DONOR ACCEPTOR LUMINESCENT MOLECULES AND THEIR PHOTOPHYSICAL STUDIES

Submitted in partial fulfillment of the requirements for the award of
Master of Science in CHEMISTRY

By

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DEPARTMENT OF CHEMISTRY
SCHOOL OF SCIENCE & HUMANITIES

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **G HAVILA DIVYA DHARSHINI (39910007)** who carried out the project entitled “**DONOR ACCEPTOR LUMINESCENT MOLECULES AND THEIR PHOTOPHYSICAL STUDIES** ” under my supervision from January 2021 to March 2021.

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DECLARATION

I G. HAVILA DIVYA DHARSHINI , hereby declare that the Project Report entitled "**DONOR ACCEPTOR LUMINESCENT MOLECULES AND THEIR PHOTOPHYSICAL STUDIES"** done by me under the guidance of **Dr.V. KAVITHA M.Sc., M.Phil, Ph.D., (INTERNAL GUIDE)** Professor, Department of Chemistry, Sathyabama Institute of Science and Technology and **Dr. S.EASWARAMOORTHI, Senior Scientist, (EXTERNAL GUIDE),** Inorganic and Physical Chemistry Laboratory, CSIR-Central Leather Research Institute is submitted in partial fulfilment of the requirements for the award of Master of Science degree in Chemistry.

DATE:

PLACE:

G. HAVILA DIVYA DHARSHINI

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ABSTRACT

In donor- acceptor conjugated system, donor and acceptor mesomeric units associated with π conjugated chromophores provide simple operational, sensitive, selective and non destructive methods. Donor – Acceptor luminescent molecules was synthesized by π conjugated system using Triphenylamine (donor) and N,N – Dimethylformamide (acceptor) as the solvent. Along with this photophysical properties have also been discussed by Ultra Violet – Visible Spectroscopy (UV – Visible) and Fluorescence Spectroscopy.

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LIST OF ABBREVIATIONS

ABBREVATIONS	EXPANSIONS
DCM	Dichloromethane
DMF	Dimethylformamide
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
TS	Triphenylamine Salicylaldehyde
DESA	Di Ethyl Salicylaldehyde
AIE	Aggregation Induced Emission
UV- Visible	Ultra Violet- Visible
H	Hydrazine
THF	Tetrahydrofuran
ECIPT	Excited-State intramolecular Proton transfer

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Among the different classes of sciences such as analytical, biological and medicinal fields, fluorescence has become an indispensable analytical technique. In a fluorescent donor–acceptor p-conjugated system (D-p-A), an acceptor (A) mesomeric unit and a donor (D) mesomeric units substituent to a chromophore unit, specifically p-conjugated chromophores in well-architecture manner so they have a great range of fluorescence wavelength.

1.1 LUMINESCENCE

- Luminescence is emission of light by a substance not resulting from heat.
- It is a form of cold- body radiation
- It can be caused by electrical energy, chemical reactions and many other processes.
- It occurs when an electron returns to the electronic ground state from an excited state and loses its excess energy as a photon.

1.1.1.TYPES OF LUMINESCENCE

- Fluorescence
- Phosphorescence

1.1.1.1 Fluorescence

It is a type of luminescence. It occurs in gas, solid or liquid chemical system. When a beam of light is incident on certain substances they emit visible light or radiations. This is known as Fluorescence. It starts immediately after the absorption of light as soon as the incident light is cut off. It returns to the Ground state from the Singlet excited state.

1.1.1.2 Phosphorescence

When light radiation is incident on certain substances they emit light continuously even after the incident light is cut off. This type of delayed fluorescence is called Phosphorescence. It returns to the Ground state from the Triplet excited state.

1.2 DONOR – ACCEPTOR

A donor is a high energy orbital with one or more electrons. It is an atom or group of atoms whose highest filled atomic orbital or molecular orbital is higher in energy than that of a reference orbital.

An acceptor is a low energy orbital with one or more vacancies. It is an atom or group of atoms whose lowest unfilled atomic or molecular orbital is lower in energy than that of a reference orbital.

1.3 CONJUGATED π SYSTEM

- A bridge is required to connect the Donor and Acceptor, and this bridge is referred to as a π system.
- It may be a simple double bond or a thiophene bridge, (depends on the compound).
- A conjugated system is a system of connected p orbitals with delocalized electrons in a molecule, which in general lowers the overall energy of the molecule and increases stability. It is conventionally represented as having alternating single and multiple bonds.

CHAPTER 2

LITERATURE SURVEY

2.1 ESIPT- active multi - colour aggregation - induced emission features of Triphenylamine – Salicylaldehyde- based unsymmetrical azine family.

In recent years, there has been a lot of interest in the creation of multi-color aggregation-induced emission (AIE)-featured azine molecules with excited-state intramolecular proton transfer (ESIPT) characteristics. The construction of donor-acceptor-structured triphenylamine-functionalized unsymmetrical azine molecules (L1–L4) prepared from 4-(hydrazonomethyl)-N,N-diphenylaniline with various salicylaldehyde derivatives is defined in this paper. We were able to tune the optical properties of the newly synthesised molecules by adjusting the electron donation potential at the ESIPT moiety. In a THF/water mixture, both of the compounds displayed the AIE activity as well as the excited-state intramolecular proton transfer phenomenon. Furthermore, in the aggregated state, the tuning of a peripheral substituent in the salicylaldehyde moiety resulted in different emission colours. The crystal structures of all of the compounds (L1–L4) showed that the solid-state structure contains several weak interactions that lead to various supramolecular networks. These molecules also exhibited a strong positive solvatochromic effect, as evidenced by their solvent polarity-dependent emission activity. Dual emission bands in the solid and solution states, lifetime values, and the HOMO, LUMO energy difference of the keto and enol types all strongly support the presence of ESIPT in all compounds (L1–L4). In addition, the presence of two separate electron donation groups (triphenylamine and diethylamino) in L3 caused pH-dependent emissive features in solution. (Balamurugan Tharmalingam and Baskaran Vijaya Pandiyan – 2020)

2.2 Hybridization of Triphenylamine and Salicylaldehyde: A Facile Strategy to Construct Aggregation-Induced Emission Luminogens with Excited-State Intramolecular Proton Transfer for Specific Lipid Droplets and Gram-Positive Bacteria Imaging

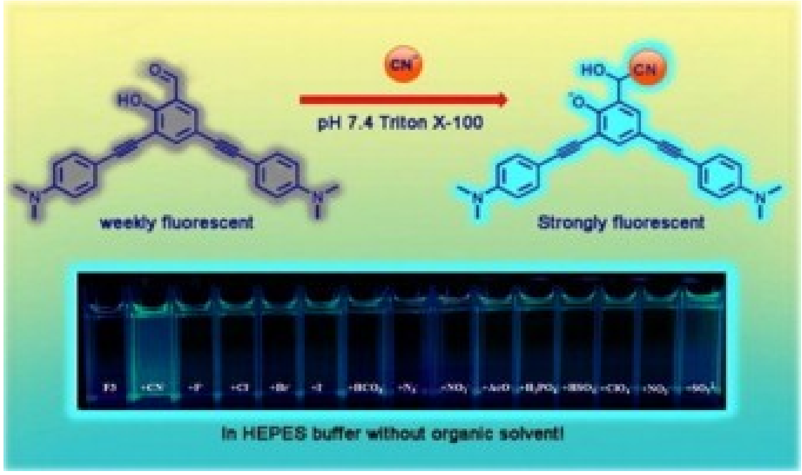
Due to various their high solidstate emission efficiencies and massive Stokes changes, aggregation induced emission luminogens (AIEgens) with an excited state intramolecular proton transfer (ESIPT) mechanism have gotten a lot of attention in bioimaging applications.Triphenylamine salicylaldehyde (TS) derivatives are produced and synthesised using a rational hybridization of triphenylamine and salicylaldehyde units as the intramolecular rotor and ESIPT generator, respectively. In the aggregated state, TS derivatives show high emission and broad Stokes shifts (>140 nm) due to the AIE and ESIPT effects.Their solid-state emission ranges from 490 to 590 nm focusing on the substituents in the triphenylamine units. The TS derivatives are able to directly stain the lipid droplets in the cells in a washfree manner and effectively image the lipid rich tissue in vivo due to their excellent biocompatibilities and suitable lipophilicities. Moreover, TS and methoxyl substituted TS (TSOMe) are seen to stain gram positive bacteria with high selectivity due to their effective hydrophilicity. (Yu Bi and Na Zhao – 2020)

2.3 Electrospun nanofibrous sheet doped with a novel triphenylamine based salicylaldehyde fluorophore for hydrazine vapor detection

The Suzuki cross-coupling reaction was used to successfully synthesise a novel triphenylamine-based salicylaldehyde fluorophore (compound 1). Following that, depending on the solid state, the identification of hydrazine vapour from an electrospun nanofiber sheet combined with compound 1 was identified. Moreover, using the electrospinning method, cellulose acetate (CA) was combined with an electrospun nanofiber sheet centred on compound 1 with an average diameter of 324.6 ± 91.6 nm. According to the study of fluorescence images using ImageJ, the sensing nanofiber sheet exhibited a sensitive and selective reaction to hydrazine vapour with a linear concentration range of 0.2-1 % w/v in aqueous solution. Even so, it showed increased selectivity with hydrazine across 21 useful interferences.The sensitivity and selectivity of the nanofibrous mat in recognizing hydrazine through naked-eye detection under backlight 365 nm with fluorescent turn-off mode were first discovered. Additionally, 1H-NMR titration and HRMS were used to investigate the formation of compound 1 and the hydrazone product (compound 1-HZ), which indicated the formation of hydrazine with a proton chemical shift of 7.95 ppm, HRMS of compound 1-HZ at m/z = 380.1764 [1-HZ+H]+).The nanofibrous mat has been shown to be an useful methodology for detecting water vapour in both water and industrial chemical environments.(Apisit Karawek, Pipattra Mayurachayakul – 2021)

2.4 Novel salicylaldehyde derivatives as fluorescence turn-on sensors for cyanide ion

Using sonogashira coupling, a new series of fluorescent probes with diphenylacetylene as a fluorogenic unit and salicylaldehyde as a CN receptor were successfully synthesized. The fluorophores revealed fluorescence “turn-on” in response to CN in aqueous media in the presence of Triton-X 100 non-ionic surfactant, with a detection limit of 1.6 μM. The internal acid catalysed addition of cyanide allows in the conversion of the aldehyde to cyanohydrin, which results in the turn-on signal. The detection of cyanide with the naked eye is possible down to 5n mol using paper sensor strips. (Nakron Niamnont and Akachai Khumsri – 2014)



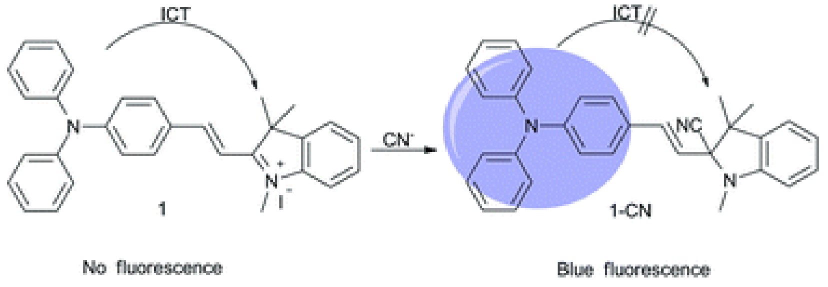
2.4.1 Novel salicylaldehyde derivatives as fluorescence turn-on sensors for cyanide ion

2.5 A naked eye fluorescent chemosensor for Zn^{2+} based on triphenylamine derivative and its bioimaging in live cells

In the system MeCN:H2O (V/V = 6:4, pH = 7.0), a novel Zn2+ fluorescent probe N-(4′-(diphenylamino)-4-hydroxy-[1,1′-biphenyl]-3-yl)methylene)-2-hydroxybenzohydrazide (TPA-HPH) with a larger Stokes change (210 nm) was designed and synthesised, which was shown to be highly selective and responsive. Meanwhile, when Zn2+ was applied to the TPA-HPH solution, it was observed that the colour of the solution changed from colourless to yellow. The probe's fluorescence intensity had a strong linear relationship with Zn2+ ion concentration in the range of 0–10 M under optimised conditions, with a low detection limit of 7.3 10^{-10} M. It was suggested that the fluorescent mechanism be used. TPA-HPH could also provide on-site monitoring and live cell imaging for the Zn2+ ion. (Bo Liu and Yanhong Tan – 2019)

2.6 A triphenylamine-based colorimetric and “turn-on” fluorescent probe for detection of cyanide anions in live cells

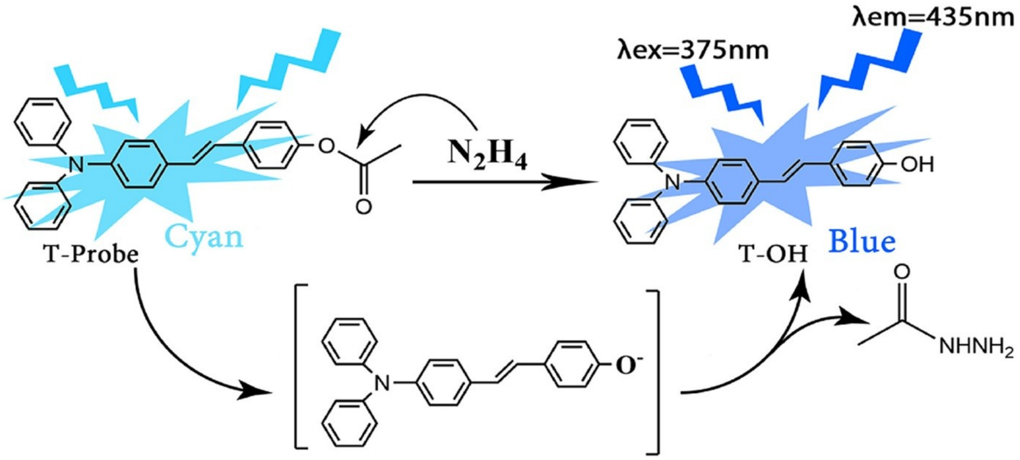
For the detection of cyanide anions, a colorimetric and "turn-on" fluorescent probe has been produced. The nucleophilic addition of cyanide to the indolium group of the probe resulted in a shift in colour from purple to colourless, as well as a rise in fluorescence. In aqueous ethanol solution, the probe showed high sensitivity and selectivity for cyanide anions over other different anionic species. The detection limit was as low as 21 nm. This probe's utility in mapping cyanide anions in biological systems was demonstrated in a live cell imaging experiment. (Yan Song and Yaoxian Li – 2015)



2.6.1 A triphenylamine-based colorimetric and “turn-on” fluorescent probe for detection of cyanide anions in live cells

2.7 Novel application of a fluorescent dye based on triphenylamine: Rapid detection of hydrazine in living cells and in vitro

This work mainly presented a new application of the triphenylamine-based fluorescent dye T-Probe in the rapid detection of hydrazine (N_2H_4) both in vivo and in vitro, based on the multi-functionalization of organic compounds.In the presence of other competitive species (such as K+, Cu^{2+}, Ni^{2+}, NO_2^-, NO_3^-, SCN^-,S^{2-}, SO_4^{2-}, SO_3^{2-}, HSO_3^- , Cl^-, CO_3^{2-}, OAc^-, NH_4^+, HS^-, Cys, BSA, Aniline CH_3NH_2, N_2H_4, etc.), this important biological intermediate displayed high selectivity and rapid response to N_2H_4 in DMSO/PBS buffer (4/6, v/v) solution. Uv–Visible, dynamic light scattering, X-ray diffraction, fluorescence spectrophotometric measurements, and DFT/TD-DFT calculations were used to further investigate the sensing property of N_2H_4 .The results showed that the target sensor T-Probe had a high anti-interference capacity, specificity, extremely high detection limit (8.47 nM), and particularly rapid response speed (within 3 min) to N_2H_4, with the entire detection process visible through "naked-eye" fluorescence colour shift (from Cyan to Blue) under 365 nm UV lamp irradiation.To verify the sensing process, 1H NMR and fluorescence titration experiments were also carried out. In a wider sense, the fluorescent dye T-Probe could provide a new analytical tool for detecting N_2H_4 in real water samples and analysing biological sample monitoring in living cells. (Xiujuan Li and Cheung-Hin Hung – 2020)



2.7.1 Novel application of a fluorescent dye based on triphenylamine: Rapid detection of hydrazine in living cells and in vitro

2.8 Triphenylamine - based stimuli- responsive solid state fluorescent materials

Smart fluorescent materials respond to pressure, heat, light, pH, and other external stimuli with a regulated fluorescence response. The fluorescence efficiency and colour are largely shaped by molecular structure and supramolecular assembly through weak intermolecular interactions. Non-planar molecular structures, in particular, play an important role in the development of solid state fluorescent materials.Triphenylamine (TPA), a non-planar propeller molecule with fascinating optoelectronic properties, offers a great opportunity for creating a range of molecular fluorescent materials due to its synthetic viability. By incorporating an acceptor group into the phenyl unit of a TPA donor, for example, a donor–acceptor (D–A) aggregation induced emissive (AIE) fluorophore can be formed.This analysis mainly focuses on TPA-based smart fluorescent materials with distinct and reversible fluorescence switching in response to various stimuli. The production of different types of stimuli-responsive materials became aided by molecular engineering of the TPA fluorophore, and the conformational flexibility of non-planar phenyl groups commonly resulted in polymorphism induced fluorescence tuning. A detailed analysis of TPA derivative structure–property relationships could lead to the formation of new TPA-based smart fluorescent materials with a wide range of properties. (Parthsarathy Gayathri and Mehboobali Pannipara – 2020)

2.9 Electrochemical characterization of small organic hole-transport molecules based on the triphenylamine unit

Electrochemical and spectroelectrochemical processes are used to investigate the hole-transport properties of a collection of substituted triphenylamine-containing organic compounds. In both the oxidative and reductive scans, some substituted tirphenylamines produced irreversible electron-transfer reactions. The cyclic voltammograms of the p-phenylenediamine series, on the other hand, are well identified. In dichloromethane solution, N,N′-bis(4-nitrophenyl)-N,N′-diphenyl-1,4-phenylenediamine (NPD) identified different reversible oxidation redox couples at +1.00 and +1.28 V vs. Ag/AgCl. At 1.12 V, there is a reversible reduction redox couple, and at 1.87 V, there is an irreversible wave with Ep,c. The oxidation redox couples of cyano-substituted p-phenylenediamine (CPD) remained similar.NPD and CPD seem to be more difficult to oxidise than amino-substituted p-phenylenediamine (APD). At +0.40 and +0.70 V, APD has two reversible oxidation redox couples and two extra irreversible oxidation waves at +1.26 and +1.52 V. The oxidation products of the above reactions were analyzed using an optically transparent thin-layer electrode (OTTLE) in combination with UV/Vis/NIR spectroscopy.In spectroelectrochemical tests, the electrogenerated cation and dication of the substituted p-phenylenediamine are very stable. The oxidation of the compound APD showed a distinct absorption pattern which differed from compound NPD and compound CPD. (Sung Jie Yeh and Che Yu Tsai – 2003)

2.10 Review on fluorescent donor–acceptor conjugated system as molecular probes

Donor and acceptor mesomeric units associated with -conjugated chromophores provide simple effective, responsive, selective, and non-destructive methods of detection in a donor–acceptor conjugated system. Fluorescein, alcidine, cyanine, rhodamine, borondipyrromethenes, coumarin, squarine, bipyridine, and the thiophene ring are one of the donor–acceptor conjugated fluorescent probes discussed in this report. There has also been discussion of photophysical and optical properties. The importance of these probes in the biological system is also discussed. We described the importance of these sensors in in vitro and in vivo control, imaging, and sensing .We examined at a few probes to see how they were made, what properties they had, and how they compared to many other methods. We mentioned the different types of probes, such as intensity-based, turn-on/off, and colorimetric probes. (Jaswal S and Kumar J – 2020)

2.11 Turn-on fluorescence sensor based on the aggregation of pyrazolo[3,4-*b*]pyridine-based coumarin chromophores induced by Hg^{2+}

The aggregation-induced emission (AIE) of the pyrazolo[3,4-b]pyridine-based coumarin chromophore was used to create a new fluorescent sensor (PPC-S) for Hg2+ (PPC-O).Given the desulfurization reaction with Hg2+, AIE inactive PPC-S can be transformed into PPC-O with AIE activity, which can be used to detect Hg2+ fluorescence turn-on in aqueous solutions with good selectivity and sensitivity. (Weigang Ju and Pengfei Wang – 2013)

2.12 Photophysical and crystallographic study of three integrated pyrazolo[1,5-*a*]pyrimidine–triphenylamine systems

The structures of three new intramolecular charge transfer (ICT) fluorophores with triphenylamine and pyrazolo[1,5-a]pyrimidine moieties 4a-c were solved using X-ray crystallography (XRC) With measured CE-B3LYP structural energies of 104.3, 125.6, and 123.8 kJ/mol, compounds 4a, 4b, and 4c crystallise in the tetragonal P42/n, triclinic P-1, and monoclinic P21/c space groups, respectively. Fluorescence, UV–Vis, XRC, and computational methods were used to analyse the influence of substitutes on the molecular and photophysical properties of 4a–c in both solution and solid state. The 2-phenyl (4b) and 2-anisyl (2c) derivatives showed higher absorption coefficients (4b, ε = 76400 → 119600 M−1cm−1 and 4c, ε = 66200 → 89200 M−1cm−1) than the 4a (2-Me, ε = 9933 → 21667 M−1cm−1), while the relative quantum yield () in various polarity solvents was as high as φ = 0.98 for 4a, φ = 0.86 for 4b and φ = 0.83 for 4c.Lippert–Mataga correlation was used to measure the difference between the excited and ground state dipole moments (Δμ) for these dyes, with 4b suffering the most changes Δμ of 26.9 D. Probe 4c has been found to be effective as a fluorescent indicator for qualitative water content sensing in organic solvents. The solid-state emission data show that the antiparallel molecular packing of the crystal structure for 4a-c, with energy framework diagrams influenced by dispersion forces, may cause photophysical properties to be affected by changing the donor-acceptor intramolecular coupling. As a result, the combination of these XRC and photophysical findings may be a useful tool for developing material science applications. (Mario Macias and Jaime Portilla – 2021)

2.13 Multi-Step Synthesis, Physicochemical investigation and optical properties of pyrazoline derivative: A Donor-π-Acceptor chromophore

From heterocyclic chalcone and 2-hydrazinylbenzo[d] thiazole, the latest extended-bond pyrazoline derivative (ENTD) was synthesised. The composition of the ENTD was calculated using spectroscopic techniques, and its purity was measured using elemental analysis. To see the effect of the solvent with pyrazoline derivative (ENTD) on the basis of different polarity, physicochemical ENTD parameters such as the molar absorption coefficient, transition dipole moments, Stokes shift, oscillator frequency, and fluorescence quantum yield were calculated in ten different solvents.The interaction of the ENTD chromophore with cationic and anionic surfactants has also been investigated. The intensity of the ENTD's fluorescence spectrum was found to increase as the surfactant concentration was increased. This suggests that ENTD and surfactants have a complex relationship. As a result, the ENTD chromophore can be used as a probe to determine the CMC of surfactants. (Qasim Ullah and Salahuddin Syed – 2021)

CHAPTER 3

AIM AND SCOPE

3.1 AIM

The aim of the project is to synthesis the donor – acceptor luminescent molecules by using electron withdrawing substituent and electron donating substituent in the molecules.

3.2 OBJECTIVE OF WORK

- To design and synthesize the donor – acceptor molecular system which exhibits luminescent properties.
- To study the photophysical properties of synthesized molecular probe.
- To analyse the absorbance and emission of the synthesized molecules by using Uv-Visible Spectroscopy and Fluorescence Spectroscopy.

CHAPTER 4

MATERIALS AND METHODS

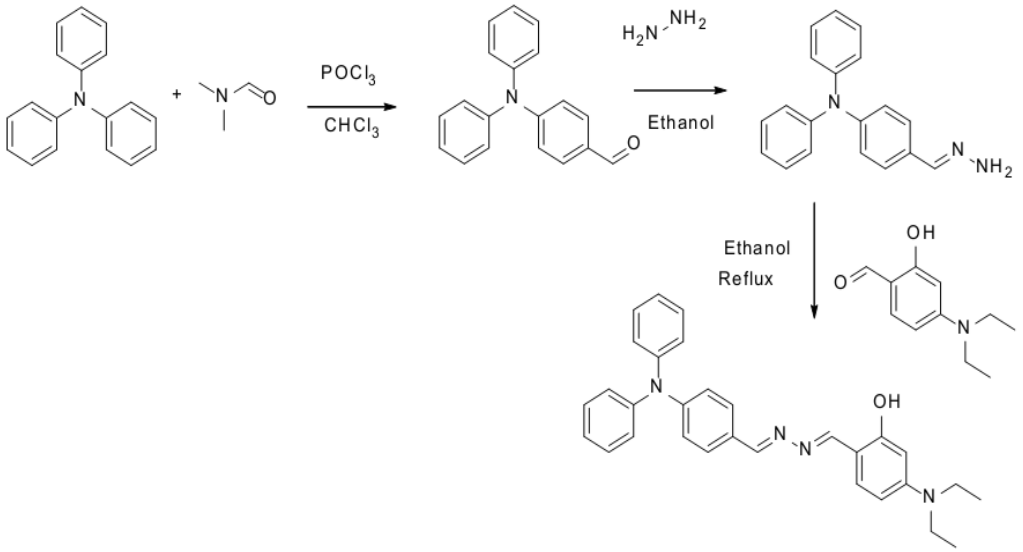
CLEANING OF APPARATUS

All the apparatus are washed with tap water followed by distilled water. It is cleaned with acetone and dried before using them.

4.1 MATERIALS AND CHEMICAL REQUIRED

- Triphenylamine
- N, N – dimethylformamide (C_3H_7NO)
- Hydrazine (N_2H_4)
- Phosphorous oxy chloride ($POCl_3$)
- Tetrahydrofuran (C_4H_8O)
- Dichloromethane

4.2 REACTION FOR TPA-H-DESA



4.2.1 REACTION FOR TPA-H-DESA

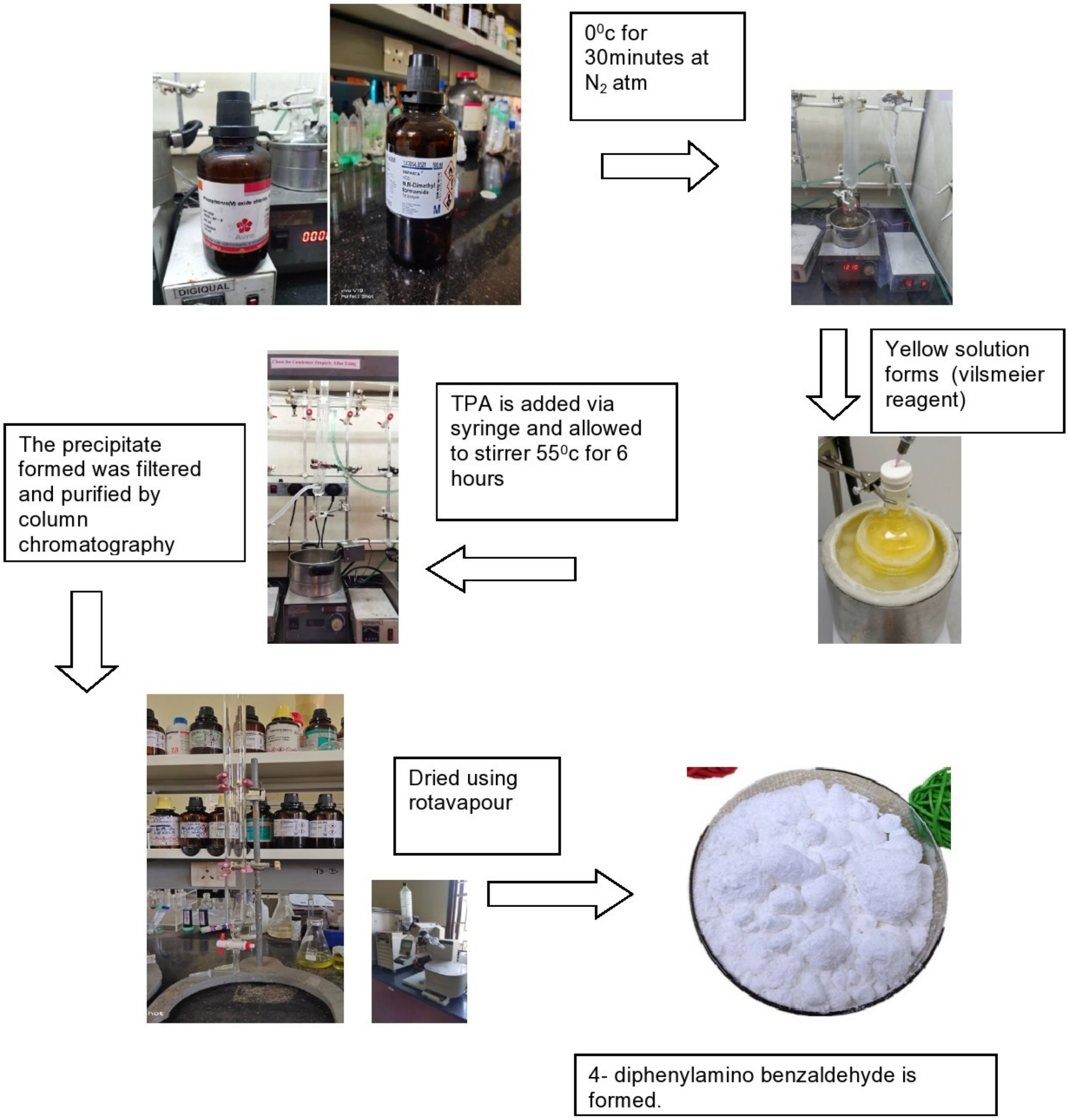
In this reaction, it involves 3 steps namely: Formylation reaction, Amine aldehyde condensation and Again Amine aldehyde condensation.

4.2.1 FORMYLATION REACTION

To introduce the functional group in Triphenylamine .It is the primary step.

4.2.1.1 Procedure

In a 100 ml two neck RB flask closed with rubber septum, 1.001g (0.0039 M) of phosphorous oxy chloride (POCl3) was taken to that add 0.44g (0.0061 M) of DMF was added drop wise under N_2 atm, and it is allowed to stirrer at 0°C for 30 minutes till vilsmeier regent forms (yellow colour solution). To that 1g (0.0041 M) of solid triphenylamine dissolved in 10 ml of DCM was added slowly via syringe. Then the reaction mixture was again kept in a stirrer at 55°C for 6 hours. After that reaction, the mixture was poured in 500 ml of beaker containing ice with constant stirring. The precipitate is formed. The formed precipitate was filtered, and purified using column chromatography. (5% ethyl acetate in hexane).It is dried using rotavapour. And then it is weighed. We get the yield 0.91 g (81%) of pure compound as pale yellow crystals.



0^0c for 30minutes at N_2 atm

Yellow solution forms (vilsmeier reagent)

TPA is added via syringe and allowed to stirrer 55^0c for 6 hours

The precipitate formed was filtered and purified by column chromatography

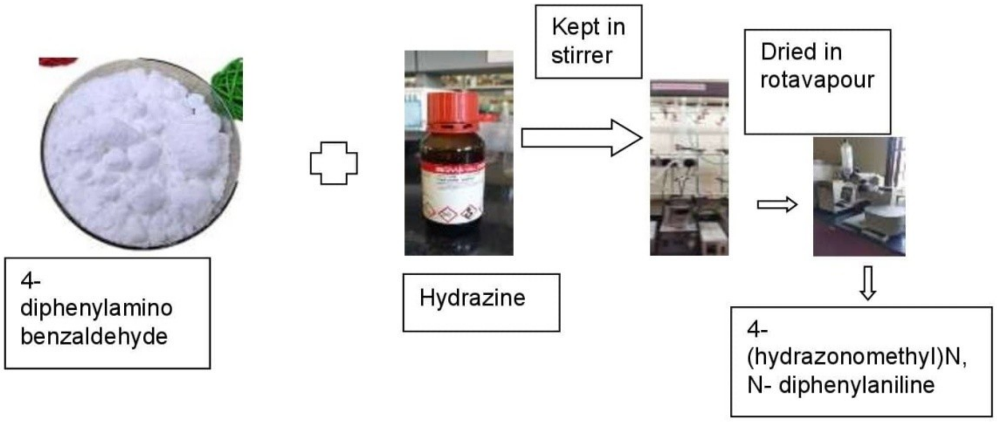
Dried using rotavapour

4- diphenylamino benzaldehyde is formed.

4.2.1.1 Schematic flowchart of Formylation reaction

4.2.2 Amine Aldehyde Condensation

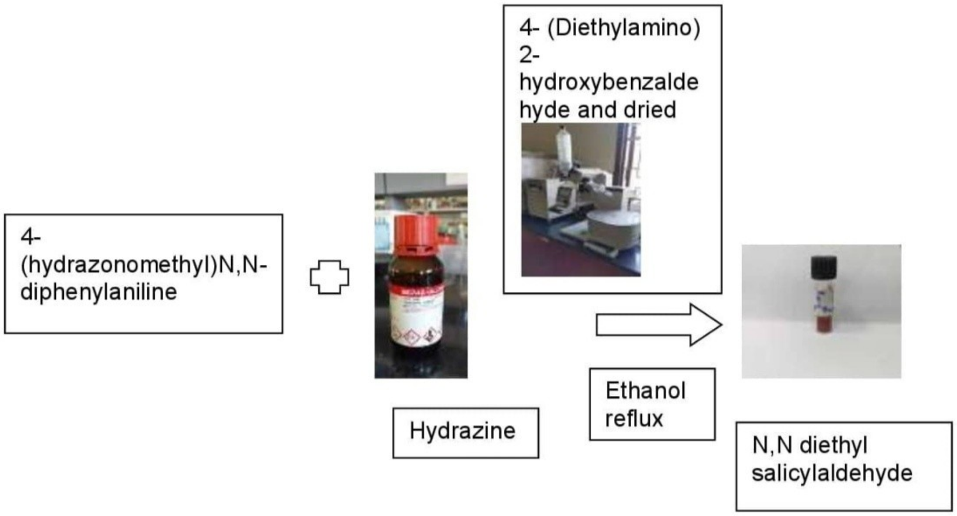
4- diphenylamino benzaldehyde and hydrazine is added and kept in a stirrer and dried in a rotavapour and we get the yield 4- (hydrazonomethyl)N,N-diphenylaniline



4.2.2.1 Flowchart of Amine Aldehyde Condensation

4.2.3 Amine Aldehyde Condensation

4- (hydrazonomethyl)N,N- diphenylaniline and hydrazine is added and kept in a stirrer and dried in a rotavapour and we get the yield 4- (hydrazonomethyl)N,N-diphenylaniline



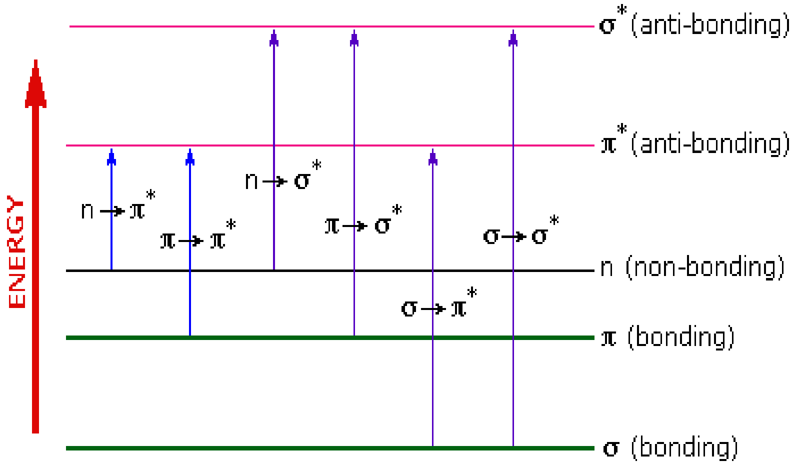
4.2.3.1 Flowchart of final step Amine Aldehyde Condensation

4.3 CHARACTERIZATION TECHINQUE

4.3.1 ULTRA VIOLET – VISIBLE (UV –Vis) SPECTROSCOPY

UV-VIS spectroscopy is a type of absorption spectroscopy in which light of UV-Vis region (200-800 nm) is absorbed by the molecule. Absorption of the UV-Vis radiations results in the excitation of the electrons from the ground state to higher energy state. The energy of the UV-Vis radiation that are absorbed is equal to the energy difference between the ground state and higher energy states. Generally, the most favoured transition is from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). For most of the molecules, the lowest energy occupied molecular orbitals are s orbital, which correspond to sigma bonds. The p orbitals are at somewhat higher energy levels, the orbitals (nonbonding orbitals) with unshared paired of electrons lie at higher energy levels. The unoccupied or anti-bonding orbitals ($\pi^*$and σ^*) are the highest energy occupied orbitals. All the compounds (other than alkanes), the electrons undergo various transitions. Some of the important transitions with increasing energies are: $n \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $\sigma \rightarrow$

π^* and $\sigma \rightarrow \sigma^*$.



4.3.1 UV-VIS spectroscopy (Electronic transition)

PRINCIPLE OF UV-VIS SPECTROSCOPY

UV –Vis spectroscopy obeys the Beer-Lambert law, which states that: *when a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the incident radiation as well as the concentration of the solution.* The expression of Beer–Lambert Law is, $A = \log (I_0/I) = £Cl$

Where, A = absorbance

I_0= intensity of light incident upon sample cell

I = intensity of light leaving sample cell

C = molar concentration of solute

l = length of sample (cm)

£ = molar absorptivity

From the Beer-Lambert law it is clear that greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption. This is the basic principle of UV spectroscopy.

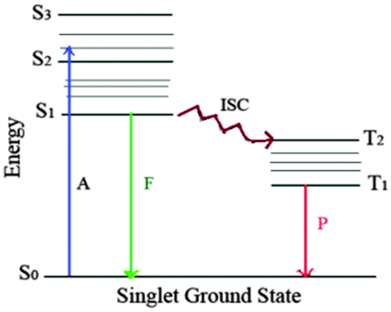
4.3.2 FLUROSCENCE SPECTROSCOPY

Fluorescence spectroscopy measures the intensity of photons emitted from a sample after it has absorbed photons. Most fluorescent molecules are aromatic. Fluorescence is an important investigational tool in many areas of analytical science, due to its high sensitivity and selectivity. It can be used to investigate real-time structure and dynamics both in solution state and under microscopes, particularly for bio-molecular systems.

PRINCIPLE AND INSTRUMENTATION

Fluorescence occurs when a fluorescent capable material (a fluorophore) is excited into a higher electronic state by absorbing an incident photon and cannot return to the ground state except by emitting a photon. The emission usually occurs from the ground vibrational level of the excited electronic state and goes to an excited vibrational state of the ground electronic state. Thus fluorescence signals occur at longer wavelengths than absorbance. The energies and relative intensities of the fluorescence signals give information about structure and environments of the fluorophores.

The component parts necessary within a typical Fluorescence Spectrometer (Spectrofluorometer) are a sample holder, incident photon source (typically a xenon lamp), monochromators used for selecting particular incident wavelengths, focussing optics, photon-collecting detector (single, or preferably multiple channel) and finally a control software unit. An emission monochromator or cut-off filters are also usually employed. The detector is usually set at 90 degrees to the light source. The intrinsic sensitivity of fluorescence is also its biggest problem and care must be taken to record a true fluorescence signal of the analyte of interest. A fluorescence emission spectrum is recorded when the excitation wavelength of light is held constant and the emission beam is scanned as a function of wavelength. An excitation spectrum is the opposite, whereby the emission light is held at a constant wavelength, and the excitation light is scanned as a function of wavelength. The excitation spectrum usually resembles the absorbance spectrum in shape. Most materials are not naturally fluorescent. However, useful data, particularly in fluorescence microscopy can be obtained by staining non-fluorophores with an active label.



4.3.2.1 Jablonski Diagram

CHAPTER 6

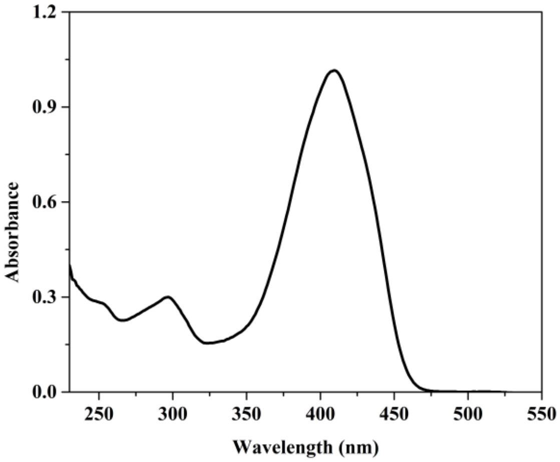
RESULTS AND DISCUSSION

- ✓ N,N diethyl salicylaldehyde was produced by Formylation and Amine aldehyde condensation method using Triphenylamine, DMF and other solvents etc …
- ✓ The optical properties of N,N diethyl salicylaldehyde can be measured by using UV-visible spectroscopy and fluorescence spectroscopy.

PHOTOPHYSICAL STUDIES

5.1 Uv- Visible Spectroscopy

We have a prepared a stock solution for 10^{-3} molar concentration. Then it is diluted to 10^{-6} concentration. From that absorbance is measured using Shimadzu Uv 1800 in the range 800 – 400 nm. We get the maximum absorbance at 410nm.



5.1.1 Uv- Visible spectroscopy absorbance graph

5.1.2 MOLAR EXTINCTION COEFFICIENT

The term molar extinction coefficient (ε) is a measure of how strongly a chemical species or substance absorbs light at a particular wavelength. It is an intrinsic property of chemical species that is dependent upon their chemical composition and structure.

According to Beer-Lambert's law, $A = \epsilon cl$.

Where, A = Absorbance value

ϵ = Molar Extinction Coefficient

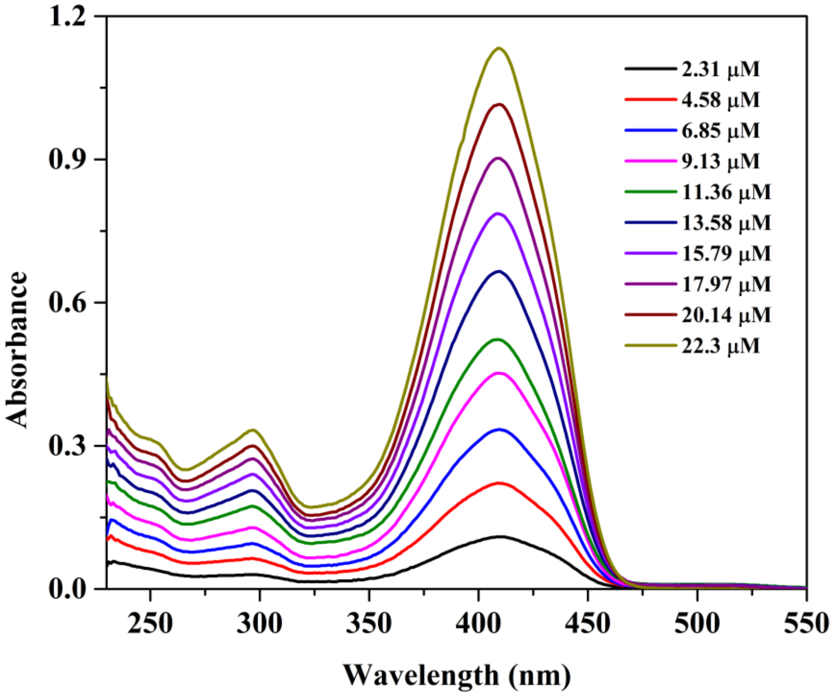
C = Concentration

L = Pathlength of the Cuvette (10mm)

Molar extinction coefficient is calculated by $\epsilon = A/Cl$

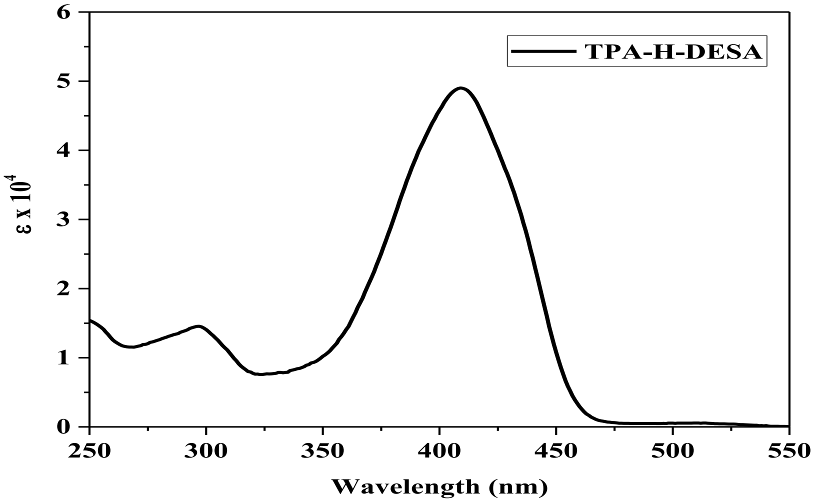
Beer- Lambert's law obeys for less than 10^{-3} molar concentration.

If concentration is high, Due to scattering, absorbance is not measured correctly. So I taking very dilute solution of THF in the range of 10^{-6} molar concentration. We get 10 molar extinction coefficient value. Since, we are preparing for organic dye. We are also going to measure the molar extinction coefficient of the dye. For this measurement, we will make 10 known concentration (1×10^{-5} to 1×10^{-6})and the absorbance is measured using known concentration.



5.1.2.1 10 different concentration of Molar extinction coefficient

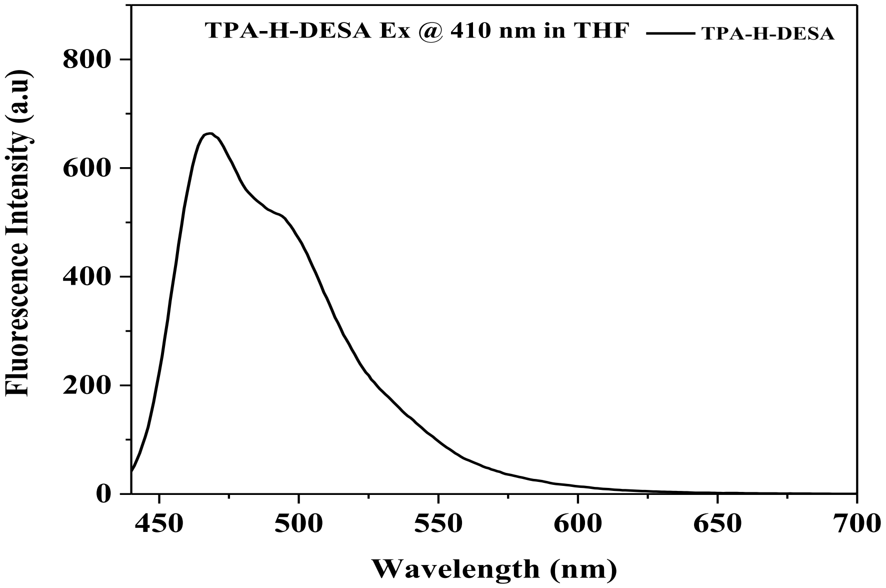
By this known concentration, we measure the molar extinction coefficient value and plotted in the graph 5.1.2.2



5.1.2.2 Average molar extinction value

5.2 Fluorescence Spectroscopy:

The emission property of N,N- diethyl salicylaldehyde was measured in THF solvent shown in fig 5.2.1. we get absorbance at 400nm in Uv- Visible spectroscopy. We are expected to get excitation at 400nm. After measuring the emission spectrum of the compound it gives a emission intensity at 470nm along with this we got another shoulder peak at 490 nm.

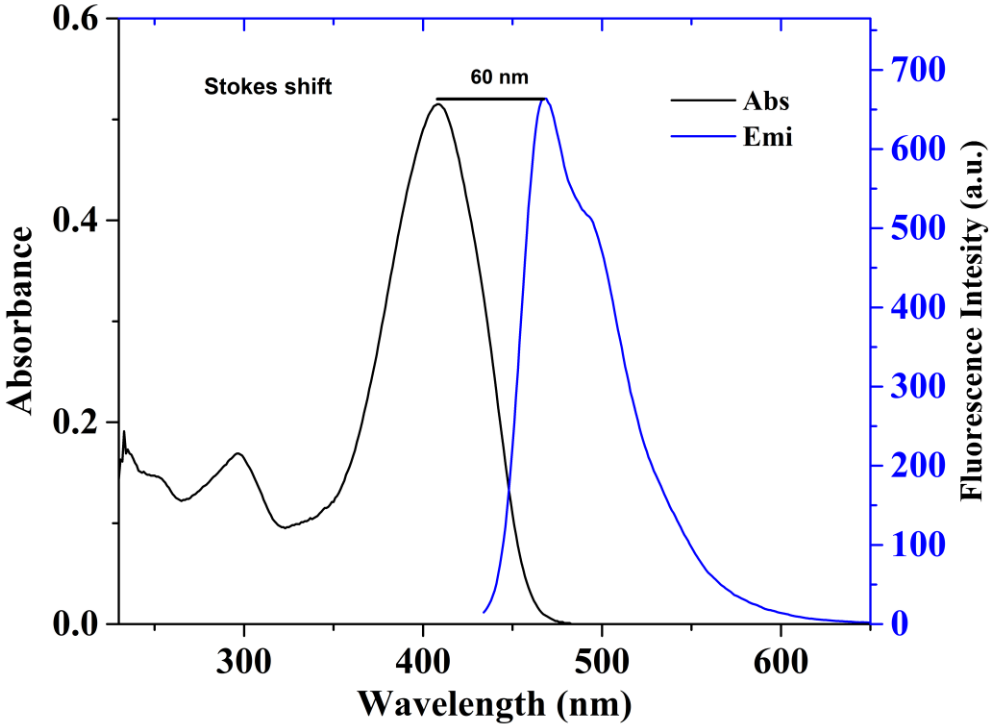


5.2.1 Fluroscence Spectroscopy graph

5.2.1 STOKES SHIFT

The difference between the maximum wavelength of the excitation light and the maximum wavelength of the emitted fluorescence light is a constant. This phenomenon is known as Stokes shift.

Stokes shift is used to measure the difference between absorbance maxima and the fluorescence maxima. We get the Stoke shift at 60nm.



5.2.1.1 Stokes shift of Absorbance and Emission

SUMMARY AND CONCLUSION

Donor- Acceptor luminescent molecules was synthesized by using Triphenylamine, N,N- dimethylformamide, $POCl_3$, Dichloromethane and Hydrazine are used in this reaction as solvent. It can be synthesized by Formylation reaction and Amine Aldehyde Condensation. Further, photophysical studies of the compound were carried out by using UV- VISIBLE SPECTROSCOPY and FLUORESCENCE SPECTROSCOPY.

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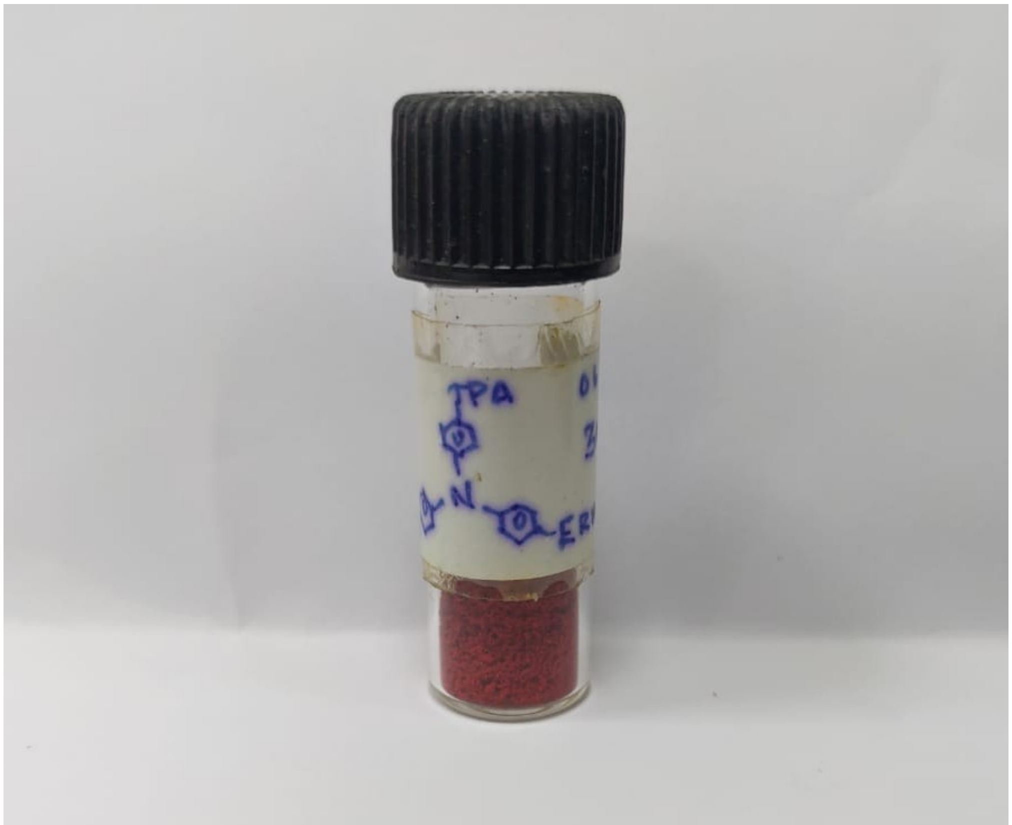
Geo tagged Photos

1. N,N- Diethyl salicylaldehyde

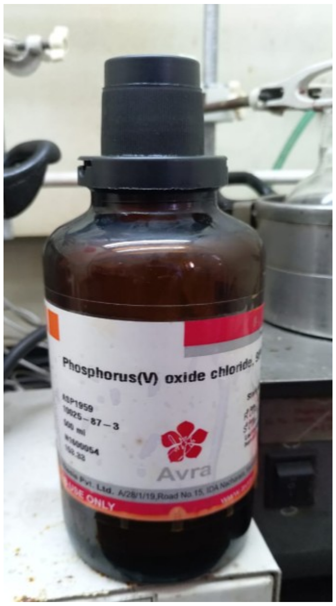


2. Uv- Visible Spectroscopy

3. Fluorescence Spectroscopy

4. Rotavapour

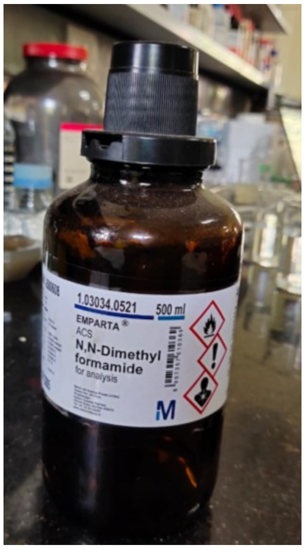
5. $POCl_3$



6. Hydrazine


SIGMA-ALDRI
225819-100ML
Lot # BCBR
Hydrazine hydrate
reagent grade, N_2H_4 50-60 %
Hydrazinium hydroxide

7. DMF



8. Condenser (stirrer)

9. Column Chromatography

10. Ethanol