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Photo Physical Properties of Sugar Derivatives with ICT Dye

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Abstract
Photo physical techniques were employed to study hydrogen-bonding self-assemblies forming sugar derivatives interaction with 4-dicyanomethylene 2, 6-dimethyl-4H-pyran (DDP) dye in aqueous medium. Hydrogen-bonding self-assemblies were investigated by addition of sugar derivatives to DDP dye which is an Intramolecular Charge Transfer (ICT) based fluorescent probe, results in a fluorescence enhancement accompanied with a shift towards the red region. The coexistence of DDP dye with sugar derivatives signifies the presence of heterogeneous micro environment of DDP dye surrounded by varying proportion of the solute and water molecules around the dye moiety. sugar derivatives influence the excited state characteristics of DDP dye resulting in the formation and promotion of different distinguishable micro environment. The hydrophobicity of sugar derivatives along with the hydrogen-bonding properties of sugar -water and sugar - sugar largely influence the photo physical nature of DDP dye is emphasized.
Keywords: *DDP dye; Sugar derivatives; Hydrogen-bonding; fluorescence emission.*

1. Introduction
DDP Dye (4-Dicyanomethylene-2,6-dimethyl-4H-pyran) DDP dye is a water-soluble fluorophore with electroluminescent properties. The structure of DDP dye is similar to that of DCM dye, a well-known ICT dye. DCM molecules possess a D-π-A configuration, showing a typical ICT effect. Possibility of the Twisted Intramolecular Charge Transfer (TICT) phenomenon [1-9], of DCM dye is completely eliminated. Derivatives derived from DCM have been widely applied in nonlinear optical materials, logic gates, photovoltaic sensitization, sensing, and other fields. Compared with cyanine dyes, the excellent photo physical and photochemical properties of DCM derivatives are much conducive to the application in realtime evaluation, detection of analytes, and long-term tracking imaging. In DDP dye which contains a strong acceptor moiety (dicyanomethylene, $C(CN)_2$) in the 4th position and a substituted donor moiety (methyl) in the 2nd and 6th positions. DDP dye has a significant advantage over DCM dye in terms of water solubility, and its photo physical nature can be probed by the addition of hydrogen bonding to study the nature of host-guest interaction [21-26]. DCM dye, on the other hand, is not soluble in water, so no such studies could be carried out in an aqueous solution (Figure 1). In recent years it was proved that DDP dye exhibits excellent fluorescence quantum efficiency, large stokes shift and solvatochromic behavior in the presence of more electron-releasing moieties and acts as an ideal that is used as the host molecule. In this work, influence of spatical structure of DDP dye molecule and its environment effect on the relaxation process in excited S_1 state of this molecule is examined [21-26].

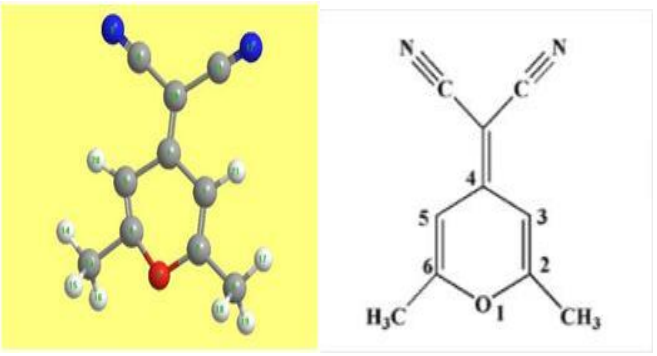

Figure 1 Structure of Dicyanomethylene-2,6-dimethyl-4H-pyran (DDP dye)

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1.1. Fluorescence Spectral Techniques

Fluorophores commonly used to probe structural, functional and dimensional information of a bio-molecule, or solutes situated in a highly heterogeneous environment are divided into two major classes [9]; intrinsic and extrinsic. Intrinsic fluorophores are those, which occur naturally in biological macromolecules, and in proteins. The dominant intrinsic fluorophore is the indole group of the amino acids that are fluorescent in nature. In addition to all these advantages the fluorescence lifetime of the probes is in the nanosecond and picosecond time scale [10,14] which could be carried out in a picosecond or femtosecond lifetime domain instrument, which seems to be the limiting factor.

2. Materials and Methods

2,6-dimethyl-4pyrone; malononitrile; acetic anhydride and Glucose, fructose, maltose, Sugar derivatives and sucrose Powder, the porcine pancreas was purchased from Sigma-Aldrich are the chemicals used in the study. Ultrapure water was used throughout the experiments.

2.1. Preparation of DDP dye and Trypsin Solutions for Spectral Studies

Sugar derivatives was dissolved in ultra-pure water to form a $5x10^{-5}$ mol L^{-1} solution and then preserved at -20°C; different concentrations of sugar derivatives (2.0 M, 4.0 M, 6.0 M, and 8.0 M) were prepared where the concentration of DDP dye ($7.1x10^{-5}$ mol L^{-1}) was fixed for steady-state absorption, emission and time-resolved fluorescence spectral studies.

3. Instrumental Techniques

3.1. Fluorescence Spectral Analysis

All fluorescence spectra were recorded on a F-7100 FL spectrophotometer (Hitachi, Japan) at the International Research Center (IRC), Satyabama Institute of Science and Technology, equipped with a 150 W xenon lamp source and a 10 mm diameter quartz cell. For analysis, the solution was transferred to the quartz cell and the emission slit and excitation slit were set at 10.0 nm. The fluorescence emission spectrum varied from 390 nm to 600 nm, and the excitation wavelength was chosen as 370 nm. Time-resolved fluorescence spectra of DDP dye in the presence and absence of trypsin at various concentrations were analyzed using Fluorolog-3 at the Department of Medical Physics, Anna University, with Δex370 nm and Δem436 nm.

4. Results and Discussion

4.1. Absorption Analysis

The UV–Visible absorption spectra of DDP dye with the addition of sugar derivatives at different concentrations were investigated by a UV–Vis spectrophotometer (Figure 2). DDP dye exhibits absorption peaks at 248±2nm and 348±2nm accompanied by a shoulder around 360nm in water as shown in Figure 2. The absorption peaks at 248± 2 nm and 348±2nm are attributed to n→π* and charge transfer (CT) transitions respectively.

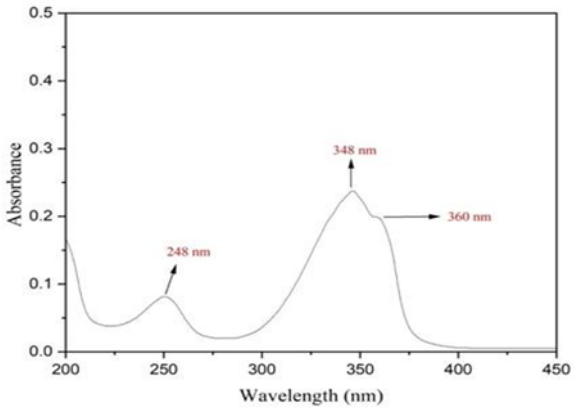

Figure 2 Absorption spectra of DCM dye (7.1x10-5 M) in Water

Addition of Sugar derivatives like Sucrose, Fructose, Maltose, Glucose and lactose results no significant change in the absorbance at the longest wavelength absorption maximum of DDP dye figure 3-5. The absorbance at the ICT absorption maximum remains unaltered even in the presence of very high concentration of sugar derivatives. The increase in the absorbance around 280 ± 10 nm is attributed to the strong absorbance of sugar derivatives. Further, an isosbestic point in the absorption spectrum of DDP dye with all the sugar derivatives used in this study is correlated to the formation of a ground state complex. Our earlier studies of DDP dye with hydrogen-bonding assemblies of amides derivatives also resulted in an isosbestic point which signifies the presence of equilibrium between dye and sugar. In the present

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investigation, we account for the role of Sugar derivatives that possesses hydrogen-bonding as well as hydrophobic moieties on the variation in the excited state nature of DDP dye. The existence of more than one environment of dye in equilibrium in the presence of Sugar derivatives which associated to be the bound and free dye component.

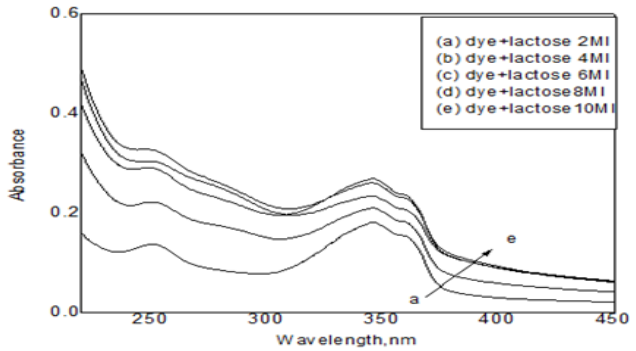

Figure 3 Absorption Spectra of DDP dye with Varying Concentrations of Sugar Derivatives in Water

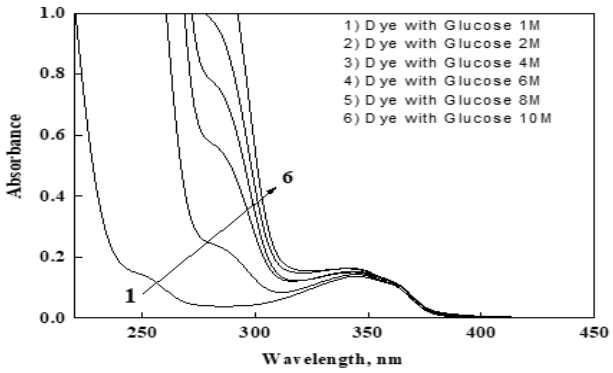

Figure 4 Absorption Spectra of DDP dye with Varying Concentrations of Glucose in Water

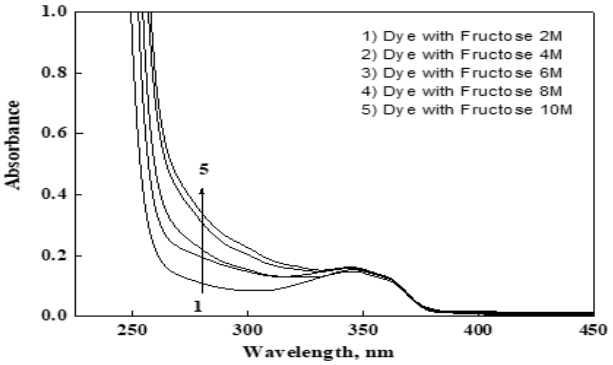

Figure 5 Absorption Spectra of DDP Dye with Varying Concentrations of Fructose in Water

4.2. Intramolecular Charge Transfer (ICT) Behaviour of DDP Dye

DDP is an example of a donor-acceptor molecule. Its structure is comprised of an electron-donating methyl group and an electron-accepting di-cyano group, where it participates in intramolecular charge transfer. During this process, the excited free electron moves from the donor to the acceptor before relaxing back to a less polar ground state. The intramolecular charge transfer is mediated by a π molecular orbital (MO) that extends from the donor to the accept or by over lapping the p-orbitals from the constituent carbon atoms or from lone pairs. In the ground state of a conjugated system, the highest occupied molecular orbital (HOMO) is fully occupied and electrons cannot move. However, if an electron from the donor group is excited into the lowest unoccupied molecular orbital state, it is free to migrate along the delocalized orbital. The existence of an overlap of the HOMO and LUMO wave functions and transition cannot be attributed to pure charge transfer character. Electron density redistribution clearly suggests $\pi \rightarrow \pi^*$ transition character, except for the small fraction of $\sigma \rightarrow \pi^*$ coming from donor methyl groups for DDP dye. The position of the absorption maxima in the spectra of the DDP dye is because of the bands that formed with the participation of π-type Molecular Orbitals delocalized on the Atomic Orbitals (AO) of the pyran ring and with anyone of the methylene group. The molecule are electrostatic potential (MEP) of DCM dye shows that nitrogen atoms of the cyano group and oxygen of the pyran cycle are responsible for the proton-acceptor properties in the ground and excited states of the molecules which give strong evidence for DDP dye where charge-transfer to occur. The presence of both hydrophilic and hydrophobic moieties in the solutes behaves as an ideal host molecule. The majority of the research in the literature on the probe–host interactions took place in non–aqueous and organic solvents, but in the present investigation, the photo physical studies of these probes are carried out in the water, which is considered of biological importance.

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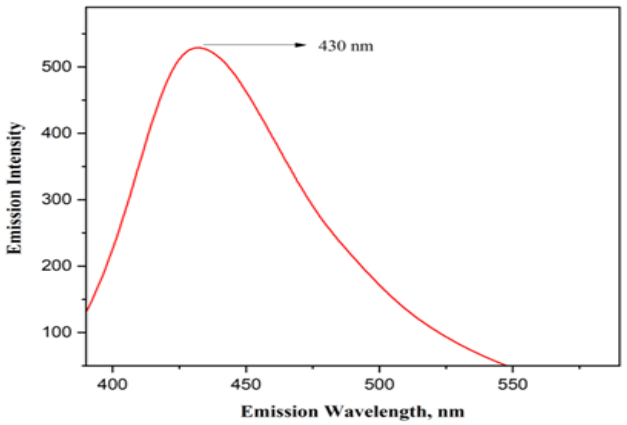

Figure 6 Emission Spectra of DDP Dye in Water

4.3. Fluorescence Spectra Analysis

The fluorescence spectrum of DDP dye in water exhibits a broad peak at approximately 436 ± 2 nm when excited at the longest wavelength absorption maximum, and this peak is assigned to the LE state emission. It is shown in figure 6. Addition of Sugar derivatives to DDP dye results in a fluorescence enhancement its shown in figure 7-11. A broad emission maximum around 430 to 440 nm resulted on the addition of Sugar derivatives as observed in the case of Sugar derivatives. A close observation on the emission spectra reveals the presence of emission peaks of almost similar intensity separated by a few nm only. Interestingly, with a further increase in the concentration of Sugar derivatives resulted in broad emission maxima at 435 ± nm with a larger fold of enhancement at the longest wavelength emission. The emission spectral studies of Sugar derivatives with DDP dye reveals that the two emission peaks of DDP dye are partially separated and coalesce to form a single peak at higher concentration of Sugar derivatives. The extent of fluorescence enhancement is accompanied with no considerable shift in the emission towards the red or blue region.If hydrophobic influences on the excited state properties of DDP dye would have been more predominant than hydrogen-bonding influences, a blue shift in the emission maxima would have resulted. The pattern of shift clearly reveals that apart the presence of microhetrogeneous population of the Sugar derivatives definitely governs the emissive nature of the dye. The fluorescence enhancement of DDP dye in the presence of Sugar derivatives is larger in terms of fluorescence enhancement. The influence of Sugar derivatives-solvent hydrogen-bonding properties on the photo physical behavior of fluorescent probe results either in an increase or decrease in the fluorescence emission and lifetime.

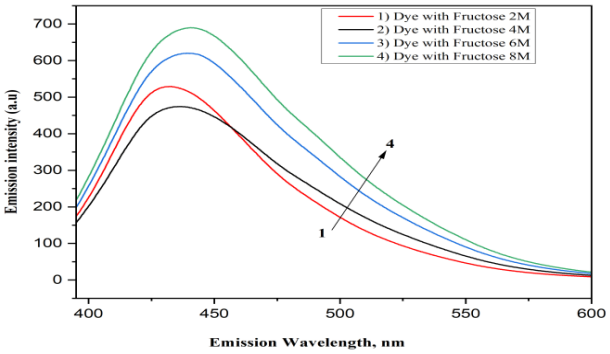

Figure 7 Emission Spectra of DDP dye with Different Concentration of Fructose

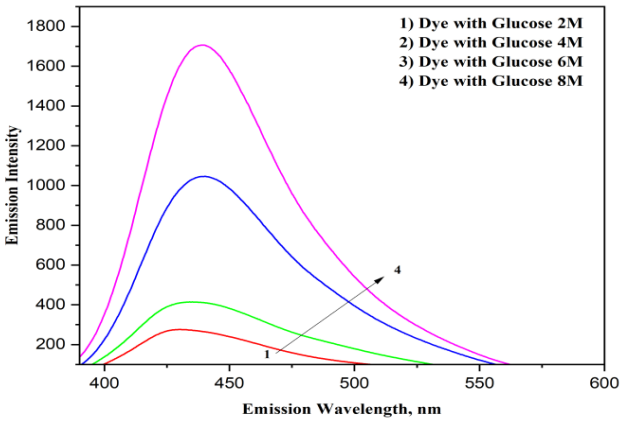

Figure 8 Emission Spectra of DDP Dye with Different Concentration of Glucose

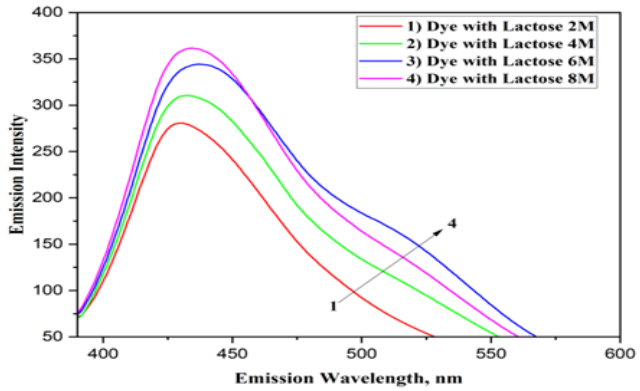

Figure 9 Emission Spectra of DDP dye with Different Concentration of Lactose

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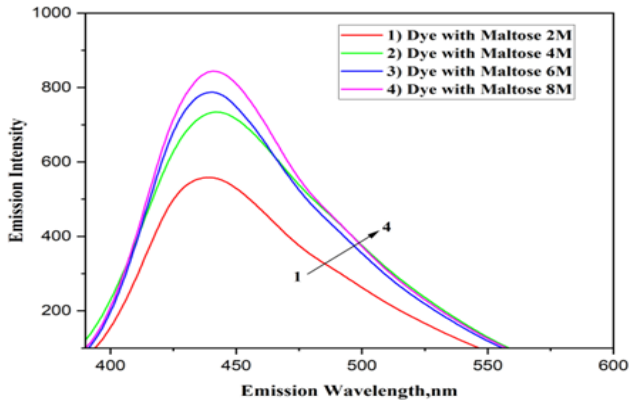

Figure 10 Emission Spectra of DDP Dye with Different Concentration of Maltose

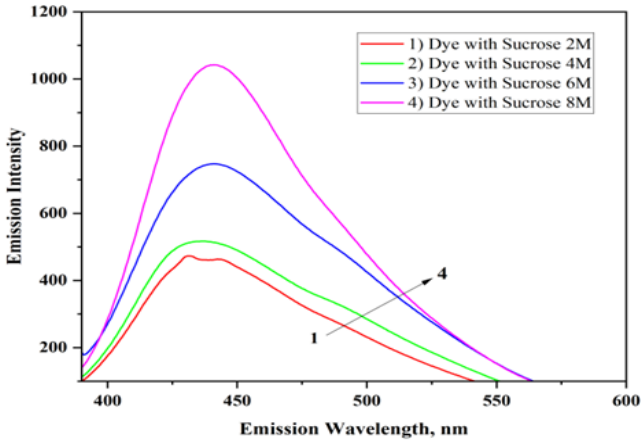

Figure 11 Emission Spectra of DDP Dye with Different Concentration of Sucrose

This provides an excellent approach to study in depth regarding the interaction of water soluble fluorophores in the presence of large macromolecules.

4.4. Mechanism of Fluorescence Enhancement of DDP Dye with Sugar Derivatives

This mechanism signifies that the increase in the fluorescence intensity accompanied with a shift in the emission is attributed to the change in the microenvironment around the fluorophore resulting in the stabilization or destabilization of the charge transfer (CT) state. Interaction of Sucrose, lactose, maltose, glucose and fructose with fluorescent probes involving a change in the polarity around the fluorophore has been well documented in this studies. literature involving probe–protein interaction [17] is examined and proved. Herein, DDP is an ICT based dye which exhibits only fluorescence enhancement and no characteristic shift is observed. On the contrary, another mechanism signifies an intermolecular energy transfers from the protein molecule to the probe resulting in a LE [15–19]. This mechanism was ruled out since there were no new emissive peaks arising from DDP dye on the addition of Sugar derivatives. The emission intensity in the spectral range of 435 ± 10 was almost similar which authenticates that the local excited (LE) state emission is stabilized to a larger extent. Apart from these mechanisms, LE is also correlated to the binding of the dye to the protein molecule resulting in the formation of a stable complex in the excited state [20] such that free dye and bound dye exists in solution. This mechanism was ruled out in our present study since there exists no free dye component in aqueous phase on the immediate addition of Sugar derivatives a complete change in the micro environment. The increase in the fluorescence intensity of DDP dye on the addition of Sugar derivatives results in a red shift in the emission maximum and this is attributed to hydrogen-bonding interaction. This mechanism results in the stabilization of the CT state emission of the flourophore. The presence of Sugar derivatives around the dye molecules compete with water molecules in forming hydrogen-bonding interaction such that the variation in the micro environment of dye is influenced by the concentration of Sugar derivatives. The nature of the solute influences the excited state properties of DDP dye is illustrated from this present study.

Summary and Conclusion

The interaction between DDP dye and other proteins or enzymes to determine photo physical properties are more broadly applicable. This could involve using fluorescence spectral techniques to monitor changes in the dye's emission spectra or fluorescence lifetime in the micro- environment presence of different molecular aggregates components. Overall, further investigations using advanced computational methods and a broader range of biological targets could help to expand our understanding of the interaction between DDP dye and biomolecules, with potential applications in

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biosensors and other optical technologies.

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