

# Pyrrolidinyl Group as Charge Donor for the Excited State Intramolecular Charge transfer in 3-(4-methoxyphenyl)-1-(4-(pyrrolidin-1-yl) phenyl) Prop-2-en-1-one

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**Abstract:** The absorption and steady state emission properties of a chemically synthesized chalcone, 3-(4-methoxyphenyl)-1-(4-(pyrrolidin-1-yl) phenyl) prop-2-en-1-one (MPPP) containing asymmetrical donor and acceptor groups has been investigated both experimentally and theoretically. The ground state, MPPP has a significant intramolecular charge transfer (ICT) character and a great sensitivity to the hydrogen bond donating ability of the medium as reflected from the absorption spectra in pure non polar, polar and neutral solvents. On the other hand, its excited singlet state exhibits high ICT characters as manifested by the drastic solvatochromic effects. These results are consistent with the data. The absorption spectra of the compound MPPP undergoes minor changes with increasing polarity of the solvents and the fluorescence spectra experiences a distinct bathochromic shifts in the both position and fluorescence quantum yields, increases reaching a maximum before decrease with increasing the solvent effects. The quantum yields decrease with increase in the solvent polarity. The magnitude of change in the dipole moment was also calculated using Austin Model 1 (AM1). These results suggest that the evidence about the intramolecular charge transfer in the emitting singlet state of this compound. The solvent dependence of quantum yields of MPPP was interpreted on the basis of positive and negative solvatokinetic as well as hydrogen bonding effects. Intramolecular charge (ICT) transfer took place from pyrrolidine nitrogen to  $\alpha$ ,  $\beta$  unsaturated carbonyl in the ground state.

**Keywords:** Chalcone, Solvatokinetic, Intramolecular charge transfer, Dipole moment, AM1 method.

## 1. INTRODUCTION

The photophysical properties of organic molecules has achieved a significant importance in recent times owing the wide applications in various fields [1]. Fluorescence spectroscopy is the most widely used technique in the area of cellular biology and biomedical to understand the microenvironment of molecular assemblies of macromolecules and more recently even in pollution control [2, 3]. Although, large number of fluorescent molecules has been developed yet search is still under way. The fluorophore thus developed should have easy to synthesize and good photophysical properties because on photoexcitation, redistribution of electronic charges at each atom (especially on the acid and basic centers) of the molecule does take place. Moreover, on photoexcitation, fluorophores containing both an electron donor and an electron acceptor exhibit an internal charge-transfer (ICT) state or twisted internal charge transfer (TICT) state [4]. Thus, the organic molecule having intramolecular charge transfer (ICT) properties are of continuing theoretical and experimental interest.

Chalcones, the biochromophoric molecules separated by a keto-vinyl chain, constitute an important class of privileged structure that has a wide range of biological properties [5]. Chalcones are widely used for various optical applications such as optical substances, photorefractive polymers [6], holographic recording materials and fluorescent probes for sensing of metal ions [7, 8], biological macromolecules [9, 10], and microenvironment in micelles [11]. Therefore, studies of the photophysical properties of chalcones have significant importance [12-15]. In the last decades, several studies were done on substituted enone derivatives with different bridge structures in various polar solvents because substituted enone derivatives are very effective photoinitiators. Various groups have studied photophysical properties of substituted chalcones involving mostly asymmetric donor-acceptor (D/A) chalcones [16] and to a lesser extent symmetrical donor acceptor chalcones [17, 18]. In such system, carbonyl group acts as acceptor while substituted phenyl group act as donor. Such D/A molecules are good example in which very large changes in charge distribution can be induced in the excited state upon absorption of light photons. This phenomena leads to large generation of dipole (due to photoinduced intramolecular charge transfer, ICT). This results in a strong interaction with the surrounding medium to cause not only solvent reorganization but also some time to structural rearrangement in the solute itself.

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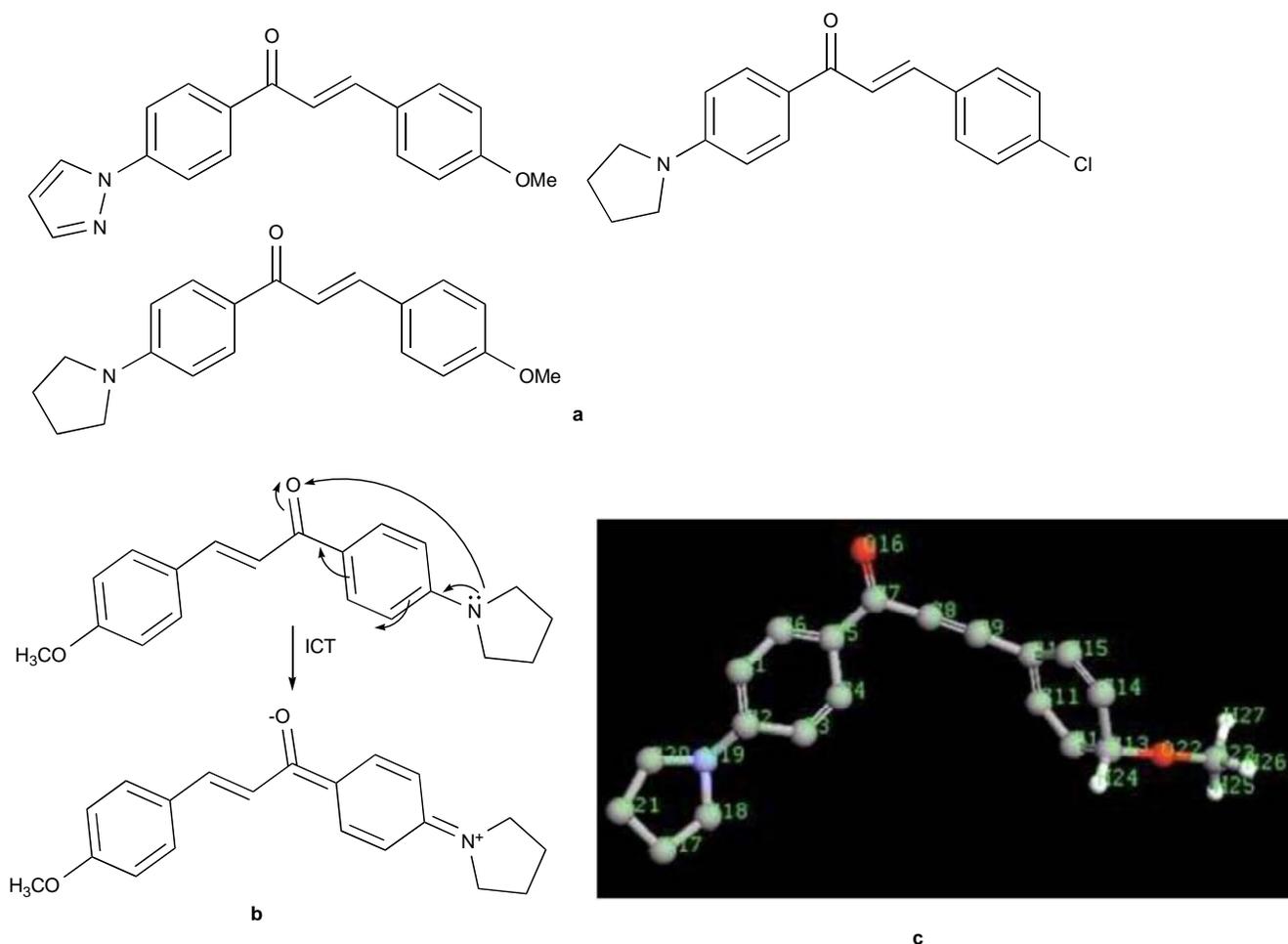
Our research effort is focused on synthesis, characterization and evaluation of various substituted chalcones for their antimalarial and antifilarial activity [19, 20]. To diversifying our research interest, we initiated photophysical properties of some of the chalcones synthesized in our laboratory. We choose bichromophoric systems for the study of photoinduced electron transfer which has an immense application in the area of photophysics, photochemistry, polymer physics, optics technology and laser physics [21]. We choose three chalcones viz. 3-(4-Chloro-phenyl)-1-(4-pyrazol-1-yl-phenyl)-propenone (CPPP-1), 3-(4-Chloro-phenyl)-1-(4-pyrrolidin-1-yl-phenyl)-propenone (CPPP-2), 3-(4-Methoxy-phenyl)-1-(4-pyrrolidin-1-yl-phenyl)-propenone (MPPP), for fluorescence studies (Figure 1a). Among all three, only one compound MPPP had shown fluorescence. In this paper, we described the ground state and excited state intramolecular charge transfer (ICT) characteristics of 3-(4-methoxyphenyl)-1-(4-(pyrrolidin-1-yl) phenyl) prop-

2-en-1-one (MPPP) (Figure 1b) in various solvents containing donor and acceptor in the same molecule. The optimized molecular structure is shown in (Figure 1c). We have used experimental and theoretical methods.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials and Methods

Synthesis and characterization of the MPPP is reported elsewhere [19, 20]. Briefly, the compound 3-(4-methoxyphenyl)-1-(4-(pyrrolidin-1-yl) phenyl) prop-2-en-1-one was synthesized by the Claisen-Smith condensation procedure. To a solution of 4-fluoroacetophenone (5.12 gm, 40 mmol) in 5 ml anhydrous DMF, pyrrolidine (2.84 gm, 40 mmol) and  $K_2CO_3$  (6.9 gm, 50 mmol) were added. The reaction mixture was refluxed for 18hs at 110 °C. On completion, as checked by thin layer chromatography (TLC), the DMF was evaporated in vacuo and re-



**Figure 1:** a: Structure of various chalcone analogs.

**b:** Molecular structure and intramolecular charge transfer process in MPP.

**c:** Optimized molecular structure of MPPP by AM1 method using Argus Lab software.

dissolved into water (50 ml). The aqueous solution was extracted with chloroform (3 x 50 ml) and the combined organic solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo to yield crude 4-pyrrolidine acetophenone. The intermediate was purified by flash column chromatography and characterized by mass (Macromass G spectrophotometer) and NMR prior to use in the next step. The remaining other two intermediates were prepared by the similar method.

To a stirred solution of column purified 4-pyrrolidine acetophenone (1.13 gm, 6 mmol) and 4-methoxy benzaldehyde (0.816 gm, 6mmol) in a minimum amount of methanol (normally 10ml), NaOH pellets (600 mg) were added at 0 °C. The reaction mixture was allowed to draw closer to room temperature and stirred for 18-20 hrs. Appearance of off-white to yellow solids in solution within few minutes to several hours indicated successful synthesis of chalcone. The product was filtered and washed with ice cold water (3 x 10 ml). The title compound was purified by column chromatography using chloroform, methanol as eluent. The remaining other two substituted 1, 3-diarylpropenone were prepared by the similar method.

## 2.2. Chemicals and Instruments

Chemicals and solvents used for the synthesis were procured from Sigma-Aldrich, Spectrochem India Pvt. Ltd and were used without further purification. HPLC grade solvents were used for spectroscopic studies. UV-vis spectra were recorded on Carry 100 Bio Varian EL 0010386 and emission spectra were recorded on a Shimadzu RF-5301 PC Fluorospectrophotometer using cuvette of 1.0 cm path length. Austin Model 1 (AM1) method was used to calculate the ground state dipole moment.

## 3. RESULTS AND DISCUSSION

### 3.1. Preparation of the Compound

Stock solution of the compound MPPP (1 X 10<sup>-3</sup> mol L<sup>-1</sup>) in various solvents viz. Methanol, acetone, acetonitrile, 1, 4-dioxane, THF, DMF, DMSO, carbon tetrachloride and ethyl acetate were prepared for all spectral studies. All solvents were checked for any emission in the desired wavelength before fluorescence studies.

### 3.2. Effect of Solvents on the Absorption and Fluorescence Spectra

The UV-visible absorption and fluorescence spectra of MPPP were analyzed in various non polar, polar and neutral organic solvents viz. acetonitrile, ethyl acetate, carbon tetra chloride, THF, DMF, DMSO, acetone, methanol, 1,4-dioxane, and the corresponding spectroscopic data are collected in Table 1. For UV-Visible absorption and fluorescence maxima measurements, the concentration was taken 1X 10<sup>-6</sup> M in all solvents.

#### 3.2.1. Absorption Spectra

We recorded the absorption spectra of MPPP in neutral, polar and hydrogen bonding organic solvents (Figure 2) and spectroscopic values are summarized in Table 1. It is apparent from the absorption spectra that the compound MPPP in all solvents except in THF showed two absorption bands in the region of ~250-297 nm with higher intensities and ~314-393 nm with lower intensities respectively while the same compound showed single band at 314 nm in THF. These absorption spectra of MPPP in different solvents attribute the charge transfer from pyrrolidine moiety to

**Table 1: Absorbance and Emission Parameters of MPPP in Different Organic Solvents**

Solvents	$\lambda_{abs}$ (nm)	$\lambda_{flu}$ (nm)	$\nu_{abs}$ (cm <sup>-1</sup> )	$\nu_{flu}$ (cm <sup>-1</sup> )	$\nu$ (cm <sup>-1</sup> )
Dioxane	368	466	27173	21459	5714
Carbon Tetra Chloride (CCl <sub>4</sub> )	297, 348,375	460,455	28735	21739,21978	6996,6757
Tetra Hydro Furan (THF)	314	468	31847	21367	10480
Acetonitrile	296,368,379	481	27173	20790	6383
Ethylacetate	378	469	26455	21321	5134
Methanol	395	484	25316	20661	4655
Acetone	378	472	26455	21186	5269
DMF	248,387	467	25839	21413	4426
DMSO	301,393	476	25445	21008	4437

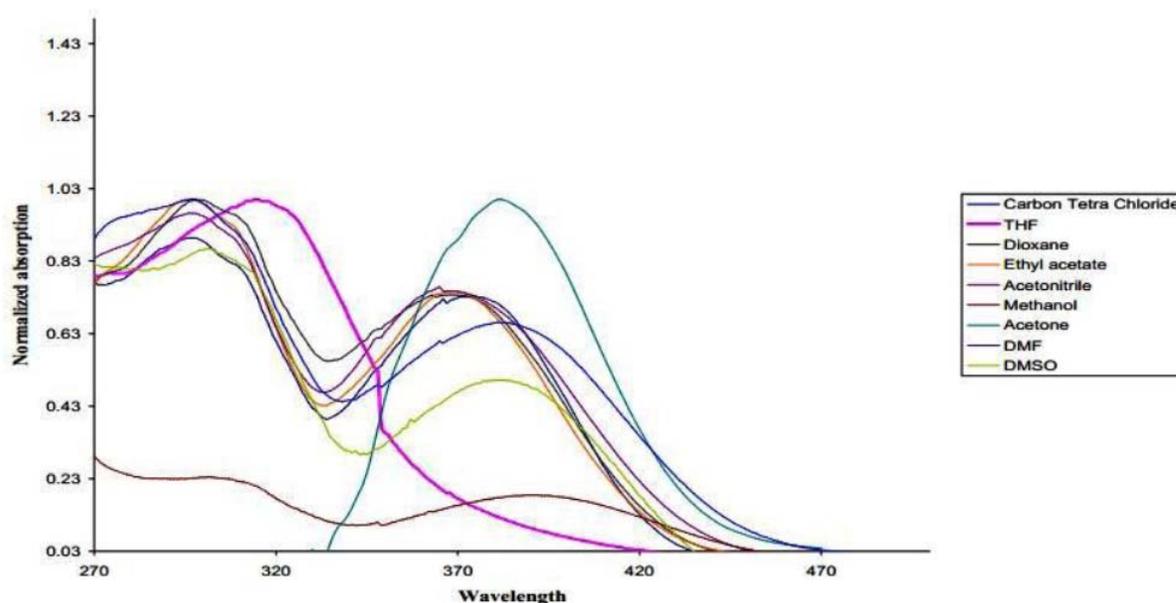
$\alpha$ ,  $\beta$  unsaturated carbonyl in the ground state. It is documented that absorption maxima of lower wavelength such as  $\sigma \rightarrow \sigma^*$  transition with higher intensities is independent of solvent polarity while higher wavelength (lower energy) absorption maxima such as  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  (with lower intensities) depend on solvent polarity as well as hydrogen bonding efficiency of solvent [22]. Absorption spectrum of MPPP in methanol showed two bands viz. longer wavelength (LW) with a maximum at  $\sim 393$  nm and a shorter wavelength band (SW) at  $\sim 248$  nm. The SW band is ascribed as  $\pi - \pi^*$  transition of the pyrrolidine substituted benzoid system whereas the LW bands can be attributed to  $\pi - \pi^*$  transition of the, unsaturated carbonyl of MPPP [23, 24]. These two bands in absorption spectrum can be assigned to the transition from ground ( $S_0$ ) to  $S_2$  ( $L_b$ ) and  $S_1$  ( $L_a$ ) states from Platt's notation [25, 26].

Moreover, the compound showed bathochromic shift of higher wavelength absorption band (lower energy) in polar solvent like methanol suggesting the possibility of intermolecular hydrogen bonding in ground state ( $S_0$ ) between nitrogen of pyrrolidine, and acidic proton of methanol, thus provides higher stability of the solute solvent complex in the ground state [25]. (Figure 2) Carbon tetrachloride being a non polar solvent cannot accept proton but showed the absorption band at  $\sim 375$  nm similar to the polar solvents which have tendency to accept proton. We assume that there must be trace amount of water is present in solvent, resulted intermolecular hydrogen

bonding with pyrrolidine nitrogen of the compound [26, 27]. This hydrogen bonding gave rise to bathochromic shifts. Further, solvents like Dioxane, DMF, acetone and ethyl acetate have high hydrogen bond accepting capability than the methanol [27]. Dioxane being less polar solvent showed absorption band at  $\sim 368$  nm, while absorption band is shifted around  $\sim 17$  to 25 nm in more polar solvent like in DMF (387 nm) and in DMSO (393 nm).

Methanol and DMSO showed absorption band at approximately  $\sim 395$  nm, though methanol is less polar than DMSO. This anomaly can be explained by the fact that methanol, having intermolecular hydrogen bonding property showed intermolecular hydrogen bonding with pyrrolidine nitrogen as well as carbonyl oxygen, that is responsible for higher stability of the solute-solvent system in ground state resulted shifting in band position.

In THF, MPPP showed single absorption band around 314 nm because the nature of solvated electrons is significantly different in THF than other polar solvents. This difference is due to the presence of many preexisting attractive solvent cavities that are inherent in THF. Due to the dislike character of THF solvent molecules are unable to pack efficiently, thus crating spatial voids. This difference in absorption maxima of THF can also be explained that there is large conformational disorder due to the different groups is involved in solvation in THF than other solvent [28].



**Figure 2:** Normalized absorption spectra of MPPP in various solvents; carbon tetra Chloride, Tetrahydrofuran, 1, 4-Dioxane, Ethyl acetate, acetonitrile, MeOH, acetone, DMF and DMSO.

### 3.2.2. Fluorescence Spectra

We recorded the fluorescence emission spectra of MPPP in various solvents as shown in Figure 3 and observed band maxima are listed in Table 1. MPPP showed single emission wavelengths in between 455-484 nm depending on solvent polarities. Unlike absorption spectra, emission spectrum bands are broad, in the large visible region and more sensitive to solvents which suggest that greater charge transfer in solute-solvent complex takes place in excited state [24].

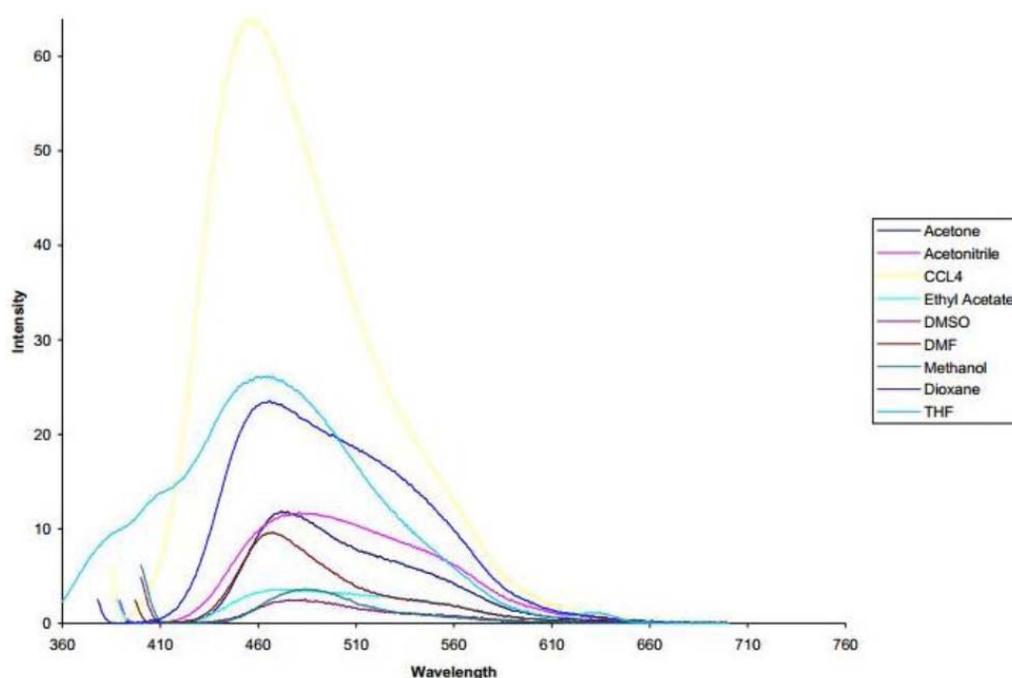
It is apparent that fluorescence spectrum shows bathochromic shifts as solvent polarity is increased. The red shift in the emission maximum from 455 nm in carbon tetrachloride to 484 nm in methanol clearly suggested that MPPP possess significant intramolecular charge transfer resulting in intramolecular polarization in the excited state due to  $\pi-\pi^*$  transition, since it contain both electron donor groups such as pyrrolidine group and electron acceptor methoxy group. This suggests that MPPP is significantly solvated in the S1 excited state, resulted in a large dipole moment difference between the S1 excited state and the ground state [26].

This fluorescence band can be assigned to transition involving the whole electronic system of the compounds with a considerable charge transfer (CT) character. Such a CT originates from the nitrogen to

the carbonyl group which is characterized by a higher electron accepting character, it means this visible band occur due to intramolecular charge transfer (ICT) [22].

A large red shift in the emission band maxima reflects the greater delocalization of the cloud of the carbonyl group and the lone pair of nitrogen of pyrrolidine moiety with the aromatic moiety. In solvents more polar than carbon tetra chloride and ethyl acetate, the emission maxima shift to the longer wavelength (red shift).

The fluorescence intensity is maximum in CCl<sub>4</sub> which is a non-polar solvents, thus molecule shows a high intramolecular charge transfer state which is stabilized by polar and non polar solvents. In this case, the donor group is nitrogen of aromatic moiety of the molecule, and the acceptor is carbonyl group similar to that absorption spectra. Contrary to the non hydrogen bonding solvents (Dioxane, THF, EA) the emission spectra of MPPP are more red shifted (484 nm) in hydrogen bonding solvent (methanol) Figure 3. This change in spectra is due to the formation of donor-acceptor complex in alcoholic solution. The fluorescence spectrum in each solvent is broader, that is having a broader full width at half the maximum height (FWHM). The FWHM of the fluorescence spectra increases in the polar solvents. Comparing with other studied system, we have assigned the lower energy emission band to the emission from the charge transfer (CT) state [25]. It is found that the peak positions of the



**Figure 3:** Fluorescence spectra of MPPP in different organic solvents.

emission bands are independent of excitation wavelength over a large range of absorption band. The excitation spectra of both the bands are independent of emission wavelength and agree reasonable with the absorption spectrum. So we can say that only one species is present in the ground state and the Charge transfer (CT) band is generated through the Lower energy (LE) state.

Unlike the absorption spectra, the fluorescence spectra of MPPP in basic (aprotic) solvent such as dioxane, exhibits dual emission band as shown in Figure 3. The excitation spectra exhibit a broad band at around ~368nm and a small shoulder at ~540 nm indicating the presence of two moieties in ground state. While in other basic solvents like ethyl acetate and DMF, fluorescence spectra showed single broad peak of less intensity unlike two intense bands in absorption spectra. Based on these observations we conclude that only one moiety is active in ground state of MPPP.

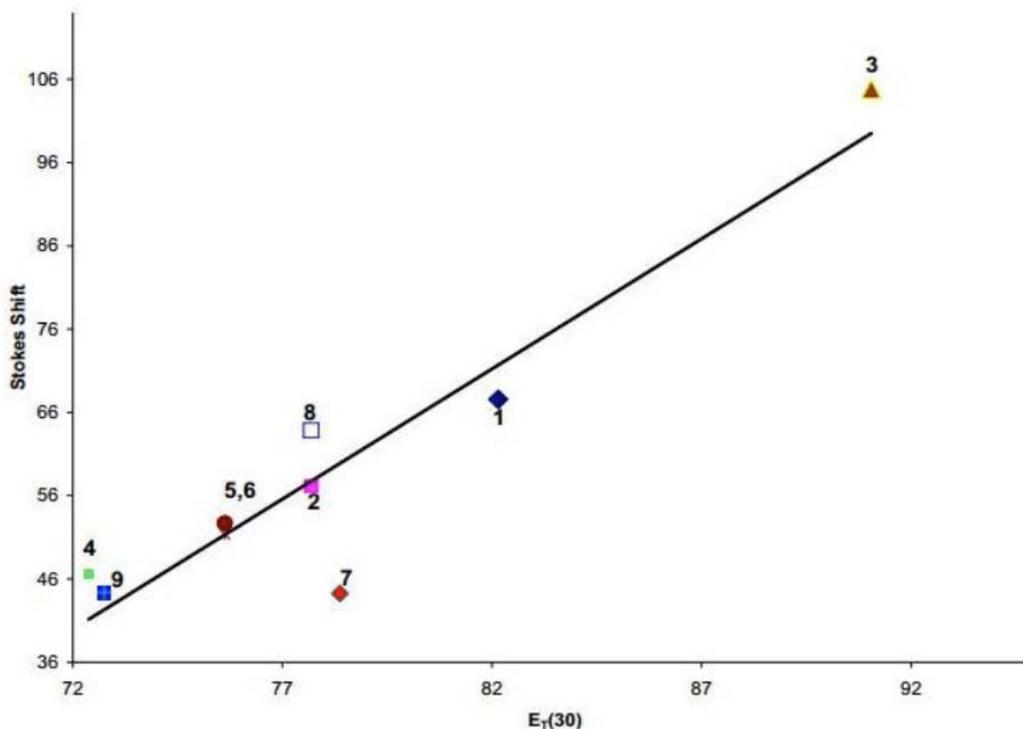
A qualitative analysis of the red shift of lower energy emission band indicated that the emissive species must possess high dipolar character [10]. In methanol, the emission maxima was maximum and markedly shifted to the red region than the other solvents, this indicate that MPPP's excited state is more polar than the ground state.

### 3.3. Stokes Shift

The fluorescence spectrum was exploited to establish correlation between peak wave numbers of fluorescence spectra and the empirical Dimorth polarity parameter  $E_T(30)$  of the solvents [14] as shown in Figure 4 and calculated  $E_T(30)$ , normal  $E_T$  and fluorescence quantum yield shown in Table 2. Figure 4 shows excellent linear correlation in case of solvent like DMSO, ethyl acetate, acetone, dioxane. However, a little deviation from linearity of Stokes shifts versus  $\Delta f$  in protic solvents like methanol; acetonitrile and THF were also seen. The maximum deviation was observed in DMF. This suggested that some additional factors affecting the system, thus making it non-linear.

In general, protic solvents have a nature to form intermolecular hydrogen bonded complex and the weak hydrogen bonding interaction significantly influences the properties in the ground state as well as in the excited state.

In earlier studies [29], it was explained that aromatic amines present in the molecules show a large departure from the linearity for the protic solvents due to the formation of hydrogen bond between protic solvents and lone pair electron of amino group in  $S_0$  state, but in excited state this bond break down due to



**Figure 4:** Graph between peak wave number ( $\Delta\nu$ ) and Dimorth Polarity parameter  $E_T(30)$ ; (1) carbon tetra Chloride, (2) 1, 4-Dioxane, (3) Tetrahydrofuran, (4) MeOH, (5) Ethyl acetate, (6) acetone, (7) DMF, (8) Acetonitrile and (9) DMSO.

Table 2: Dimorph Polarity Parameter and Fluorescence Quantum Yield

Solvents	$E_T(30)$	$E_T(\text{normal})$	$\rho_f$	$\Delta f$
Dioxane	77.69	77.48	0.50	0.0294
Carbon Tetra Chloride (CCl <sub>4</sub> )	82.15	82.09	0.32	0.0112
Tetra Hydro Furan (THF)	91.05	90.85	0.087	0.2088
Acetonitrile	77.69	77.48	0.02	0.3049
Ethyl acetate	75.63	75.63	0.004	0.1996
Methanol	72.38	72.17	0.019	0.3088
DMF	78.37	73.79	0.025	0.2752
DMSO	72.75	72.63	0.029	0.2632

the formation of reverse hydrogen bonding i.e., between amino proton and lone pair of protic solvent. This straight line formation in case of  $E_T(30)$  parameters reflects a dispersive and specific interaction in these parameters [30]. Non linearity in case of solvents like DMF, acetonitrile, THF and methanol showed deviation.

The linear correlation between  $E_T$  values and Stokes shift ( $\Delta\nu$ ) are in good agreement with an extensive intramolecular charge transfer upon excitation of the molecule. Moreover, polarizability scale can also be represented as a function of refractive index i.e.  $(n^2-1)/(2n^2+1)$  [31] as shown in

Figure 5. Thus electron redistribution of electrons generates the spectral shift Figure 5. The graph shows that MPPP possesses a strong intramolecular charge transfer by increasing polarization in its excited state.

### 3.4. Fluorescence Quantum Yield

Compound showed fluorescence in all studied solvents, the intensity was maximum in acetone. The fluorescence quantum yields ( $\phi_s$ ) of MPPP in solvent of different polarities were calculated using the following equation [32]. 2-Amino pyridine in 0.1M H<sub>2</sub>SO<sub>4</sub> was used as standard reference,  $\phi_r = 0.60$  [33]

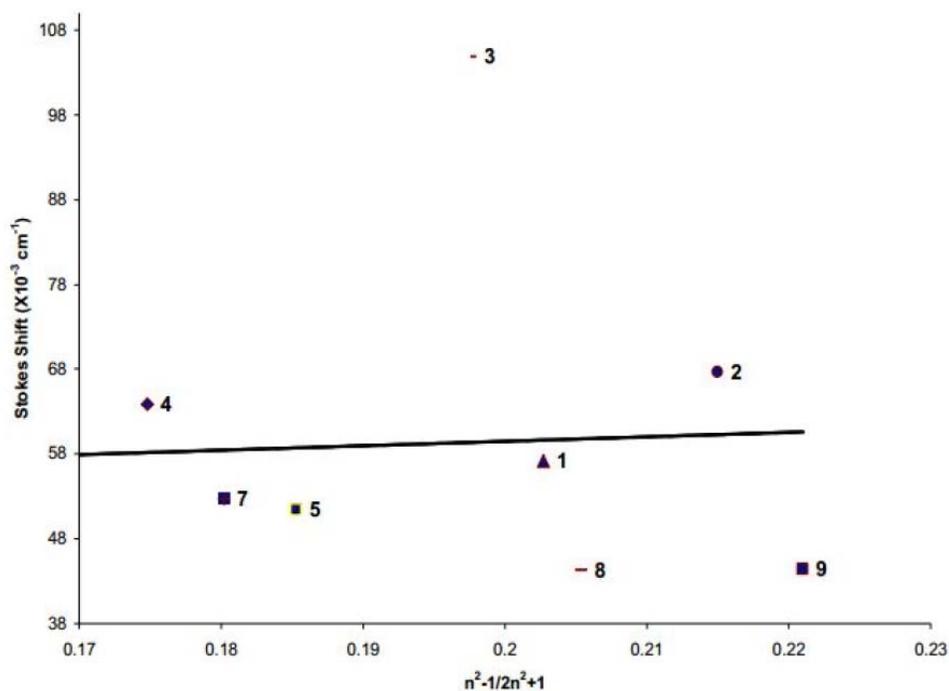


Figure 5: Graph between peak wave number  $\Delta\nu$  ( $\times 10^3\text{cm}^{-1}$ ) and index of refraction; (1) 1, 4-Dioxane, (2) carbon tetra Chloride, (3) Tetrahydrofuran, (4) Acetonitrile.

$$\phi_s = [(A_r F_s n_s^2 / (A_s F_r n_r^2))] \phi_r \quad (1)$$

Where A is absorbance at the excitation wave length, F the integrated emission area and n the refraction index of the solvents used. Subscripts refer to the reference (r) or sample (s) compound.

The fluorescence quantum yields ( $\phi_s$ ) depends strongly on the solvent polarity and the acceptor strength of the keto-phenyl group (Table 2) [26].

MPPP shows significant quantum yield ( $\phi_s$ ) which depends on solvent polarity, acidity and basicity of the solvents as shown in Table 2. Figure 6 represents a relationship between  $\phi_s$  and the solvent polarity parameter  $E_T(30)$ . It is clear from the Figure 6 that the fluorescent quantum yield increases with the increasing the solvent polarity from  $\text{CCl}_4$  to dioxane, reaching to its maximum in 1, 4 dioxane. Further, increase in solvent polarity leads to a dramatic decrease in quantum yield, which is very less in case of ethyl acetate. As we know that solvent ethyl acetate, DMF and acetone have high bond accepting capability, thus these solvents can either accept or donate hydrogen from pyrrolidine nitrogen of MPPP. A very efficient electron transfer from ethyl acetate to MPPP in excited state is responsible for the very low  $\phi_s$  [14].

Based on previous photophysical studies, two mechanisms had been proposed for substituted chalcones to explain the increase or decrease in

quantum yield of fluorescent compound by changing the solvent polarity [34]. The “Negative solvatokinetic effect” explains an increase in the fluorescence yield  $\phi_s$  with a suitable enhancement of the ICT character. Several suggestions have been given such as, ‘proximity effect’, ‘biradicaloid charge transfer’ and ‘conformational changes’ to explain “Negative solvatokinetic effect”. Thus, solute-solvent complexes formed in the ground state results in an effective non-radiative loss and quenching of the MPPP fluorescence occur in excited state due to hydrogen bond interaction [35]. Further, a decrease in the fluorescence quantum yield by strong ICT falls under “Positive solvatokinetic effect”. Thus, both “Negative and Positive solvatokinetic effect” have significant contributions on MPPP fluorescence quantum yields. Therefore, as solvent polarity changes from  $\text{CCl}_4$  to 1, 4-dioxane, fluorescence quantum yields increases (0.32 to 0.50) as it is governed by “Negative solvatokinetic effect. However, in solvent with higher polarity from THF to methanol, the fluorescence quantum yields decreases (0.087 to 0.019) due to strongly intramolecular charge transfer (ICT), i.e. “Positive solvatokinetic effect”. It can be attributed from second mechanism that a strong ICT interaction occurs between solute and solvent [34].

### 3.5. Solvatochromasim

The UV-vis and fluorescence spectral results of MPPP in various organic solvents are summarized in

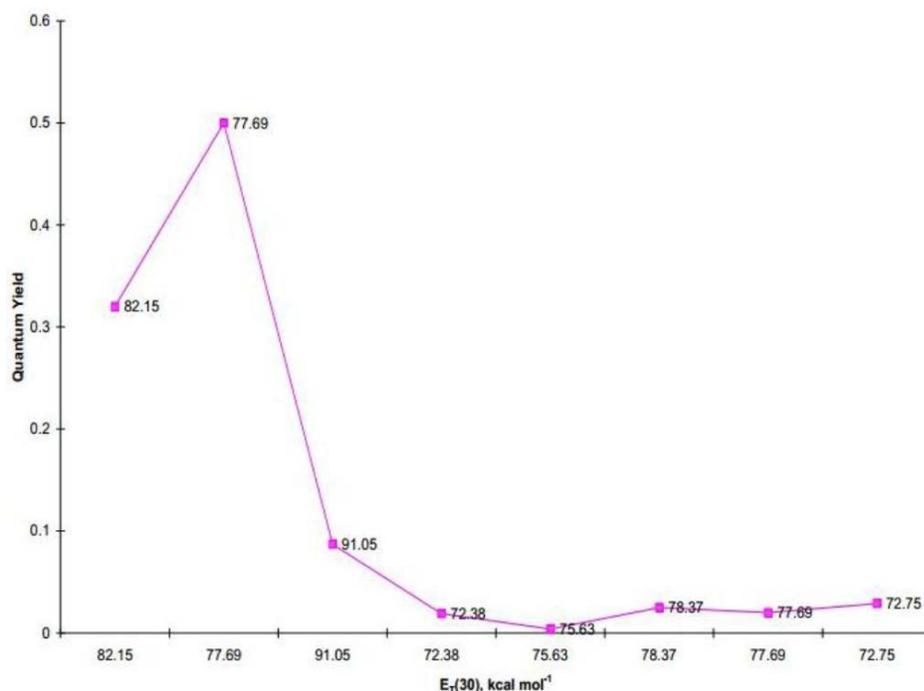


Figure 6: Change in fluorescence quantum yield ( $\phi$ ) of MPPP with the Dimorth solvent polarity parameter.

Table 1. Solvatochromic behaviour of compound MPPP in ground and excited state helps to determine the change in dipole moment upon excitation ( $\mu^*$ ) using Lippert-Mataga equation [25].

$$v_a - v_f = [2/hca^3] \Delta f (\mu^* - \mu)^2 \quad (2)$$

$$\Delta f = [\epsilon - 1/2\epsilon + 1] - [n^2 - 1/2n^2 + 1] \quad (3)$$

Where,  $h$  is Planck's constant,  $c$  is the speed of light, and  $a$  is Onsager cavity radius,  $\epsilon$  and  $n$  are the dielectric constant and refractive index of the solvent, respectively. The absorption and emission frequencies are  $v_a$  and  $v_f$  respectively.  $(\epsilon - 1) / (2\epsilon + 1)$  expresses the spectral shifts produced by two factor namely the solvent dipole reorientation and electron redistribution in solvent molecules while  $(n^2 - 1) / (2n^2 + 1)$  expresses the spectral shifts due to electron redistribution. The difference between these two items represents the spectral shifts caused by the solvent molecular reorientation. This is shown in the plot of Stoke shift and solvent parameter ( $\Delta f$ ) Figure 7. A linear relationship between the Stokes shifts and solvent parameters in aprotic solvents predicts large dipole moment of the emissive species. The ground ( $\mu$ ) and excited state ( $\mu^*$ ) dipole moment of MPPP was calculated using solvatochromic method and was found 5.58 and 5.90 D respectively. The change in dipole

moment from the ground state to excited state suggested that the charge transfer occurs through the relaxation of ground state to excited state. Thus, the solvent dependent emission shifting was observed.  $\Delta f = [\epsilon - 1/2\epsilon + 1] - [n^2 - 1/2n^2 + 1]$  a function which is independent of polarisability effect. Further, Dipole moment ( $\mu^*$ ) of excited state was calculated from spectroscopic values using the following equation [36].

$$(\mu^* - \mu) = \Delta\mu = \sqrt{m \times 81 / (6.2/a)^3 \times 11307.6} \quad (4)$$

Where 'a' is Onsager cavity radius.  $\Delta\mu$  is extracted from the slope ( $m$ ) of the plot of stokes shift versus  $E_T^N$ . The value of Onsager cavity radius ( $a$ ) was calculated from the following equation (5) [22],

$$a = \sqrt[3]{3M / 4\pi dN} \quad (5)$$

Here,  $M$  is molecular weight of the compound,  $N$  is Avogadro number, and  $d$  is the density ( $d = 0.15 \text{ g/cm}^3$ ). By using the Eq. 5, Onsager cavity radius was calculated to be  $8.55 \text{ \AA}$ . Thus, using calculated  $\Delta\mu$ , dipole moment of MPPP molecule in the excited state was calculated.

#### 4. CONCLUSION

Photoinduced charge transfer in MPPP using various solvents is discussed. It is apparent from the

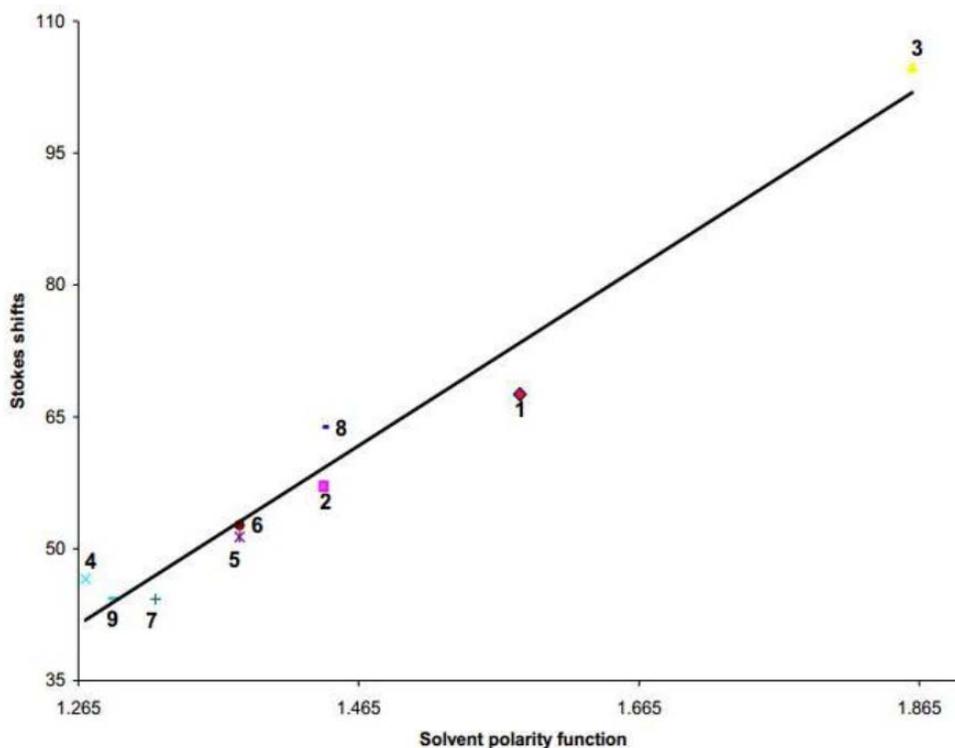


Figure 7: Graph between Stokes shift and solvent polarity function ( $\Delta f$ ) of MPPP; (1)1, 4-Dioxane, (2) carbon tetra Chloride, (3) Tetrahydrofuran, (4) Acetonitrile (5) Ethyl acetate, (6) MeOH, (7) acetone, (8) DMF and (9) DMSO.

experiments that MPPP is very sensitive to the environment polarity due to intramolecular charge transfer (ICT). Moreover, due to the high fluorescence quantum yields, MPPP may be used to probe the solvent polarity and hydrogen bonding properties as well as its microenvironment in biological macromolecules of interest.

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