

# Influence of Inorganic Salts and Bases on the J-Band in the Absorption Spectra of Water Solutions of 1,1'-Diethyl-2,2'-cyanine Iodide

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We studied the influence of inorganic salts and bases on the absorption spectra and kinetics of the formation of the J-band in water solutions of 1,1'-diethyl-2, 2'-cyanine (PIC) iodide. The absorption spectra of diluted ( $10^{-5}$  to  $10^{-6}$  mol/L) solutions of PIC containing significant amounts of neutral or basic inorganic salts showed an intense and narrow J-band, with the half-width at the full maximum (HWHM) of less than 4 nm at room temperature. The position of the maximum of the J-band depended on the anion of the salt. Spectra had shape concurrent with that previously assigned in published materials to pure J-aggregates. Kinetics of the absorption spectra during the formation of the J-band in diluted solutions showed isosbestic points, indicating that PIC molecules undergo a transition from monomer state directly to "J-aggregate" state, without intermediate states, such as dimers or trimers. Absorption spectra of concentrated solutions of PIC containing some inorganic salts showed two J-bands. The "red" J-band had the maximum at 579 nm in all solutions. The position of the maximum of the "blue" band depended on the anion of the salt. Its intensity strongly depended on the concentration of the inorganic salt. Possible mechanisms of the influence of inorganic anions on the formation of the J-band in the spectra of diluted and concentrated solutions of PIC are discussed.

## 1. Introduction

In 1936 Scheibe<sup>1</sup> and Jelley<sup>2</sup> reported that the absorption spectra of concentrated solutions of some cyanine dyes showed a new, very narrow and intense band, red-shifted with respect to the absorption spectra of diluted solutions. The solutions also showed a very strong fluorescence, nearly resonant with the absorption. The new band received the name "J-band" in honor of Jelley. Later it was attributed to the formation of a special type of molecular aggregates, J-aggregates.

In subsequent years, significant efforts have been made to establish the nature of the J-band. Initially, papers were devoted primarily to absorption and fluorescence spectra of cyanine dyes at different conditions. After the development of laser techniques other optical characteristics of J-aggregates have been studied using different fascinating methods, including nonlinear spectroscopy,<sup>3</sup> time-resolved fluorescence,<sup>4–13</sup> accumulated photon-echo technique,<sup>9–11</sup> Raman spectroscopy,<sup>4</sup> femtosecond pump-probe spectroscopy,<sup>14,15</sup> electro-modulation spectroscopy,<sup>16</sup> near-field scanning optical microscopy,<sup>17</sup> and atomic force microscopy.<sup>18</sup> It was found that, in addition to the J-bands in the absorption and fluorescence spectra, aggregates of some cyanine dyes show high second- and third-order nonlinearity and optical activity.

Of all cyanine dyes, PIC shows the narrowest and the most impressive J-band. In early works it was noticed that the position of the maximum of the J-band depends on the medium. Scheibe<sup>19</sup> observed that the J-band at a mica/solution interface was red-shifted at approximately 5 nm compared to that in water solutions. Later, Cooper<sup>20</sup> found that at low temperatures, the J-band in the absorption spectrum of PIC in water/ethylene glycol glasses splits on two very close bands, with the maxima

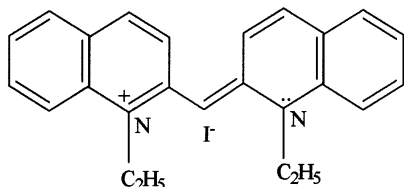
at 572 and 575 nm. Nakatsu et al.<sup>21</sup> observed a J-band with the maximum at 580 nm in the absorption spectrum of PIC iodide powder suspended on a quartz-glass plate. Daltrozzi et al.<sup>22</sup> and Renge and Wild<sup>23</sup> reported that anions of inorganic salts have a significant effect on the J-band in the spectra of PIC and that the position of the maximum of the J-band depended on the anion of the salt.

It was noticed many times, including in the pioneer paper of Jelley,<sup>2</sup> that inorganic ions decrease the threshold concentration of dye molecules, required for the appearance of the J-band. Only one explanation to this phenomenon was given so far, which is promotion of aggregation of dye molecules by inorganic salts due to an increase of the effective dielectric constant of the solvent.<sup>24</sup> The doublet structure of the J-band observed in some experiments has been ascribed to different staking configurations of PIC molecules in aggregates.<sup>23</sup>

There are two published theories explaining the nature of the J-band. Scheibe<sup>25</sup> and Frank and Teller<sup>26</sup> proposed that the J-band is the result of the formation of an excitonic state through the electronic coupling of the tightly packed dye molecules. This theory received further development in numerous publications and is currently overall accepted.<sup>27–39</sup> However, recently Egorov<sup>40</sup> suggested that the J-band could have a different nature. According to his theory the J-band originates from an electron transfer between neighbor molecules in aggregates and unusual resonance between electronic motion and environmental nuclear motion. Both theories relate the J-band with aggregation and do not take into account a possible role of inorganic ions.

Most of the experimental data published support the hypothesis of the aggregational nature of the J-band. Indeed, the J-band usually appears in the spectra of concentrated solutions or films and glasses and disappears under dilution. Progress in experimental technique made possible the direct observation of the macrostructure of cyanine dyes J-aggregates in aqueous solu-

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**Figure 1.** Structural formula of PIC Iodide.

tions. Von Berlepsch and co-workers<sup>41</sup> reported that at concentration  $10^{-3}$  mol/L PIC, J-aggregates in solutions look like cylindrical rods with diameters  $2.3 \pm 0.2$  nm.

However, recently we observed that inorganic salts and bases cause complete transformation of the absorption spectra of very diluted,  $10^{-8}$  mol/L, water solutions of 5,6-dichloro-2-[3-[5,6-dichloro-1-ethyl-3-(3-sulfopropyl)-2(3*H*)-benzimidazolylidene]-1-propenyl]-1-ethyl-3-(3-sulfopropyl)benzimidazolium hydroxide (TDBC) from a monomer shape to a J-aggregate shape and that kinetics of the absorption spectra exhibit an isosbestic point.<sup>42</sup> Formation of relatively large (if any) tightly packed molecular aggregates in such diluted solutions is questionable. In this paper we report on the study of the influence of inorganic salts and bases on diluted and concentrated solutions of PIC. Data obtained suggest that inorganic ions may play a more important role in the formation of the J-band than simply promotion of aggregation due to an increase of the effective dielectric constant of the solvent.

## 2. Experimental Details and Results

We studied the influence of different inorganic salts and bases on the absorption and fluorescence spectra and kinetics of diluted and concentrated water solutions of PIC iodide. The structural formula of the dye is shown in Figure 1. The dye was purchased from Aldrich and used as received. The concentration of PIC in the solutions studied ranged from  $10^{-6}$  to  $10^{-3}$  mol/L.

Absorption spectra and kinetics were recorded with a Perkin-Elmer Lambda-12 UV-vis spectrometer. All solutions exhibiting the J-band in the absorption spectra had a J-band in their fluorescence spectra, nearly resonant to absorption. Fluorescence spectra were recorded with a Perkin-Elmer Lambda 50-B luminescence spectrometer. However, for the purpose of this paper, emphasis is made on the absorption spectra.

Absorption spectra of the solutions depended on the concentrations of both PIC and inorganic ions. Weak acidic salts did not have significant effects on the absorption spectra of the solutions. Strongly acidic salts and acids bleached the solutions, most probably due to the protonation of PIC.<sup>24</sup>

Neutral and basic salts and strong bases initiated the appearance of the J-band in the absorption spectra of the solutions independent of the concentration of PIC. However, the amount of salt (base) required strongly depended on the concentration of PIC.

**I. Influence of Inorganic Salts and Bases on the Absorption of Diluted ( $10^{-6}$  to  $10^{-4}$  mol/L) Solutions of PIC.** Absorption spectra of diluted ( $10^{-4}$  mol/L and lower) solutions of PIC in distilled water had only one maximum at 522 nm and a short wavelength shoulder at approximately 480 nm. Figure 2a shows the absorption spectrum of a  $3 \times 10^{-5}$  mol/L solution of PIC in pure water measured at room temperature. This spectrum looks like a typical spectrum of PIC<sup>+</sup> cation in monomeric form<sup>43</sup> and does not indicate on any significant amount of dimers or other aggregates present in the solution. Therefore, one can conclude that at concentrations  $10^{-4}$  and lower, PIC in pure water exists mostly in a monomeric form.

Addition of inorganic salts in the amount of 0.2–0.5 mol/L (a typical amount used to promote the J-band in concentrated solutions of PIC<sup>14,24</sup>) had no significant effect on the absorption spectra of diluted solutions. However, when the concentration of the salts approached the limit of solubility, the absorption spectra of the solutions suddenly changed very significantly. Parts b–f of Figure 2 illustrate the changes that took place in the absorption spectra of  $3 \times 10^{-5}$  mol/L water solutions of PIC after addition of significant amounts of NaCl, KBr, KOH, NaI, and Na<sub>2</sub>SO<sub>4</sub>. Spectra were measured in a 1 cm cell at 25 °C. Solutions were liquids and did not show noticeable increases of viscosity. The J-band was very narrow, with a HWFM less than 4 nm in solutions containing NaCl, KBr, and Na<sub>2</sub>SO<sub>4</sub>. It was broader in solution containing KOH. Solutions containing NaI showed two J-bands with maxima at 578 and 583 nm.

Absorption spectra of the solutions containing NaCl, KBr, and Na<sub>2</sub>SO<sub>4</sub> showed no significant changes during a few hours after the preparation. However, the J-band and the overall absorption of the solutions containing KOH and NaI significantly decreased in a few minutes.

The position of the maximum of the J-band in diluted solutions of PIC depended on the anion of the salt/base. It was at 572 nm in solutions containing SO<sub>4</sub><sup>2-</sup>, at 573 nm in solutions containing Cl<sup>-</sup>, at 575 nm in solutions containing Br<sup>-</sup>.

Inorganic salts caused not only the appearance of the J-band, but also the transformation of other parts of the absorption spectra of diluted solutions of PIC. Thus, instead of the maximum at 522 nm, belonging to monomers of PIC<sup>+</sup>, absorption spectra of the solutions containing NaCl and KBr (Figures 2b,c) showed two peaks at 495 and 532 nm.

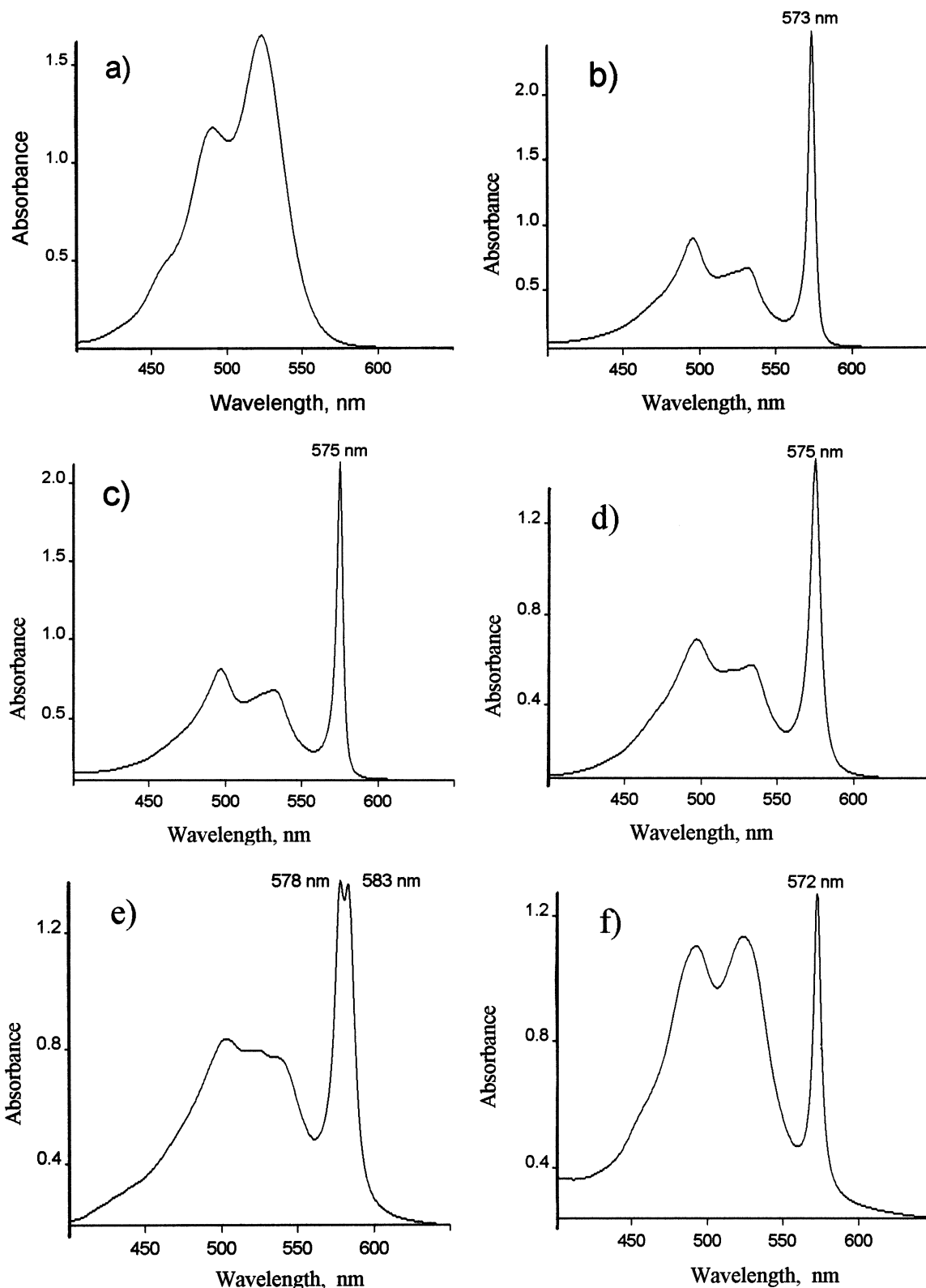
The absorption spectra of diluted solutions of PIC containing inorganic salts and bases depended on temperature. Thus, at 50 °C and higher the absorption spectra of all solutions looked almost identical to the absorption spectrum of PIC<sup>+</sup> monomers (Figure 2a) and did not show a J-band. Cooling of the solutions to room temperature led to the appearance and growth of the J-band. Transformation of the absorption spectrum of  $3 \times 10^{-5}$  mol/L water solution of PIC containing NaCl during its cooling from 54 to 23 °C is shown in Figures 3a,b. Figure 3a shows 30 spectra measured with a time interval of 24 s between each consecutive spectrum and Figure 3b shows the selection of five spectra at different temperature.

Three isosbestic points are clearly seen in Figures 3a,b. This is an interesting result, because it indicates that PIC molecules in diluted solutions exist in only two forms: as monomers and “J-aggregates”.

When the concentration of PIC was  $5 \times 10^{-6}$  mol/L, addition of NaCl, KBr, and NaI had a similar effect on the absorption spectra of the solutions; however, bigger amounts of salt were required.

**II. Influence of Inorganic Salts and Bases on the Absorption of Concentrated ( $5 \times 10^{-4}$  to  $10^{-3}$  mol/L) Solutions of PIC.** Absorption spectra of concentrated solutions of PIC in pure water differ from those of diluted solutions. Figure 4 shows the absorption spectrum of a  $6 \times 10^{-4}$  mol/L water solution of PIC. The spectrum was measured in a 0.5 mm cell at 25 °C. The spectrum had two maxima, one at 522 nm and the other at 480 nm, and a weak J-band at approximately 580 nm. In previously published papers<sup>43,44</sup> the maximum at 480 nm was attributed to dimers of PIC.

When the solution was heated to 50 °C, the J-band disappeared, the maximum at 480 nm became smaller and the maximum at 522 nm became bigger. When the solution cooled back to room temperature, its absorption spectrum returned to



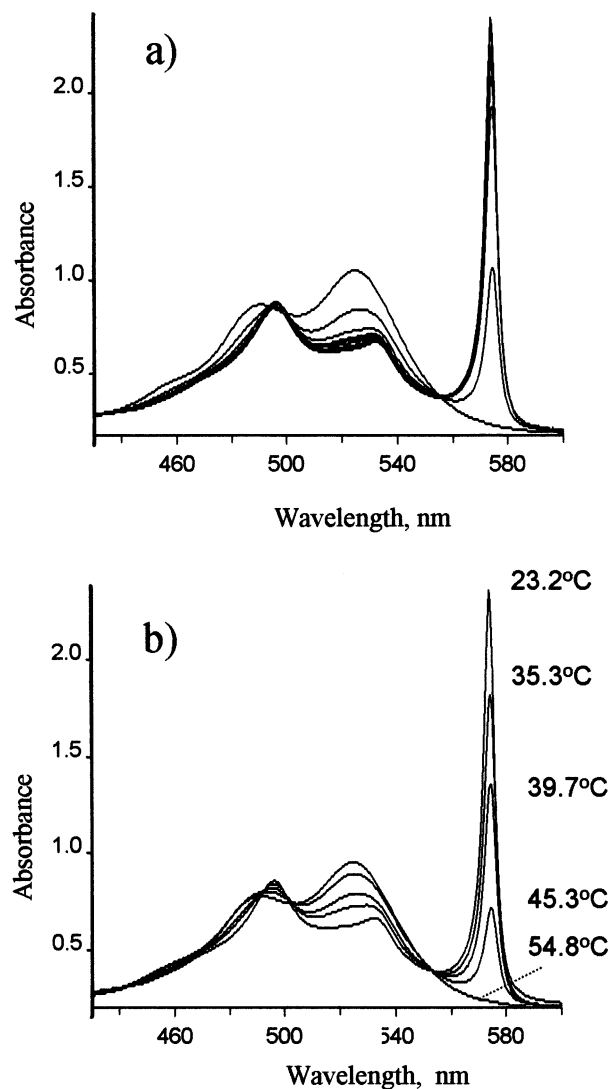
**Figure 2.** Absorption spectra of  $3 \times 10^{-5}$  mol/L solutions of PIC in distilled water (a) and containing 4.95 mol/L of NaCl (b), 3.59 mol/L of KBr (c), 7.56 mol/L of KOH (d), 1.1 mol/L of NaI (e), and 1.3 mol/L of  $\text{Na}_2\text{SO}_4$  (f). Spectra were measured in a 1 cm cell at 25 °C.

the initial state. Figure 5a shows the kinetics of the absorption spectra of the solution while it cooled from 50 to 25 °C. Spectra were measured with 24 s time intervals in a 0.5 mm cell. Figure 5b shows an enlarged picture of the absorption spectra in the J-band area.

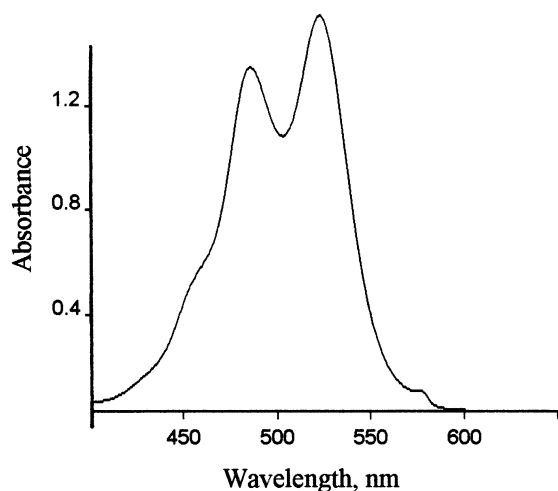
Addition of inorganic salts in relatively small amounts had a significant effect on the absorption spectra of concentrated water solutions of PIC. Figure 6 shows the transformation of the

absorption spectra of  $6 \times 10^{-4}$  mol/L water solutions of PIC containing 0.13 (a), 0.19 (b), and 0.26 (c) mol/L of  $\text{Na}_2\text{SO}_4$  observed while the solutions cooled from 50 to 25 °C. Spectra were measured in a 0.5 mm cell. Figure 7 shows an enlarged picture of the absorption spectra in the J-band area.

Comparing Figures 5, 6a, and 7a one can conclude that the addition of 0.13 mol/L of  $\text{Na}_2\text{SO}_4$  led to a relative increase of the absorption at 480 nm and the intensity of the J-band, without

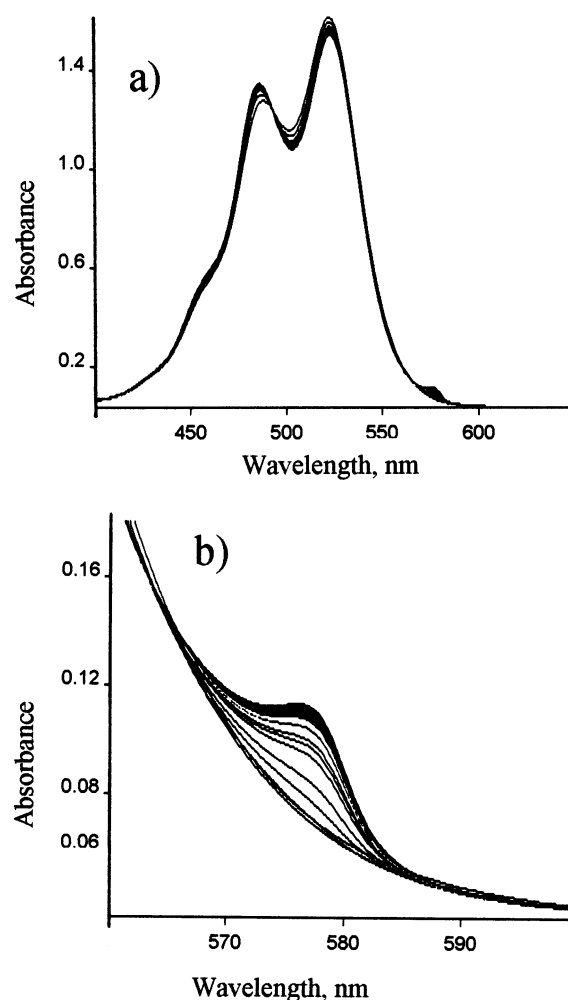


**Figure 3.** Transformation of the absorption spectrum of a  $3 \times 10^{-5}$  mol/L water solution of PIC containing 4.95 mol/L of NaCl under the change of temperature: (a) 30 absorption spectra measured with 24 s time intervals between each; (b) five spectra corresponding to different temperatures. The optical path is 1 cm.



**Figure 4.** Absorption spectrum of a  $6 \times 10^{-4}$  mol/L solution of PIC in distilled water at 25 °C. The optical path 0.5 mm.

noticeable changes in the position of its maximum. More significant changes of the absorption spectra took place when the concentration of  $\text{Na}_2\text{SO}_4$  in the solution was 0.19 mol/L.



**Figure 5.** (a) Absorption spectra of a  $6 \times 10^{-4}$  mol/L solution of PIC in distilled water measured while it cooled from 50 to 25 °C. (b) Enlarged picture of the J-band area. Spectra were measured with 24 s time intervals in 0.5 mm cell.

Although the increase of the absorption at 480 nm was not that significant, very interesting changes took place in the J-band area. Figure 7b shows that while the solution cooled from 50 to 25 °C, initially one J-band, with the maximum at 579 nm appeared and later, at a cooler temperature, another J-band, with a maximum at 572 nm.

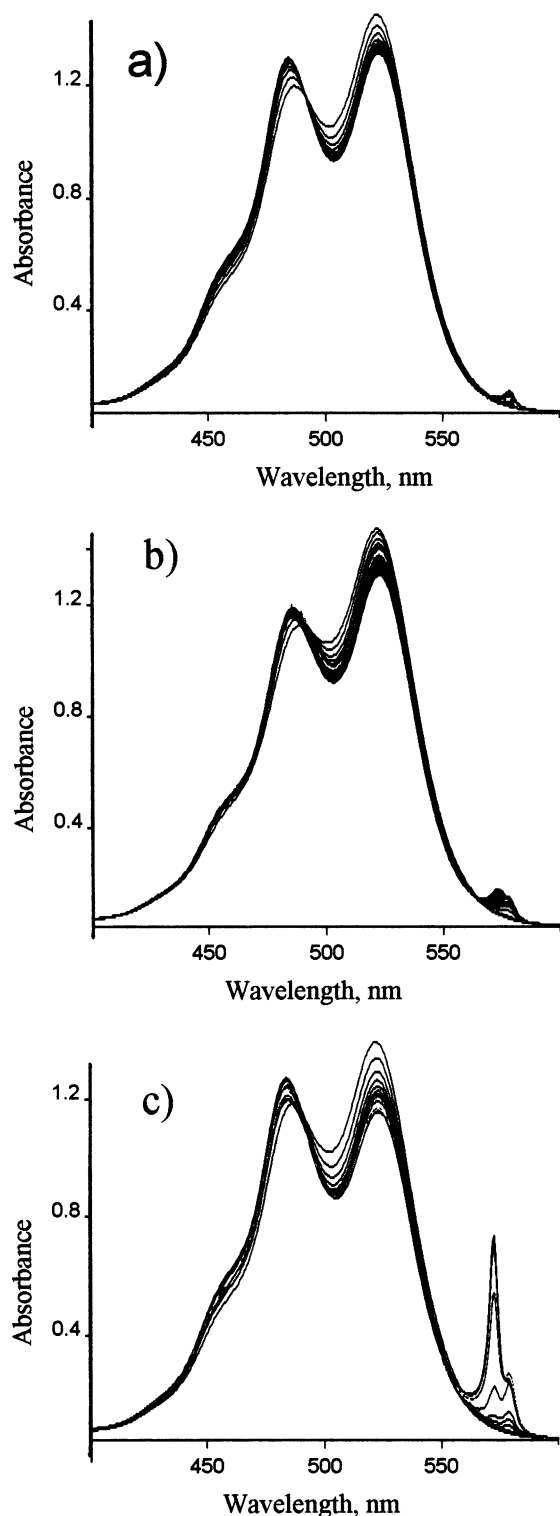
When the concentration of  $\text{Na}_2\text{SO}_4$  was 0.26 mol/L, two bands appeared simultaneously, one at 579 and the other at 572 nm (Figure 7c). The band at 579 nm reached its maximum soon, whereas the band at 572 nm continued to grow.

We observed similar kinetics in the  $6 \times 10^{-4}$  mol/L water solution of PIC containing small amounts of NaCl. When the solution containing 0.047 mol/L of NaCl cooled from 50 to 25 °C, initially a J-band with the maximum at 580 nm appeared, but soon after it was dominated by another band with the maximum at 573 nm (Figures 8 and 9).

Bases catalyzed the growth of the J-band and the transformation of the absorption spectra of concentrated solutions of PIC also. However, the concentration of base required was greater than the concentration of salts. Independent of the amount of the base added, we observed only one J-band, with the maximum at 579 nm.

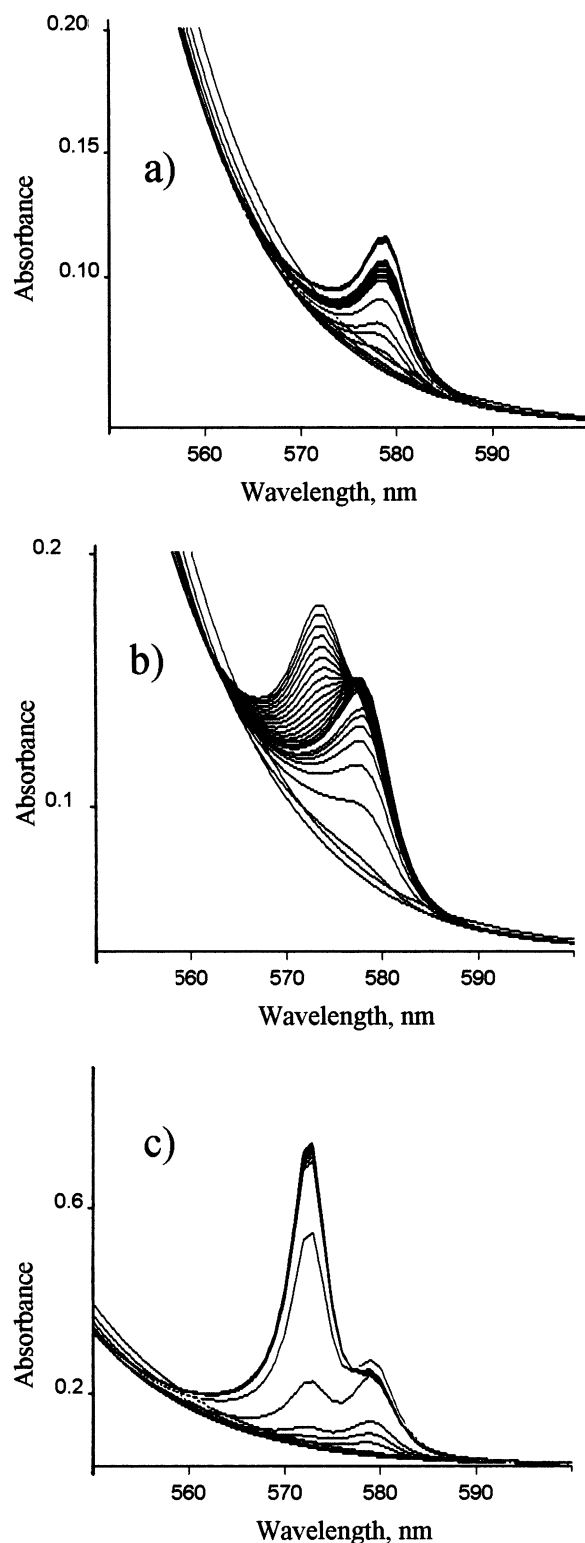
### 3. Discussion

The results presented in the previous section indicate that inorganic salts have a very significant influence on the formation



**Figure 6.** Absorption spectra of  $6 \times 10^{-4}$  mol/L water solutions of PIC containing 0.13 (a), 0.19 (b), and 0.26 (c) mol/L of Na<sub>2</sub>SO<sub>4</sub>, measured while they cooled from 50 to 25 °C. Spectra were measured with 24 s time intervals in 0.5 mm cell.

of the J-band in the absorption spectra of water solutions of PIC. To determine the mechanism of this influence, one should consider different processes that could be initiated by inorganic salts in the solutions. One of them mentioned in published materials is increase of the effective dielectric constant of the solvent.<sup>24</sup> Other possible processes are crystallizations of PIC and salts caused by a shift in the ionic balance in the solutions. Indeed, it is well-known that the presence of a common ion

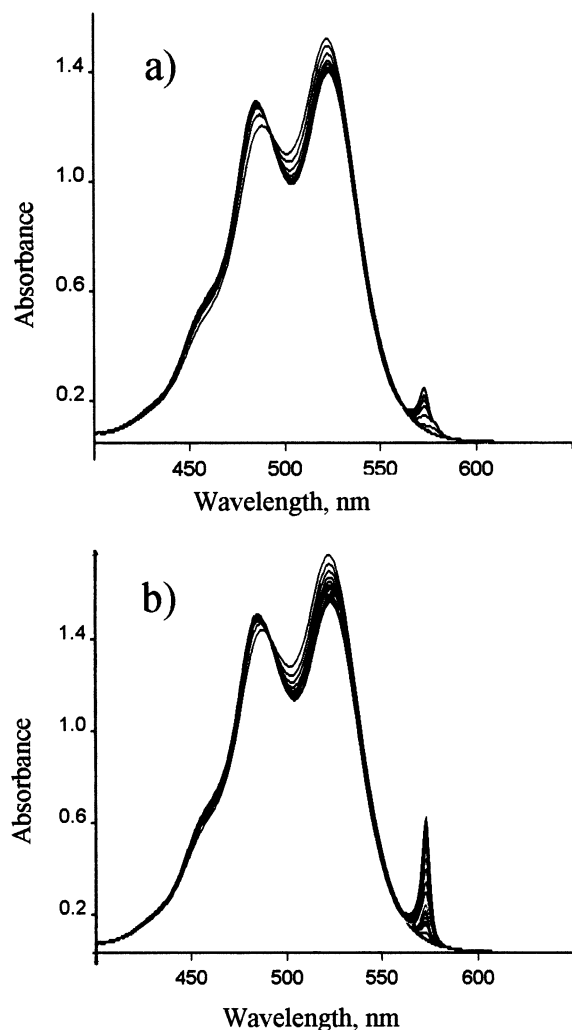


**Figure 7.** Enlarged picture of the absorption spectra shown in Figure 6 in the J-band area.

from another source decreases the solubility of a salt.<sup>45</sup> The solubility of PIC in pure water at room temperature is relatively low (the limit of solubility is about  $10^{-3}$  mol/L). It is probable that inorganic salts could decrease the solubility of PIC. On the other hand, the solubility of inorganic salts in water could be affected by the presence of PIC. Crystallization of both PIC and inorganic salts could take place in the solutions studied.

Changes in the absorption spectra of diluted solutions of PIC presented in Figure 2 took place when the concentration of the



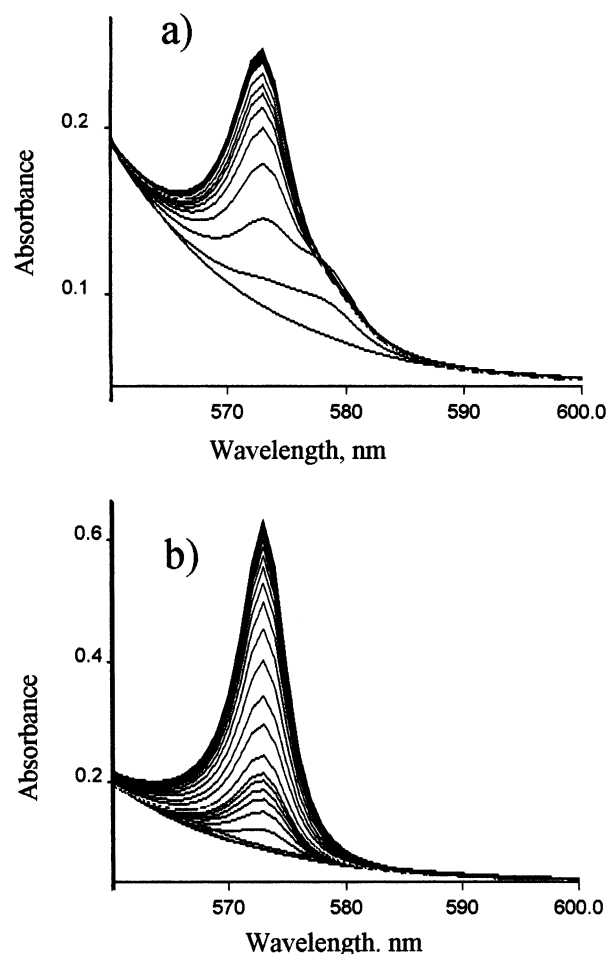


**Figure 8.** Absorption spectra of  $6 \times 10^{-4}$  mol/L water solutions of PIC containing 0.047 (a) and 0.091 (b) mol/L of NaCl, measured while they cooled from 50 to 25 °C. Spectra were measured with 24 s time intervals in 0.5 mm cell.

salts approached the limit of solubility. They had a jump-like, not a smooth character. These facts suggest that the J-band and the transformation of the absorption spectra of the solutions were initiated more likely by a shift in an ionic balance and crystallization than by an increase of the effective dielectric constant of the solvent.

PIC is known to form salt not with iodide only, but with bromide and chloride. When the concentration of  $\text{Br}^-$  or  $\text{Cl}^-$  ions in the solution is much greater than concentration of  $\text{I}^-$  ion,  $\text{PIC}^+$  should rather crystallize with bromide or chloride than with iodide. It is possible that  $\text{PIC}^+$  could form some type of crystals or aggregates with  $\text{SO}_4^{2-}$  and  $\text{OH}^-$ . The dependence of the maximum of the J-band on the anion of the salt and a double structure of the J-band in the diluted solution of PIC containing NaI (Figure 2) could be results of crystallization of  $\text{PIC}^+$  with different anions.

Crystallization and a key role of anions in the position of the maximum of the J-band could lead to the dependences presented in Figures 6–9 of the kinetics of the absorption spectra of  $6 \times 10^{-4}$  mol/L solutions of PIC on the concentration of inorganic salts. Indeed, when the concentration of PIC is relatively high, a small amount of inorganic anions may shift the ionic equilibrium and cause crystallization (or aggregation) of PIC. In solution in pure water or containing a very small amount of inorganic salts,  $\text{PIC}^+$  should crystallize with  $\text{I}^-$ . This results in



**Figure 9.** Enlarged picture of the absorption spectra shown in Figure 8 in the J-band area.

a single J-band with a maximum at 580 nm (figures 5, 6a, and 7a). A small increase of the intensity of the J-band and the absorption near 480 nm in the solution containing 0.13 mol/L of  $\text{Na}_2\text{SO}_4$  compared to that in the solution in pure water could be due to a promotion of aggregation of PIC caused by an increase of the effective dielectric constant of the solvent.<sup>24</sup> In solutions containing more significant amounts of inorganic salt,  $\text{PIC}^+$  can crystallize as with  $\text{I}^-$ , as with an anion of inorganic salt, leading to the appearance of two J-bands (Figures 6b, 7b, 8a, and 9a). A further increase of the concentration of inorganic salt should cause the domination of crystallization with anions of inorganic salts over crystallization with  $\text{I}^-$  (Figures 6c, 7c, 8b, and 9b).

Suggesting that crystallization of  $\text{PIC}^+$  with inorganic anions could be responsible for the observed influence of inorganic salts on the absorption spectra of the solutions studied, we are not sure how it leads to the formation of the J-band. As mentioned in the Introduction, the overall accepted theory<sup>25–39</sup> relates the J-band with the aggregation and formation of an excitonic state among tightly packed dye molecules in aggregates. According to Kobayashi<sup>4</sup> and Renge<sup>23</sup> spectra similar to those observed for diluted solutions of PIC (Figure 2b,c) correspond to the situation when all dye molecules aggregated, forming at least 10–15 molecular J-aggregates, and there are no monomers or dimers of PIC left in the solutions. Such a situation seems unlikely in  $10^{-5}$  to  $10^{-6}$  mol/L dye solutions. Formation of PIC crystals of different sizes, starting from two to three molecular microcrystals or crystals of inorganic salts, containing single  $\text{PIC}^+$  cations as impurity seems more probable.

In addition, the excitonic theory predicts that the position of the maximum of the J-band should depend on the number of coupled chromophores. One would expect that the aggregation of PIC monomers in highly diluted solutions should be consecutive. The dependence of the position of the maximum of the J-band on the number of molecules in aggregates should appear in the kinetics of the absorption spectra. However, kinetics of the absorption spectra of diluted solutions of PIC (Figure 3) show isosbestic points and do not indicate any changes in the position of the maximum or HWFM of the J-band. It seems that the J-band is caused rather by some kind of a phase transition of the monomeric substance of the dyes than by a consecutive process.

Phase transition like behavior of the kinetics of absorption spectra could be explained in the frame of the excitonic theory if PIC molecules in diluted solutions even at high temperature form 10–15 molecular clusters but do not interact with each other significantly and have optical properties identical to PIC<sup>+</sup> monomers. Then, crystallization could lead to a sudden change of the structure and an immediate formation of an excitonic state among 10–15 tightly packed molecules. However, existence of 10–15 molecular clusters of PIC with optical characteristics identical to monomers and, in the meantime, absence of monomers and dimers in 10<sup>-5</sup> to 10<sup>-6</sup> mol/L solutions of PIC seem unlikely.

The low concentration of PIC in the solutions showing a complete transformation of the absorption spectra from a monomer shape to “J-aggregate” shape reported in this paper and the even lower concentration of TDBC in the solutions showing similar transformations reported earlier<sup>42</sup> do not exclude the possibility that the J-band could be a result of a mono- or a bimolecular process. Thus, according to Egorov,<sup>40</sup> an electron transfer from one PIC molecule to another can lead to a narrow and intense band in the absorption spectrum. Other possibilities, such as an electron transfer from an inorganic anion to a PIC<sup>+</sup> cation and changes of the geometrical structure or conformation of PIC due to crystallization also might be considered. In any case, additional research is required to determine the exact nature of the J-band in the absorption spectra of highly diluted solutions of cyanine dyes.

#### 4. Conclusion

Experimental data on the influence of inorganic ions on the absorption spectra of water solutions of PIC presented in this paper, which include (1) the transformation of the absorption spectra of the diluted solutions from a monomer shape to “J-aggregate” shape, (2) isosbestic points in the kinetics of the absorption spectra, (3) the dependence of the position of the maximum of the J-band on the anion of the salt, and (4) the double structure of the J-band in diluted and concentrated solutions of PIC at room temperature, suggest that inorganic anions may play a key role in the origin of the J-band.

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