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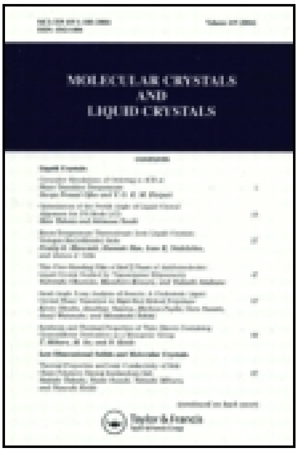

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I. K. Katrunov [a], A. V. Sorokin [a], S. L. Yefimova [a] & Yu. V. Malyukin [a]

[a] Institute for Scintillation Materials, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, Kharkov, Ukraine

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Manifestation of Exciton-Lattice Interaction in J-Aggregates

I. K. KATRUNOV, A. V. SOROKIN, S. L. YEFIMOVA, AND YU. V. MALYUKIN

Institute for Scintillation Materials, STC "Institute for Single Crystals",
National Academy of Sciences of Ukraine, Kharkov, Ukraine

The inverse correlation between the exciton-lattice interaction strength and the exciton delocalization length is shown for dielectric organic nanoclusters – J*-aggregates. Since the exciton delocalization length defines all optical properties of* J*-aggregates, it allows one to control them via the exciton-lattice interaction. We demonstrate the exciton self-trapping suppression in amphi-PIC* J*-aggregates as a result of the exciton-lattice interaction weakening due to the formation of a surfactant shell around* J*-aggregates. The control over optical properties via the exciton-lattice interaction for other types of* J*-aggregates is discussed.*

Keywords Exciton delocalization; exciton-lattice interaction; *J*-aggregates

Introduction

The electron-lattice interaction (ELI) is a ubiquitous fundamental phenomenon in solid-state physics. For semiconductors and metals, ELI can be changed by varying the charge density on the Fermi level through a chemical doping [1] or using the electric field effect [2]. It does not work for bulk dielectric crystals, but there is a certain possibility to control ELI in their nano-sized analogs [3]. The short-range ELI was demonstrated to be anomalously large for the localized electron states which can be produced by a static disorder or a spatial confinement of electron wave functions as well [4]. This transforms the ELI to a potentially useful instrument to tailor the modern materials with important functional properties.

One of the most suitable objects to examine ELI in dielectric nanoparticles is, probably, organic luminescent nanoclusters called *J*-aggregates [5–8]. *J*-aggregates are molecular aggregates formed by dye molecules, typically polymethines and porphyrines, organized in well-ordered molecular chains (linear or closed) [5–8]. The molecular chain ordering results in the electron excitation delocalization and the Frenkel exciton formation [5–8]. Therefore, a fingerprint of the formation of *J*-aggregates is the appearance of a very narrow intense excitonic band (called a

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Address correspondence to Yu. V. Malyukin, Institute for Scintillation Materials, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60, Lenin Ave, Kharkov 61001, Ukraine. E-mail: malyukin@isma.kharkov.ua

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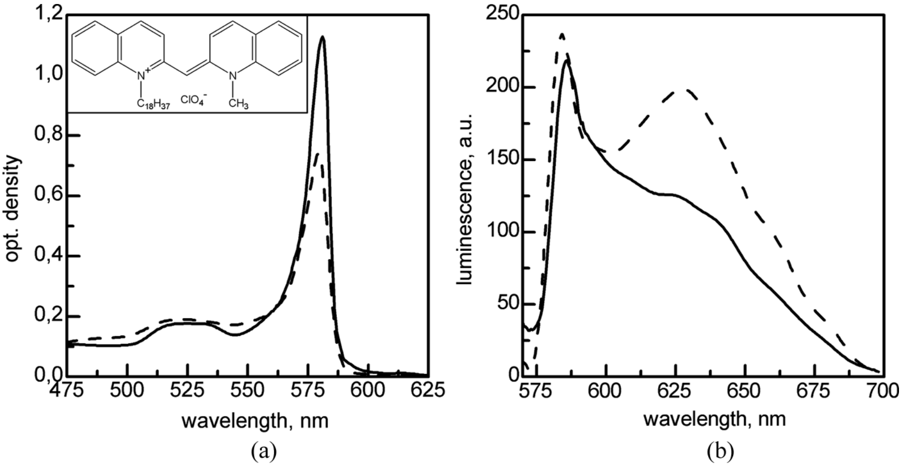
J-band) in the absorption spectrum which is red-shifted relative to the monomer band (Fig. 1a) [5–8]. Spectral properties of *J*-aggregates are governed by the exciton delocalization length which is usually equal to up to tens of monomers, rather than by the physical length of aggregates [8]. Due to the excitonic nature of electronic excitations, *J*-aggregates reveal a number of unique spectral properties such as very narrow spectral lines (tens of cm^{-1} at the liquid helium temperature) which are not characteristic of organic molecules, large extinction coefficients (hundreds of thousands of $cm^{-1} \cdot M^{-1}$), giant third-order optical nonlinearities up to 10^{-5} esu, *etc*. Such optical properties make *J*-aggregates very promising objects for many applications, e.g., the spectral sensibilization in photovoltaics, nonlinear optical devices, luminescent probes in biology and medicine, *etc*. [5–8].

However, one of the reasons that inhibit wide applications of *J*-aggregates is a low quantum yield of their luminescence [9]. Recently, we have revealed that the cationic surfactant CPB added to a *J*-aggregate solution can increase the luminescence quantum yield of *J*-aggregates of several cyanine dyes by up to 15 times [9]. It has been suggested that CPB forms a molecular shell around J-aggregates, though the microscopic nature of the "J-aggregate-surfactant" complex is still not clear. To explain the significant luminescence quantum yield enhancement, it has been proposed that the surfactant shell formation results in suppressing the exciton self-trapping (ST) in *J*-aggregates [9,10]. As the exciton ST is caused by the strong ELI (the exciton-lattice interaction in such a case) [11], it was one of the first evidences of the control over luminescence properties of *J*-aggregates via changing the ELI.

As a rule, the exciton ST in *J*-aggregates are not taken into consideration due to the suggested weak ELI [6,8]. In experiments, the exciton ST was clearly observed only for *J*-aggregates of amphi-PIC [12–14]. So, the main aim of this work is to show the ELI influence on the exciton delocalization length (N_{del}) and luminescent properties of amphi-PIC *J*-aggregates.



(a) (b)

Figure 1. Absorption (a) and luminescence (b) spectra of amphi-PIC *J*-aggregates in the presence (solid line) and the absence (dashed line) of surfactant CPB at $T = 80\,K$. On the inset – structural formula of amphi-PIC dye.

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Experimental

The amphi-PIC (1-methyl-1′-octadecyl-2,2′-cyanine perchlorate) dye was obtained from the dye collection of Dr. I.A. Borovoy (Institute for Scintillation Materials, NAS of Ukraine) with a purity controlled by thin-layer chromatography. The cationic surfactant CPB (cetylpyridinium (hexadecylpyridinium) bromide) was purchased from Sigma Aldrich (USA) and used as-received. To prepare amphi-PIC J-aggregates, the dye was dissolved in dimethylformamide (DMF), and then doubly distilled water was added to obtain a binary solution DMF/water with 90-% water content. To prepare amphi-PIC *J*-aggregates with surfactant CPB, the required amount of the surfactant was added in the stock solution of the dye in DMF. At temperatures below the vitrifying temperature ($T_{vitr} = 265\,K$), this binary solution forms a homogeneous vitrescent matrix. The concentration of amphi-PIC in the solution was $5 \times 10^{-5}\,M$, and the concentration of CPB was $10^{-3}\,M$.

Luminescence 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. Absorption spectra were registered with the use of a microspectrometer USB4000 (Ocean Optics, USA) supplied with an incandescent lamp. Solutions were placed in a small cell 1 mm in thickness into a cryostat and cooled down to the liquid nitrogen temperature. The luminescence intensity was measured in the temperature range of 80–240 K with a step of 5 K. The temperature was controlled within 1 K.

Results and Discussion

Due to the amphiphilic nature of amphi-PIC dye molecules, they form nano-scale cylinders composed from rings 3.5 nm in diameter in DMF/water binary solutions. These rings are composed from 25–30 dye molecules [15]. As was shown earlier, the exciton ST in amphi-PIC *J*-aggregates strongly depends on the static disorder degree which can be changed, by varying the water content in a DMF/water binary solution [12–14,16]. The method of *J*-aggregate preparation described in this study allows one to obtain *J*-aggregates with a small disorder degree that is characterized by the Gaussian form of the long-wavelength edge of the *J*-band (Fig. 1a). At a high disorder degree in *J*-aggregates, the long-wavelength edge of the *J*-band becomes Lorentzian [16]. However, despite a small disorder degree in *J*-aggregates obtained, we can observe the exciton ST luminescence (Fig. 1b) in such samples. This fact and the shape of the *J*-band red tail will be essential for our further analysis. In the luminescence spectrum (Fig. 1b), two bands are resolved: one band almost resonant to the *J*-band ($\lambda_{max} = 584\,nm$) corresponds to the free exciton emission, and the second band is red-shifted ($\lambda_{max} = 628\,nm$) and associated with the self-trapped exciton emission [12–14].

Recently, we have shown that the presence of cationic surfactant CPB in a DMF/water binary solution at room temperatures causes drastic changes in the optical properties of amphi-PIC *J*-aggregate: the *J*-band intensity increases, the *J*-band becomes narrow, the value of N_{del} grows (from 4 monomers in solutions without CPB up to 11 monomers in solutions with CPB), and the luminescence quantum yield increases slightly (from 0.3 up to 0.5) [15]. In a frozen matrix at the liquid nitrogen temperature, the CPB addition causes the same effect: the *J*-band becomes more intense and narrower ($\Delta\nu_{FWHM} = 415\,\mathrm{cm}^{-1}$ as compared with $\Delta\nu^{CPB}_{FWHM} = 320\,\mathrm{cm}^{-1}$) and shifts to a longer wavelength (from $\lambda_{max} = 579\,\mathrm{nm}$ to $\lambda^{CPB}_{\max} = 580.5\,\mathrm{nm}$) (Fig. 1a). We can find N_{del} from the relation [8]

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

where $\Delta\nu^{mon}_{FWHM}$ and $\Delta\nu^{J}_{FWHM}$ are the full widths at a half maximum (FWHM) of a monomer and *J*-aggregate absorption bands, respectively. Relation (1) gives us only the lower limit of N_{del} due to an uncertainty in the determination of $\Delta\nu^{mon}_{FWHM}$ [8]. As a rule, the $\Delta\nu^{mon}_{FWHM}$ value is determined in a dilute solution of the dye, where no aggregation occurs [8]. Taking $\Delta\nu^{mon}_{FWHM} = 1200\,\mathrm{cm}^{-1}$ from [16], we obtain $N_{del} = 11$ monomers and $N^{CPB}_{del} = 20$ monomers, i.e., the CPB shell leads to increasing the exciton delocalization. In the luminescence spectrum, one can see that the addition of CPB suppresses the luminescence of ST excitons and results in a band shift: $\lambda^{CPB}_{free} = 586\,\mathrm{nm}$ and $\lambda^{CPB}_{ST} = 626\,\mathrm{nm}$ (Fig. 1b).

How does CPB shell affect the ELI in amphi-PIC *J*-aggregates? There are two possibilities to calculate the exciton-lattice coupling constant *g*: from the exciton ST depth (E_{SF}) which is a distance between maxima of the luminescence of free and ST excitons [11,17] and from a slope of the Urbach edge (exponential form of the long-wavelength tail) of the *J*-band [11,18]. Within the first approach, the EL coupling constant can be estimated from the relation [17]

$$g = \frac{E_{SF}}{B} + 1, \tag{2}$$

where *B* is the half-width of the exciton band. In its turn, $B = 2J$, where *J* is the dipole-dipole interaction strength in a molecular chain. Taking long-range interactions into account, we can find *J* from the absorption spectrum [8]:

$$J = \frac{\lambda^{J}_{\max} - \lambda^{mon}_{\max}}{2.4}. \tag{3}$$

Here, $\lambda^{J}_{\max}$ and $\lambda^{mon}_{\max}$ are maxima of the *J*- and monomer bands, respectively. Thus, we found $J = 740\,\mathrm{cm}^{-1}$ and $J^{CPB} = 765\,\mathrm{cm}^{-1}$, and $B = 1480\,\mathrm{cm}^{-1}$ and $B^{CPB} = 1530\,\mathrm{cm}^{-1}$. So, it follows from relation (2) that $g = 1.8$ and $g^{CPB} = 1.7$, i.e., the ELI in *J*-aggregates with the surfactant becomes, indeed, weaker. Note that $g > 1$ both in the absence and presence of CPB, which indicates the exciton ST appearance [11]. That's why, despite the ST suppression, its luminescence band is still observed in the spectrum (Fig. 1b). However, such an approach is rough enough due to an uncertainty in the determination of a ST exciton emission maximum, which can be blurred by the emission from unrelaxed states [12–14].

In the second approach, it is possible to find the exciton-lattice coupling constant from a slope of the long-wavelength tail of the excitonic band, which has exponential form (Urbach edge), by using the Urbach–Matthiessen rule [11,18]

$$\alpha(E) = \alpha_0 \exp\left(-\sigma \frac{E_0 - E}{kT}\right), \tag{4}$$

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where $\alpha(E)$ is the absorption coefficient, α_0 and E_0 are coordinates of the intersection of straight lines which are approximations of Urbach edges at different temperatures on a semilogarithmic plot, and σ is the Urbach edge slope.

In its turn, σ also depends on the temperature as

$$\sigma = \sigma_0 \frac{2kT}{\hbar\omega_p} \tanh\left(\frac{\hbar\omega_p}{2kT}\right), \tag{5}$$

where $\hbar\omega_p$ is an energy of the principal interacting phonon mode, and σ_0 is the limit of σ at high temperatures. The quantities σ_0 and g have a simple reciprocal relationship,

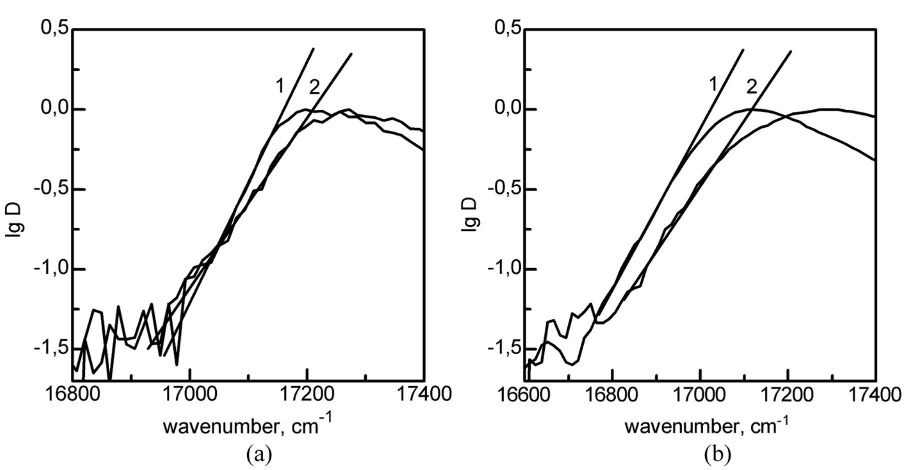
$$g = \frac{s}{\sigma_0}, \tag{6}$$

where the dimensionless parameter s is called the steepness index which depends only on the dimensionality and a geometry of the lattice. The index s is equal to 1.5 and 1.24 for 3D simple cubic lattices and 2D square lattices, respectively. For 1D chains, s is found to be temperature-dependent, by scaling as $T^{1/3}$ [11,18].

The long-wavelength edges of amphi-PIC *J*-bands at liquid nitrogen and room temperatures appeared to be exponential and can be approximated by straight lines on the semilogarithmic plot (Fig. 2). It is obvious from Figure 2 that the Urbach edges in the presence of CPB are steeper at both temperatures pointing to smaller g values, according to formula (6). Such a comparison is of importance because presents different media, where *J*-aggregates are spread: a glass-like matrix at low temperatures and a solution at room temperature, for which ELI is different.

To determine σ_0, we plot the Urbach edges for amphi-PIC *J*-aggregates in the absence (Fig. 3) and the presence (Fig. 4) of CPB at different temperatures.

Analyzing the temperature dependence of the slopes of Urbach edges according to (5), we have found the following parameters: $\sigma_0 = 0.65$ and $\omega_p = 220\,\text{cm}^{-1}$ in the absence of CPB, and $\sigma_0^{CPB} = 0.8$ and $\omega_p^{CPB} = 225\,\text{cm}^{-1}$ in the presence of CPB, i.e.,



(a) (b)

Figure 2. The slopes of Urbach tails for a *J*-band in the presence (1) and the absence (2) of CPB at various temperatures: (a) 80 K, (b) 290 K.

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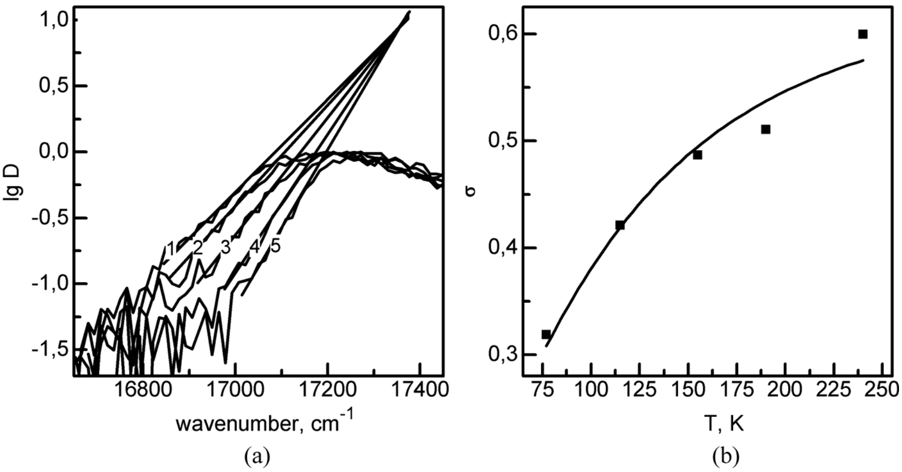
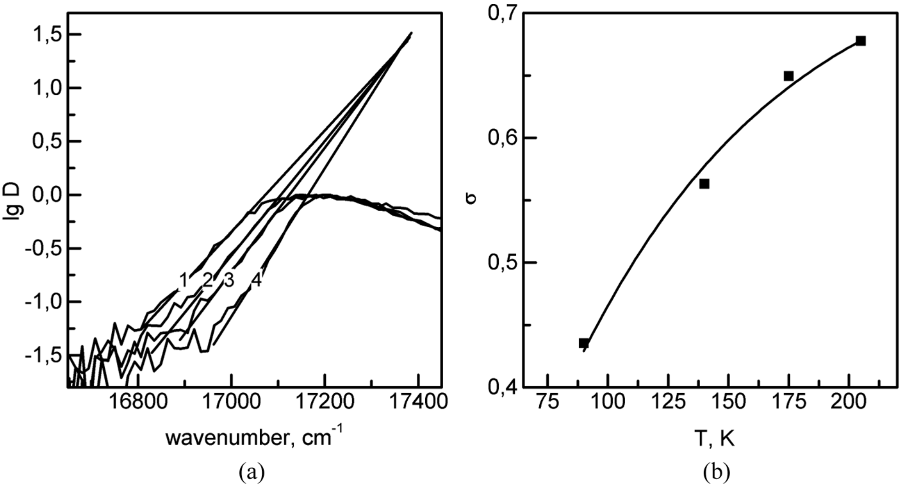


(a) (b)

Figure 3. (a) Temperature dependence of Urbach tails for a *J*-band in the absence of surfactant CPB. Temperatures designation: 1 – 220 K, 2 – 190 K, 3 – 155 K, 4 – 105 K, 5 – 80 K; (b) Temperature dependence of Urbach slopes and its approximation by (5).

$\sigma_0 < \sigma_0^{CPB}$. The calculation of the exciton-lattice coupling constant g within this approach is complicated due to the uncertainty of the steepness index s. Indeed, an exciton in amphi-PIC *J*-aggregates is delocalized on a strongly curved segment of the molecular ring consisting on 25–30 molecules [15]. In such case, the value of s should lie between those for 1D and 2D cases and requires separate numerical calculations, similar to [18]. For estimation, we choose $s = 1$ as the limit of the s(T) dependence for a linear 1D chain at the temperatures under consideration [18]. This gives $g = 1.55$ and $g^{CPB} = 1.25$, which confirms the ELI weakening.



(a) (b)

Figure 4. (a) Temperature dependence of Urbach tails for a *J*-band in the presence of surfactant CPB. Temperatures designation: 1 – 205 K, 2 – 175 K, 3 – 140 K, 4 – 90 K; (b) Temperature dependence of Urbach slopes and its approximation by (5).

Thus, the surfactant shell formation around amphi-PIC *J*-aggregates leads to the ELI weakening, which results in an increase of the exciton delocalization length both at low and room temperatures and the exciton ST suppression. This result confirms the idea of Drabold *et al.* [4] of the manipulation of optical properties of dielectric nanoclusters through the exciton-lattice interaction. The result obtained can be spread out on other types of a *J*- aggregate with regard for data from [9,10]. Indeed, the CPB shell formation around *J*-aggregates of three different cyanine dues at room temperature results in an increase in both the exciton delocalization length and the luminescence quantum yield [9]. Simultaneously, this leads to the steeper Urbach edges of *J*-bands pointing to the ELI weakening [10].

Conclusions

Using amphi-PIC *J*-aggregates which reveal clearly the exciton self-trapping as a model object, we have experimentally proved an increase of the exciton delocalization length at the exciton-lattice interaction weakening. Thus, we have obtained a possibility to manipulate by optical properties of *J*-aggregates via the exciton-lattice interaction by forming, for example, a surfactant shell around *J*-aggregates. The results obtained can be spread out on *J*-aggregates of other cyanine dyes, for which the exciton self-trapping was not postulated.

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