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Anomalous Surfactant-Induced Enhancement of Luminescence Quantum Yield of Cyanine Dye J-Aggregates

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Formation of the "J-aggregate-surfactant" complex for three cyanine dyes (L-21, LC-1 and PIC) in binary solutions containing cationic surfactant CPB at the concentration higher than the critical micelle concentration has been observed. The complex formation causes a significant increase of J-aggregate luminescence quantum yield and a decrease of radiative lifetime. The model of exciton self-trapping suppression in the "J-aggregate-surfactant" complex that causes changes of luminescence parameters has been proposed.

Introduction

J-aggregates are ordered luminescent nanoassemblies of noncovalently coupled luminophores such as cyanines, porphyrines and some other dyes.[1–7] Since their first discovery by Jelley and Scheibe,[1–4] J-aggregates ("Jelley" aggregates) have been of fundamental interest due to their intermediate position between dissolved molecules and structurally ordered crystals. Their optical properties possess an excitonic nature due to a high degree of ordering of dye molecules in J-aggregate chains. That results in the appearance of a narrow absorption band (so-called J-band) bathochromically shifted with respect to a monomer band and an almost resonant luminescence one. Spectral properties of J-aggregates are governed by the exciton delocalization length, which is usually equal to up to tens monomers,[1–8] rather than the physical length of aggregates.[8] Beside the change of the exciton delocalization length, there is another way to affect the J-aggregate spectral properties. That is the change of molecular arrangement in the J-aggregate chain. If molecular arrangement is changed from "side-by-side" (or "head-to-tail"), which is typical for J-aggregates, to "face-to-face" (or "head-to-head"), excitonic absorption band shifts hypsochromically with respect to the monomers one.[3,4] Such aggregates are called H-aggregates (aggregates with hypsochromic band, H-band) and they are typically nonluminescent. In some cases both J- and H-band could be observed in the absorption spectrum.[4,9,10] This case corresponds to the "herringbone" type arrangement of dye molecules[4,9,10] with two molecules per unit cell. H- and J-bands are upper- and lower Davydov components of the exciton band.[11] Luminescent spectrum of "herringbone" aggregates reveals only one band that corresponds to J-aggregate luminescence. Since photophysical properties of J-aggregates are size and arrangement dependent,[1–4,8–10] it is of great interest to control them by enhancing the aggregation and increasing the coupling strength.

There are several ways to affect the dye aggregation in solutions: an addition of salts, changing solution acidity, temperature, solvent ratio (for binary solutions), using different templates etc.[1–4,7,12–14] Surfactants can provoke the aggregation too.[7,14–28] It was shown that the addition of surfactants at a concentration below the critical micelle concentration (cmc) enhances the aggregation[7,14–28] and sometimes changes J-aggregate morphology.[14,25] As a rule, at surfactant concentrations above the cmc, dye molecules are solubilized by surfactant micelles that prevents their aggregation.[7,14–27] Nevertheless, it was shown that the addition of surfactants at concentrations above the cmc can promote the aggregation of polymethine dyes.[15–17,26–28] In ref 15, the influence of a number of anionic surfactants (sulfonates, sulfates, and their derivatives) on the aggregation of well-known cationic dye PIC was studied. The addition of some surfactants at concentrations below the cmc was found to provoke both J- and H-aggregate formation. At the same time, J-aggregate formation at concentrations much above the cmc was also revealed.[15] In the presence of nonionic surfactants the aggregation of PIC was not observed.[15] In ref 16, the effect of a zwitterionic surfactant on TDBC J-aggregate formation was investigated. It was shown that the addition of the surfactant at concentrations above the cmc changes the J-aggregate spectral characteristics: the absorption J-band becomes narrower and more intense, the luminescence band of J-aggregates also becomes narrower and the fluorescence quantum yield increases. In case of cationic surfactants, the destruction of J-aggregates was observed.[16] The interaction of cationic dye amphi-PIC with anionic and cationic surfactants was investigated in ref 17. The addition of an anionic surfactant at the concentrations above the cmc was found to destroy amphi-PIC J-aggregates, while cationic surfactant CPB causes the increase of the J-band intensity and its narrowing at concentrations below and above the cmc. Recently, a strong aggregation of cationic dye L-21 enhanced by the cationic surfactant CPB at a concentration above the cmc has been reported.[28] The formation of a "J-aggregate-surfactant" complex with a "herringbone" structure of J-aggregates was found that leads to a strong increase of J-aggregate luminescence intensity. However, the structure of such a complex and the reason for the significant increase of J-aggregate luminescence intensity was not analyzed. The aggregation of tetra(*p*-hydroxyphenyl)porphyrin in Triton X-100 micelles was reported in refs 26 and 27. Porphyrin J-aggregates are formed in a large hydration (hydrophilic) layer of nonionic Triton X-100 micelles and their formation is induced by an addition of trihalo acetic acids or ionic surfactants.

We report the study of the influence of cationic surfactant cetylpyridinium (hexadecylpyridinium) bromide (CPB) on the aggregation of three cyanine dyes 3,3′-dimethyl-9-thienylthiacarbocyanine iodide (L-21), 5,5′,6,6′-tetrachloro-1,1,3,3′-

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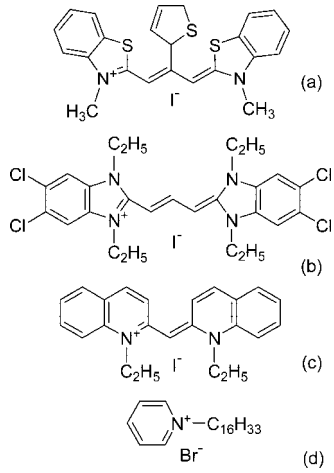

Figure 1. Molecular structures of the dyes and surfactant investigated: (a) L-21; (b) JC-1; (c) PIC; (d) CPB.

tetraethylbenzimidazolylcarbocyanine iodide (JC-1 or TTBC) and 1,1′-diethyl-2,2′-cyanine iodide (PIC) (Figure 1) and luminescence quantum yield of J-aggregate formed.

Experimental Section

L-21 was obtained from the dye collection of the Department of Combinatorial Chemistry (Institute for Molecular Biology and Genetics NAS of Ukraine). JC-1 was synthesized by Dr. I. Borovoy (Institute for Scintillation Materials NAS of Ukraine). The purity of the dyes was controlled by thin layer chromatography. PIC and CPB were purchased from Sigma Aldrich and used as-received.

J-aggregates of L-21 were prepared by the addition of appropriate amount of the surfactant CPB to a stock solution of the dye L-21 in dimethylformamide (DMF). Then the solution was diluted with a water buffer Tris-HCl (0.05 M, pH = 8) in the ratio 1:19. JC-1 aggregates were prepared in a similar way from a stock solution of the dye JC-1 and the surfactant CPB in DMF. Then the solution was diluted with a water-borate buffer ($Na_2B_4O_7$−HCl, pH = 8.5) in the ratio 1:9. PIC J-aggregates were prepared by dissolving the dye PIC (0.25 mM) and the surfactant CPB (1 mM) in an aqueous NaCl (0.2 M) solution under moderate heating (<80 °C). Then the solutions were cooled down to room temperature.

Luminescence and luminescence excitation spectra were recorded using a spectrofluorimeter based on two grating monochromators MDR-23 and a xenon lamp. One of the monochromators was used to select a required wavelength (fwhm ∼ 0.5 nm), the other one was used for the luminescence collection. For absorption spectra registration the spectrofluorimeter was supplied with an incandescent lamp.

Absolute quantum yields of photoluminescence for all solutions were measured using a homemade integrating sphere (diameter of 100 mm), which provides a reflectance > 99% over the 400−1000 nm range. As an excitation source, a diode-pumped Nd^{3+}:YAG laser (λ = 532 nm) was used. The absolute quantum yield was calculated using the method developed by de Mello et al.[29] and successfully applied for solutions by Porres et al.[30] The experimental setup was adjusted and tested on a standard dye (rhodamine 6G in ethanol, $C = 10^{-6}$ M) as described in ref.[29]

To measure the time-resolved luminescence spectra, a mode-locked Nd^{3+}:YAG laser (second harmonics, λ_{exc} = 532 nm) and a time-correlated photon counting system were used. The instrumental function of the setup was 0.5 ns. The CFS_LS software package (Center for Fluorescent Spectroscopy) was used to process the experimental luminescence decay curves.

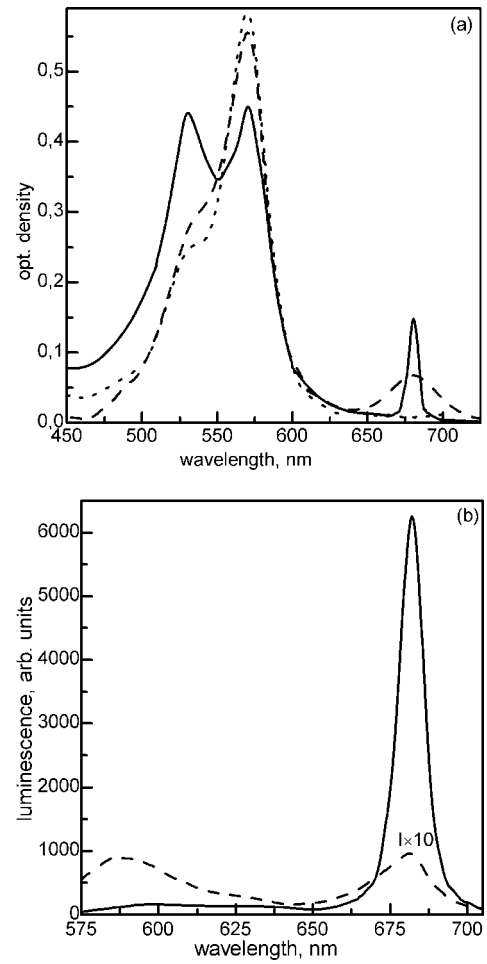

Figure 2. Absorption (a) and luminescence (b) spectra of L-21 dye ($C = 10^{-4}$ M) in a binary solution DMF: water buffer Tris-HCl (pH = 8.0) (1:19) in the absence (dashed lines) and presence (solid lines) of CPB ($C = 10^{-3}$ M). Dotted line = absorption spectrum of L-21 monomers ($C = 10^{-6}$ M) in the solution (the intensity was normalized for clear presentation).

Results

L-21 J-Aggregates. Due to a weak solubility of L-21 in water, L-21 J-aggregates were prepared in a binary solution from a stock dye solution in DMF. Alkalescent medium is found to be required for the dye aggregation. So, the samples were prepared in DMF: water Tris-HCl buffer (pH = 8) in the ratio 1:19. Absorption and luminescence spectra of L-21 dye in such a binary solution show weak and quite wide bands ($\Delta\nu^{abs}_{fwhm}$= 800 cm^{-1} and $\Delta\nu^{lum}_{fwhm}$= 475 cm^{-1}) that belong to J-aggregates (Figure 2, dashed lines). The addition of the cationic surfactant CPB at the concentration above the cmc (6.2×10^{-4} M, see ref 31) provokes significant changes in the spectra (Figure 2, solid lines). In the absorption spectrum, the J-band (λ_{max} = 680 nm) becomes more intense and very narrow ($\Delta\nu_{fwhm}$ = 175 cm^{-1}). Moreover, an intense hypsochromically shifted band (H-band) emerges at λ_{max} = 530 nm (Figure 2a, solid line). It should be noted that the absorption spectrum of the solution without CPB also reveals a short-wavelength shoulder in the monomer band and this shoulder is more intensive in the solution at high dye concentration (Figure 2a, dashed line). Recently it has been shown that both H- and J-bands belong to L-21 J-aggregates of

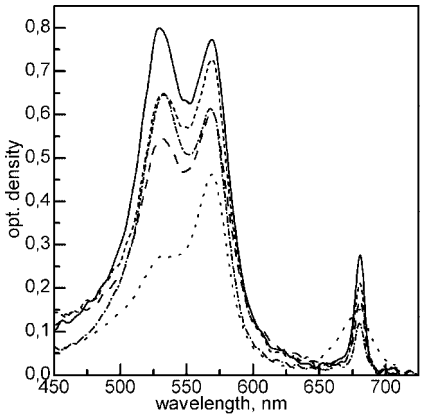

Figure 3. Absorption spectra of the L-21 dye in a solution with CPB at different CPB concentrations: dotted line, 0; short dash dotted line, 2.5×10^{-4} M; solid line, 1×10^{-3} M; short dashed line, 2×10^{-3} M; dashed line, 3×10^{-3} M.

the "herringbone" type.[28] The luminescence band ($\lambda_{max} = 682$ nm) of J-aggregates (Figure 2b, solid line) also becomes much narrower ($\Delta\nu_{fwhm} = 200$ cm^{-1}) and very intense (more than 60 times as compared to J-aggregate luminescence in the absence of CPB), while the intensity of the monomer band decreases.

Significant spectral and structural changes observed seem to be associated with a specific "J-aggregate-surfactant" complex formation in the solutions with CPB.[28] To examine this assumption, the aggregation of L-21 dye has been analyzed in the solutions containing CPB at the wide concentration range (from 2 times lower the cmc up to more than 5 times higher) (Figure 3). At all surfactant concentrations examined, despite some fluctuation of aggregate band intensities, the features of the absorption spectra were the same and the destruction of aggregates as a result of dye solubilization by CPB micelles was not observed. That is evidence of the "J-aggregate-surfactant" complex formation. It should be noted that this complex is not typical, since both the dye and the surfactant possess cationic nature. Similar complex formation is reported only for a zwitterion dye and a zwitterion surfactant,[16] and it was supposed that such a complex is formed as a result of the electrostatic attraction between a positively charged part of the dye and a negatively charged part of the surfactant and vice versa.

JC-1 J-Aggregates. The interaction between another cationic dye JC-1 and CPB also leads to the formation of the "J-aggregate−surfactant" complex. Similar to L-21 J-aggregates, JC-1 ones are prepared in a binary solution DMF:water buffer (pH = 8.5) at the ratio1:9. At JC-1 dye concentration of 10^{-5} M, absorption and luminescence spectra show the appearance of J-aggregate bands with maxima: $\lambda_{abs} = 592$ nm and $\lambda_{lum} = 594.5$ nm (Figure 4, dashed lines). A comparison of the absorption spectra at different dye concentrations (Figure 4a, dotted and dashed lines) has revealed a weak H-band (λ_{max} is about 500 nm) as a shoulder in the short-wavelength edge of the monomer band ($\lambda_{max} = 514$ nm). The addition of CPB causes the transformation of the JC-1 absorption spectrum (Figure 4a, solid line). The intensity of the H-band ($\lambda_{max} = 502$ nm) increases significantly, the J-band becomes narrower ($\Delta\nu_{fwhm} = 265$ cm^{-1} instead of 380 cm^{-1} in the absence of CPB) and shifts toward the long-wavelength region ($\lambda_{max} = 595$ nm). Similar transformation of the JC-1 J-aggregate absorption spectrum was observed in ref 10 under the increase of the dye concentration. The luminescence band of JC-1 J-aggregates in solutions with CPB is narrower ($\Delta\nu_{fwhm} = 185$ cm^{-1} instead of

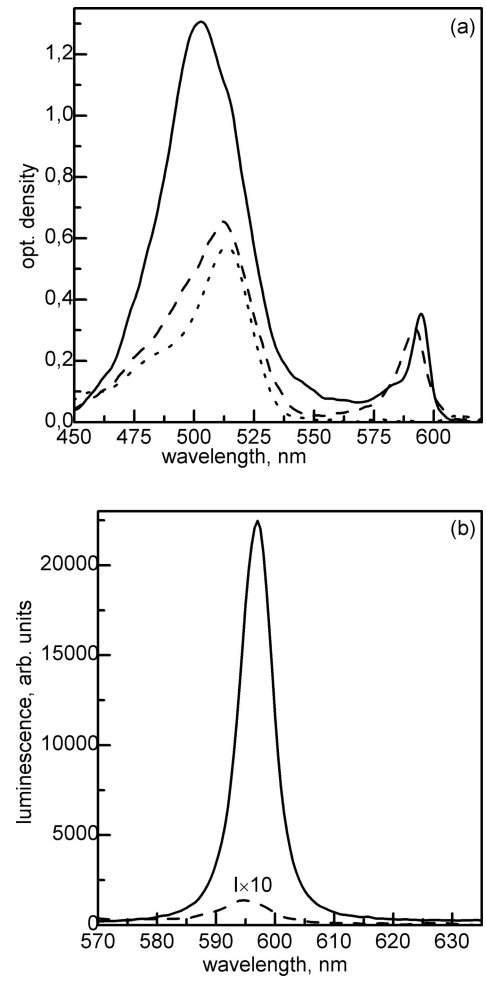

Figure 4. Absorption (a) and luminescence (b) spectra of the JC-1 dye ($C = 10^{-5}$ M) in a binary solution DMF: water borate buffer (pH = 8.5) (1:9) in the absence (dashed lines) and presence (solid lines) of CPB ($C = 10^{-3}$ M). Dotted line = absorption spectrum of JC-1 monomers ($C = 10^{-6}$ M) in the solution (the intensity normalized for clear presentation).

300 cm^{-1} in the absence of CPB) and red-shifted ($\lambda_{max} = 597$ nm), and its intensity increases significantly (more than 50 times) (Figure 4b, solid line).

The increase of JC-1 concentration causes the change of the J-aggregate structure which becomes of a strongly pronounced "herringbone" type (Figure 5a, dashed line), similar to JC-1 J-aggregates in solutions with CPB (Figure 4a, solid line). The intensity of J-aggregate luminescence increases too (Figure 5b, dashed line). The addition of CPB causes just small increase of the absorption H- and J-band intensities (about 15%) (Figure 5a, solid line). At the same time, the intensity of JC-1 J-aggregate luminescence increases significantly (about 10 times) (Figure 5b, solid line).

PIC J-Aggregates. It has been found that CPB also affects the aggregation of the well-known PIC dye. Contrary to L-21 and JC-1 aggregates, PIC J-aggregates are formed in an aqueous NaCl solution. To analyze the influence of CPB on PIC J-aggregate spectra, a small dye concentration was used.[32] The absorption spectrum shows that the J-band ($\lambda_{max} = 573$ nm) is not intense (Figure 6a, dashed line). The analysis of absorption spectra of PIC at different dye concentrations (Figure 6a, dotted and dashed lines) revealed that the short-wavelength band with $\lambda_{max} = 482.5$ nm belongs to H-aggregates. So, the structure of PIC J-aggregate is also of the "herringbone" type, but slightly differs from those for JC-1 and L-21 J-aggregates. The "her-

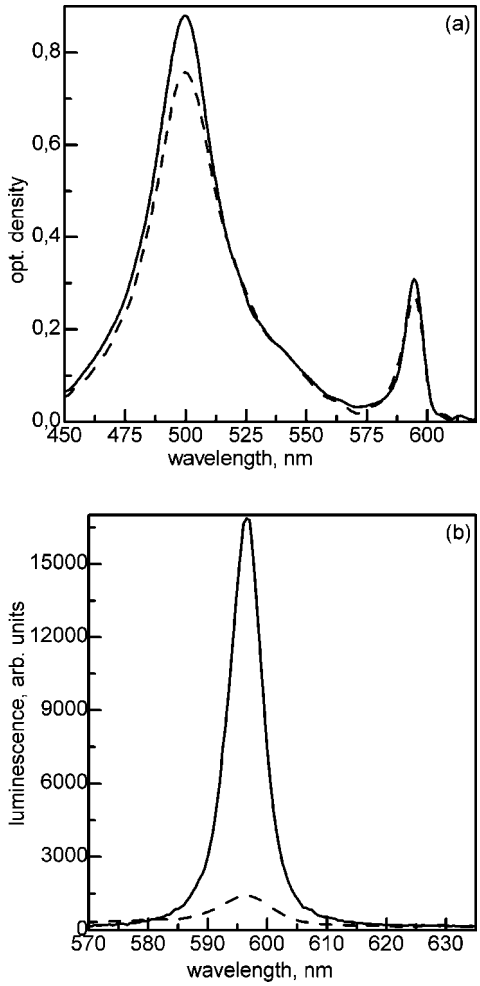

Figure 5. Absorption (a) and luminescence (b) spectra of the JC-1 dye ($C = 10^{-4}$ M) in a binary solution DMF:water borate buffer (pH = 8.5) (1:9) in the absence (dashed lines) and presence (solid lines) of CPB ($C = 10^{-3}$ M).

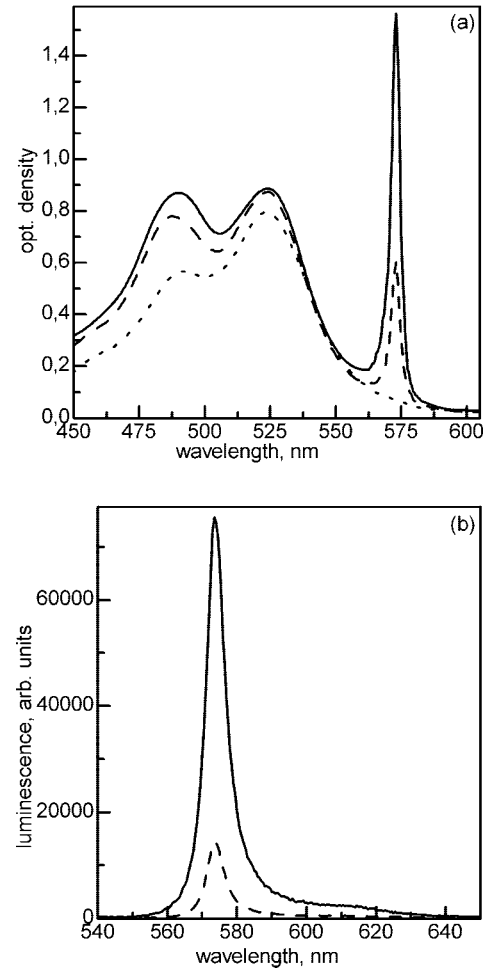

Figure 6. Absorption (a) and luminescence (b) spectra of the PIC dye ($C = 2.5 \times 10^{-4}$ M) in a water solution with NaCl (0.2 M) in the absence (dashed lines) and presence (solid lines) of CPB ($C = 10^{-3}$ M). Dotted line = absorption spectrum of PIC monomers ($C = 10^{-6}$ M) in the solution (the intensity normalized for clear presentation).

ringbone" structure of PIC J-aggregate caused by nonplanar structure of PIC molecules[33] was proposed in refs 34–36 and is confirmed by the perpendicular polarization of J- and H-bands of PIC J-aggregates.[37,38] Indeed, it is known that Davydov-split components (H- and J-bands) must be polarized perpendicularly.[11] As it follows from Figure 6a (dashed line), the ratio of H- and J-bands is much smaller than that for L-21 and JC-1 dyes that can be associated with other angle of the molecular arrangement in the molecular chain.

Similar to J-aggregates of L-21 and JC-1, PIC J-aggregates also forms the complex with CPB that results in the increase of J-aggregate luminescence intensity (about 5 times) and luminescence band narrowing ($\Delta\nu_{fwhm} = 200$ cm^{-1} instead of 240 cm^{-1} in the absence of CPB) (Figure 6b, solid line). The addition of CPB causes the increase of H- and J-bands intensities and slight narrowing of the J-band ($\Delta\nu_{fwhm} = 125$ cm^{-1} instead of 130 cm^{-1} in the absence of CPB) (Figure 6a, solid line). However, the intensity of the H-band slightly increases (about 10%), while the J-band becomes about 2 times more intensive (90%). Such a redistribution of the band intensities points to the rearrangement of PIC J-aggregates molecular packing in solutions containing CPB.

Quantum Yield Measurements. As was shown above, formation of the "J-aggregate-surfactant" complex is accompanied by both strong increase of the J-aggregate luminescence intensity and significant redistribution of the bands in the absorption spectra. So, to prove whether the complex formation effects exciton dynamics in J-aggregates, the absolute quantum yield (φ) of J-aggregate luminescence has been measured in solutions in the presence and absence of CPB (Table 1). The addition of CPB is found to cause the significant increase (up to 15 times) of quantum yield for all J-aggregates investigated. Let us note that the quantum yield of JC-1 J-aggregates slightly increases (in the 1.5−5% range) also with an increase of JC-1 dye concentration. Thus, the dye-concentration-induced changes of J-aggregate structure observed also for L-21 and PIC J-aggregates seem to result in some enhancement of luminescence quantum yield. However, the addition of CPB causes much stronger increase in quantum yield of JC-1 J-aggregate luminescence (Table 1) than the change of the J-aggregate structure as a result of the dye concentration increase.

TABLE 1: Luminescence Quantum Yields (φ) for Different J-Aggregates in the Absence and Presence of CPB

	L-21	JC-1 (low concn)	JC-1 (high concn)	PIC
φ	0.025	0.015	0.05	0.025
φ^{CPB}	0.175	0.19	0.19	0.38

Luminescence Decay Time Measurements. Table 2 represents the results of luminescence decay time (τ) measurements for J-aggregates formed in the solutions in the presence and absence of CPB. For J-aggregates of all the dyes investigated

TABLE 2: Luminescence Decay Times (τ), Radiative Lifetimes (τ_0) and the Relative Changes of N_{del} (Δ^{τ}_{rel}) for Different J-Aggregates in the Absence and Presence of CPB

	L-21	JC-1 (low concn)	JC-1(high concn)	PIC
τ, ns	<0.1	0.25	0.55	0.4
τ^{CPB}, ns	0.45	0.8	0.8	0.7
τ_0, ns		16.65	11	16
τ_0^{CPB}, ns	2.55	4.2	4.2	1.85
$\Delta^{\tau}_{rel} = \tau_0/\tau_0^{CPB}$		3.95	2.6	8.65

TABLE 3: Rotational Correlation Times (τ_{corr}) for Different J-Aggregates in the Absence and Presence of CPB

	L-21	JC-1(low concn)	JC-1(high concn)	PIC
τ_{corr}, ns	0.45	0.55	0.8	2.3
τ_{corr}^{CPB}, ns	2.1	1.3	1.3	3.2

the addition of CPB causes the significant increase of luminescence decay time.

Using measured values τ and φ, we can calculate radiative lifetime (τ_0):[39]

$$\tau_0 = \tau/\phi \quad (1)$$

The results presented in Table 2 show that the addition of CPB causes a significant decrease of radiative lifetime for J-aggregates of all dyes investigated. This feature will be discussed below. Let us also emphasize the decrease of radiative lifetime for JC-1 J-aggregates in solutions at high dye concentration as a result of luminescence quantum yield increase due to the J-aggregate structure change. However, this decrease is smaller than that caused by the CPB influence (Table 2).

Using the method described in ref 39, luminescence anisotropy decay for all J-aggregates in solutions with and without CPB have been measured that allowed us to estimate the rotational correlation time (τ_{corr}) for the J-aggregates (Table 3). In the solutions containing CPB the rotation correlation time increases that points to hindering J-aggregate rotational diffusion.[39] Increasing JC-1 concentration also causes the increase of rotational correlation time that can be associated with an increase of JC-1 J-aggregate size. However, the effect of CPB on J-aggregate rotational diffusion is stronger (Table 3).

Discussion

Formation of the specific "J-aggregate-surfactant" complex is shown to be observed for J-aggregates of three cyanine dyes (L-21, JC-1, and PIC) in solutions containing CPB at postmicellar concentrations. The exciton nature of electron excitations in J-aggregates supposes high degree of molecular arrangement.[1–4] Since the complex formation results in the improvement of J-aggregate exciton properties (for example, absorption and luminescence intensity increase), we suppose that surfactant molecules do not penetrate between the dye ones in the J-aggregate chain. Indeed, if pyridinium ions incorporate in a J-aggregate chain, they act as an electron acceptor and a fluorescence quencher.[14] The strong inhibition of J-aggregate rotation in the solutions with CPB (Table 3) allows us to suppose that the J-aggregate core is covered with a shell of surfactant molecules. Moreover, the increase of a counterion concentration in a solution (OH^- and Cl^- in case of L-21 and JC-1 solutions or Cl^- in case of the PIC solution) screens the strong electrostatic repulsion between positively charged dyes and surfactant molecules and facilitates J-aggregate covering with the surfactant. Indeed, the addition of CPB to the dye solutions without a buffer or a salt causes the dye monomer solubilization by spherical micelles and, consequently, in such solutions J-aggregates do not form.

TABLE 4: Spectral Characteristics of J and Monomer Bands in the Absence and Presence of CPB

	L-21	JC-1 (low concn)	JC-1 (high concn)	PIC
$\Delta\nu^{mon}_{FWHM}$, cm^{-1}	770	675	675	990
$\Delta\nu_{FWHM}$, cm^{-1}	800	380	300	130
$\Delta\nu^{CPB}_{FWHM}$, cm^{-1}	175	265	250	125
N_{del}		4	7	86
N_{del}^{CPB}	28	9	10	93
$\Delta^{\nu}_{rel} = N_{del}^{CPB}/N_{del}$		2.25	1.4	1.1

The main question is why does the "J-aggregate-surfactant" complex formation results in the strong increase of J-aggregate luminescence quantum yield? The improvement of J-aggregate structure as a result of J-aggregate being covered with CPB molecules and, consequently, increasing exciton delocalization length seems to be a reasonable answer. This assumption is confirmed by J-band narrowing (Table 4) and decreasing the radiative lifetime of the J-aggregates luminescence[40] (Table 2) in solutions containing CPB. Exciton delocalization length can be estimated using equations:[41,42]

$$N_{del} = \frac{3(\Delta\nu^{mon}_{FWHM})^2}{2(\Delta\nu^{J}_{FWHM})^2} - 1 \quad (2)$$

$$N_{del} = \frac{\pi^2\tau_{mon}}{8\tau_J} \quad (3)$$

where $\Delta\nu^{mon}_{FWHM}$ and $\Delta\nu^{J}_{FWHM}$ are full widths on half-maximum of monomer and J-aggregate absorption bands; τ_{mon} and τ_J are luminescence decay times for dye monomers and J-aggregates, respectively. $\Delta\nu^{mon}_{FWHM}$ and τ_{mon} values can be obtained from experimental study of diluted solutions (at low dye concentration). Though eq 2 is considered to be less accurate because the bandwidth of the monomers forming J-aggregates may differ from that of monomers in a dilute solution,[41,42] it can be used for the estimation of exciton delocalization length change. The spectral widths of J- and monomer bands in solutions in the absence and presence of CPB and calculated exciton delocalization lengths are given in Table 4. As the J-band of L-21 J-aggregates in a solution without CPB is too broad, $N_{del} < 1$. This fact can be explained by the formation of small aggregates with a wide variation of exciton delocalization lengths that leads to J-band broadening. N_{del} for PIC J-aggregates is much larger than $N_{del} \sim 20-30$ reported in refs 1–4 (Table 4), evidently, due to an overestimation of monomer bandwidth in our case. However, we can calculate the relative change of exciton delocalization length under the effect of surfactant CPB: $\Delta_{rel} = N_{del}^{CPB}/N_{del}$, and this value will be independent of the monomer spectral characteristics. We can not calculate the exciton delocalization length using eq 3, because our experimental setup does not allow us to measure the luminescence decay time for dye monomers. However, using eq 3, we can calculate the relative change of N_{del} under the effect of CPB: $\Delta_{rel} = N_{del}^{CPB}/N_{del} = \tau_J/\tau_J^{CPB}$. To indicate the equation used to calculate the change of N_{del}, we applied a superscript "τ" for Δ_{rel} determined from eq 3 and "ν" for Δ_{rel} determined from eq 2. The comparison of Δ^{τ}_{rel} and Δ^{ν}_{rel} for JC-1 and PIC J-aggregates (the data for L-21 are not correct and were excluded from the consideration) revealed that for JC-1 (low concentration) $\Delta^{\nu}_{rel} = 2.25 < \Delta^{\tau}_{rel} = 3.95$; for JC-1 (high concentration) $\Delta^{\nu}_{rel} = 1.4 < \Delta^{\tau}_{rel} = 2.6$; for PIC $\Delta^{\nu}_{rel} = 1.1 < \Delta^{\tau}_{rel} = 8.65$ (Tables 2 and 4). Thus, the value of Δ^{ν}_{rel} is revealed to be much less than Δ^{τ}_{rel} for

all J-aggregates examined. So we can conclude that the radiative lifetime decreases not only due to the increase of the exciton delocalization length. There seems to be another process that affects the exciton dynamics in J-aggregates.

Let us consider the change of JC-1 J-aggregate spectral parameters due to the dye concentration increase to be a "pure" case of the J-aggregate structure improvement. As one can calculate from the data shown in Tables 2 and 4, the changes of exciton delocalization length in that "pure" case ($\Delta_{JC-1} = N_{del}^{high\ concn}/N_{del}^{low\ concn}$), are $\Delta_{JC-1}^{\nu} = 1.75 \sim \Delta_{JC-1}^{\tau} = 1.5$, where superscripts "$\nu$" and "$\tau$" indicate the origins of the calculations. Thus, in this "pure" case the improvement of J-aggregate structure is the only process causes the radiative lifetime decrease. The influence of J-aggregate structure improvement caused by the increase of JC-1 concentration on luminescence properties of JC-1 J-aggregates is similar to that caused by the "J-aggregate−surfactant" complex formation (Tables 1–4), but its contribution is smaller, especially, in the luminescence quantum yield increase (Table 1). Thus, we can conclude that there is another process that governs the change of J-aggregate luminescence properties under effect of CPB.

Another process affecting the lifetime and the luminescence yield is the self-trapping of excitons in the J-aggregate molecular chain.[43] The exciton self-trapping is exciton localization in a potential well as a result of a self-induced lattice distortion. For such self-trapped exciton states N_{del} is lower than that for free exciton state, depending on a strength of exciton−phonon coupling, that leads to the decrease of the radiative lifetime.[40] If the exciton self-trapping leads to the decrease of the exciton energy, the self-trapped excitons can be lost from the luminescence cycle and, consequently, the luminescence quantum yield decreases. It is very important to emphasize that in 1D chain a free exciton state can spontaneously transform into a self-trapped exciton state without overcoming the self-trapping barrier as in case of 2D and 3D lattices.[43] The theory of exciton self-trapping in a 1D chain was successfully applied to explain Stokes shifts, temperature broadening of luminescence bands, nonexponential luminescence decay and temperature dependence of radiative lifetimes of J-aggregates.[44–50] Moreover, the luminescence band that belongs to self-trapped excitons was observed directly for amphi-PIC J-aggregates at liquid nitrogen temperature.[44–46]

We suppose that the "J-aggregate−surfactant" complex formation leads to J-aggregate structure "strengthening" and, consequently, increase of the energy of molecular chain distortion, which becomes comparable to the exciton−phonon coupling energy or exceeds it. As a result, the suppression of exciton self-trapping in J-aggregates occurs that causes the increase of J-aggregate luminescence quantum yield and the radiative lifetime decrease. Indeed, as self-trapping occurs in the excited state, it should not affect the absorption bandwidth significantly,[43,51] excepting an appearance of the Urbach edge due to a strong exciton−phonon interaction.[43] Therefore the exciton delocalization length calculated from J-band spectral width can differ from that calculated from lifetime, which is dependent on self-trapping efficiency. The assumption concerning the self-trapping suppression in L-21, JC-1, and L-21 J-aggregates at CPB addition is confirmed by the fact that at room temperature the addition of CPB to the amphi-PIC J-aggregate solution results in J-band narrowing and an increase of luminescence band intensity.[17] At liquid nitrogen temperature the strong decrease of self-trapped exciton luminescence band intensity is observed.[52] Thus, we can conclude that the "J-aggregate−surfactant" complex formation leads to the suppression of exciton self-trapping. If we compare the contributions of the two processes (structure improvement and exciton self-trapping inhibition) to the luminescence properties change (Tables 1 and 2), we can conclude that the exciton self-trapping inhibition is the main process that affects the luminescence quantum yield increase and radiative lifetime decrease.

Conclusions

Formation of the "J-aggregate-surfactant" complex for J-aggregates of three cyanine dyes (L-21, JC-1 and PIC) has been observed in solutions containing surfactant CPB at concentrations higher than critical micelle concentration. The J-aggregates of all dyes investigated reveal the "herringbone" type structure. The complex formation enhances the cyanine dyes aggregation and improves J-aggregate structure that manifests via an increase of aggregate absorption H- and J-bands intensities and J-band narrowing. Moreover, complex formation causes the change of J-aggregate luminescence parameters, namely, a strong enhancement of luminescence quantum yield (up to 15 times) and the decrease of radiative lifetimes. Two processes are considered to be responsible for the changes of spectral characteristics, the increase of exciton delocalization length due to the J-aggregate structure improvement and a suppression of the exciton self-trapping. The exciton self-trapping inhibition is supposed to be the main process that causes the changes of luminescence properties.

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