

Dynamics of Formation of 1,1'-Diethyl-2,2'-Cyanine Iodide J-Aggregates in Solution

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The dynamics of the formation of 1,1'-diethyl-2,2'-cyanine iodide (PIC) J-aggregates in water solutions have been studied using UV/vis spectroscopy. The appearance and growth of the J-aggregates' band at 573 nm took place simultaneously with the decrease of the absorption of the sample at 525 and 485 nm. The experimental dependence of the intensity of the absorption at 573 nm versus time has the shape of a reverse exponential curve, $J_{573} = J_0(1 - \exp(-kt))$. Two possible explanations of the experimental data are given. The first one is that if J-aggregates are simple chains of molecules, then only three PIC molecules in aggregate may be enough to produce a J-band in the absorption spectrum of the solution. The second one is that J-aggregates are not simple chains of molecules but consist of "unit cells" of nonlinear structure. At a high concentration of PIC the full width at half-maximum of the J-band increased with time, but the position of its maximum did not change. Possible explanations of this phenomenon are discussed.

Introduction

J-aggregates have been the subject of keen interest in the scientific community for many years. This interest is based on the following: (1) their applications in photography; (2) their unique optical properties; (3) they are considered to be intermediates between single molecules and bulk phases, making them ideal models to investigate the change of physical properties between these two extremes.

J-aggregates are formed by some cyanine dyes in aqueous solution and several matrixes. Since their discovery by Scheibe¹ and Jelley,² J-aggregates have been studied using different methods, including simple absorption spectroscopy, time-resolved fluorescence,^{3–9} the accumulated photon-echo technique,^{7–9} Raman spectroscopy,¹⁰ femtosecond pump–probe spectroscopy,¹¹ electromodulation spectroscopy,¹² near-field scanning optical microscopy,¹³ and atomic force microscopy.¹⁴

The formation of J-aggregates can be detected by the intense narrow absorption band (J-band) red-shifted with respect to the absorption spectrum of the monomer. The appearance of this band was explained by the formation of an excitonic state through the electronic coupling of the tightly packed dye molecules.¹⁵ A model of N identical molecules aligned one-dimensionally was proposed to explain the absorption spectrum of the J-aggregates^{16,17} and their other optical properties.^{18–22} It was discussed that J-aggregates form a helical structure,²³ a herringbonelike arrangement that is described by a centered, rectangular unit cell containing two identical molecules,^{24,25} and a helix-like, cylindrical chiral structure.²⁶ Still, the linear chain model is most often applied to J-aggregates.^{27,28}

Despite various spectroscopic experiments and theories regarding J-aggregates, some questions still remain. One of these concerns the effective size of J-aggregates or the number of monomers N interacting with each other and producing a new excitonic state. Different authors have estimated that effective sizes for PIC J-aggregates range from 4 to 100 molecules. This

implies that the effective size of J-aggregates may be different in different conditions. If this were indeed the case, it would be interesting to determine the minimum number of PIC molecules in aggregate needed to produce a J-band.

This question may be answered by studying the process of formation of J-aggregates. It is well-known that the formation of J-aggregates in solution depends on both the concentration and temperature. At low concentrations and high temperatures, PIC in solution exists in monomer form. At relatively high concentrations and low temperatures, the process of aggregation takes place. The first step of aggregation is considered to be the dimerization,²⁹ or coupling, of two molecules. The dimerization causes a change of the absorption spectrum of the solution, and can thus be detected. The next steps of aggregation are the couplings of three, four, and more molecules. When the number of monomers in the aggregate reaches a critical number N required to form a new excitonic transition, the J-band in the absorption spectrum appears. An estimate of the critical number N can be obtained by analyzing the absorption kinetics of the solution.

In this paper I report on the kinetics of formation of J-aggregates of PIC in water solutions that demonstrate that if J-aggregates are simple chains of molecules, then three molecules of PIC in aggregate may be enough to form a J-band in the absorption spectrum of the solution. This means that the effective size of PIC J-aggregates, in some cases, may be three molecules. Another possible explanation of the data obtained is that J-aggregates are not simple chains of molecules, but consist of "unit cells". In this case the number of molecules required to produce a J-band is equal to the number of PIC molecules in the unit cell.

Experimental Details and Results

Samples were prepared by dissolving PIC in a 0.2 mol/L water solution of NaCl. PIC was purchased from Aldrich and used as received. Concentrations of PIC in the solutions studied were 10^{-3} , 5×10^{-4} , 3×10^{-4} , 2×10^{-4} , and 10^{-4} mol/L. The optical spectra and kinetics were recorded with a Perkin-

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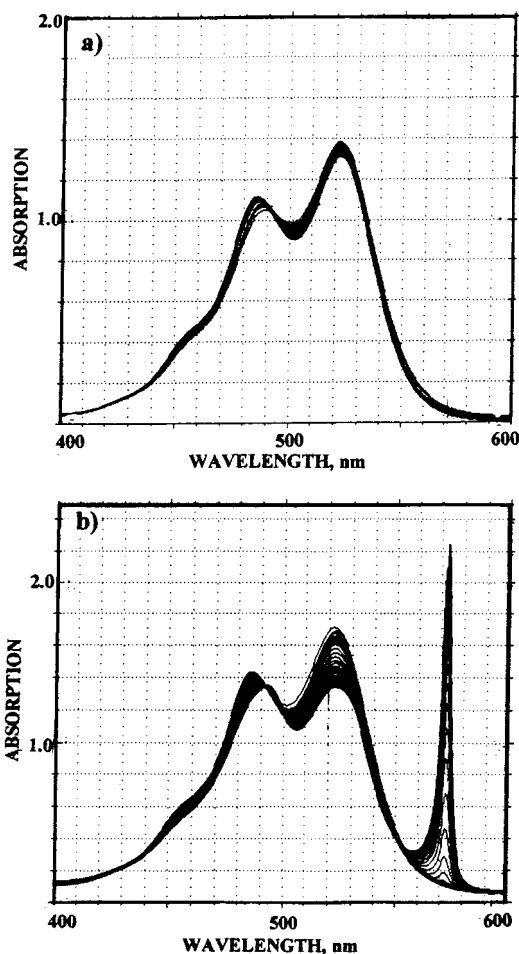


Figure 1. Temporal evolution of the absorption spectra of 2×10^{-4} mol/L (a) and 3×10^{-4} mol/L (b) solutions of PIC in water with NaCl during cooling.

Elmer Lambda 12 UV/vis spectrophotometer. At room temperature, the absorption spectra of the solutions of concentrations 10^{-3} , 5×10^{-4} , and 3×10^{-4} mol/L had three maxima: at 525 nm, which corresponds to the PIC monomer, at 490 nm, and at 573 nm, which is the well-known absorption maximum of PIC J-aggregates. The absorption spectra of the solutions of concentrations 2×10^{-4} and 10^{-4} mol/L at room temperature had only two maxima: at 525 and 485 nm.

The solutions were placed in a small 1 mm thick cell and heated to approximately 80 °C. As the solutions cooled to room temperature, the absorption spectra and kinetics at different wavelengths were measured. The solutions in the cell reached room temperature in less than 10 min.

Figure 1 shows the absorption spectra of the solutions of concentrations 2×10^{-4} (Figure 1a) and 3×10^{-4} (Figure 1b) mol/L measured continuously for 20 min while the solutions cooled. The recording time of each spectrum was 30 s. Immediately after heating, the absorption spectra of both solutions looked similar: they both had only two maxima, at 523 and 490 nm. As the temperature decreased, initially in both solutions the absorption at 525 nm decreased and the absorption in the region of 490 nm increased with a shift to 485 nm. Approximately 5 min later in both solutions this process slowed significantly. No other changes were observed in the solution of concentration 2×10^{-4} mol/L during 20 min of measurement. In the solution of concentration 3×10^{-4} mol/L approximately 5 min after the beginning of the measurements, the appearance and very fast growth of the absorption band at 573 nm were

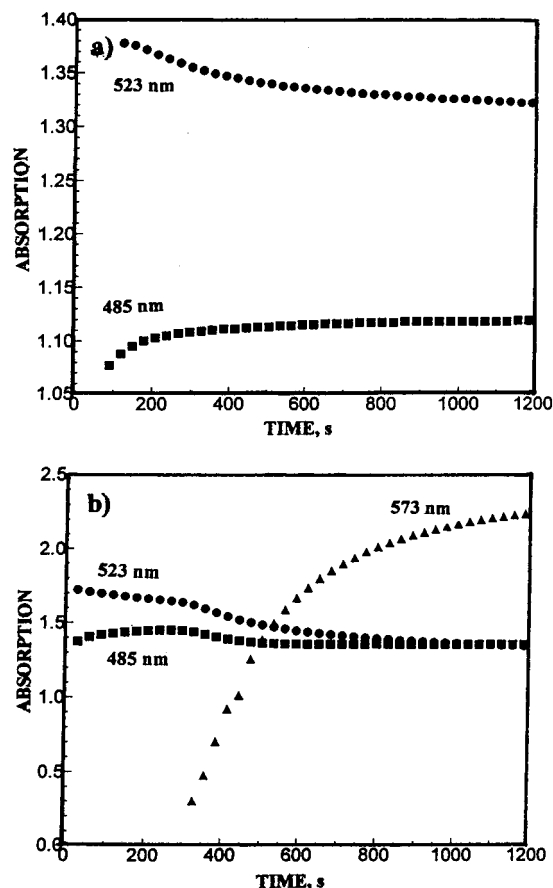


Figure 2. Kinetics of the absorption in water solutions of PIC at 2×10^{-4} mol/L (a) and 3×10^{-4} mol/L (b).

observed, with a simultaneous decrease of absorption at 525 and 485 nm. The position of the absorption maximum at 523 nm did not change. The absorption peak at 485 nm shifted to 492 nm in the process of growth of the J-band.

Figure 2 shows the absorption kinetics in solutions of concentrations 2×10^{-4} (Figure 2a) and 3×10^{-4} (Figure 2b) mol/L. At 2×10^{-4} mol/L, the absorption at 525 nm monotonically decreased with time and the rate of the decrease continuously slowed. In the meantime, the absorption at 485 nm monotonically increased with time. The rate of its increase continuously slowed as well. A similar picture was observed in the solution of concentration 10^{-4} mol/L, but the range of change of absorption at 485 and 523 nm was smaller.

At 3×10^{-4} mol/L the absorption at 525 nm continuously decreased with time. Initially the rate of its decrease behaved the same way as in the solution of concentration 2×10^{-4} mol/L: it slowed. Approximately 5 min after the decrease started, the rate of the decrease of absorption at 525 nm became faster. The absorption at 485 nm initially increased with time, but then decreased. The decrease started approximately at the same time, when the rate of the decrease of absorption at 525 nm changed. Finally, both processes, the change of the rate of the decrease of absorption at 525 nm and the beginning of the decrease of absorption at 485 nm, coincided in time with the appearance of a J-band at 573 nm.

Figure 3 shows the time correlation among the rates of absorption kinetics at 485, 523, and 573 nm in the solution of concentration 3×10^{-4} mol/L.

Similar absorption kinetics have been observed for the solutions of concentrations 5×10^{-4} and 10^{-3} mol/L. In the solution of concentration 5×10^{-4} mol/L, the J-band at 573

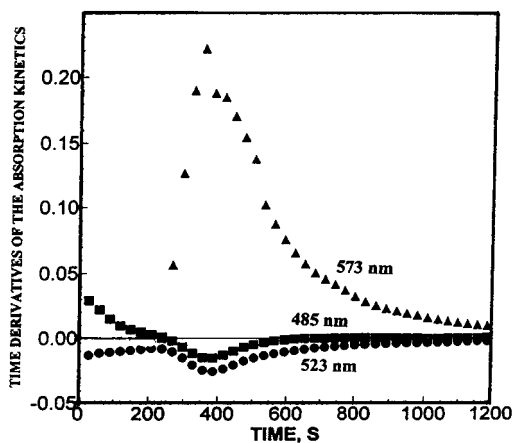


Figure 3. Time dependence of the rates of the absorption kinetics in water solutions of PIC at 3×10^{-4} mol/L.

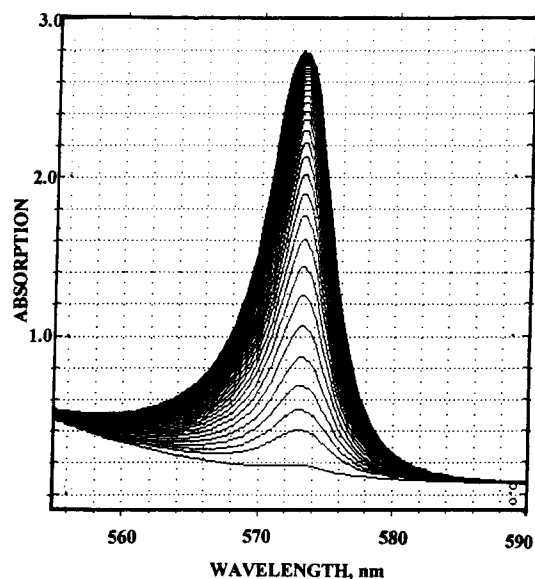


Figure 4. Dynamics of the formation of the J-band in a 5×10^{-4} mol/L solution of PIC in water with NaCl. The time interval between each spectrum is 15 s.

nm appeared approximately 4 min after the beginning of the measurements and, in the solution of concentration 10^{-3} mol/L, $3\frac{1}{2}$ min after the beginning of the measurements.

In all three solutions where the formation of a J-band was observed, the position of its maximum did not change in the process of growth. The full width at half-maximum (fwhm) of the J-band of the solution of concentration 3×10^{-4} mol/L did not change significantly as well and was approximately 4 nm. In the solution of concentration 5×10^{-4} mol/L, the fwhm of the J-band increased from 4 to 6 nm (Figure 4). In the solution of concentration 10^{-3} mol/L, the fwhm of the J-band increased from 4 to 14 nm.

Discussion

The purpose of the experiment was to observe the dynamics of formation of J-aggregates with the hope of obtaining some information about how many molecules of PIC in aggregates are required to produce a J-band in the absorption spectrum of the solution. The process can be observed in one of two different ways: (1) by changing the concentration of the dye, because PIC forms J-aggregates only at high concentrations or (2) by keeping the concentration constant and changing the temperature, because PIC does not form J-aggregates at high temper-

ature. In the first case, it is very difficult to control the concentration of dissolved PIC and the kinetic model cannot be used. Therefore, the second method was chosen. The concentration of PIC in solution was constant during the experiment, but the temperature was not. The changing temperature complicates the interpretation of experimental data, but some conclusions can be made without hesitation.

(1) The formation of J-aggregates is very sensitive to the concentration of PIC in the solution. Indeed, at 3×10^{-4} mol/L an intense J-band was formed while at 2×10^{-4} mol/L the formation of a J-band was not observed.

(2) J-aggregates in the solutions studied are formed from monomers of PIC and intermediates with absorption at 485 nm. This conclusion can be made from analysis of the data presented in Figures 2 and 3. Indeed, the formation and the growth of the J-band are accompanied by a decrease of the absorption at both 523 and 485 nm. Moreover, there is a very good correlation among the time dependencies of the absorption values at 485, 523, and 573 nm.

(3) It looks like the absorption spectrum of PIC J-aggregates in the solution studied consists not only of a narrow J-band at 573 nm, but also a band in the region of 490 nm. Indeed, in the process of formation of J-aggregates, the short wavelength maximum in the absorption spectrum moved from 485 to 492 nm and its shape slightly changed. Such a change was not observed in the solution of concentration 2×10^{-4} mol/L. The fact that the absorption spectrum of PIC J-aggregates shows a band in the region of 490 nm has been discussed in several papers.^{12,30}

(4) The position of the maximum of the J-band at 573 nm probably does not depend on the number of PIC molecules in the J-aggregate. In all solutions studied the position of the maximum of the J-band did not change with time, while it is reasonable to assume that the number of PIC molecules in the J-aggregate has to increase in the process of growth and has to be greater in solutions of higher concentration.

An estimate of the number of PIC molecules in the aggregate required to produce a J-band can be obtained from an analysis of the absorption kinetics shown in Figure 2.

The first step is to try to determine which intermediates have absorption at 485 nm. Kaiser and others proposed earlier²⁹ that absorption at 485 nm corresponds to the dimer of PIC and that the dimerization is the first step of formation of J-aggregates. Such a suggestion is reasonable. Hence, the decrease in absorption at 523 nm and the increase in absorption at 485 nm observed in the solutions studied is attributed to formation of dimers of PIC.

If we make the assumption that absorption in the region of 485 nm is caused by dimers, then J-aggregates are formed from dimers and monomers of PIC. The aggregates must form from a combination of monomers and dimers. Otherwise it is difficult to explain the difference between the absorption kinetics in solutions of concentrations 2×10^{-4} and 3×10^{-4} mol/L.

Aggregation has to be a consecutive process. Initially two molecules, and then three, four and more molecules (or two, three, four, and more dimers), become connected together. When the number of PIC molecules in the aggregate reaches a critical number N , the J-band appears.

The question is how each step of aggregation influences the absorption characteristics of the solution. Two possibilities exist. The first is that the formation of each intermediate aggregate causes a change in the absorption spectrum of the PIC molecules in it. The second is that the formation of each intermediate aggregate does not change the absorption spectrum of the

solution and only when a certain number of PIC molecules are incorporated does the absorption spectrum of the aggregate suddenly change.

If J-aggregates are simple chains of PIC molecules, it is reasonable to assume that in the beginning the addition of each monomer into the chain changes the absorption spectrum of the aggregate. Otherwise it is difficult to explain why, for example, when the aggregate consists of 19 PIC molecules its absorption spectrum is like that of a monomer, and when another PIC molecule is attached a J-band suddenly appears.

Sudden changes in the absorption spectra of the aggregate with the addition of a monomer are possible if J-aggregates are not simply chains of molecules but consist of unit cells and each cell is a nonlinear geometrical structure. In this case until a unit cell is formed absorption characteristics of molecules in aggregate may be like those of monomers and dimers. Then the formation of a unit cell changes the character of the bond between molecules and the spectral characteristics of the aggregate.

The absorption spectra of the solution studied (Figure 1b) do not show the appearance of any intermediates before the formation of the J-band other than those with absorption in the region of 485 nm. Likewise, no shift in the position of the maximum of the J-band with time is observed. If we assume that the absorption in the region of 485 nm belongs to dimers and J-aggregates are linear chains of PIC molecules, then the formation of the smallest J-aggregate can be written as



where N_1 is the number of monomers M and N_2 is the number of dimers D required to produce a J-band in the absorption spectrum of J-aggregate J. To simplify the problem in the first approximation, continuous formation of dimers from monomers



can be neglected. Indeed, as can be seen from Figure 2b, when a J-band appears, the rate of decay of absorption at 523 and 485 nm changes. Such changes are not observed in solutions of lower concentration (Figure 2a). Thus, likely they are caused by formation of J-aggregates and not by possible temperature effects. The formation of J-aggregates must therefore be faster than the continuous formation of dimers.

If we neglect the backward reaction



then the rate of formation of J-aggregates should be proportional to the concentration of monomers to the power N_1 and the concentration of dimers to the power N_2 :

$$d[J]/dt = k[M]^{N_1}[D]^{N_2} \quad (4)$$

Depending on N_1 and N_2 , eq 4 leads to different types of dependence of the concentration of J-aggregates [J] on time.³¹

The J-band at 573 nm does not overlap significantly with the rest of the absorption spectrum of the solution. The absorption at 573 nm may then be assumed proportional to the concentration of J-aggregates in the solution. The fact that there was no change observed in the shape of the absorption spectrum of the solution in the region of 523 nm indicates that overlap among the absorption spectra of monomers, dimers, and J-aggregates in the region of 523 nm is minor. As a first approximation the absorption at 523 nm may be assumed proportional to the concentration of PIC monomers in the

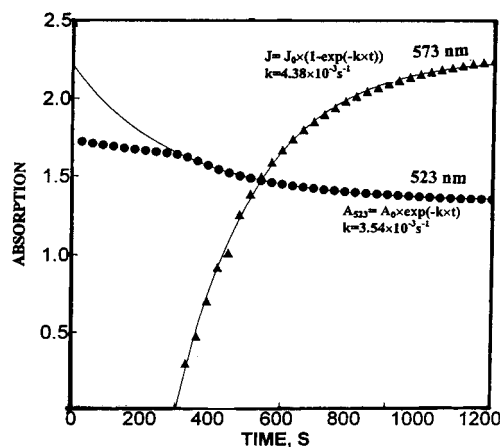


Figure 5. Theoretical (solid lines) and experimental absorption kinetics in water solutions of PIC at 3×10^{-4} mol/L.

solution. Unfortunately in the region of 485–490 nm there is evidently significant overlap of the absorption spectra of monomers, dimers, and J-aggregates, and it does not appear possible to separate them.

A few different equations have been used to fit the experimental absorption kinetics at 523 and 573 nm. Amazingly the best fit was obtained with simple exponential dependencies

$$J_{573} = J_0(1 - \exp(-k_1 t)) \quad (5)$$

for the absorption at 573 nm and

$$A_{523} = A_0 \exp(-k_2 t) \quad (6)$$

for the absorption at 523 nm. The agreement between the theoretical curves in eqs 5 and 6 and the experimental kinetics is shown in Figure 5. Moreover, rate constants k_1 and k_2 obtained as a result of fitting the experimental kinetics with these equations are relatively close: $k_1 = 4.38 \times 10^{-3} \text{ s}^{-1}$ and $k_2 = 3.54 \times 10^{-3} \text{ s}^{-1}$. The fact that k_2 is slightly less than k_1 can be explained by the possible slight overlap of the absorption spectra of monomers, dimers, and J-aggregates in the region of 523 nm.

The simple exponential dependencies in eqs 5 and 6 arise if only one monomer and one dimer are required to produce a J-band and the concentration of monomers is much greater than the concentration of dimers or if the concentration of dimers is approximately constant. That means that under the assumptions made above (and if we treat J-aggregates as simple chains of molecules) one of the possible explanations of the absorption kinetics shown in Figure 2b is that only one dimer and one monomer are required to produce a J-band in the absorption spectrum of the solution.

It should be emphasized that three is the number of PIC molecules participating in initial J-aggregate formation. Aggregation, evidently, does not stop at this number. The equilibrium number of monomers in the J-aggregate should depend on the concentration of the solution, temperature, solvent, and other factors and can be very large.

Three is the number of PIC molecules required to produce a J-band in the absorption spectrum of the solution. The number of PIC molecules in the aggregate required to cause its superradiant emission or high second-order nonlinear optical susceptibility could be different.

Finally, the conclusion about three molecules was obtained under the assumption that J-aggregates are simple chains of

molecules and intermediates with absorption in the region of 485 nm formed prior to J-aggregates are dimers of PIC. If they are not dimers, but other types of aggregates, the number may be different.

It is important to mention that there are other mechanisms that will lead to the absorption kinetics given by eqs 5 and 6. One of them is a chain reaction where T is a trimer and I is the



last intermediate before the J-aggregate is formed. Intermediate steps between $D + M \rightarrow T$ and $I + M \rightarrow J$ in reaction 7 are omitted. Reaction 7 will lead to eqs 5 and 6 if all but the last step of the reaction go very fast or only the last step of the reaction changes the spectral characteristics of the aggregates. In this case, the number of molecules of PIC required to produce a J-band can be relatively large. But as was discussed above, if we assume that J-aggregates are chains of PIC molecules, it is difficult to explain why the last step affects the spectral characteristics of aggregates and the others do not.

If we assume that J-aggregates are not simply chains of PIC molecules, but consist of unit cells and the last step in reaction 7 reflects the formation of a unit cell, then it is possible that this step changes the spectral characteristics of aggregates. The data gathered do not allow identification of this unit cell. PIC J-aggregates are formed only when the concentration of PIC molecules in the solution is close to the limit of solubility. That suggests that the unit cell may be nothing other than the unit cell of a crystal of PIC. The minimum number of PIC molecules in aggregate required to produce a J-band is the number of PIC molecules in a unit cell of a PIC crystal.

As for the number of PIC molecules in a unit cell, it is certainly greater than two, because Figures 1 and 2 clearly show that J-aggregates are formed from both monomers and intermediates with absorption at 485 nm. The absence of other intermediates indicates that the number is relatively small. From another perspective, highly nonlinear concentration dependence suggests that the number is large. Further research is required to determine the exact number of PIC molecules in a unit cell.

An interesting conclusion can be drawn from an analysis of the change in J-band with time. As mentioned above, in a solution of concentration 3×10^{-4} mol/L, the fwhm of the J-band did not change significantly during the time of the experiment, at concentration 5×10^{-4} mol/L it increased from 4 to 6 nm (Figure 4), and at concentration 10^{-3} mol/L it changed from 5 to 14 nm. These changes can be explained with the assumption that at least two processes take place. The first is the formation of small J-aggregates at different points of the solution. The second is the growth of J-aggregates. Growth should be faster in more concentrated solutions. Growth leads to inhomogeneous broadening and causes an increase of the fwhm of the J-band.

Another interesting detail of the evolution of the J-band, as was mentioned above, is that the position of its maximum does not change noticeably with time in all solutions studied. As follows from an earlier proposed model^{16–22} describing J-aggregates in solution as consisting of N identical molecules aligned one-dimensionally, both the absorption maximum and fwhm of the J-band should depend on the number of molecules

in the aggregate. The dependence of the position of the maximum of the J-band on the number of molecules in the aggregate is expected for helix-like aggregates as well.²³ According to experimental data, this is not always the case. Apparently, in the solutions studied, the position of the maximum of the J-band does not reflect the size of J-aggregates.

Conclusion

Data gathered here allow several conclusions to be made. First, J-aggregates are formed from monomers of PIC and an intermediate with absorption in the region of 485 nm. Second, if these intermediates are dimers of PIC and J-aggregates are simple chains of PIC molecules, then three molecules of PIC is the minimal number required to produce a J-band in the absorption spectrum of the solution. Third, the position of the maximum of the J-band does not depend on the number of PIC molecules in the aggregate.

If J-aggregates are not simple chains of PIC molecules, but consist of unit cells of nonlinear structure, then it is possible that more than three PIC molecules are required to produce a J-band. Further research is required for a deeper understanding of the evolution of optical properties of J-aggregates in the process of growth. Such research is now under way.

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