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Control of Exciton Migration Efficiency in Disordered *J*-Aggregates

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Using luminescent exciton traps, an efficiency of the exciton migration in *J*-aggregates of an amphiphilic analogue of pseudoisocyanine (amphi-PIC) dye in solutions, has been investigated. Applying a modified Stern−Volmer equation for analysis of the *J*-aggregate luminescence quenching by the trap, the quenching of 50% of amphi-PIC *J*-aggregate luminescence accessible for trapping at the ratio amphi-PIC/DiD = 120:1 has been revealed. To increase the exciton migration efficiency, the *J*-aggregate structure was improved by the formation of a "*J*-aggregate−surfactant" complex. The *J*-aggregate structure improvement is confirmed by the about 3 times increase in the exciton delocalization length that leads to the 1.3 times enhancement in the exciton migration efficiency in solutions with the surfactant. To the best of our knowledge, such a control of the exciton transport parameters in *J*-aggregates in solutions has not been demonstrated yet.

Introduction

J-Aggregates (Jelley aggregates or Scheibe polymers) are luminescent nanoscale supramolecular ensembles formed by well-ordered molecular chains (linear or closed) of dye molecules, typically polymethines (cyanines, merocyanines, or squaraines) and porphyrines.[1–3] They were discovered in the 1930s independently by E. Jelley and G. Scheibe in a concentrated water solution of cyanine dye PIC by appearance of a new very narrow and intense absorption band (called the *J*-band) bathochromically shifted relative to the monomeric band, and near resonant luminescence band.[4–6] The spectral properties of the novel type of dye aggregates were found to be explained within Frenkel's exciton model,[7] and now it is the main concept.[1–3,8] Due to the excitonic nature of electronic excitations, *J*-aggregates reveal a number of unique spectral properties such as very narrow spectral lines for organic molecules (tens of cm^{-1} at liquid helium temperatures), large extinction coefficients (hundreds of thousands of cm^{-1}·M^{-1}), giant third-order optical nonlinearities up to 10^{-5} esu, and so on.[1–3,8–10]

One of the unique properties of *J*-aggregates is exciton migration over hundreds of monomers.[1–3,11–24] Due to this feature, *J*-aggregates can be considered as optical antenna for energy delivery purposes.[20,24,25] Exciton properties of *J*-aggregates are similar to those of light-harvesting complexes (LHC), which provide extremely fast and efficient energy transport of the absorbed sunlight to the photochemical reaction center of plants and photosynthetic bacteria.[26,27] Indeed, it was shown that the *J*-aggregates of cylindrical structure are the most promising artificial systems to mimic LHCs.[20,24]

The amphiphilic dye 1-methyl-1′-octadecyl-2,2′-cyanine perchlorate (amphi-PIC, Chart 1) also forms the cylindrical *J*-aggregates in aqueous solutions.[28,29] Amphi-PIC *J*-aggregates stand out in the *J*-aggregate family by one of the largest static disorder degrees, which can be controlled.[30] Amphi-PIC *J*-aggregates easily solubilize other molecules, such as cyanine and squaraine dyes, which can be used as exciton traps for

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CHART 1: Structural Formulas of the Dyes and the Surfactant Investigated: (a) amphi-PIC; (b) DiD; (c) CPB
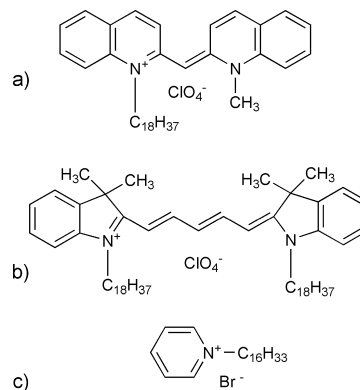
J-aggregates.[13,23,31] It has helped us to reveal quite effective exciton transport in the amphi-PIC *J*-aggregates.[13,23,31]

Despite a number of works devoted to the exciton transport study in *J*-aggregates, there is no experimental evidence of the possibility to affect the exciton transport efficiency.[1–3,11–24] Thus, the goal of the present study is to find ways for increasing exciton transport efficiency in *J*-aggregates. As an exciton trap, amphiphilic cyanine dye 1,1′-dioctadecyl-3,3,3′,3′-tetramethylindodicarbocyanine perchlorate (DiD, Chart 1) embedded into the *J*-aggregate was used.[13,31]

Experimental Section

The amphi-PIC dye was obtained from the dye collection of Dr. I. A. Borovoy (Institute for Scintillation Materials NAS of Ukraine) with the purity controlled by thin layer chromatography. DiD dye and cationic surfactant cetylpyridinium (hexadecylpyridinium) bromide (CPB) were purchased from Sigma Aldrich and used as received. Sample solutions containing amphi-PIC *J*-aggregates with the DiD dye were prepared as follows. DiD and amphi-PIC were dissolved in dimethyl formamide (DMF) to form a mixture at a given ratio; then, doubly distilled water was added to obtain a binary solution of DMF/water with 90% water content. The concentration of

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amphi-PIC in all solutions was 5×10^{-5} M. To prepare solutions with CPB, surfactant was dissolved in the dye solution in DMF. The concentration of CPB in the final DMF/water solution was 10^{-3} M (the critical micelle concentration for CPB is 6.2×10^{-4} M[32]).

To prepare amphi-PIC *J*-aggregates in polymer films, the dye solution in DMF (10^{-3} M) was mixed with an aqueous 2% poly(vinyl alcohol) (PVA, $M_w \sim 61\,000$ g/mol, Sigma Aldrich) solution (2 g of PVA per 98 mL of doubly distilled water) at a 1:9 ratio. The solution was poured onto a glass substrate, and water was evaporated in the dark for 6–7 h. The obtained films, which were not fully dried out, were stretched at weak heating (30–35 °C) by a factor of 4.

Luminescence spectra were recorded using a spectrofluorimeter on the base of two MDR-23 grating monochromators and a xenon lamp. One of the monochromators was used to select a required wavelength (FWHM ~ 0.5 nm), and the other one was used for the luminescence collection. In all experiments, the luminescence excitation wavelength was 530 nm. For absorption spectra registration, the microspectrometer USB4000 (OceanOptics, USA) supplied with an incandescent lamp was used. All measurements were done at room temperature. For polarized absorption measurements, a polarizer was placed in front of a stretched film and turned from 0 to 90° with regard to the stretching axis. After each polarizer turning, a signal without a film was measured and saved as a reference. The absolute quantum yield of photoluminescence was measured using an 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 ($\lambda = 532$ nm) was used. The absolute quantum yield was calculated using the method developed by de Mello et al.[33] and successfully applied for solutions by Porres et al.[34] The experimental setup was adjusted and tested on a standard dye (rhodamine 6G in ethanol, $C = 10^{-6}$ M), as described in ref 33.

Results and Discussion

Structure of amphi-PIC *J*-Aggregates. Before the analysis of exciton migration, it would be useful to clear up the structure of amphi-PIC *J*-aggregates. Due to their amphiphilic nature (see Chart 1), the aggregation of amphi-PIC molecules should be governed by the same laws as surfactant micelle formation.[32,35] Namely, the aggregation must be a threshold process and take place after exceeding a certain "critical" concentration (which is called the critical micelle concentration in the case of surfactants).[32,35] Indeed, such a critical aggregation concentration in the case of amphi-PIC dye appears to be 10^{-6} M (Figure 1). That is a very low value as compared to surfactants[32] and points to the efficient aggregation ability. As the dye possesses a large, nearly flat "head" and due to the high translation symmetry resulting in an exciton formation, it was supposed that amphi-PIC *J*-aggregates are cylinders formed by rings composed of 25–30 monomers with a diameter of 3.5 nm dictated by the dye's hydrocarbon "tail".[28] However, cryo-TEM images of amphi-PIC *J*-aggregates revealed large double-wall structures.[29] Here, we have to make some remarks to gain a better understanding of the results presented in ref 29. At low dye concentrations usually used for amphi-PIC *J*-aggregate preparation (10^{-4} M and less; see, for example, refs 13, 23, and 28–31), *J*-aggregates are too small to obtain their image using cryo-TEM. To resolve *J*-aggregates, the dye concentration was increased up to 10^{-2} M.[29] For surfactants, it is known that there is a so-called second critical micelle concentration. The increase of the surfactant concentration higher than the second critical
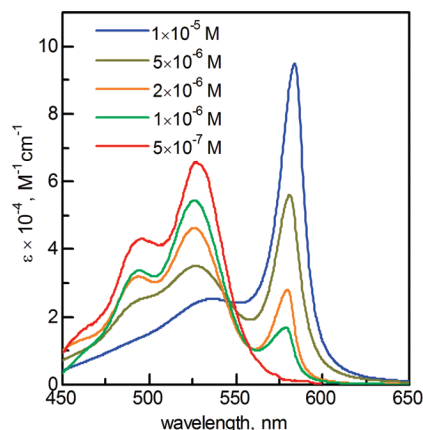

Figure 1. Absorption spectra of amphi-PIC *J*-aggregates at different dye concentrations.

micelle concentration causes the micelle structure transformation from a monolayer to a bilayer (lamellar).[35] Thus, we suppose that at low dye concentrations amphi-PIC *J*-aggregates exist in a form of monolayer cylinders with a diameter of 3.5 nm, proposed in ref 28.

A theory of excitons in cylindrical aggregates was developed by J. Knoester and co-wokers[8,36] and successfully applied to explain the optical properties of tubular *J*-aggregates of carbocyanine[20,37–39] and porphyrin[40] dyes and chlorosomes of green bacteria.[41] In cylindrical aggregates, their symmetry restricts the optically allowed transitions from the ground state to three superradiant components: one that is polarized along the axis of the cylinder and two that are degenerated and polarized perpendicular to this axis. The absorption band corresponding to the latter transitions is shifted toward shorter wavelengths as compared to the transition polarized along the axis.[8,36–41] It is interesting that for *J*-aggregates of one of the 5,5′,6,6′-tetrachlorobenzimidacarbocyanine dye derivatives, namely, C8O3,[20] two species revealing 2-fold and 3-fold exciton band splitting were observed.[37] *J*-aggregates with a 3-fold split *J*-band appeared to be large double-wall aggregates that were confirmed by a direct cryo-TEM observation. Two shorter-wavelength bands for transitions oriented perpendicular to the cylinder axis appeared due to the different radius of outer and inner layers.[20,37–39] Smaller *J*-aggregates with 2-fold splitting were not resolved by cryo-TEM, and the optical spectroscopy experiments allowed the single-wall tubular structure to be proposed for them.[37] In ref 37, it was stated that small monolayer aggregates are formed at low dye concentrations, hence our conclusion about the formation of single-wall amphi-PIC *J*-aggregates at low dye concentrations is correct.

Contrary to *J*-aggregates of carbocyanine dyes,[20,37–39] amphi-PIC *J*-aggregates reveal only one wide *J*-band (Figure 1). It could be supposed that the exciton bands, corresponding to the different optical transitions, are hidden within the wide *J*-band. To clear up this assumption, polarization experiments with PVA-film-embedded amphi-PIC *J*-aggregates were carried out. As the spectral positions (581 nm in PVA film vs 583 nm in a solution) of the *J*-band and the *J*-bandwidth (675 cm^{-1} in PVA film vs 650 cm^{-1} in a solution) do not change significantly (Figure 2), we suppose that the amphi-PIC *J*-aggregate structure does not change. To orient *J*-aggregates, the film was stretched by a factor of 4 and then polarized absorption was measured following ref 37. It has been revealed that the *J*-band is polarized perpendicularly to the cylinder axis (Figure 2); i.e., there are no optical transitions polarized along the cylinder axis and excitons are formed in the molecular rings packed into cylinders.
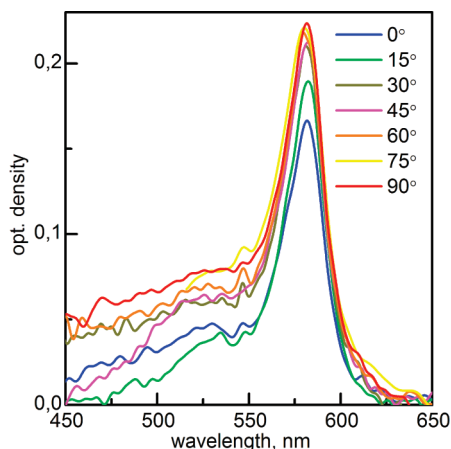
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Figure 2. Absorption spectra of the *J*-aggregates in a stretched PVA film for different polarization angles of the light with respect to the stretching axis.
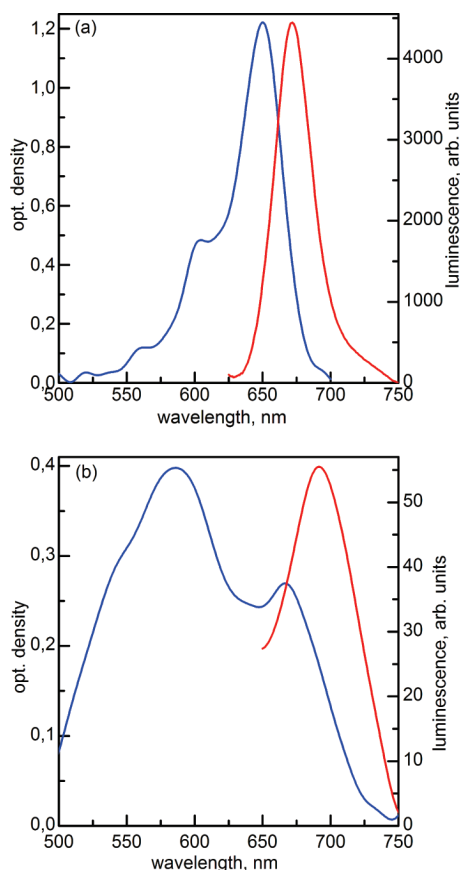

Figure 3. Absorption (blue) and luminescence (red) spectra of DiD dye in (a) DMF and (b) DMF/water (1:9) solution.

Figure 4. (a) Absorption (red) and the DiD luminescence excitation (blue, $\lambda_{reg} = 680$ nm) spectra of amphi-PIC *J*-aggregates with the DiD trap (amphi-PIC/DiD = 20:1) in a DMF/water (1:9) solution. The inset represents the DiD absorption band. (b) Luminescence spectra of amphi-PIC *J*-aggregates (green) and amphi-PIC *J*-aggregates with the DiD trap (dark yellow), $\lambda_{exc} = 530$ nm.

Exciton Transport in amphi-PIC *J*-Aggregates. The DiD dye is well dissolved in DMF and reveals quite narrow absorption and luminescence bands centered at $\lambda_{abs} = 650$ nm and $\lambda_{lum} = 675$ nm, respectively (Figure 3a). In a binary DMF/water solution used for the preparation of amphi-PIC *J*-aggregates, the DiD absorption spectrum is strongly broadened and reveals two maxima ($\lambda_1 = 585$ nm and $\lambda_2 = 665$ nm). The intensity of the dye luminescence ($\lambda_{lum} = 690$ nm) is weak (Figure 3b). That points to the formation of nonfluorescent aggregates of the dye in the presence of water due to strong hydrophobicity caused by long hydrophobic tails $C_{18}H_{37}$ (Chart 1). However, in the presence of amphi-PIC *J*-aggregates, a strong sensitized luminescence of DiD at the excitation within

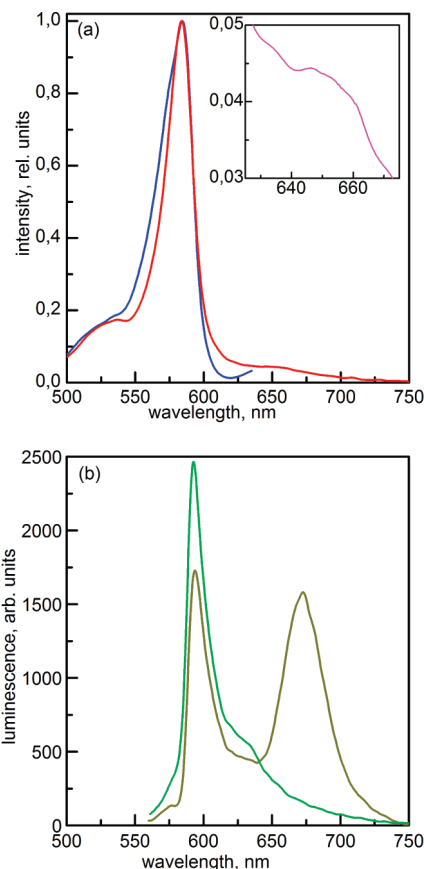the *J*-band is observed (Figure 4b). The spectral position of absorption ($\lambda_{abs} = 650$ nm, an inset in Figure 4a) and luminescence ($\lambda_{lum} = 675$ nm, Figure 4b) maxima corresponds to that of DiD in DMF (Figure 3a); i.e., DiD molecules are solubilized by amphi-PIC *J*-aggregates. In the DiD luminescence excitation spectrum, the band that corresponds to the *J*-band is observed (Figure 4a). Moreover, in the presence of DiD molecules, the luminescence of amphi-PIC *J*-aggregates is quenched (Figure 4b), so DiD can be considered as an exciton trap for *J*-aggregates. In ref 42, it was shown that more than 90% of hydrophobic dye DiO, which belongs to the same carbocyanine family as DiD and possesses the same hydrocarbon tails, is incorporated into the surfactant micelles. Thus, by analogy, we can conclude that hydrophobic DiD molecules are almost totally solubilized by the micelle-like amphi-PIC *J*-aggregates.

To investigate the exciton migration efficiency in amphi-PIC *J*-aggregates using a DiD trap, the concentration of DiD was varied (the ratio amphi-PIC/DiD was changed from 1000:1 to 10:1), similar to that in our previous work with the squaraine dye Sq-2Me as an exciton trap.[23] The increase of the DiD portion leads to the redistribution of *J*-aggregate and DiD luminescence band intensities (Figure 5a). It was found that, at high DiD concentration (the ratio amphi-PIC/DiD = 10:1), DiD luminescence intensity decreases and the band is red-shifted as compared to that at the ratio amphi-PIC/DiD = 20:1 (Figure 5a). That points to the formation of DiD associates inside *J*-aggregates like it was in DMF/water solution (Figure 3b). Moreover, at
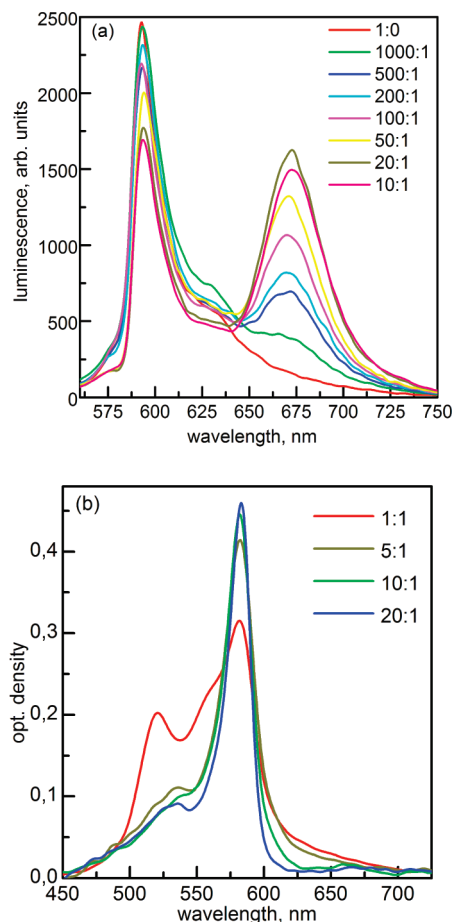
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Figure 5. Luminescence (a) and absorption (b) spectra of the *J*-aggregates with the DiD trap at different amphi-PIC/DiD ratios.

Figure 6. (a) Stern−Volmer and (b) modified Stern−Volmer plots for amphi-PIC *J*-aggregate luminescence quenching by the DiD trap.

the ratio amphi-PIC:Sq-2Me ≤ 10:1, the *J*-band decreases (Figure 5b), which points to *J*-aggregate destruction. Thereby, the solutions with smaller concentrations of the trap were chosen for the analysis. Since *J*-aggregate luminescence quenching and sensitized DiD dye luminescence are observed even at a very small ratio of amphi-PIC/DiD = 1000:1 (Figure 5a), we consider DiD to be a very effective exciton trap.

To estimate the efficiency of the exciton migration in the *J*-aggregate, the luminescence quenching was analyzed using the well-known Stern−Volmer equation:[23,43]

$$F_0/F = 1 + K_{SV}[Q] \qquad (1)$$

where F_0 and F are the *J*-aggregate luminescence intensities in the absence and presence of the trap, respectively, [Q] is the quencher concentration, and K_{SV} is the Stern−Volmer constant. The value $1/K_{SV}$ gives us the concentration of the trap that quenches 50% of the *J*-aggregate luminescence.[23,43]

The plot F_0/F against [Q] does not follow the linear law and shows downward curvature toward the *X*-axis (Figure 6a) that is a characteristic feature of the existence of donors (excitons in our case), which are not accessible to a quencher.[23,43] In such a case, the modified Stern−Volmer equation should be used:[23,43]

$$\frac{F_0}{F_0 - F} = \frac{1}{f_q \cdot K_{SV} \cdot [Q]} + \frac{1}{f_q} \qquad (2)$$
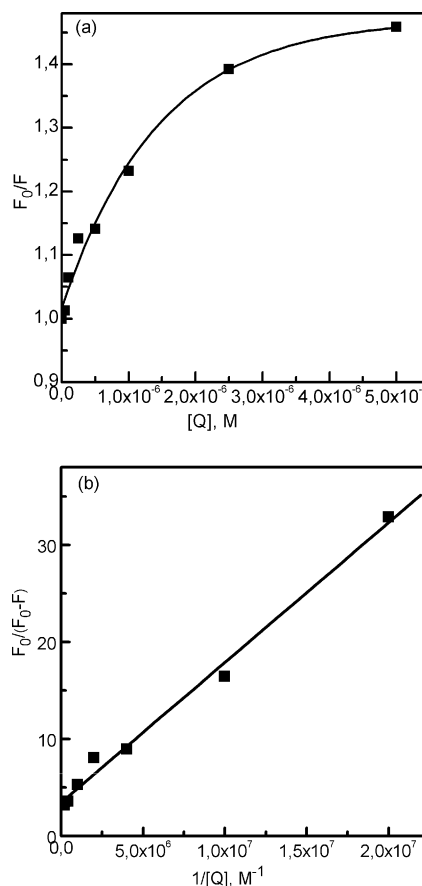
where f_q is the fraction of the initial fluorescence which is accessible to a quencher (in the case of *J*-aggregates, this is a fraction of trapped excitons). The plot of $F_0/(F_0 - F)$ versus $1/[Q]$ for amphi-PIC *J*-aggregate luminescence quenching by DiD is linear and yields $1/f_q$ as the intercept and $1/(f_q \cdot K_{SV})$ as the slope (Figure 6b). Thus, we obtain $f_q = 0.3$, i.e., only 30% of the excitons are trapped by the DiD. This value is much less as compared to that obtained using the squaraine dye Sq-2Me as an exciton trap (80%).[23] However, $K_{SV} = 2.4 \times 10^6$ M^{-1}; thus, taking into account that the concentration of amphi-PIC in a binary solution is 5×10^{-5} M, we obtain that 1 DiD molecule quenches 50% luminescence of 120 amphi-PIC molecules forming the *J*-aggregate. This parameter, which characterizes the exciton migration efficiency, turned out to be larger than that obtained using a squaraine trap ($N_{\text{amphi-PIC/Sq-2Me}}$ = 80:1).[23] As the molecular rings where excitons are formed consist of 25−30 molecules, we could suggest exciton migration between the rings packed into the cylinders. This assumption is supported by the fact that *J*-aggregate luminescence is not fully quenched even at an amphi-PIC/DiD = 10:1 ratio, i.e., when about three DiD molecules fall on one amphi-PIC ring.

Thus, the DiD exciton trap reveals much smaller exciton trapping characteristics (30%) but much larger exciton transport efficiency as compared to the squaraine dye. To understand the feature observed, we have to take into account the peculiarities of a squaraine dye.[44,45] Namely, it should be emphasized that both ground and excited singlet states of squaraines involve significant intramolecular charge transfer (near 80% of electron density is concentrated on the cyclobutene fragment).[44,45] Taking into consideration the significant red shift of the squaraine
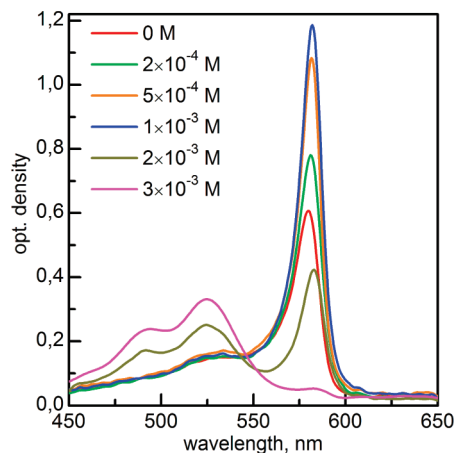
Figure 7. Absorption spectra of the amphi-PIC *J*-aggregates with CPB at different surfactant concentrations.

Figure 8. Luminescence spectra of the *J*-aggregate with the trap at different amphi-PIC/DiD ratios in the presence of CPB.

spectral bands during the dye solubilization by amphi-PIC *J*-aggregates,[23] we suppose that the dye Sq-2Me used in our previous study is not only an exciton trap (energy acceptor) but also an electron acceptor.[46] The redistribution of electron density within *J*-aggregate molecular chains during the charge transfer to the squaraine dye could be the reason for the observed exciton migration suppression. Contrary to that, DiD acts only as an exciton trap and the exciton transport parameters obtained using it can be used correctly.

"*J*-Aggregate−Surfactant" Complex. The following question arises: can we increase the exciton migration efficiency in *J*-aggregates? It could be supposed that the main parameter, which may affect the exciton transport, is structural perfection of a molecular chain, i.e., minimal static disorder. Amphi-PIC *J*-aggregates are known to possess a significant static disorder, which can be changed by varying the water content in a binary solution DMF/water.[47] However, in the binary solvent mixture used in the experiments (DMF/water = 1:9), static disorder is quite small and cannot be significantly decreased by further increasing water content.[47] Another way to decrease static disorder in *J*-aggregates is the formation of a "*J*-aggregate−surfactant" complex.[48] Recently, it has been demonstrated that *J*-aggregates of different cyanine dyes interact with CPB surfactant (Chart 1), which leads to a structural improvement and a suppression of exciton self-trapping in the *J*-aggregates.[48] For amphi-PIC *J*-aggregates, the addition of CPB results in a suppression of exciton self-trapping at low temperatures as well.[49] Thus, it was interesting to analyze how the "amphi-PIC *J*-aggregates−CPB surfactant" complex formation will affect the exciton transport in amphi-PIC *J*-aggregates.

The CPB addition up to the surfactant concentration $C_{CPB} = 10^{-3}$ M (amphi-PIC/CPB = 1:20) leads to *J*-band narrowing (from $\Delta\nu_{FWHM} = 650$ cm^{-1} to $\Delta\nu_{FWHM}^{CPB} = 410$ cm^{-1}) and about 2 times increase in *J*-band intensity (Figure 7). However, the further increase of the CPB concentration causes a *J*-band destruction (Figure 7) unlike *J*-aggregates of other dyes.[48] Interestingly, DiD molecules destroy the *J*-aggregates at much lower concentrations and do not affect the *J*-band width and intensity (Figure 5b). Therefore, we could suppose that CPB and DiD interact with amphi-PIC in different ways: DiD molecules are incorporated into the *J*-aggregate molecular ring, while CPB ones, whose concentration is up to 20 times higher than that of amphi-PIC molecules, apparently form a kind of shell around the *J*-aggregate. Such a CPB shell formation was supposed for *J*-aggregates of other cyanine dyes.[48] Though the microscopic structure of the "*J*-aggregate−surfactant" complex
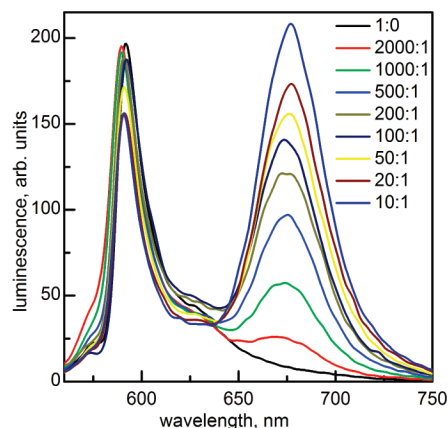
is still unknown, it could be assumed that coulomb repulsions between positively charged heads of amphi-PIC dye and CPB surfactant are screened by counterions, while hydrophobic interactions promote the complex formation.

The spectral transformation observed at CPB concentrations up to 10^{-3} M (Figure 7) points to the structural improvement of the amphi-PIC *J*-aggregates and, consequently, to the static disorder decrease.[1–3,8,30] We can estimate N_{del} using the following equation:[8,50]

$$N_{del} = \frac{3 \cdot (\Delta\nu_{FWHM}^{mon})^2}{2 \cdot (\Delta\nu_{FWHM}^{J})^2} - 1 \qquad (3)$$

where $\Delta\nu_{FWHM}^{mon}$ and $\Delta\nu_{FWHM}^{J}$ are full widths at half-maxima (FWHM) of monomer and *J*-aggregate absorption bands, respectively. Equation 3 gives us only the lower limit of the N_{del} value due to uncertainty in $\Delta\nu_{FWHM}^{mon}$ value determination.[50] As a rule, the $\Delta\nu_{FWHM}^{mon}$ value is determined in a dilute solution of the dye, where no aggregation occurs.[50] Taking $\Delta\nu_{FWHM}^{mon} = 1200$ cm^{-1} from ref 30, we obtain $N_{del} = 4$ monomers in the absence of CPB and $N_{del}^{CPB} = 11$ monomers in the presence of CPB. Such about 3 times increase in *J*-aggregate delocalization length is evidence of improvement of amphi-PIC *J*-aggregate structure in the complex with CPB surfactant.

Exciton Transport in the Case of the "*J*-Aggregate−Surfactant" Complex. To clear up whether structural improvement of *J*-aggregates affects the exciton transport parameters, luminescence spectra of amphi-PIC *J*-aggregates with DiD trap at different concentrations were analyzed (Figure 8). The DiD sensitized luminescence intensity is revealed to increase with increasing DiD concentration in the *J*-aggregate−CPB complex. Moreover, the excitation energy trapping by DiD is detected even at the amphi-PIC/DiD ratio = 2000:1 (Figure 8). Let us note that, in the case of squaraine dye, the addition of CPB into a binary solution of DMF/water = 1:9 causes the Sq-2Me trap expulsion from the amphi-PIC *J*-aggregates. In such a solution, the Sq-2Me sensitized luminescence is nearly not observed, while the *J*-aggregate luminescence is restored as compared to the solution without CPB.

The Stern−Volmer plot of *J*-aggregate luminescence quenching by the DiD trap in the presence of CPB does not follow the linear law and the modified Stern−Volmer equation (eq 2) was used to analyze the exciton transport efficiency (Figure 9). The modified Stern−Volmer plot confirms an enhancement of the exciton transport in *J*-aggregates in the solutions containing
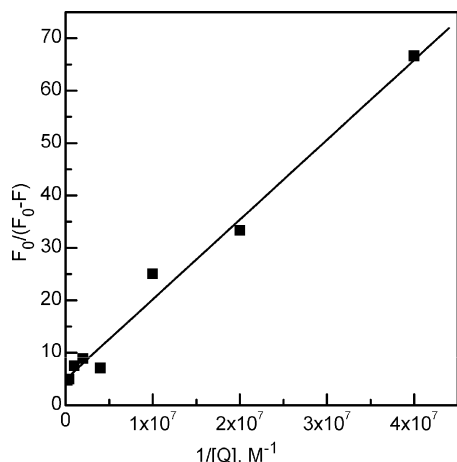
Figure 9. Modified Stern–Volmer plot for amphi-PIC *J*-aggregate luminescence quenching by the DiD trap in the presence of CPB.

CPB. The value of K_{SV}^{CPB} obtained is 3.2×10^6 M^{-1}, so 1 DiD molecule quenches the luminescence of 160 amphi-PIC molecules forming the *J*-aggregate that is 1.3 times larger than in the absence of CPB. Let us note that in the presence of CPB $f_q^{CPB} = 0.2$; i.e., only 20% of the excitons are trapped by the DiD trap. The decreasing trapped exciton fraction can be explained by shortening the exciton radiative lifetime due to the *J*-aggregate structure improvement.[48] Unfortunately, our experimental setup, reported in ref 48, does not allow the amphi-PIC *J*-aggregate luminescence decay time to be measured. However, shortening of the exciton radiative lifetime in the case of the "amphi-PIC *J*-aggregate–CPB surfactant" complex could be proved indirectly by measuring the absolute luminescence quantum yield. Amphi-PIC *J*-aggregates reveal a small quantum yield of ~0.3%, that could be explained by a significant disorder degree.[30] However, in the presence of CPB, it grows up to 0.5%, i.e., more than 1.5 times. Such an increase in luminescence quantum yield appears to be much smaller than it was for other *J*-aggregates[48] and again could be referred to the much larger disorder degree compared to other *J*-aggregates.[30]

Conclusions

Exciton migration in amphi-PIC dye *J*-aggregates, which possess a monolayer cylindrical structure formed by rings composed of 25–30 molecules with a diameter of ~3.5 nm, has been investigated using steady-state optical spectroscopy. Using cyanine dye DiD as an exciton trap, it has been found that 50% of amphi-PIC *J*-aggregate luminescence accessible for trapping is quenched at the ratio amphi-PIC/DiD = 120:1, i.e., one trap molecule per four amphi-PIC rings. Due to the micelle-like structure of amphi-PIC *J*-aggregates and large DiD hydrophobicity, the almost total solubilization of the trap molecules by the *J*-aggregates has been considered. It has been revealed that only a small part of excitons (about 30%) reach the trap even at the ratio of three trap molecules per one amphi-PIC ring. Polarized absorption measurements of the *J*-aggregates embedded in a PVA film oriented by the film stretching have shown that excitons are mainly formed inside the rings and there are no optical transitions polarized along the axis of the *J*-aggregate's cylinder. Despite that, the exciton migration between rings has been assumed due to good migration efficiency and small exciton trapping even at high DiD concentration. Surfactant CPB is found to interact with amphi-PIC *J*-aggregates, forming a "*J*-aggregate–surfactant" complex. The surfactant shell formation around the *J*-aggregates has been

supposed. The amphi-PIC *J*-aggregate structure in the case of the "*J*-aggregate–surfactant" complex appears to be more perfect, which results in about 3 times increase in the value of the exciton delocalization length. The improvement of *J*-aggregate structure leads to the 30% enhancement of the exciton migration efficiency; i.e., 50% amphi-PIC *J*-aggregate luminescence accessible for trapping is quenched at the ratio amphi-PIC/DiD = 160:1.

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(46) The electron transport in *J*-aggregates is a well-known phenomenon (see, e.g., refs 1–3 and 18), but it has not been adequately described theoretically yet, because Frenkel excitons do not transfer a charge. Recently, a novel concept of CT excitons mixed with Frenkel excitons in *J*-aggregates has been proposed (see, e.g., Eilmes, A. *Chem. Phys. Lett* **2001**, *347*, 205; Ogawa, T.; Tokunaga, E.; Kobayashi, T. *Chem. Phys. Lett.* **2005**, *410*, 18). However, this concept requires detailed experimental and theoretical investigations.

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