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# INTERACTION OF 4-FLUOROPHENYLACETYLENE WITH TRIETHYLAMINE IN SOLUTIONS

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**ABSTRACT**

In non-polar aprotic solvent cyclohexane, 4-Fluorophenylacetylene interacts with triethylamine in the excited state and forms a transient, emissive, weak bimolecular complex, known as exciplex. The fluorescence quenching of 4-Fluorophenylacetylene by triethylamine in cyclohexane is complex. In the lower range of triethylamine (which acts also as a quencher) concentration fluorescence quenching is predominantly dynamic and in higher concentrations the quenching phenomena is complicated. In polar protic solvent ethanol, the fluorescence quenching is dynamic throughout the entire range of quencher concentration, and the formation of exciplex is not observed.

**Keywords:** Non-Polar Aprotic Solvent; 4-Flurophenylacetylene, Triethylamine; Exciplex; Polar Protic Solvent; Complex Quenching; Dynamic Quenching.

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## INTRODUCTION

Hydrogen bonding is incredibly common in nature.[1] It is an electrostatic interaction between two atoms having different electronegativity.[2] It influences several physical properties of a molecule as aggregates, mainly in the solution phase.[3] X-H-D represents a typical H-bonding interaction in which D is the donor and X-H is the acceptor species.[4] Though a very simple interaction, it tremendously affects protein folding [5], organizing DNA molecules[6], water and carbohydrates[7], and various biomolecules including synthetic polymers.[8] H-bonding plays a key role in the determination of the 3D structure of proteins and nucleic bases.[9,10] Folding of the proteins affects the biological activity in our body, which is also controlled by H-bonding. Polymers like cellulose, and nylon fibers strengthen by H-bonding.[11,12] There is a large number of reports where H-bonds are formed between unconventional donors and acceptors.[13] These include hydrogen bonds with π bond electrons[14], methyl group as acceptors[15] hydridic hydrogen as acceptors[16], noble gas atoms[17], and metal atoms in charge neutral state.[18] Further, hydrogen bonds that show blue shifts in the donor stretching frequency have also been reported.[19] Three and four-centered, bifurcated and trifurcated hydrogen bonds are also known from the literature of carbohydrates and amino acids.[20] To investigate the effect of H-bonding in the excited state, several investigations have been done with Phenylacatylene and its various fluorine derivatives as representatives in the gas phase. Size-selected IR spectroscopy and theoretical calculations (Ab-initio techniques and higher level DFT) reveal the formation of two types of complexes in the gas phase in the excited state. They are N•••π type and C-H•••N complexes. The N•••π type complex formation leads to a non-fluorescent excited state while C-H•••N type exciplex shows fluorescence.[21,22] It is quite enigmatic as the N donor atom interacts with π electron cloud directly must lead to a non-fluorescent excited state but the experiment shows a different result.[21,22] To explore the underlying fact about what is actually going on, 4-Fluorophenylacetylene in the solution phase (Cyclohexane and Ethanol) where H-bonding sites are in dynamic equilibrium which is totally absent in the gas phase, has been studied. The selection for the molecule is due to the fact that it has three different sites in which weak electrostatic interactions are possible that may lead to different quenching behavior in different solvents. Site C is acetylenic and therefore more prone to form a typical H-bond. Site A and site B are suitable for weak electrostatic interaction between the incoming nucleophile and the π electron clouds. In site D, the Florine atom acts as a very weak hydrogen bond donor because of the counterbalance of the -I and +R effect. Therefore, investigation of the mode of quenching in solution phase is of interest to uncover the type of excited state perturbation through quenching which will probably offer a suitable understanding of the compound's excited state behavior. Figure-1 shows different sites in the molecule. For quenching to occur in both static and dynamic mode, the quencher must come in contact with the fluorophore binding sites.


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This can be a method to understand the localization of the fluorophores and their permeability to the quencher.

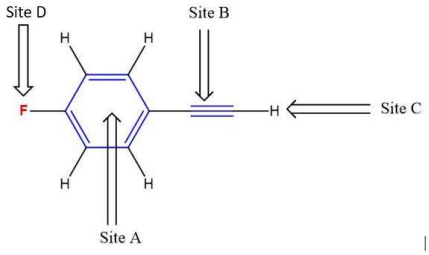


Fig.-1: Various Hydrogen Bonding Sites of 4-Fluorophenylacetylene

## EXPERIMENTAL

The materials used are 4-Fluoerophenylacetylene(4FPHA) (Fluorophore), triethylamine (TEA) (Quencher, Q), cyclohexane, and ethanol (as solvent). UV-visible spectrophotometer (JASCO-530) and Varian CARY eclipse fluorescence spectrophotometer were used for recording absorption and steady-state fluorescence spectra respectively. Time-resolved fluorescence measurements were performed at a magic angle of 54.7 using 265 nm picosecond LED based on an IBH-TCSPC fluorescence spectrometer. The stock solution of 4FPHA and TEA were prepared as 50 mM and 200 mM respectively in cyclohexane and ethanol. Then 1mM sample solution of 4FPHA was prepared and taken in a cuvette in which TEA solution was increasingly added. Spectroscopic data was recorded using UV-VIS spectrophotometer, Spectrofluorometers, and TCSPC. Each experiment was repeated four times to avoid discrepancies.

## RESULTS AND DISCUSSION

Figure-2 (Left panel) shows absorption spectra of 4FPHA with varying concentrations of TEA as a quencher. As absorption spectra may be used to distinguish between static and dynamic quenching, it has been examined carefully and shows almost no decrease in intensity which is an indication of collisional quenching as it only affects the excited state of the molecule. Static quenching is attributed to complex formation in the ground state henceforth should affect the absorption spectra. Too little change in absorption is due to the dilution effect.4FPHA shows a strong absorption peak at 277 nm wavelength and strongly emits at 299 nm. Figure-2 (Right panel) shows the optical density corrected area normalized fluorescence emission spectra of 4FPHA titrated against the increasing concentration of TEA, which has no shift of the peaks.

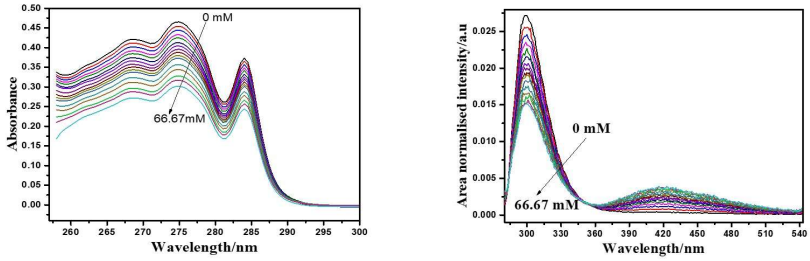


Fig.-2: Absorption Spectra (Left panel) and Area Normalized Fluorescence Emission Spectra (Right panel) of 4FPHA Titrated Against Increasing Concentration of TEA in Cyclohexane

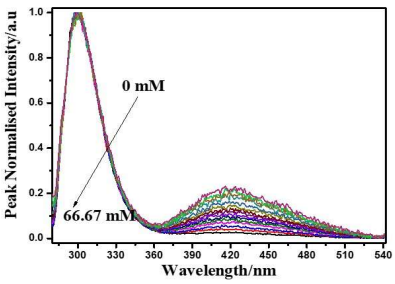


Fig.-3: Peak Normalized Emission Spectra of 4FPHA Titrated Against TEA

With the increase of relative amounts of TEA in the solution the fluorescence intensity at 299 nm gradually decreases which is accompanied by a new emission band centered at around 418 nm. The introduction of a new emission band at around 418 nm reveals the formation of an excited state of new emissive species are known as exciplex.[23] Figure-3 shows peak normalized emission spectra which suggests the formation of exciplex.[23]An integrated area vs. [Q] is plotted separately for the 299 nm band and rising 418 nm band to focus on their contrast in one graph (Fig.-4).

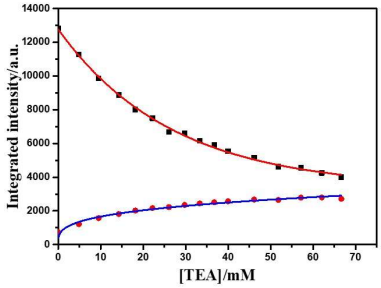


Fig.-4: Integrated Area vs. [Q] Plot for 299 nm (red) and 418 nm (blue) Bands

The exciplex formation may be considered an excited state reaction between the fluorophore and the quencher. Change of Fluorescence intensity may be explained in terms of the Stern-Volmer equation which mainly describes collisional quenching,

$$\frac{F_0}{F} = 1 + k_q \tau_0 [Q]$$

In the Stern-Volmer equation, $F_0$ and F are the intensity of fluorescence when the quencher is absent and present respectively, $k_q$ is the bimolecular quenching constant, $\tau_0$ is the lifetime of excited state when quencher is absent.[25] A linear plot with intercept 1 is expected to be observed. Figure-5 shows Stern-Volmer plot for the emission spectra. The almost linear behavior with intercept 0.99±0.012, slope 0.03±($1.7\times10^{-4}$) mM, and $k_q = 7.6\times10^9 \pm (1.16\times10^2)$ $M^{-1}$ indicates the quenching as dynamic one. Though this value is lower than the typical diffusion-controlled quenching which is almost $1\times10^{10}$, it may indicate the lower quenching efficiency or steric shielding of the fluorophore. The linear Stern-Volmer plot may suggest a single class of fluorophore where all the sites are equally amenable to the quencher.

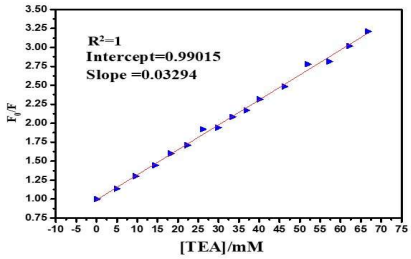


Fig.-5: Stern-Volmer for 418 nm Band in Cyclohexane

The best way to investigate the type of quenching and formation of new species is by performing Time Correlated Single Photon Counting (TCSPC) experiment. The decrease in lifetime should occur in case of collisional quenching as in this rate process, the population in the excited state decreases due to non-radiative and other non-fluorescent processes leading to the decrease in quantum yield. In the case of static quenching lifetime does not change as we measure the photons that emit fluorescence of uncomplexed molecules which have the same lifetime $\tau_0$. Therefore, to further understand the dynamic or static behavior of the excited state of 4FPHA in the presence of TEA, time-resolved fluorescence measurements were carried out. Figure-6 (Left panel) shows the plots of time-resolved fluorescence decay curves and Fig.-6 (Right panel) shows the lifetime vs. [Q] plot. The lifetimes and the amplitudes obtained by fitting the fluorescence decay curves using a non-linear iterative reconvolution procedure are listed in Table-1. The fluorescence decay data of 4FPHA in cyclohexane was found to fit single exponentially with a lifetime of

4.30ns. Upon addition of TEA, the fluorescence decay collected at 299 nm was found to fit in the bi-exponential function. It is clear from Table-1 that with the increase in the concentration of TEA, the lifetime of the faster decay component decreases accompanying the increase in the corresponding amplitude.

Table-1: Time-Resolved Fluorescence Measurement Data of 4-Fluorophenylacetylene Monitored at 300 nm as a Function of Triethylamine Concentration in Cyclohexane

| [TEA]/mM | $\tau_1$/ns | $\tau_2$/ns | $a_1$ | $a_2$ | $\chi^2$ |
|---|---|---|---|---|---|
| 0 | 4.30 | - | 1.00 | - | 1.11 |
| 2.5 | 4.03 | - | 1.00 | - | 1.08 |
| 5.0 | 3.78 | - | 1.00 | - | 1.13 |
| 7.5 | 3.52 | - | 1.00 | - | 1.02 |
| 10.0 | 3.26 | - | 1.00 | - | 1.00 |
| 12.5 | 3.09 | - | 1.00 | - | 1.02 |
| 15.0 | 2.90 | - | 1.00 | - | 1.06 |
| 17.5 | 2.77 | - | 1.00 | - | 1.02 |
| 22.5 | 2.43 | 0.42 | 1.15 | -0.15 | 1.05 |
| 27.5 | 2.17 | 1.62 | 1.18 | -0.18 | 1.04 |

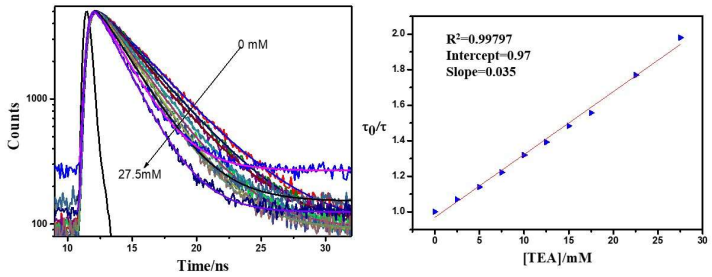


Fig.-6: Time-Resolved Fluorescence Decay Curves Recorded by Monitoring the Fluorescence at 299 nm (Left panel) as a Function of Triethylamine Concentration and Lifetime Ratio vs. [TEA] (Right panel)

Again, from the lifetime vs. [Q] plot, it is observed that the plot fits well in the linear form. In the case of dynamic quenching, always $\frac{F_0}{F} = \tau_0/\tau$. So, it demands a linear relationship with a positive slope of the $\tau_0/\tau$ with the quencher concentration. Comparing the slopes of the lifetime decay vs. [Q] plot with the stern-Volmer plot it can be concluded that basically quenching is dynamic in nature. However, we can't really eliminate the possibility of having static quenching as we have a structure-less new emission band as proof. So, fluorescence intensity decreases both by exciplex formation and collisional quenching. In the C–H•••N binding mode, the nitrogen lone pair is involved in the hydrogen bonding and is therefore unlikely to form an exciplex. Therefore, the interaction of triethylamine with the extended π electron cloud of the 4FPHA molecule through multiple C–H•••π contacts can be the possible structure of the exciplex. We propose here the exciplex formation by 4FPHA with TEA in cyclohexane due to the interaction of the excited state dipole of the 4FPHA with the C-H dipole of TEA. This can be justified by the fact that the emission band at 418 nm is broad and structure-less, unlike the 299 nm band due to emission from the locally excited state. 4FPHA in EtOH absorbs at around 274 nm wavelength and emits fluorescence at around 300 nm. There is almost no change in features of absorption spectra of EtOH but it gives strikingly different spectra where 418 nm bands which appeared in cyclohexane are totally absent and show almost natural fluorescence quenching (Fig.-2 and 7, Right panel). Area normalized spectra show no shift of the peaks with respect to TEA concentration (Fig.-7, Right panel).

In the Stern-Volmer plot, the intercept is 1.05±0013 and the slope is 0.009±(.8×$10^{-5}$) mM which gives a $k_q$ value of 1.89×$10^9$±(1.61×$10^2$) $M^{-1}$ which is quite lower than the typical value of the collisional quenching which is 1×$10^{10}$. This explains that there is some sort of inaccessibility of the fluorophore sites or ineffectiveness of the quencher in protic solvent EtOH. Though this type of quenching is purely dynamic, the lower binary quenching constant may be the attribution of solvation of the incoming nucleophiles i.e. TEA in EtOH or it might be the case of H-bonded 4FPHA in EtOH which is sometimes accessible or sometimes inaccessible to the quencher. To figure out the actual nature of the quenching phenomenon in

the excited state of the 4FPHA in EtOH, time-resolved fluorescence measurements were done for consistency.

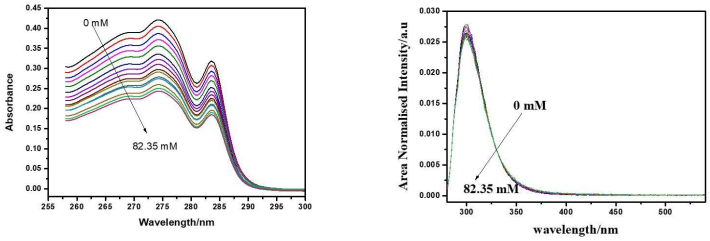


Fig.-7: Absorption Spectra (right panel) and Area Normalized Fluorescence Emission Spectra (left panel) of 4FPHA in EtOH Titrated with Varying Concentrations of TEA

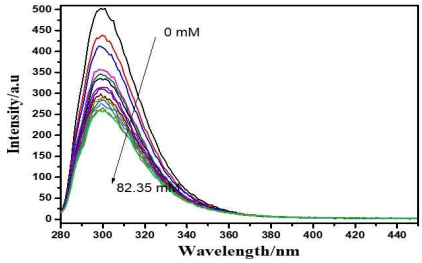


Fig. -8: Fluorescence Spectra of 4FPHA in EtOH Titrated Against TEA

The Stern-Volmer plot for 4FPHA-TEA in EtOH is linear (Fig.-9).

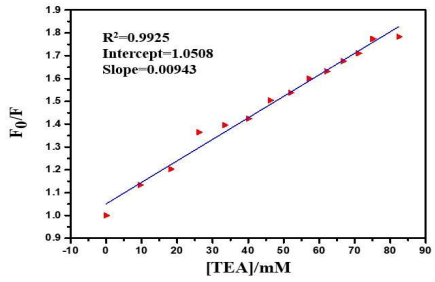


Fig.-9: Stern-Volmer Plot of 4-Fluorophenylacetylene with Respect to Triethylamine Concentration in EtOH

Figure-10 (Left panel) shows the time-resolved decay curves. The lifetimes and the amplitudes obtained by fitting the fluorescence decay curves using a non-linear iterative reconvolution procedure are listed in Table-2. Comparing the slopes of both $\tau_0/\tau$ vs. [Q] and Stern-Volmer plot we can reach firmly in a firm conclusion that in this case, no static quenching is possible as they are almost consistent and henceforth it is purely diffusion controlled. Moreover, dynamic quenching is also extensively diminished due to the inaccessibility of the quencher binding sites over the shielded intermolecularly hydrogen-bonded region of the fluorophore which can be inferred from the low value of the slope in both Stern-Volmer and $\tau_0/\tau$ vs. [Q] plot.

Table-2: Time-resolved Fluorescence Measurement Data of 4FPHA Monitored at 300 nm as a Function of TEA Concentration in ETOH

| [TEA]/mM | τ/ns | $\chi^2$ |
|---|---|---|
| 0 | 5.00 | 1.02 |
| 10 | 4.54 | 0.97 |
| 20 | 4.10 | 0.96 |
| 30 | 3.80 | 1.05 |
| 40 | 3.55 | 1.02 |
| 50 | 3.38 | 0.98 |
| 60 | 3.13 | 1.07 |

| | | |
|---|---|---|
| 80 | 2.77 | 1.00 |
| 100 | 2.53 | 1.00 |
| 120 | 2.23 | 1.00 |
| 140 | 2.06 | 1.00 |

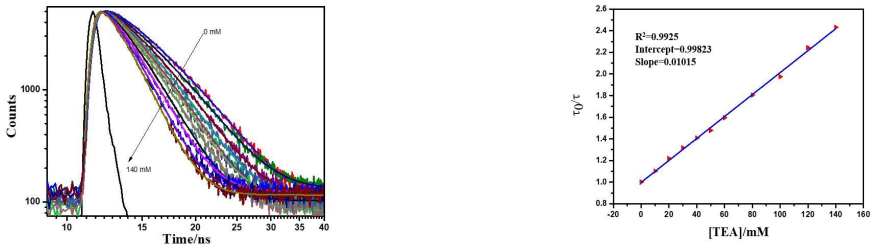


Fig.-10: Time-Resolved Decay Curves of 4FPHA Monitored at 300 nm Wavelength as a Function of TEA Concentration (left panel) Life Time Ratio vs. Concentration of TEA Plot of 4FPHA in ETOH

## CONCLUSION

The exact correlation of Stern-Volmer plots obtained from fluorescence and time-resolved measurement confirm purely dynamic quenching. In the case of cyclohexane, it can be concluded that quenching phenomena follow some complex mechanism in which both diffusion-controlled collision and exciplex formation decrease the fluorescence intensity. But in ethanol, as some number of accessible sites are buried under the solvent cage through extensive intermolecular H-bonding, it's becoming difficult for the incoming dipole to interact electrostatically with π-electron cloud to form exciplex. Because this type of field interaction is not well known it is expected that they should come in contact with the fluorophores to interact. From the Stern-Volmer plots in both cases, the obtained $k_q$ value is lower compared to what is expected from a dynamic collision. This is the indication of inaccessibility of all probable quenching sites in the fluorophore. 4-Fluorophenylacetylene has two π electron clouds to share. But perhaps they are not equally accessible to the quencher. It can be speculated that the structure of exciplex would be the interaction of π electron in 4FPHA with the C-H dipole in the excited state. The significant change is observed in fluorescence spectra on going from nonpolar aprotic solvent to polar protic solvent. In cyclohexane, a new emissive band is observed at around 418 nm which has no definite structure. It is observed clearly in the peak normalized spectra in cyclohexane (Fig.-4), confirming the formation of an excited state transient complex between 4-FPHA and TEA and thus generates a reacted singlet state which has fluorescence property. If this type of complex is formed in ethanol, then it is totally quenched through solvation and generates another non-fluorescent excited state. The fluorescence intensity of the 418 nm band increases exponentially with quencher concentration in cyclohexane.

## CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

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## AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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