65 (1993) 1745.
- [53] T. Atsbeha, A.M. Mohammed, M. Redi-Abshiro, J. Fluoresc. 20 (2010) 1241.
- [54] P.R. Bangal, S. Chakravorti, J. Photochem. Photobiol. A: Chem. 116 (1998) 191.