Manipulation by optical properties of luminescent ordered organic nanoclusters via exciton-phonon coupling

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Abstract. The way to manipulate by spectral properties of cyanine dye luminescent ordered nanoclusters (J-aggregates) has been demonstrated. It has been observed a surfactant shell formation around the J-aggregates of four different dyes. This leads to exciton delocalization length increasing which causes an exciton self-trapping suppression. The latter results in spectral changes observed.

Molecular aggregates, called J-aggregates, are well-ordered luminescent organic nanoclusters of non-covalently coupled luminophores such as cyanines, porphyrines and some other dyes [1-3]. High degree of dye molecules ordering in J-aggregate chains results in the appearance of an excitonic narrow absorption band (so-called J-band) bathochromically shifted with respect to a monomer band. Spectral properties of J-aggregates are governed by the exciton delocalization length, which is usually equal to up to tens monomers, rather than the physical length of aggregates [3]. Due to excitonic nature of electronic excitations, J-aggregates reveal a number of unique spectral properties such as very narrow for organic molecules spectral lines (tens of cm\(^{-1}\) at liquid helium temperatures), large extinction coefficients (hundreds of thousands of cm\(^{-1}\cdot M^{-1}\)), giant third-order optical nonlinearities up to \(10^{-5}\) esu and so on [1-3]. Such optical properties do the J-aggregates a very promising object for many applications, e.g. spectral sensitization in photovoltaics, nonlinear optical devices, luminescent probes in biology and medicine and so on [1-3].

Usually exciton-phonon interaction in J-aggregates suggested being week so exciton self-trapping in J-aggregates is not taken into consideration [3]. But there is one representative of J-aggregates family (amphi-PIC J-aggregates) for which exciton ST has been obviously demonstrated [4]. It is clear evidence of strong exciton-phonon interaction in this type of J-aggregates. Moreover, exciton-phonon coupling constant \(g\) measurement for merocyanine J-aggregates formed in Langmuir-Blodgett films demonstrates significant dependence of exciton-phonon interaction on J-aggregate preparation conditions [5]. Authors shown that for some cases exciton-phonon coupling is strong enough with \(g > 1\) and exciton self-trapping should be suggested [5].

The aim of present report is to demonstrate importance of exciton-phonon interaction taking into account and to show dependence of exciton properties like luminescence quantum yield on exciton-phonon coupling for J-aggregates of 4 different cyanine dyes (figure 1).

Sample preparation and experimental details could be found in [6-8]. Luminescence decay times for L-21 and amphi-PIC J-aggregates which was appeared to be impossible to measure using our previous setup [6] have been measured using picosecond spectrofluorimeter FluoTime 200 (PicoQuant, Germany). This lifetime spectrometer was supplied by MCP-PMT P3809U-50 (Hamamatsu, Japan).
and laser head LDH-P-FA-530 with $\lambda_{em} = 531$ nm (PicoQuant, Germany). The FWHM of instrument response function (IRF) was 96 ps.

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

Recently we have shown significant spectral changes for J-aggregates of different dyes (figure 1) caused by surfactant – J-aggregate interaction [6,7]. In particular, exciton delocalization length growth, luminescence quantum yield increase up to 15 times and lifetime decrease has been observed (Table 1).

Table 1. Exciton delocalization lengths ($N_{del}$), luminescent quantum yields ($\phi$), radiative lifetimes ($\tau_0$) and exciton-phonon coupling constants ($g$) for cyanine dyes J-aggregates in absence and presence of surfactant CPB

|        | $N_{del}$ | $\phi$, % | $\tau_0$ ns | $g$     |
|--------|----------|----------|-------------|---------|
|        | CPB      | CPB      | CPB         | CPB     |
|        | shell    | shell    | shell       | shell   |
| L-21   | < 1      | 28       | 2.5         | 6       | 1.95   | 2.2     | 0.6   |
| JC-1   | 4        | 9        | 1.5         | 19      | 16.65  | 4.2     | 1.4   | 0.85  |
| PIC    | 86       | 93       | 2.5         | 38      | 16     | 1.85    | 0.75  | 0.55  |
| amphi-PIC | 4      | 11       | 0.3         | 0.5     | 11.7   | 9       | 1.1   | 0.9   |

Figure 2 demonstrates the most obvious spectral changes for JC-1 J-aggregates at interaction with surfactant CPB. One could see J-band ($\lambda_{max} = 680$ nm) narrowing and growth, hypsochromically shifted band appearing ($\lambda_{max} = 530$ nm, so called H-band) in absorption spectrum (figure 2a). Luminescence spectrum (figure 2b) reveals significant exciton emission band ($\lambda_{max} = 682$ nm) growth with simultaneous monomer emission band ($\lambda_{max} = 585$ nm) decreasing.

On the base of anisotropy decay analysis it was suggested that the surfactant molecules form a kind of shell around J-aggregates [6]. To check this assumption, TEM images have been obtained for amphi-PIC J-aggregates in the absence and presence of CPB surfactant (figure 3). Amphi-PIC J-aggregates are revealed to be cylinders with a diameter of ~ 4 nm and 50–100 nm length (figure 3a). In the presence of CPB, elongated shapeless objects with a mean diameter of ~ 30 nm and 50–100 nm length are observed (figure 3b). Such a picture confirms the J-aggregates-surfactant complex formation and supports our idea concerning a surfactant shell creation.
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). (c) – semilogarithmic plot of J-bands from (a).

Figure 3. TEM images of amphi-PIC J-aggregates: (a) in absence and (b) in presence of CPB surfactant

It was supposed that luminescence quantum yield increasing occurs due to exciton-phonon interaction weakening and exciton self-trapping suppression as a result [7,8]. Indeed, for amphi-PIC J-aggregates exciton ST suppression at interaction with CPB surfactant could be observed directly at low temperatures (figure 4) [8].

Figure 4. Absorption (a) and luminescence (b) spectra of amphi-PIC J-aggregates in the presence (solid line) and absence (dashed line) of the surfactant CPB at T = 80 K.
At low temperatures in luminescence spectrum of amphi-PIC J-aggregates (figure 4b) two different bands are observed: narrow band ($\lambda_{\text{max}} = 585 \text{ nm}$), which was ascribed to free exciton emission, and wide band ($\lambda_{\text{max}} = 630 \text{ nm}$), which was ascribed to self-trapped exciton emission [4]. It could be seen that CPB cause the same effect on amphi-PIC J-band at low temperatures as on J-bands of other J-aggregates at room temperatures (figure 2a), namely leading to J-band ($\lambda_{\text{max}} = 580 \text{ nm}$) increasing and narrowing (figure 4a). At luminescence spectrum both emission bands decreasing could be observed (figure 4b). But if the free excitons band with $\lambda_{\text{max}} = 585 \text{ nm}$ reveals only slight decrease in intensity, the self-trapped excitons band with $\lambda_{\text{max}} = 630 \text{ nm}$ decreases significantly. Moreover, the first band decreasing could be ascribed rather to ST excitons contribution reducing than the free excitons luminescence suppression (figure 4b).

Unfortunately, ST excitons luminescence for other types of J-aggregates hasn’t been found. But it is possible to find the exciton-lattice coupling constant from a slope of long-wavelength tail of the excitonic band by using the Urbach rule [8]:

$$\alpha(E) = \alpha_0 \exp\left(-\frac{E_0 - E}{kT}\right), \quad (1)$$

where $\alpha(E)$ is the absorption coefficient,

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

where $\hbar\omega_p$ is an energy of the principal interacting phonon mode and $\sigma_0$ is the limit of $\sigma$ at high temperatures. $\sigma_0$ and $g$ have a simple reciprocal relationship:

$$g = \frac{s}{\sigma_0} \quad (3)$$

For 3D simple cubic lattices $s = 1.5$, for 2D square lattices $s = 1.24$ and for 1D chains $s$ is found to be temperature dependent, scaling as $T^{1/3}$ [8].

The application of Urbach-Martienssen rule for amphi-PIC is demonstrated on figure 5.

\[\text{Figure 5. a) Temperature dependence of Urbach tails for amphi-PIC J-band in the absence of CPB. Temperatures designation: 1 -- 80 K, 2 -- 105 K, 3 -- 155 K, 4 -- 190 K, 5 -- 220 K, 6 -- 290 K; (b) Temperature dependence of low temperature Urbach slopes and its approximation by equation (2).}\]

So, we have found such parameters: $\sigma_0 = 0.65$ and $\omega_p = 220 \text{ cm}^{-1}$ and $\sigma_0^\text{CPB} = 0.8$ and $\omega_p^\text{CPB} = 225 \text{ cm}^{-1}$, i.e. $\sigma_0 < \sigma_0^\text{CPB}$. For estimation, we choose $s = 1$ as limit of $s(T)$ dependences for linear 1D chain
at the temperatures under consideration [8]. It gives us $g = 1.55$ and $g^{CPB} = 1.25$ thus confirms exciton-phonon coupling weakening.

But comparing Urbach tails for J-band at room (figure 5a, curve 6) and low (figure 5a, curves 1-5) temperatures one could see a significant difference. Indeed, J-aggregates obviously affects by different surrounding in solutions and glass-like matrices. However, semilogarithmic plot of J-bands at room temperature reveals steeper slope in CPB presence (figure 2c), i.e. $\sigma < \sigma^{CPB}$. Analyzing literature data [1-5] we have found that interacting phonon modes are laid within range 50–300 cm$^{-1}$, that is corresponded to $\sigma/\omega_0 = 0.85–0.99$ at $T = 290$ K according to equation (2). So, averaging we obtain $\sigma/\omega_0 \sim 0.92$ which is corresponded to $\omega \sim 205$ cm$^{-1}$ in close correlation with data obtained for amphiphilic J-aggregates in low temperature cases. So, finally we could to determine the exciton-phonon coupling $g$ constants for all J-aggregates under investigation and to confirm the exciton-phonon weakening at the surfactant shell formation for all cases (Table 1).

We could to conclude that solvate shell changing for J-aggregates via surfactant addition results in multiple effects on exciton properties such as exciton delocalization increasing, exciton-phonon interaction weakening and luminescence quantum yield enhancement. The results obtained could be used for J-aggregates luminescence properties control for different applications.

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