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Solvent Impact on Fluorescence and UV-Vis Spectra: Gáti and Szalay Relationship for Sulfonimide-Based Compound

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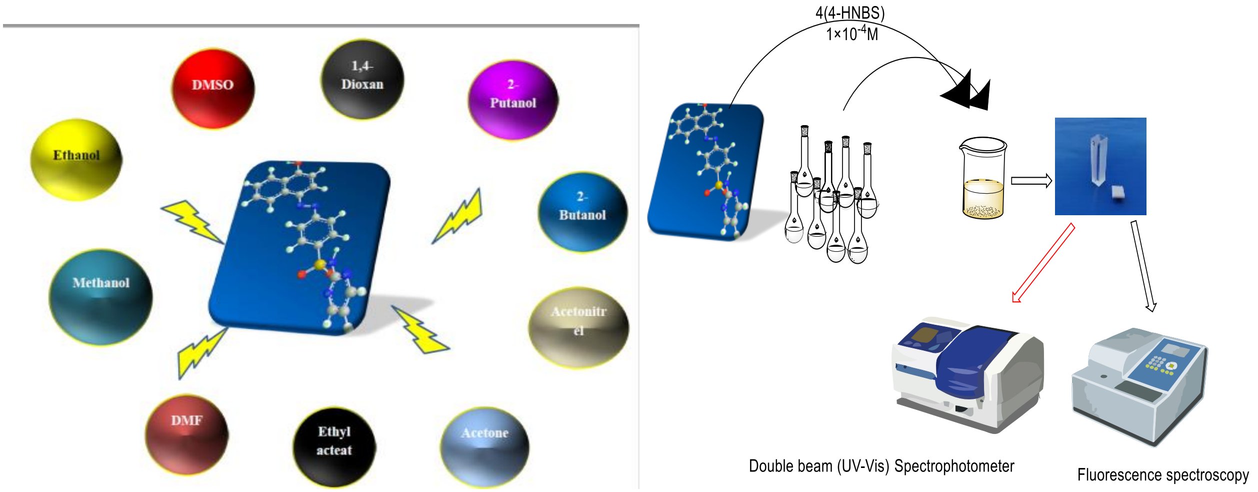
Abstract

Both absorption and fluorescence spectra are studied and measured for"4(4-HNBS),4-((4-hydroxynaphthalen-1-yl)diazenyl)-N-(pyrimidin-2-yl)benzenesulfonamide", Which is dissolved in DMF, DMSO, 2-butanol, 2-propanol, 1,4-dioxane, methanol, Ethanol, acetone, acetonitrile, and ethyl acetate when Dissolved in different solvents. Fluorescence and absorption spectra peaks are Calculated and compared. The Solvation or dielectric constant effect is presented by Using the Gáti and Szalay Relationship.

GRAPHICAL ABSTRACT



Keywords*:* Fluorescence; UV-VIS; Solvent effect; Azo compounds

1. Introduction

Organic dyes are complex unsaturated hydrocarbon compounds containing Chromophores that are responsible for their color by absorbing visible light (400–700 nm) [1]. Organic dyes have gained immense importance in spectroscopy, Environmental, and industrial applications due to their wide range of applications Over the last two decades [2]. Their spectroscopic characteristics in various solvents Are an excellent source of data about solute-solvent interactions and dipole moment Changes [3].

Azo dyes containing the (-N=N-) chromophore group are one of the most widely used Classes of organic dyes. They are extensively applied in leather [4], paper [4], textile [5][6], food [7][8], environmental applications [9], pharmaceutical applications [10][11], industrial chemical applications [11], cosmetics and pharmaceuticals [12], And biomedical research [13][14].

These dyes are synthesized mainly through diazotization and coupling reactions [15][16]. Azo dyes account for approximately 60–70% of industrial dye production [17][18][19]. They are usually modified in order to enhance dispersibility, color Properties, and particle size. Spectroscopic methods, particularly UV-Vis and Fluorescence spectroscopy, are of immense significance in qualitative and Quantitative analysis of organic dyes [20].

UV-Vis spectrophotometry measures the absorption of ultraviolet (180–380 nm) and Visible (380–780 nm) light by molecules, leading to electronic excitations in Chromophores [21]. Fluorescence spectroscopy, on the other hand, involves light Absorption and subsequent emission, producing a Stokes shift due to energy loss in Non-radiative decay. Figure 1 shows a Jablonski diagram illustrating the transitions Between energy states [22][23][24][25][26].

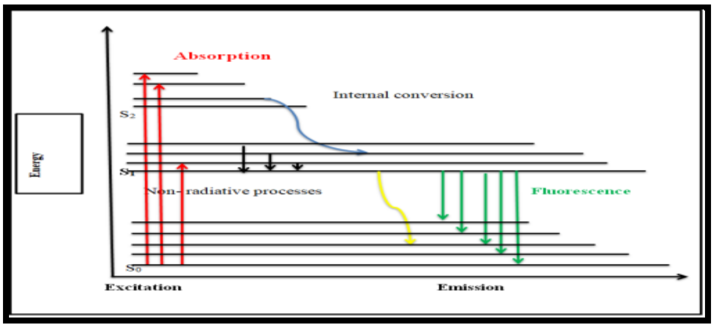


Fig. 1. Jablonski diagram

This technique is highly sensitive and widely applied for detecting fluorophores in Various environments [27]. Solvent polarity significantly affects dyes' absorption And Fluorescence spectra, influencing photophysical properties such as Stokes shifts And Spectral shapes [26][28]. These effects are widely studied in optoelectronics, Organic Light-emitting diodes, and organic photovoltaics. Fluorescence spectroscopy Is also Used for environmental monitoring, including water quality assessment and Oil Pollution detection [22]. Additionally, laser-induced fluorescence is employed in Broadband light sources for spectroscopy applications [29]. The method is effective For real-time applications, such as differentiating plant varieties post-harvest [30]. Organic dyes, especially azo dyes, are crucial in various scientific fields. Their Spectroscopic properties are widely studied using UV-Vis and fluorescence Techniques to understand their behavior and enhance their applications in diverse Sectors.

2. Experiment

2.1. Instrumentation

The instruments used in the current research were:

- UV-Vis spectrophotometer with double-beam, Libra S60 Biochrom, England, UK.
- AD Company Limited electric sensitive balance, CE HR 200, Dool, Japan.
- Spectrophotometer F96 PRO, Product: Shanghai Kingdak Company, emission Monochromatic wavelength range (200–900 nm), scanning rate.
- Laboratory equipment, involving pipettes, beakers, and different sizes Volumetric flasks.

2.2. Organic solvents used in the study

Table .1. lists the organic solvents used in the current study.

Substance	Molecular	M.wt	Company	Purity
1,4-Dioxane	$C_4H_8O_2$	88.11	B.D.H	99%
2-Butanol	C_4H_9OH	74.12	G.C.C	99%
Propanol2-	C_4H_7OH	60.094	B.D.H	99%
Acetone	$(CH_3)_2CO$	58.08	B.D.H	99%
Acetonitryl	CH_3CN	180.156	B.D.H	99%
Dimethyl formamide	C_3H_7NO	73.09	ROMIL	98%
Dimethyl sulfoxide	C_2H_6OS	78.13	Merck	99%
Ethanol	C_2H_5OH	46.0688	B.D.H	99%
Ethyl Acetate	$C_4H_8O_2$	88.11	G.C.C	99%
Methanol	CH_3OH	32.04	G.C.C	99%

3. Azo Reagent 4(4-HNBS) Studies

3.1 Comparison of the study of the effect of solvents on absorption and fluorescence

The absorption spectrum was measured by a UV-Vis spectrophotometer with double-Beam, LibraS60, Biochrom England, UK. The fluorescence spectrum was recorded By using a spectrofluorophotometer. The Spectrophotometer F96 PRO, a product of Shanghai Kingdak Company, has an emission monochromatic wavelength range of 200–900 nm and a specified scanning rate. It features dimensions of 1 × 1 × 5 cm and Is positioned at an angle of 90° with the incident beam. The selected optical Configuration aims to remove the impact of scattered incident radiation as well as the Occurrence of self-absorption.

The instrument is digitally controlled and functions within the wavelength range Between 200 and 900 nm. A specialized computer manages the operational aspects of The fluorometer, including excitation and emission wavelengths, scanning, Monochromator slit width, and detector settings, as well as the collection of spectral Data. It is used in the measurements, which were performed at room temperature.

3.2 Effect of organic solvents on 4(4-HNBS)

The absorption spectrum of the synthesized organic reagents was recorded over a wavelength range of 280–800 nm in solvents of different polarities. Solvents such as DMF, DMSO, 2-butanol, 2-propanol, 1,4-dioxane, methanol, ethanol, acetone, ethyl Acetate, and acetonitrile were utilized. Readings were derived from the dissolving of

A specified quantity to achieve a concentration of 0.0001 M of the organic Component.

4. Results and Discussion

4.1 UV-Visible and Fluorescence Technique

The red-orange solution of 4(4-HNBS) Its shape is shown below figure(2)dissolving in ethanol exhibited peaks at 461 nm, attributed to the absorption of the -N=N- group, as seen in Fig. 3. These Absorptions indicated that not all interacting molecules encompassed both compound Bands.

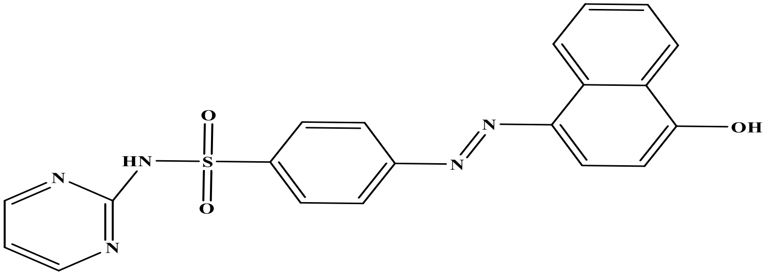


Figure 2. (E)-4-((4-hydroxynaphthalen-1-yl)diazenyl)-N-(pyrimidin-2-yl)benzenesulfonamide

4(4-HNBS)

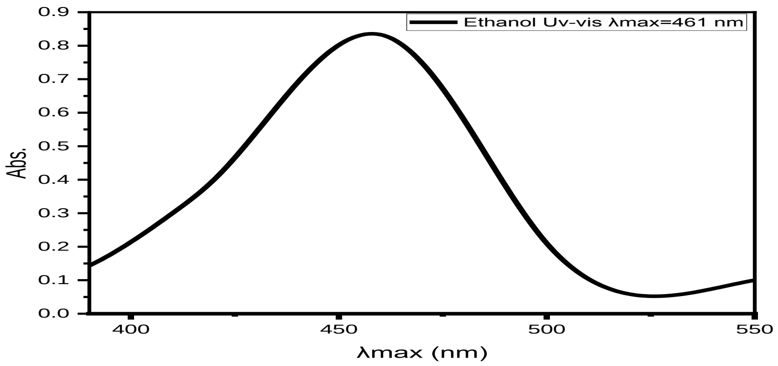


Fig. 3. 4(4-HNBS) absorption spectrum in ethanol

4.2 Effect of organic solvents on 4(4-HNBS)

In this paper, the fluorescence spectra of a 4(4-HNBS) solution dissolved in different Polarities solvents, such as 2-butanol, DMF, ethanol, DMSO, 2-propanol, methanol, 1,4-dioxane, acetone, ethyl acetate, and acetonitrile [10][11][31], were examined at a 1×10^{-4} M concentration to determine the effect of polarity on the fluorescence Spectrum. The tests were conducted on the compound in various solvents, such as DMF, 1,4-dioxane, DMSO, 2-butanol, methanol, 2-propanol, ethanol, acetone, ethyl

Acetate, and acetonitrile. It should be noted that the solvents were selected based on Their ability to dissolve the compound. Fig. 4 and Table 2 show the absorption and fluorescence spectra of solutions in Different solvent polarities, respectively. From Table 1, the fluorescence spectra Appear in the UV-visible absorption spectra of the organic compound 4(4-HNBS), Showing maximum absorption peaks due to the π-π* transitions within the detector Molecule. There are previous studies that compared absorbance and fluorescence at The same concentrations [32][33][2][34].

Table 2. Measured maximum absorption and fluorescence for the 4(4-HNBS) molecule in different solvents.

NO.	Solvents	λ_{max}	Absorption	λ_{max}	intensity
1	ACETONITRILE	450.50	0.766	588	0.811
2	Acetone	450.00	0.831	590	0.880
3	ETAC	454.00	0.417	589	0.511
4	DMF	458.00	0.856	588	0.951
5	ETHANOL	461.00	0.830	588	0.952
6	2-Butanol	464.00	0.897	589	0.860
7	METHANOL	469.50	0.815	585	0.941
8	2-Propanol	470.50	1.050	590	0.882
9	DMSO	566.00	0.505	615	0.581
10	1,4-Dioxan	450.5	0.896	586	0.911

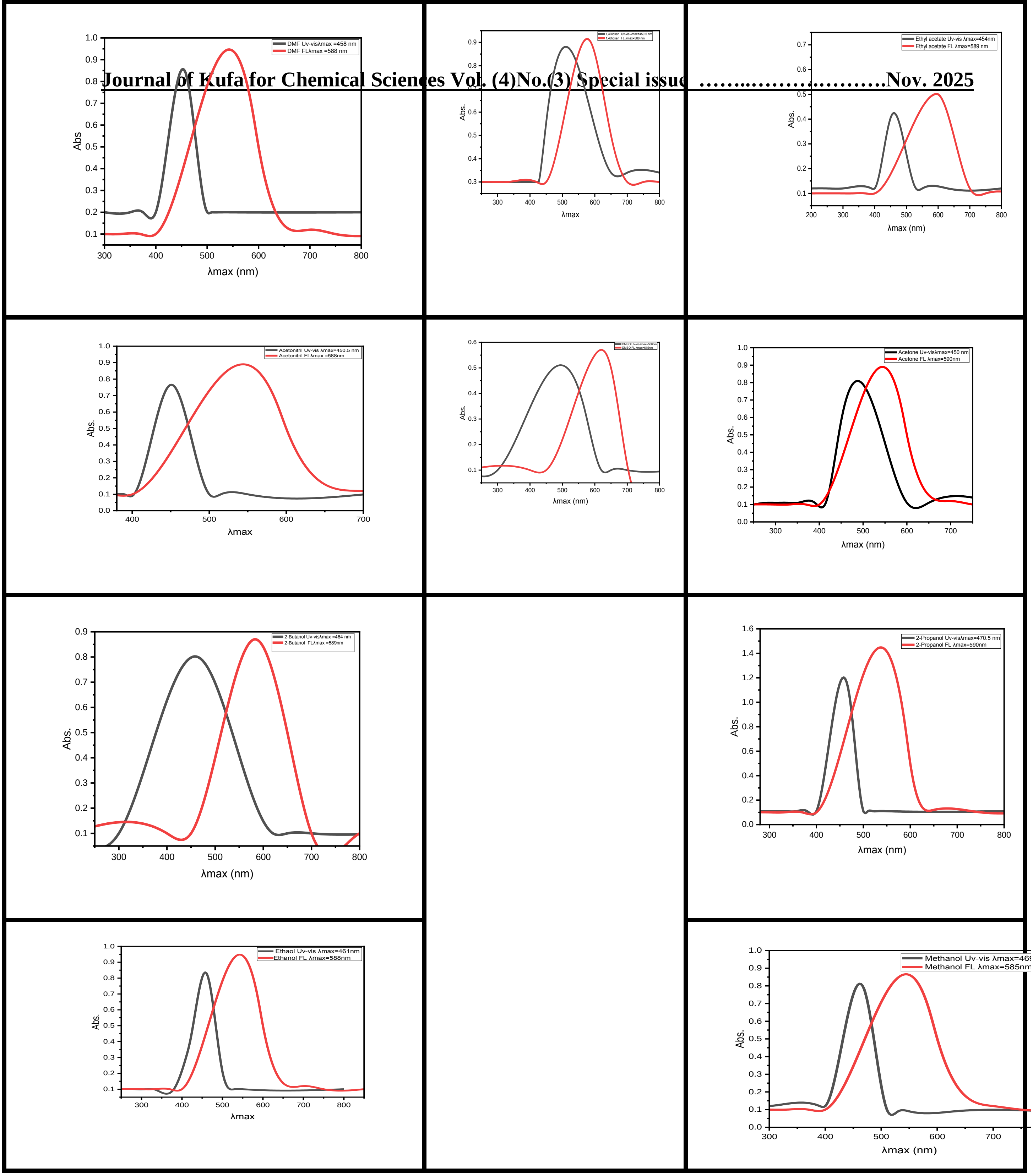


Fig. 4. Absorbance and fluorescence spectra of 4(4-HNBS) in different solvents.

When compared to fluorescence and absorption (ABSORPTION) for the same compound, there are several expected results:

1. Difference in wavelength (Stokes Shift):

- The fluorescence spectrum appears at longer wavelengths (lower energies) than The absorption spectrum.
- This occurs due to the loss of some energy in the form of internal vibrations Before the release of light [35][36][37][38][39].

2. Signal intensity:

- Absorption depends on the number of molecules that absorb light at a specific Wavelength, while fluorescence depends on the emission efficiency after Absorption.
- Some compounds may be highly absorbing, but their fluorescence may be Weak due to energy loss in other ways (such as internal transformations or Phosphorescence) [40].

3. Spectrum shape:

- The absorption spectrum is usually broader than the fluorescence spectrum Because absorption may occur from multiple vibrational states. Conversely, Fluorescence often arises from lower vibrational level of the excited electronic State. [41][42].

4. The overlap between the two spectra:

- In some cases, there may be an overlap between absorption spectra and Fluorescence, which is known as “self-fluorescence” or “internal overlap,” Especially if there is a direct transition between closely spaced energy levels [43][44].
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5. The effect of the surrounding environment:

- The properties of absorption and fluorescence can change due to a solvent or pH change, which may lead to spectra shifts or intensity changes [45][46].

•Consequently, comparing the fluorescence and absorption measurements provides Valuable Information about the behavior of the studied compound, its electronic Nature, and its Interaction with its environment [47][48].
Fluorescence is a process in which light is emitted when a molecule returns to a lower energy State after absorbing a photon in the ultraviolet or visible range. Transitions include:

S1 → S0 transitions: Occur when a molecule transitions from a singlet excited state (S1) to a ground singlet state (S0), emitting light during this process.

S2 → S0 transition does not occur directly: According to the Franck-Condon rule, a molecule In the higher excited state (S2) undergoes internal conversion (IC) to S1 before fluorescence Occurs.

Triple state interaction: Sometimes a transition from the singlet excited state (S1) to the triplet State (T1) may occur via an intersystem crossing (ISC), which subsequently leads to phosphorescence if T1 decreases to S0 by emitting light.

Thus, fluorescence usually results from the S1 → S0 transition and is of lower energy (longer Wavelength) than the absorbed radiation due to some energy being lost in vibrational or Internal cooling processes[49][50][51].

5. Solvent Effect

5.1 Study of the Impact of Solvent Dielectric Constant on the Organic Probe 4(4-HNBS)

The absorption spectrum of the probe was studied in different polar organic solvents, Including DMF, acetonitrile, DMSO, 1,4-dioxane, 2-butanol, 2-propanol, ethanol, Acetone, methanol, and ethyl acetate. This study provided valuable information about The nature of the mutual interaction between the solvent and the solute. This study Concludes that there are changes in the intensity and shape of the electronic Absorption bands. These mutual effects are classified into two types:

Firstly, specific interactions result in the binding of solvent molecules with solute Molecules through hydrogen bonds and the formation of charge transfer complexes.

Secondly, non-specific interactions involve electrostatic attractions between the Solvent and solute, attributed to dipole-induced dipole interactions, dispersion forces, And dipole-dipole interactions. Changes in the solvent may shift the absorbance Spectrum of the absorbing substance towards longer wavelengths (redshift). This Redshift is particularly pronounced in solvents with high dielectric constants because The displacement of charge to a higher state requires less energy in a high dielectric Constant solvent than in a vacuum.

Unsaturated organic molecules containing π orbitals and electrons can exhibit red and Blue shifts simultaneously when dissolved in a polar solvent. This study was Conducted over a range of nanometer wavelengths, as illustrated in Table 3, Demonstrating the key absorption bands of the prepared detector in various polar Solvents.

As most of the spectral properties of these dyes are affected by the surrounding Solvent molecules, the solvent can lead to a change in their spectral properties. It is Noted that the absorption spectra in various polar solvents are influenced by what is

Called the solvation or dielectric effect (D). The solvation or dielectric constant effect Is expressed by applying the Gati and Szaly relationship, given by Eq. 1 [49]:

$$\Delta V=[(a-b)(n^2-1/2n+1)]+b(D-1/D+1)] \qquad \textbf{Eq. 1}$$

Where:

Δ V= frequency change.

n=refractive index of the medium, and

a, b = constants

This relationship arises from the change in solvation energy or dielectric constant Effect. More precisely, the functions ØD and f(D) lead to a linear relationship when The dielectric constant controls the band shift.

$$\mathbf{f(D)} = \frac{2(D-1)}{(2D+1)} \qquad \textbf{Eq. 2}$$

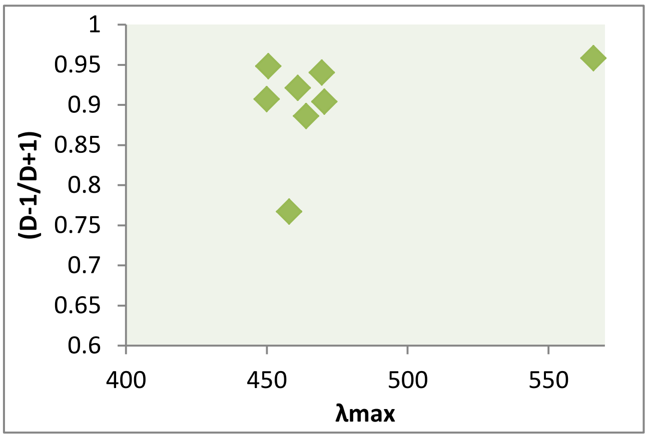
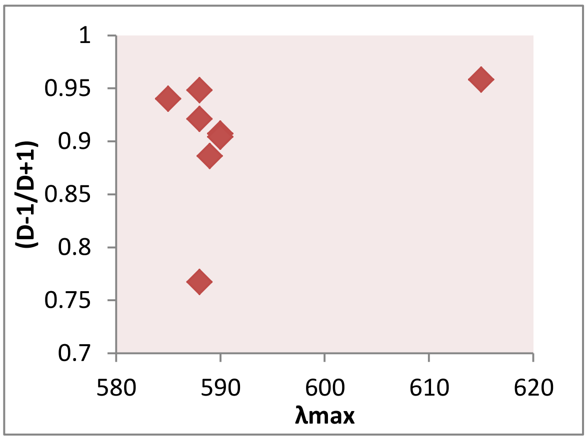
$$\mathbf{ØD}= \frac{(D-1}{(D+2)} \qquad \textbf{Eq. 3}$$

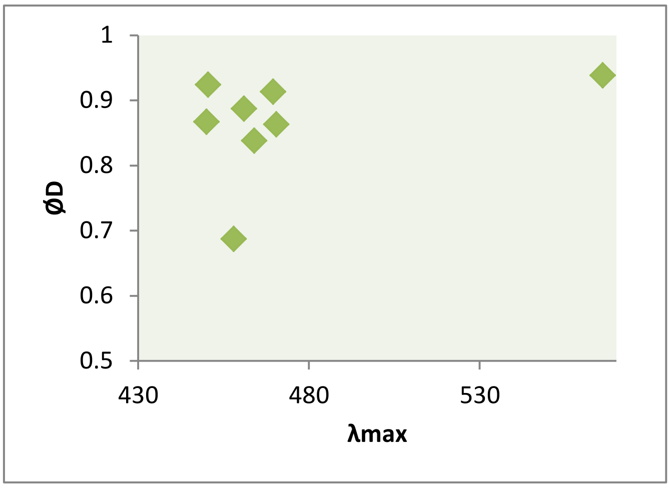
Where f(D), ØD, and (D-1)/(D+1) represent functions of the dielectric constant, and The values of these functions are given for each solvent[50]

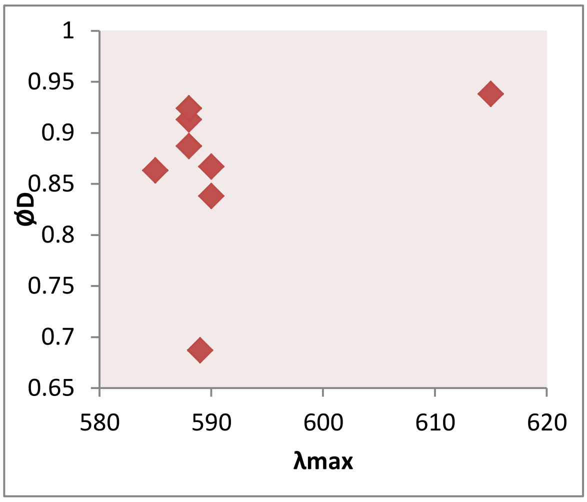
Table 3. values of the f(D), ØD, and (D-1)/(D+1) functions

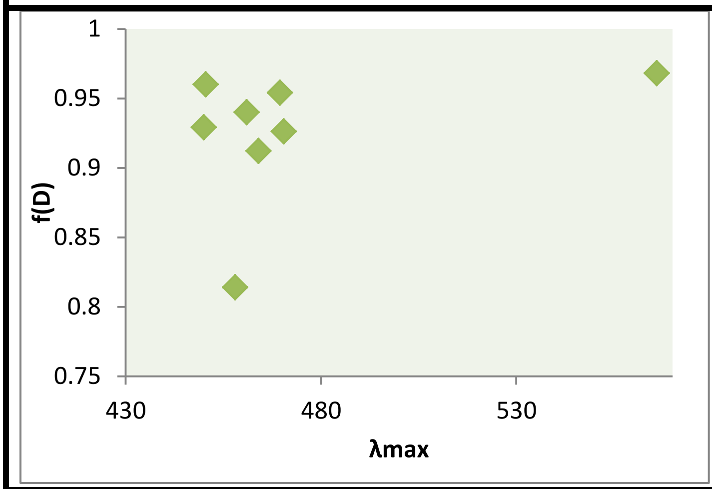
No.		Solvent	λ_{max}	D	(D-1/D+1)	ØD	f(D)	Solvent	λ_{max}	D	(D-1/D+1)	ØD	f(D)
1	Polar solvents	Acetone	450	20.7	0.907	0.867	0.929	Acetone	590	20.7	0.907	0.867	0.929
2		DMF	458	7.6	0.767	0.687	0.814	DMF	588	7.6	0.767	0.687	0.814
3		2-Butanol	464	16.56	0.886	0.838	0.912	2-Butanol	589	16.56	0.886	0.838	0.912
4		2-Propanol	470.5	19.92	0.904	0.863	0.926	2-Propanol	590	19.92	0.904	0.863	0.926
5		Methanol	469.5	32.6	0.94	0.913	0.954	Methanol	585	32.6	0.94	0.913	0.954
6		Acetonitrile	450.5	37.5	0.948	0.924	0.96	Acetonitrile	585	37.5	0.948	0.924	0.96
7		DMSO	566	47	0.958	0.938	0.968	DMSO	615	47	0.958	0.938	0.968
8		Ethanol	461	24.6	0.921	0.887	0.94	Ethanol	588	24.6	0.921	0.887	0.94
9	Non-polar solvents	ETAC	454	6	0.714	0.625	0.769	ETAC	589	6	0.714	0.625	0.769
10		1,4-Dioxane	450.5	2.3	0.393	0.302	0.464	1,4-Dioxane	450.5	2.3	0.393	0.302	0.464

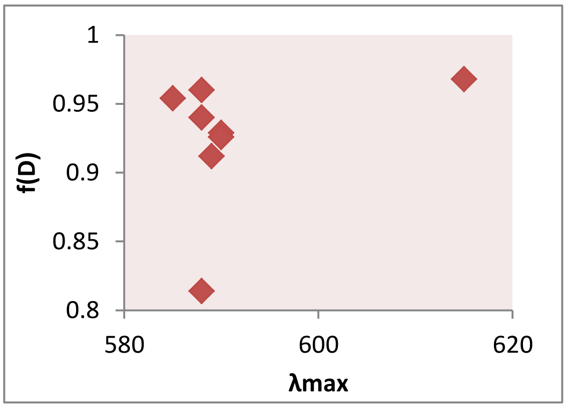
Table5. Relationship between the organic dye wavelength and the functions specific to the dielectric constants of various polar solvents

Polar solvents UV-Vis	Polar solvents FL
	



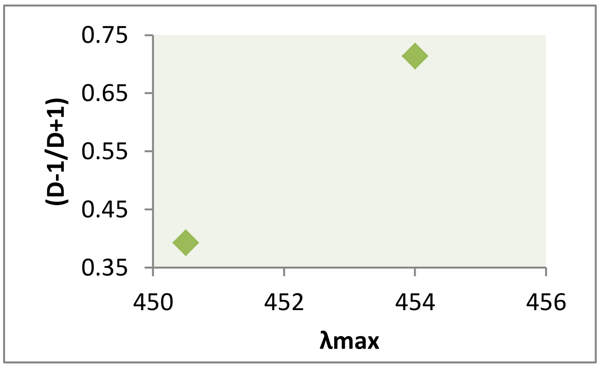


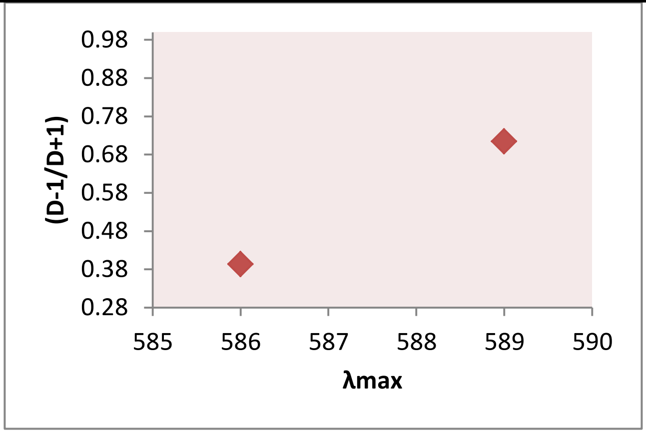


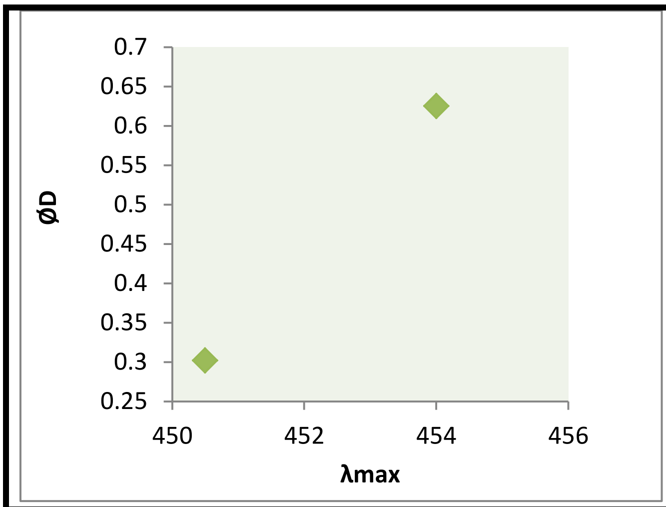


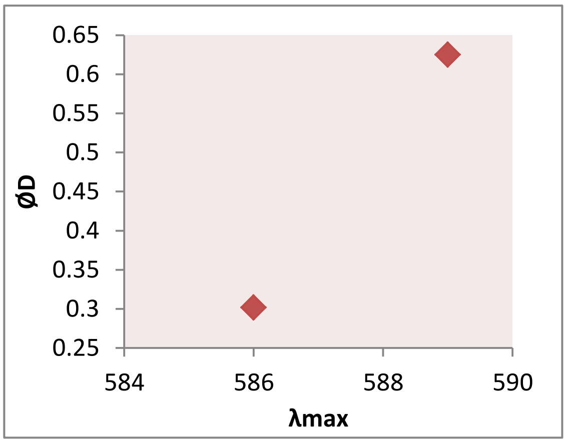
Non-polar solvents UV-Vis

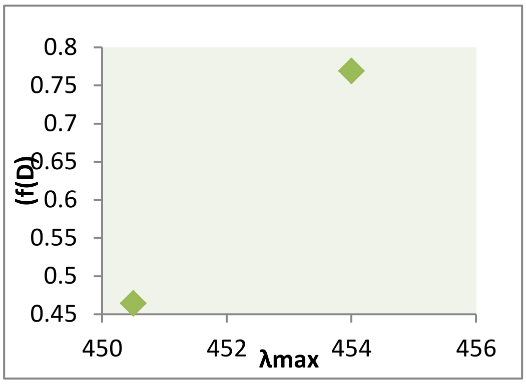
Non-polar solvents FL

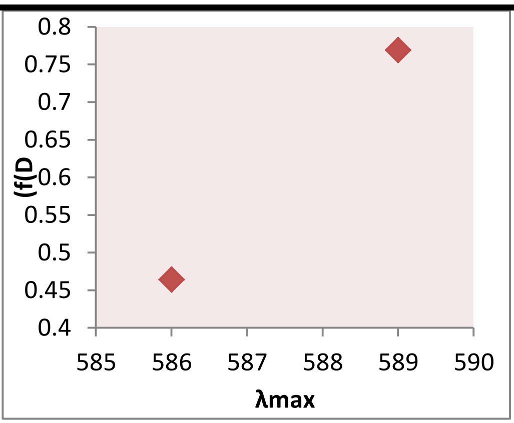












6. Conclusions

The data on absorption and fluorescence of the 4(4-HNBS) molecule in different Solvents reveal important insights into its behavior :

The absorption maxima (λ_{max}) vary with different solvents, suggesting that solvent polarity influences the molecule’s electronic structure. Polar solvents such as DMF And methanol cause a shift in absorption, indicating stabilization of the excited state.

The fluorescence maxima (λ_{max}) also show variations, with some solvents like DMSO exhibiting significant redshifts. This suggests that strong solvent-molecule Interactions, possibly involving dipole-dipole interactions or hydrogen bonding, can Affect fluorescence behavior .

Differences in fluorescence intensity suggest variations in non-radiative decay rates. Higher intensity values in solvents like ethanol and methanol imply that these solvents reduce non-radiative relaxation pathways, leading to enhanced fluorescence .

Alcoholic solvents (ethanol, 2-butanol, methanol, and 2-propanol) significantly Impact absorption and fluorescence, likely due to hydrogen bonding with the solute. These interactions can influence both energy levels and fluorescence efficiency. DMSO shows distinct behavior with a much higher fluorescence wavelength (615 nm), possibly due to strong solvation effects or charge transfer interactions stabilizing The excited state .

Overall, the data indicate that solvent polarity, hydrogen bonding, and specific solute-Solvent interactions play crucial roles in determining the properties of the 4(4-HNBS) Molecule.

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