TEMPERATURE AND CONCERNTRATION-DEPENDENT ABSORPTION AND FLUORESENCE OF THAITS J-AGGREGATE DYE, REVEAL SUPRA-MOLECULAR ARCHITECTURE.

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ABSTRACT:

The narrow and redshirted absorption bands of J–aggregates relative to the monomer absorption, coupled with their ability to coherently and incoherently delocalise exciton wave function over several hundreds of molecules has made this class of molecules very important in high technology fields. This has provided new impetus to study the properties of J–aggregates and to explore the mechanism involved in their production. We have investigated the absorption and fluorescence of THIATS J-aggregate dye as a function of Temperature and concentration in aqueous solotion.1mL of 1M solution of sodium chloride was added to each monomer solution to enhance aggregation. The formation of a beautiful intense blue colour and a shift of the absorption band from 515nm to 625nm is a tremendous indication that the THIATS monomers aggregate in aqueous solution. The monomer spectra show no fluorescence peak, while the aggregate spectra show a fluorescence peak at 638nm.Plots of absorption and fluorescence graphs show that stokes shift decreases with concentration. The temperature–dependent absorption spectra show an isobestic point at λ=530nm, which indicates an equilibrium situation between monomer and aggregate. From the data obtained, we calculated an aggregation number (n=4), an equilibrium constant(K=3.067M^{-1}), and Gibbs free energy (ΔG=-2.925KJ/mol).Furthermore, we calculated the Gibbs free energy required to construct one supramolecule of THIATS aggregate ($5*10^{-21}$J), and compared it with the thermal energy per molecule ($4.39*10^{-21}$).Consequently, our experiments have shown that they are comparable. A possible improvement on the properties of THIATS J-aggregate may be the synthesis of derivatives that will enhance its ability to delocalize exciton energy, and consequently better its application in high technology fields.

1. INTRODUCTION

1.1 J-aggregates and Applications

J-Aggregates or S-Aggregates are dyes with a narrow absorption band that is shifted to longer wavelengths or lower frequencies, with respect to the monomer absorption band, with a nearly resonant fluorescence. The shift of absorption band to longer wavelengths is called bathochromic shift. The J and the S in the aggregate name denotes Edwin E Jelly and Gunther Scheibes [1,2,3,4,5,6] in honour of their inventors.Aggregates with absorption bands shifted to shorter wavelengths with respect to the monomer band are termed Hypsochromic shift denoted as H-aggregates and exhibit in most cases low or no fluorescence. J- aggregates are characterised by sharp absorption bands that are bathocromically shifted, small stokes shift with nearly resonant fluorescence, high fluorescence yield and super radiance, small value for the full width at half maximum (fwhm) and a high absorption coefficient (high oscillator strength).

The ability of J-aggregates to coherently and incoherently delocalize exciton energy over hundreds of molecules makes them very important in high technology fields. In spectral sensitization devices, the photoinduced electron transfer is enhanced when J–aggregates are used[7].This leads to applications in silver halide photography[7],photovoltaic cells [7,8] and electrographic copy systems[9].The narrow absorption bands of J–aggregates open new fields in optical data storage in multicolour technigues[10].Through J–aggregation, the first and second optical hyperpolarisability is strongly enhanced as compared to single molecules due to   exciton energy delocalisation[11], thus allowing second and third harmonic generation(SHG,THG) applications in minimal sizes. Q–switches and optical switching devices based on J-aggregates have been developed. Thus, J-aggregates are candidates for highly integrated optical data processing and optical computers. This provides new impetus to the study of the properties of J-aggregates and to explore the mechanisms involved in their production.

 The rate of J-aggregation increases as the temperature decreases. According to Tatyana et al, the rate of J-aggregation correlates with the rate of decay of dimers or monomers and is dependent on the type of metal ion, dye structure, and temperature. The rate of formation of J-aggregates increases as the temperature decrease but increase as the dye and salt concentrations increase, however, it increases with charge density of the cation and is independent of the presence of anion. The time course of formation of J-aggregates is described in most cases by a sigmoidal curve, and the kinetics and mechanism are discussed

within the framework of autocatalysis.

1.2 The family of J-aggregates and Structure

J-aggregates belong to the family of cyanine dyes or polymethine dyes which are characterised by an intense beautiful blue colour and have one feature in common, namely, they consist of two heterocyclic units, which are connected by an odd number of methine groups (CH)n, with (n= 1,2,3,4….).The intensity of the beautiful blue colour is determined by the length of the polymethine chain [12,13] and the degree of conjugation. In conjugated systems, electron repulsion is minimized as well as the energy of the system due to electron delocalization on several atoms. The aggregation tendency of cyanine dyes increase with steric hindrance to a certain point before diminishing to low values. Figure 1 and 2 below give the structures and names of some cyanine dyes.
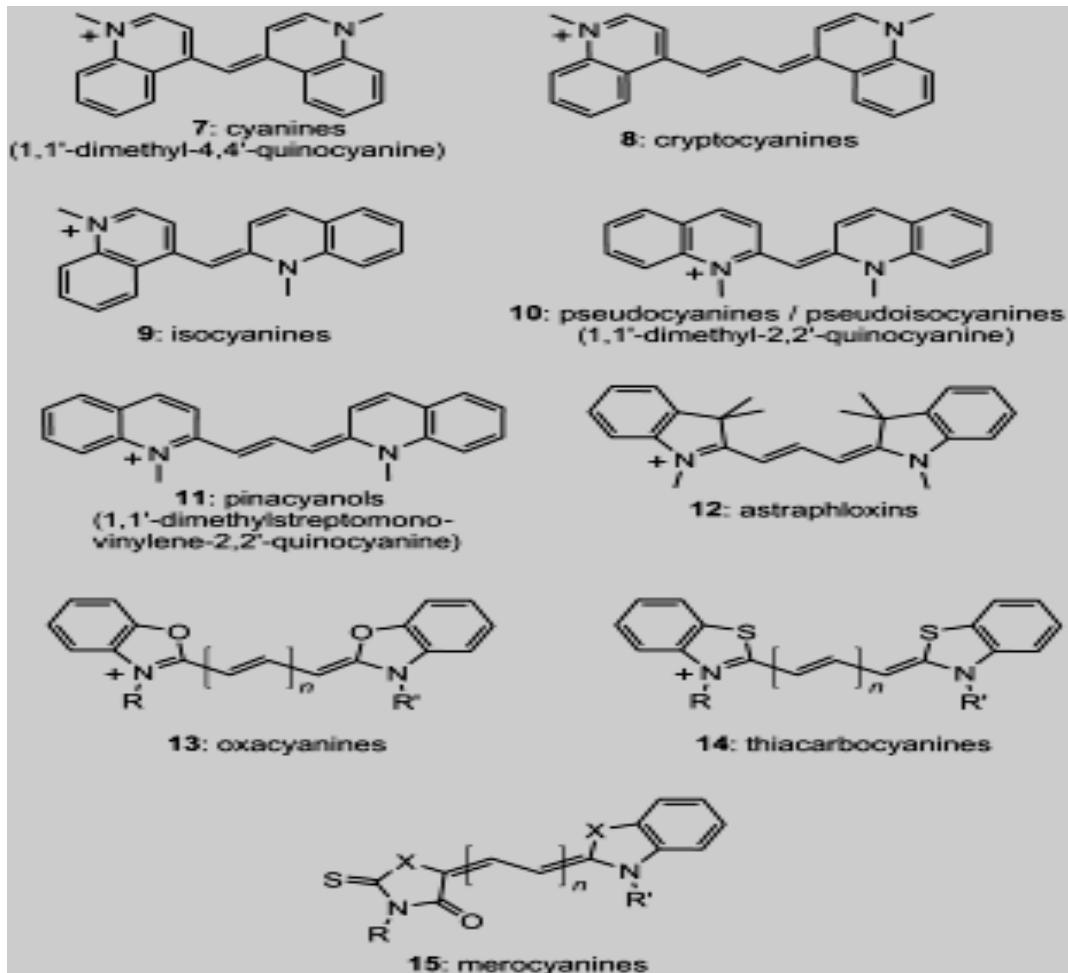

Figure 1 (polymethines and their trivial names)
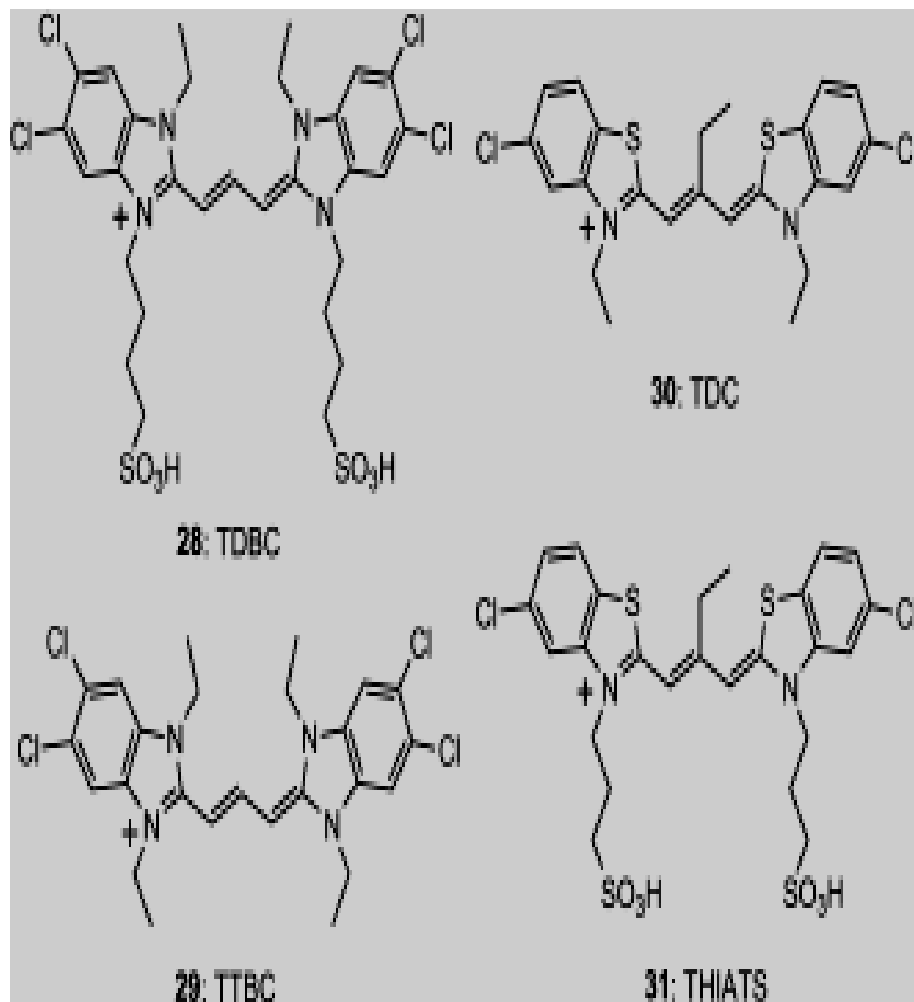
Figure 2. (31, THIATS J–Aggregate).

The supra-molecular structure of J-aggregates, for example, their aggregation number, geometrical size, and morphology, is not fully understood yet, and is controversially discussed, and factors governing the structures are often ambiguous. Despite the multitude of studies available and data available on the optical and spectroscopic properties of J-aggregate dyes, little is known about the supra-molecular structure of the aggregates.

Pseodoisicyanine Chloride (PIC) is the most investigated cyanine dye, both in homogeneous solution and at interfaces[14], Its peculiar spectroscopic behavior was attributed by Scheibe to a reversible polymerization of the chromophores due to intermolecular interactions. According to literature, the J-aggregates of PIC form elongated and rodlike supramolecular structures in aqueous solution, the detailed molecular architecture discussed is controversial. This is partly due to the nonplanar structure of its monomers. The two quinoline rings are twisted around the central methine group at an angle of 50.6 degree[15].Scheibe and Kandler showed by flow linear dichroism experiments that the sharp absorption band at 572nm of J-aggregates of PIC is polarized parallel to the aggregate axis[15].From this results, Förster concluded in 1946 that the monomers in the aggregate are not perpendicularly oriented to the aggregate direction but are aligned parallel to the the aggregate direction.

Figure 3. Transition dipoles aligned parallel to aggregate direction.

The dipole moments of the monomers are arranged parallel to each other in the aggregate direction. Several theories have been proposed to describe the structure of J –aggregates.

The excitonic theory of Kasha and co-workers[16], describes the excitonic interaction of the transition dipole moments of the chromophores with respect to their geometrical arrangement as a point dipole approximation. According to this theory, a much more pronounced displacement of the dyes is needed to afford bathochromically shifted absorption bands. This is illustrated below:
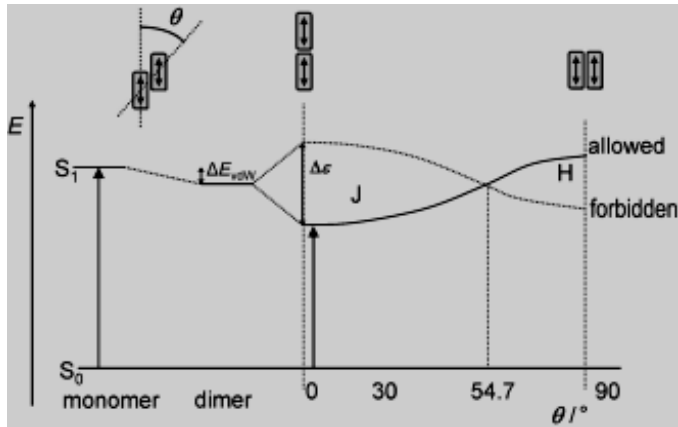
Figure 4 Schematic energy diagram for aggregate dimer

The geometry and slip angle are indicated above. Due to tortional motion, the angle between the transition dipoles change. For parallel aligned dimers, the optical excitation is only allowed from the ground state to one of the two electronic states depending on the angle θ. For θ less than 54.7degrees, the lower energy state is allowed leading to a bathochromically shifted J-band, because its transition dipole moment is different from zero, while for θ greater than 54.7 degrees, the allowed state is at higher energy leading to a hypsochromically shifted H-band.

1.3. Wave mechanics and point dipole approximation

The exciton is a microscopic particle with both particle and wave properties, consequently, we can describe it in terms of wave mechanics. The ground state wave function of the dimer molecule may be expressed as,

$$\Psi_g = \Psi_1\Psi_2$$

Where

Ψ_g = ground state wave function of dimer molecule, Ψ_1 = wave function of molecule 1, Ψ_2 = wave function of molecule 2. The Hamiltonian operator or total energy operator can be expressed as:

$$H = H_1 + H_2 + V_{12},$$

Where, H_1 and H_2 are the total energy operators for the isolated molecules , and V_{12} is the intermolecular perturbation potential or the columbic potential. The energy of the ground state can be derived from the Schrödinger equation:

$$E_g = \iint \psi_1\psi_2 H\psi_1\psi_2 d\tau_1 d\tau_2$$

$$E_g = E_1 + E_2 + \iint \psi_1\psi_2 V_{12}\psi_1\psi_2 d\tau_1 d\tau_2$$

The last term represent the Van der Waals interaction energy, while E_1 and E_2 are the ground state energies of the isolated molecules.

The excited state wave function may be written as,

$$\Psi_e = c_1\psi^*_1\psi_2 + c_2\psi_1\psi^*_2.$$

And the Schrödinger equation for the excited state can be expressed as,

$$H(c_1\psi^*_1\psi_2 + c_2\psi_1\psi^*_2) = E_e(c_1\psi^*_1\psi_2 + c_2\psi_1\psi^*_2)$$

Where ψ^*_1 and ψ^*_2 are the excited state wave functions with energy E^*_1 and E^*_2, and c_1 and c_2 are coefficients that arise from the asymmetric nature of the wave functions.

Multiplying both sides of the equation by $\psi^*_1\psi_2$ and integrating over all space for molecule 1 and 2 and repeating the process for $\psi_1\psi^*_2$, leads to two simultaneous equations containing terms symmetrical in molecules 1 and 2.

$$H_{11} = H_{22} = \iint \psi^*_1\psi_2 H\psi^*_1\psi_2 d\tau_1 d\tau_2$$

$$H_{12} = H_{21} = \iint \psi^*_1\psi_2 H\psi_1\psi^*_2 d\tau_1 d\tau_2.$$

From the determinant formed from the two equations we can calculate the excited state energies.

$$E_{1e} = H_{11} + H_{12}, \quad \psi^*_e = (½)^{1/2}(\psi^*_1\psi_2 + \psi_1\psi^*_2)$$

$$E_{2e} = H_{11} - H_{12}, \quad \psi^*_e = (½)^{1/2}(\psi^*_1\psi2 - \psi_1\psi^*_2)$$

$$E_{1e} = E_1 + E_2 + \iint \psi^*_1\psi_2(V_{12})\psi^*_1\psi_2 d\tau_1 d\tau_2 +$$

$$\iint \psi^*_1\psi_2(V_{12})\psi_1\psi^*_2 d\tau_1 d\tau_2.$$

$$E_{2e} = E_1 + E_2 + \iint \psi^*_1\psi_2(V_{12})\psi^*_1\psi_2 d\tau_1 d\tau_2 -$$

$$\iint \psi^*_1\psi_2(V_{12})\psi_1\psi^*_2 d\tau_1 d\tau_2$$

The last term is called exciton splitting integral.

$$Є = \iint \psi^*_1\psi_2(V_{12})\psi_1\psi^*_2 d\tau_1 d\tau_2$$

In the diplole- dipole approximation, it can be written as,

$$Є = M_1.M_2/r^3 - 3(M^1.r)(M^2.r)/r^5$$

Where M_1 is the transition moment of molecule 1, M_2 the transition moment of molecule 2

and r is position vector of molecule. Є represent interaction energy due to exchange of excitation energy between molecule 1 and 2.The transition energy for the dimer can be represented as:

$\Delta E_d = \Delta E_m + \Delta D \pm Є$

Where ΔD is the difference in Van der waals energy between ground and excited states, and the Exciton Splitting formula as a function of θ, is expressed as,

$\Delta Є = 2IMI^2/r^3{}_{12}(1 - 3cos^2\theta)$

Hence, the exciton model describes the resonance splitting of the aggregate molecule energy levels which were non-degenerate in the individual molecules. The nodes in the molecular exciton wave-function correspond to a change in the phase relation of exciton dipoles .
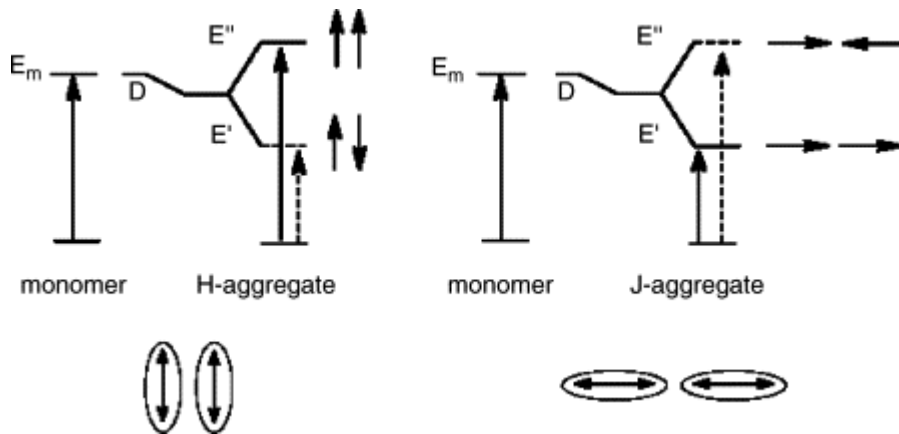
Figur 5 Phase relation of exciton dipoles

1.4. The Frankel Exciton Theory

In the molecular Frankel exciton model, the excited states are of excitonic nature with the electrons tightly bound to their molecular centers. The exciton states or collective eigenstates are delocalised electronic states caused by the strong long range dipole-dipole interactions between the monomers within the chain. The coupling of the optical

transitions by these interactions result in a band of Frankel excitons states. The width of the exciton band is proportional to the coupling energy. In the case of one molecule per unit cell, with a negative coupling energy, only transitions to states at the bottom of the exciton band are optically allowed and forms the J-band. The total oscillator strength of the coupled monomers is thus swept together in a few eigenstates, and the majority of the exciton states are not available in absorption. Consequently, the radiative rates of the bottom states are greatly enhanced compared to a single molecule, this is usually referred to as exciton superradiance[23].

The exciton motion may be coherent or incoherent, and generally, the degree of delocalisation of the exciton wave function depend crucially on the interactions between the exciton systems with other degrees of freedom in its environment. The exciton dynamics may be coherent when the intermolecular transfer of exciton energy is much faster than any relaxation scale induced by the fluctuating environment. Conversely, the exciton motion will be incoherent if the intermolecular transfer of exciton energy is slower than the relaxation scales induced by the environment leading to a hoping process between different sites. In other words, coherent transfer require fixed phase relations of the exciton wave function on different molecules, while incoherent transfer takes place when relaxation processes introduce fast intermolecular dephasing of the wave function[19].The degree of delocalisation and dephasing are fundamental quantities which can be determined experimentally using linear and nonlinear spectroscopy[20].Experiments have confirmed that the actual coherents lenght, the number of monomers on which the exciton wave function is delocalised, is much smaller than the total aggregate size[21].Figure 6 below illustrates stokes shift.
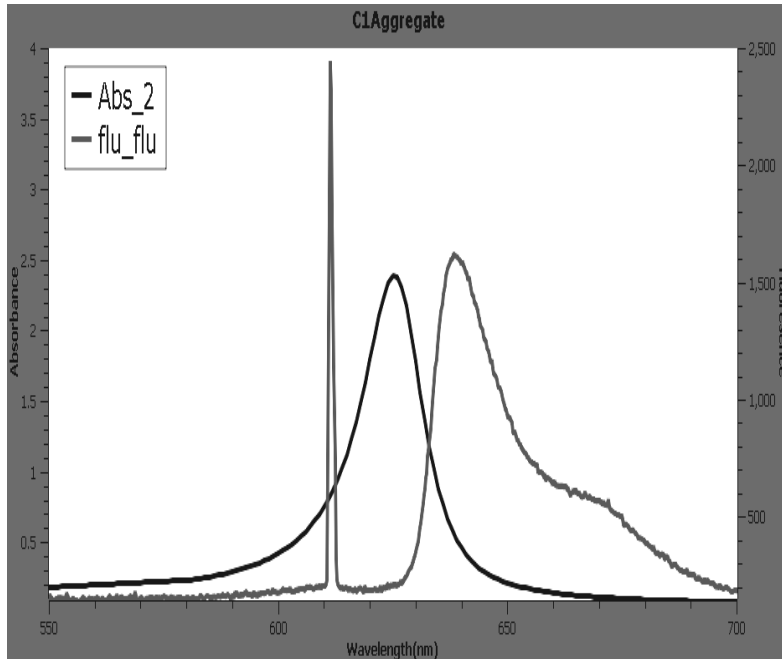
Figure 6. Stokes Shift.

Stokes shift is the difference in peak positions between the absorption and the fluorescence bands. It is named after the Irish Physicist George G Stokes. when a molecule absorbs a photon, it gains energy and is excited. One way for the molecule to relax is to emit a photon, thus losing its energy, otherwise, it will lose heat energy with solvent molecules. when the emitted photon has less energy than the absorbed photon, the energy difference is the stokes shift. If the emitted photon has more energy, the energy difference is called anti-stokes. This extra energy may come from dissipation of thermal photons in a crystal lattice, cooling the crystal in the process. The conversion of infrared light to visible light typifies ant-stokes shift.

For a fixed disorder strength, the temperature dependence of stokes shift is non-monotonic: stokes shift first increases upon heating and then goes down again. The extend of the temperature interval over which the stokes shift increases is small compared to the absorption band width, which is 170K for a disorder strength of $\sigma=0.3J$.The explanation of the behavior of stokes shift in the Frankel excton chain is similar to that for nonmonotonic behavior for disordered quantum wells. At the zero temperature of the exciton relaxation, excitons created initially at the blue tail, rapidly relax to the local states of the Density of States (DOS) tail, which are visible in fluorescence. After that, the excitons may relax

further, within the manifold of the local ground states. This possibility might be restricted because an exciton that relax into one of the local ground states may move to another similar state of an adjacent localization segment only when the latter has energy lower than the former. The typical energy difference between the local ground states is of the order of the absorption band width. Therefore after one jump, the exciton typically resides in the red tail of this band. The number of states with still lower energy greatly reduce, giving rise to an increased expectation value for the distance to such energy states. So in one jump the exciton has a strong suppressed chance to jump further during its lifetime and will generally emit a photon without further jumps. Thus the states deep in the DOS can typically not be reached by the excitons, because they occur at a low density. This explains why the stokes shift of the fluorescence spectrum does not exceed the absorption band width. Upon a small increase of temperature from zero, it become easier to reach those lower-lying states because the spatial migration to other segments may take place by thermally-activated transitions involving exciton states that are extended over several localization segments as intermediate states[22].It is this indirect hopping that is responsible for the increase of the stokes shift at temperatures small compared to the absorption band width. Further heating will thermalise the excitons and lead to real populations of higher-energy states leading to a decrease in stokes shift. Scheblykin et al , have studied in detail the temperature dependence of the stokes shift of THIATS J-aggregate .They paid particular attention to stokes shift calculated in uints of fluorescence width. Their findings are summarized in the equation below:

$$SS_{rel} = SS/(fwhm_{fl}) = SS/\sigma = \sigma/(KT.In2)$$

Where SS_{rel} is the relative stokes shift, σ is fwhm of the Gussian which is equal to the absorption spectrum of fwhm at zero temperature, while KT is the thermal energy.

The above expression indicates that the stokes shift is temperature dependent.

Fluorescence anisotropy as well as linear dichroism experiments performed by Scheblykin et al. on aligned aggregates of THIATS in a rotating cell provided evidence of the presence of two dye molecules per cell[25].They also obtained fluorescence quantum yield in the range of 10% to 40% for excitations involving the upper and lower Davydov components, thus revealing an intraband exciton relaxation. See figure 7a and 7b bellow.
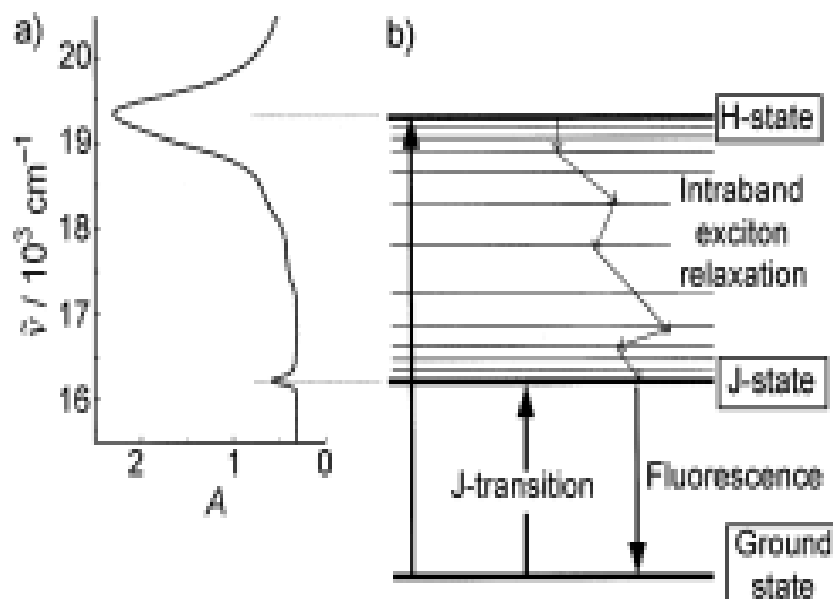

Figure 7. a Absorption spectrum of THIATS J Aggregate ,7b. Energy diagram of a molecular aggregate with DavYdov splitting of exciton bands.

Exciton-exciton annihilation experiments demonstrated an efficient exciton transport whithin this aggregate system which suggested an exciton migration over $6*10^4$ monomer units at room temperature and $6*10^6$ monomers at 77K before it decays[26],with a velocity of 2.5km/s.

1.5 Objectives

In this project, we investigate the aggregation tendency of THIATS J –aggregate (3,3´-disulphopropyl-5,5´-dicloro-9-ethyl thiacarbonine) in aqueous solutions, with the degree of aggregation depending strongly on concentration and temperature within a certain regime. We conducted absorption and fluorescence experiments to show the difference in stokes shift with increasing concentration. From the data obtained, we calculated the aggregation number, equilibrium constant and the change in Gibbs free energy with composition of the

mixture of aggregate and monomer. Furthermore, we demonstrated that at the isobestic point, the wavelength at which the absorbance of aggregate and monomer are identical , is independent of concentration, while the absorption coefficients of monomer and aggregate are in a certain proportion.

2. SAMPLE PREPARATION AND EXPERIMENTAL METHODS

The stock solution of the THIATS J-aggregate was prepared by dissolving 0.034g of the dye in 5ml of solution to obtain a concentration of 0.01M.Deionised water was used in making the solution. The stock solution was then diluted to obtain the various concentrations. 1M sodium chloride was prepared by dissolving 0.585g of sodium chloride salt in 10ml of solution. The aggregate solution for each concentration was made by adding 1ml of 1M sodium chloride to 2ml of the monomer solution.

For the concentration-dependent experiment, the absorption spectra were measured for each concentration with the absorption spectrometer Agilant Technology Model 8453 with a 1cm cuvette. Before each measurement, a background measurement was taken. For the temperature-dependent absorption, some of the concentrations of the aggregate samples were then placed in the plastic cuvette and heated in a water bath until the blue colour changes to red at 60 degrees. This was then placed in the chamber of the spectrometer and the absorbance measured for every 5 degree fall in temperature until at 20 degrees when there is no further change in the absorbance of neither aggregate nor monomer.

The fluorescence experiments were conducted for each concentration using a Helium-Neon Tunable laser with the excitation energy at 612nm.

3. RESULTS AND DISCUSSIONS

Results and discussions are subdivided into monomer absorption, aggregate absorption, Fluorescence and stokes shift, temperature-dependent absorption, and calculations.

3.1 Monomer Absorption

The maximum absorbance of the monomer occurs at 515nm, See figure 8 below. The Beer-Lambert Law requires the absorbance of the monomer to increases with concentration, however, the intensity of the blue shifted band increases with concentration due to some degree of aggregation. The lowest concentrated sample has an absorbance intensity of 0.593. While the highest concentrated has an absorbance of 2.664.The absorption of the monomer in this region of the electromagnetic spectrum may be attributed to the extended

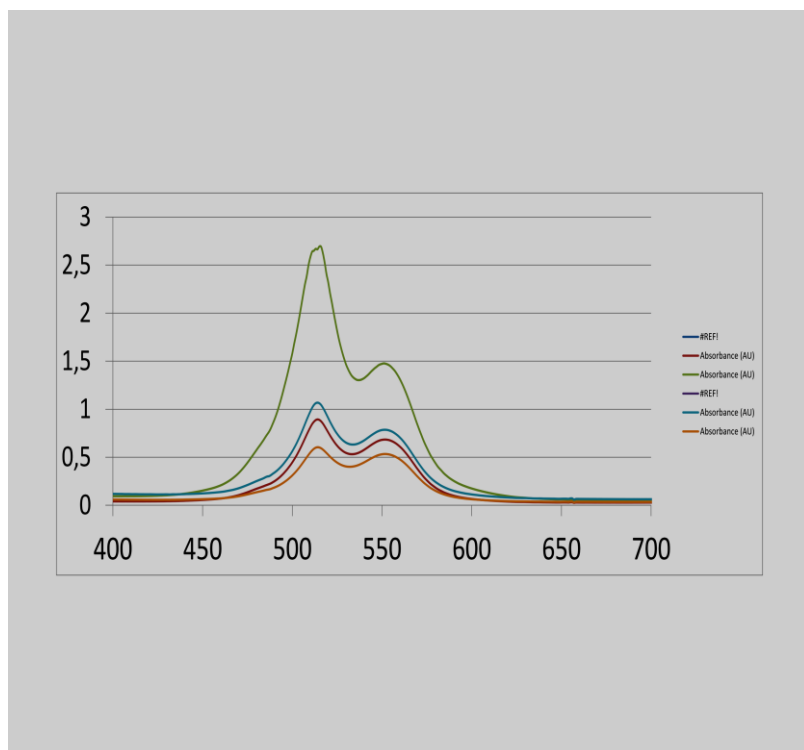conjugation of π-electrons in the molecule which minimises electron repulsion and the transition energy.

Figure 8. Monomer Absorption

3.2 Aggregate Absorption

The J-aggregate sample absorbs at λ= 625nm relative to the monomer. Hence the absorption has been bathochromically shifted or red shifted. When sodium chloride salt is added to the monomer solution, it promotes J-aggregation by increasing its effective dielectric constant [23,24], consequently, the electrostatic repulsion between dye ions is minimised ,aggregation is then accelerated. The molecules are then bonded together by electrostatic forces in assemblies of reduced dimensionality often with a chainlike configuration. The excited states are of excitonic nature with the electrons tightly bound to their molecular centers. The exciton states are delocalised caused by the strong long- range dipole-dipole interactions between the monomers. The coupling of the optical transitions of the molecules by these interactions result in the formation of a band of Frankel exciton states. In the simplest case of one molecule per unit cell and a negative coupling energy, only transitions to states at the bottom of the exciton band are optically allowed and forms

the J-band which is bathchromically shifted. The j-transition is optically allowed because it transition dipole moment is different from zero. The J-band is also strongly narrowed compared to the monomer band because the total oscillator strength of the coupled molecules is thus swept together in a few eigenstates and the majority of the exciton states are not accessible in absorption, consequently, the radiative rates of the bottom states are strongly enhanced as compared to a single molecule. As expected, for the lowest concentrated sample, the absorbance is very almost zero, while that of the highest concentration is 2.21.See figure 9 below.
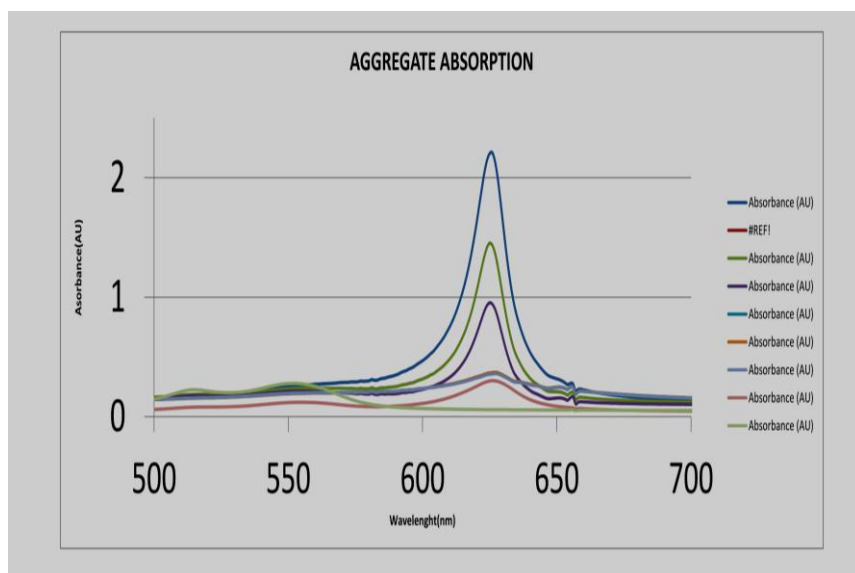

Figure9.Aggregate Absorption.

The occurrence of the J-band in the concentration regime from $2*10^{-4}$ to $7*10^{-5}$ in 1M NaCl, confirms the formation of network superstructures consisting of isolated fibers and complex fiber bundles. More of the threadlike J-aggregates could be made visible by diluting the solution; these aggregates are characterized by a diameter of 2.3nm, a length of several hundreds of nanometers, and a high stiffness. No concentration-dependent growth of the J-aggregates or elongation of the J aggregate could be observed at very high concentrations. Consequently, the appearance of the J-band at the above concentration regime is due to aggregate concentration and not aggregate growth.
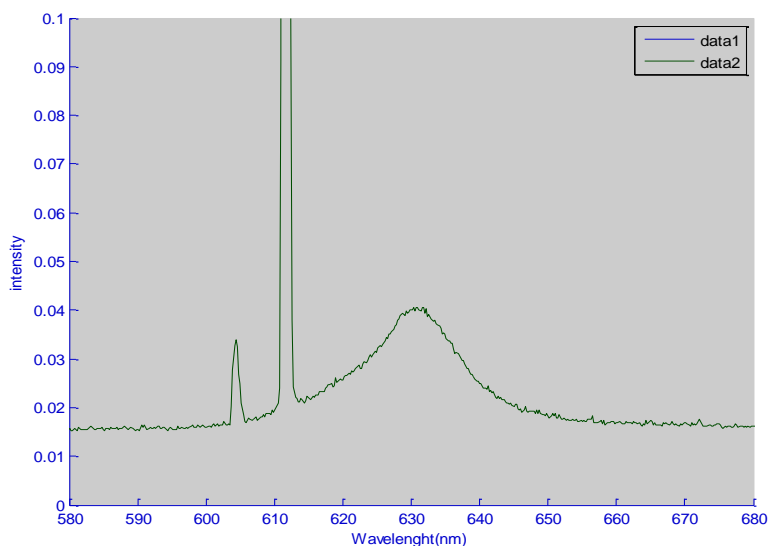
3.3 Fluorescence.

Figure 10. Aggregate Fluorescence.

The monomer of THIATS show little or no fluorescence due to lack of delocalization of exciton energy. The excitonic state with the highest transition dipole moment lay at the upper edge of the exciton band and hence, a higher absorption energy. After excitation, due to tortional motion, the energy relaxes rapidly within the exciton band down to states with vanishing transition dipole moments and finally to the ground state without emission, thus, the fluorescence is suppressed. However, the aggregate show an intense fluorescence peak at 638nm for the high concentration. The graph below show absorption and fluorescence presented on same graph to show stokes shift. The difference between the maxima of the fluorescence and the absorbance bands is the stokes shift. The tail of the absorbance graph stenches towards shorter wavelengths while that of the fluorescence stretches towards longer wavelengths. Stokes shift decreases with concentration as the table below illustrates.

Table 1. Concentration-Dependent Stokes Shift.

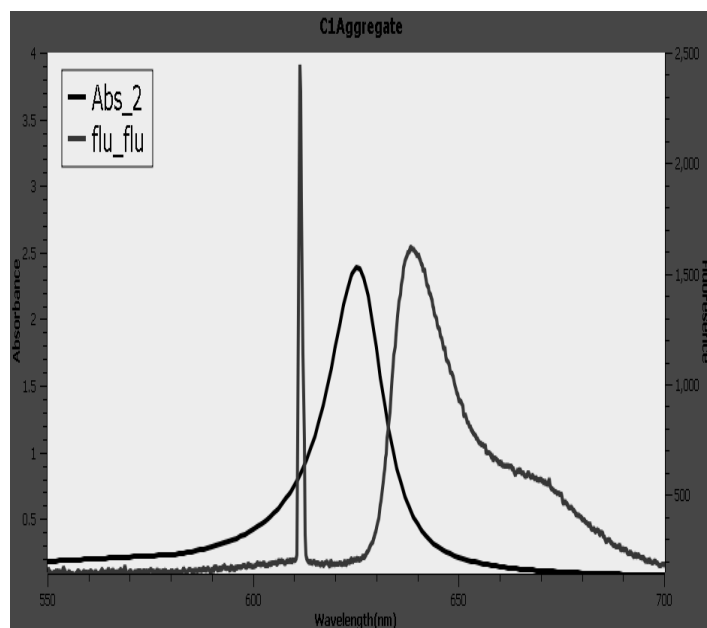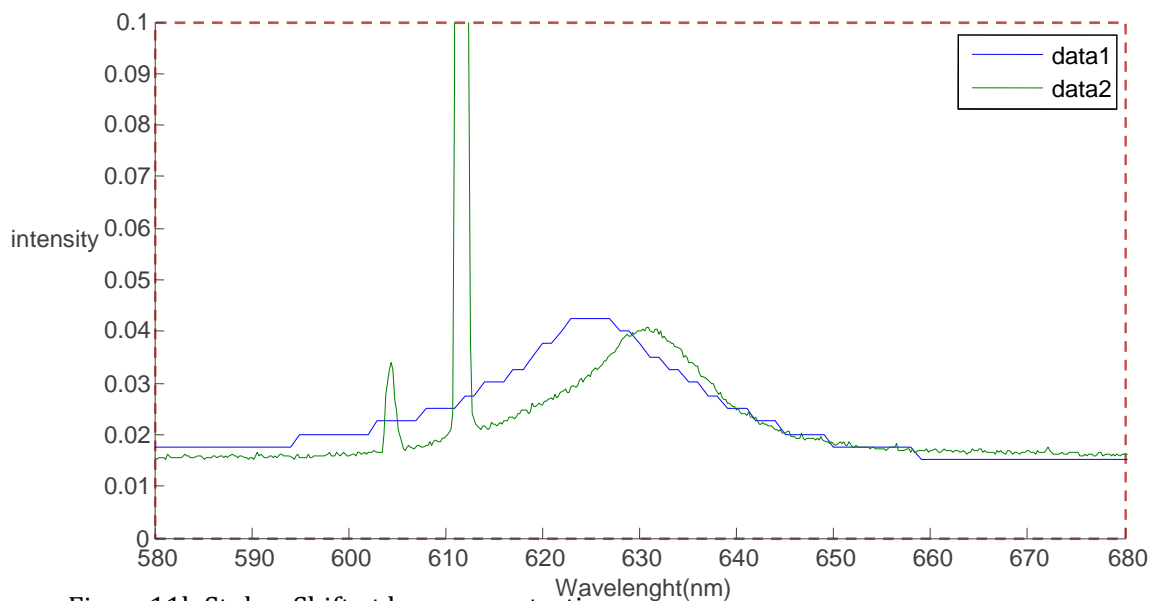| Concentration(M) of Aggregate sample	Absorbance(nm)	Fluorescence(nm)	Stokes Shift(nm)	Stokes Shift(cm^{-1})
$1*10^{-3}$M	625.5	638.8	13.3	333.9
$1*10^{-4}$M	624.3	634.9	10.6	267.4
$1*10^{-5}$M	623.5	631.5	8.2	208.4

Figure 11a. Stokes shift at high concentration

Figure11b Stokes Shift at low concentration

3.4 Temperature–Dependent Absorption.

The sample of the aggregate solution was then heated in a water bath until the intense beautiful blue colour turns red at 60 degree. An indication that the strong dipole-dipole forces between monomers are broken. This was then placed in the spectrometer and the absorbance measured every 5 degree drop in temperature. It is observed that the monomer absorption decreases in intensity while that of the aggregate increases. At 20 degrees, no further change on the absorbance intensity of neither the monomer nor aggregate occurred, which indicates the reach of the saturation point, where at the microscopic level, the rate at which the monomer is formed equals the rate at which the aggregate is formed. The two rates are beautifully balanced so that at the macroscopic level we see no changes. The appearance of only one isobestic point in the UV. vis spectra suggest that equilibrium has been established. The isobestic point is the wavelength at which monomer and aggregate have the same absorbance intensity and is independent of concentration. Figure 12a and
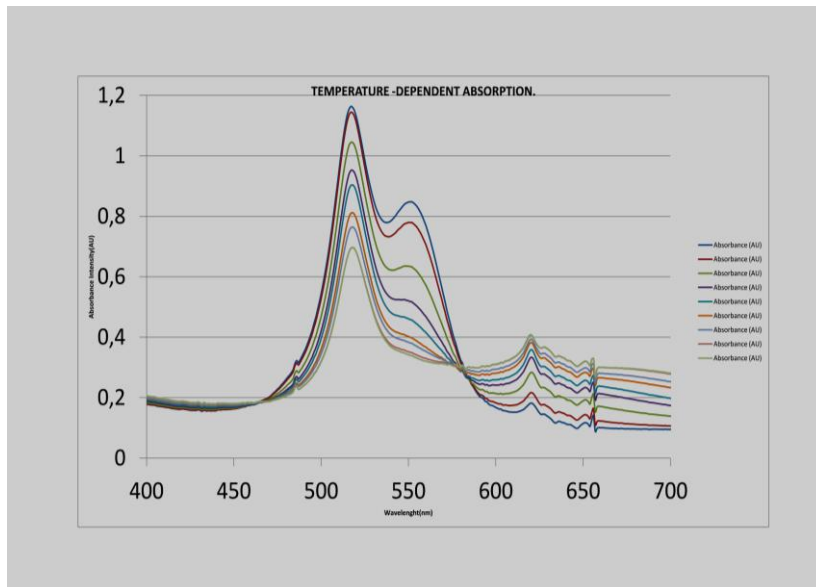
12b below illustrates this.

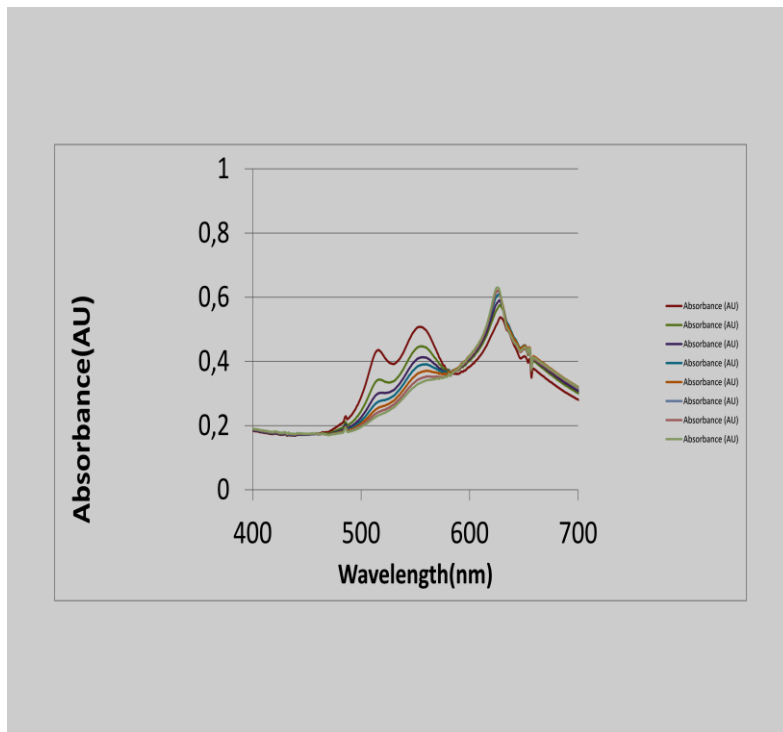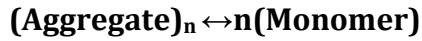*Figure 12a Temperature-dependent Absorption (low concentration)*

Figure 12b. Temperature -dependent absorption (high concentration).

The chemical equation below describes the equilibrium reaction.

(Aggregate)$_n$ ↔ n(Monomer)

A plot of the natural logarithm of the aggregate against that of the monomer is a linear graph whose gradient is n, the aggregation number; the number of monomers in a supra-molecule. See figure 13 below.
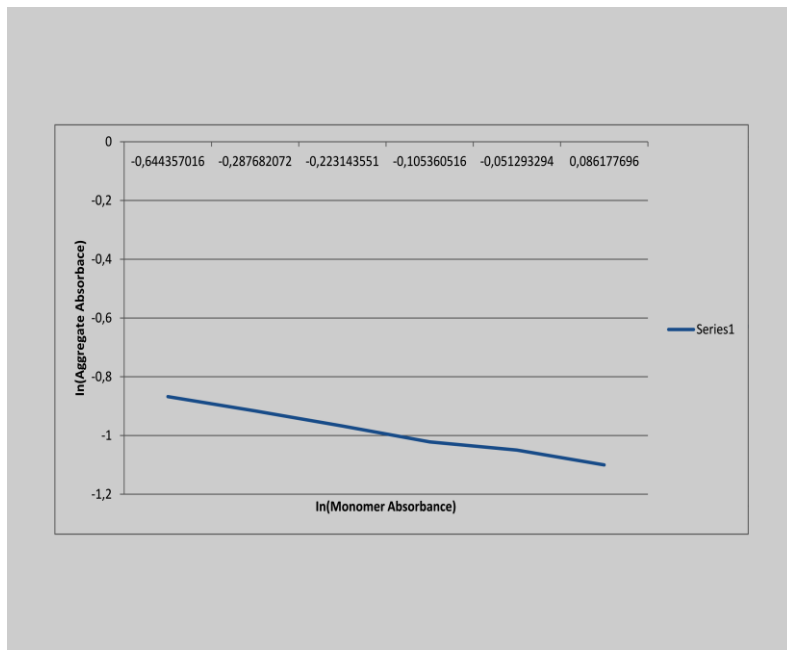
Aggregation Number, n = $\Delta InC_A / \Delta InC_m$

Figure13.Monomer absorption (In C_m) versus aggregate absorption(In C_A)

Where, C_A =concentration or absorbance of Aggregate.

C_M = Concentration or absorbance of monomer.

Δ = change in concentration.

n = ΔIn C_A /ΔIn C_M = 8/2 = 4

In the literature, the aggregation number varies in the range 4 to 10, however, we have conducted this experiment several times with some consistency.

The reaction is reversible and in equilibrium, we can write a mass action expression for the

reaction. The ratio of the concentration of products raised to their stoichiometric coefficients to those of products is always a constant, and that constant number is called equilibrium constant.

K = [Monomer]^n / [Aggregate] = [C_m]^n / [C_A].

We take the natural logarithm of both sides of the equation,

Ink = nIn[C_m] - In[C_A],

From graph, n=4 and if we plot absorbance against temperature, we obtain the concentrations of Aggregate and monomer, see figure 14 below, consequently we can calculate K,

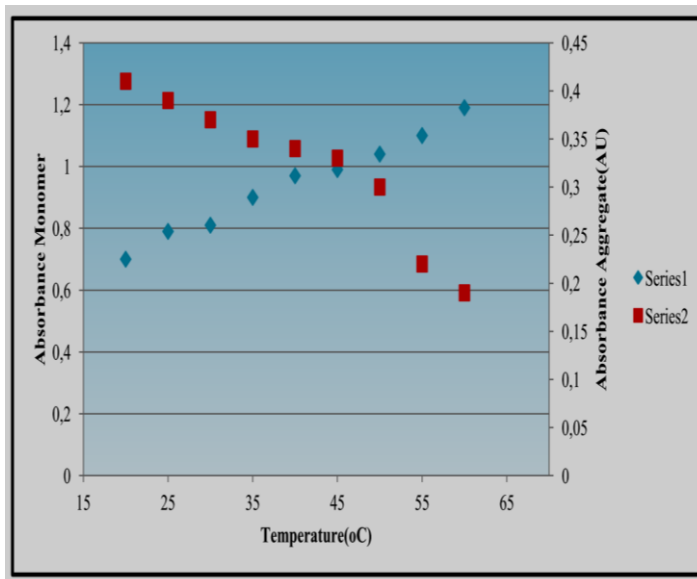Figure 14. Absorbance versus temperature.

From the graph above

[C_m]= IM and [C_A] = 0.325M

Ink = 4In[1] - In[0.325] = 1.124

K = 3.067M^{-1}

K > 1 implies the mixture is richer in the monomer than the aggregate. The extend of

aggregation is less at the specified concentration and temperature.

The Gibbs free energy is related to the equilibrium constant in the following expression:

ΔG = - R T Ink

Where

ΔG = change in Gibbs free energy

R = Molar gas Constant,

T = thermodynamic temperature.

Consequently, **ΔG** can be calculated.

ΔG = -(8.314J/K)(45+273.15)(1.124) = -2.925KJ/mol.

at 45 degree centigrade.

ΔG < 0, implies the conversion of aggregate to monomer is a non spontaneous process or is thermodynamically not feasible at the specified temperature. On the other hand, the conversion of monomer to aggregate is a spontaneous process and is thermodynamically feasible at low temperatures.

For a mole of Aggregate molecules, **ΔG = -2.925KJ**, however, for one supra-molecule of aggregate,

ΔG = ΔG/N_A = (2.925KJ/mol)/6.022*10^{23} = 5*10^{-21}J , where **N_A** is the Avogadro number of aggregate supra-molecules.

The thermal energy at **318.15K**, is expressed as,

KT = 1.38*10^{-2} J/K*318.15K =4.39*10^{-21}J

Thus, the thermal energy per molecule is comparable to the Gibbs free energy per molecule. This is the free energy or maximum non-expansion work that must be done to construct one supra-molecule of ThIATS J-aggregate.
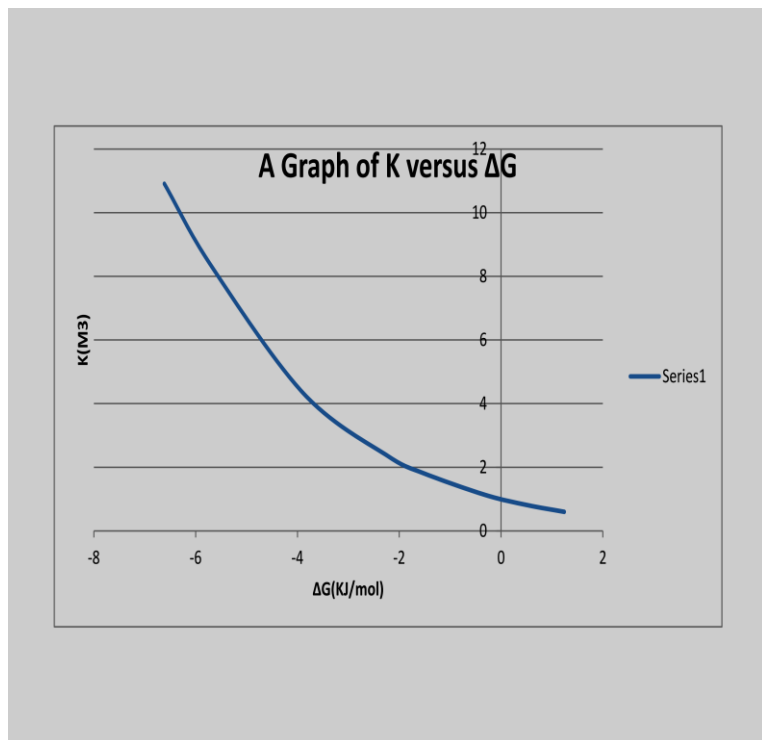
Figure 14. equilibrium constant(K) versus Gibbs free energy(ΔG).

The graph of the **K** versus **ΔG** decreases monotonically as the temperature decrease, see figure 14 above. At higher temperatures, the change in Gibbs free energy is more negative while the equilibrium constant is more positive. Thus the formation of aggregate is favoured at low temperatures. The table below shows the values of **K and ΔG at various temperatures.**

Table 2. Temperature-dependent equilibrium constant and Gibbs free energy.

Temperature(degree centigrade)	Equilibrium constant (M^{-1})	Gibbs Free Energy (KJ/mol)
20	0.6	1.244
25	0.811	0.519
30	1.132	-0.312
35	1.822	-1.536
40	2.237	-2.197
45	4.306	-3.872
50	8.328	-5.692
60	10.91	-6.615

The Gibbs free energy is related to the entropy of the system in the following expression:

ΔG = ΔH - TΔS,

Where,

ΔH = change in enthalpy or heat of reaction,

ΔS = change in entropy of the system and

T = thermodynamic temperature.

The equation above means that some of the energy taken up by the sample is actually used in the construction of J-aggregate molecules, while some of the energy called entropy is wasted or used by the surrounding molecules for their vibrations, rotations and translations. Thus, this part of the energy has been randomised and not used in doing the useful work of molecular architecture.

The change in Gibbs free energy with composition of mixture is called chemical potential and is denoted by, **γ**. In other words, the chemical potential of the aggregate is the partial molar derivative of the free energy.

$[\, dG \,/\, dn_A \,]_{T,\, P,\, n} = \gamma_A$

Where dn_A is differential change in number of moles of aggregate in mixture. Thus the chemical potential of the aggregate decreases from high values at high temperatures to low values. This is similar to the flow of water downhill to gain stability or the flow of electrons from a high electrical potential to a low electrical potential in an electric field. At the point of saturation, the chemical potential of aggregate and monomer are identical.

$\gamma_A = \gamma_M$

In the process of aggregation, the Gibbs free energy change with composition of aggregate and monomer. As the temperature decreases, the composition of aggregate increases while that of monomer decrease in the mixture. At the isobestic point, absorbance is independent of concentration or composition of aggregate and monomer but is dependent on the absorption coefficient of monomer and aggregate. This is illustrated below:

The celebrated Beer-Lambert Law requires the absorption of a solution to be proportional to its molar concentration and is expressed in the equation below:

$A = \varepsilon[C]L$,

Where,

A = absorption of sample or optical density (AU)

[C] = Molar concentration of sample (mol/dm^3) and

L = length of cuvette used in measurement (cm).

$[C] = A/\varepsilon L$.

For a mixture of aggregate and monomer, the total absorbance is calculated as follows,

$A_T = A_M + A_J = \varepsilon_M[C_m]L + \varepsilon_J[C_A]L = (\varepsilon_M[C_m] + \varepsilon_J[C_A])L$

For two measurements of total absorbance at wavelengths λ_1 and λ_2, with absorption coefficients ε_1 and $\varepsilon_2,$

$A1 = (\varepsilon_{M1}[C_m] + \varepsilon_{J1}[C_A]L$

$A2 = (\varepsilon_{M2}[C_m] + \varepsilon_{J2}[C_A])L$

Solving the two equations simultaneously,

$[C_m] = \varepsilon_{J2}A_1 - \varepsilon_{J1}A_2 / (\varepsilon_{M1}\varepsilon_{J2} - \varepsilon_{M2}\varepsilon_{J1})L$

$[C_A] = \varepsilon_{M1}A_2 - \varepsilon_{M2}A_2 / (\varepsilon_{M1}\varepsilon_{J2} - \varepsilon_{M2}\varepsilon_{J1})L$

At the isobestic point, the absorbance is a constant

$A_i = (\varepsilon_m[Cm] + \varepsilon_J[CA])L = $ constant

$dA = (\varepsilon_M d[C_m] + \varepsilon_J[C_A])L = 0$

$[C_A] \leftrightarrow n[C_m]$

Therefore,

$d[C_A] = -nd[C_m]$

Substituting in equation we have,

$\varepsilon_m d[Cm] - \varepsilon_J nd[Cm] = 0$

$\varepsilon_M = n\varepsilon_J,$

where **n** is the aggregation number or coherence length. **n** can have values that range from 4 to 10 as stated in the literature. The coherence length is the number of monomers on which the exciton wave function is delocalized. Consequently, the longer the coherence length, the stronger the absorption, therefore, we can adjust substituents on the heterocyclic units of polymethine J – aggregates to increase aggregation number and hence the strength of the absorption or the oscillator strength. For a monomer concentration of $2*10^{-4}M$, and absorbance of 2.22 the absorption coefficient is given by,

$\varepsilon_M = 2.22/2*10^{-4} = 1.1*10^4$ and

$\varepsilon_J = n\varepsilon_M = 4*1.1*10^4 = 4.1*10^4$.

The strength of the transition or oscillator strength is related to the absorption in the expression below:

f_{nm} = 4.319*10^{-9}(mol*cm2/L)*A,

Where f_{nm} = oscillator strength, and **A** the integrated absorption coefficient.

4. Conclusions

The absorption and fluorescence of THIATS J-aggregate depend strongly on temperature and concentration of the solution. The bathochromic shift increases within a certain concentration regime from 10^{-5}M to 2*10^{-4}M.The formation of J-aggregate is enhanced by the addition of sodium chloride solution to a solution of the monomer, this is accompanied by a colour change from bright red to a beautiful intense blue. The monomer spectra show no fluorescence peak because it has been suppressed by vanishing transition dipole moment caused by fast intraband relaxation to the ground state, while the aggregate spectra show an intense peak at 638nm.A plot of absorption and fluorescence data on same graph shows stokes shift which decreases with concentration. In the temperature dependent experiment, the aggregate sample was heated in a cuvette until it turns red at 60 degrees and the absorbance was measured in every 5 degree fall in temperature as the monomers are converted to aggregate. The saturation point was indicated by no further change in the absorption of neither monomer nor aggregate. The spectra shows only one isobestic point which means equilibrium is established between aggregate and monomer. From the data obtained, we calculated the aggregation number, equilibrium constant, and the Gibbs free energy of the aggregation. From the Gibbs free energy, we calculated the energy required to construct one supramolecule of the THIATS J- aggregate and then compared it with the thermal energy per molecule. The calculated aggregation number of 4 could be increased by adjusting substituents on the heterocyclic rings of the THIATS J-aggregate to enhance the degree of excitonic energy delocalization which improves on spectral properties and supramolecular architecture for applications in high technology fields. The supra-molecular structure of J-aggregates; aggregation number, geometrical size, and morphology, is not fully understood yet, and is controversially discussed, and factors governing the structures are often ambiguous. Consequently, this aspect of J-aggregates is still wide open for investigation.

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