

Control of polaron formation in J-aggregates

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It has been shown that the strong exciton-lattice interaction is realized for J-aggregates of different dyes. It causes exciton self-trapping that results in a low quantum yield of J-aggregate luminescence. It has been found that at room temperature, the self-trapped excitons relax via a nonradiative process. The possibility to influence the exciton-lattice interaction in J-aggregates is discussed.

Показано, что для J-агрегатов разных красителей реализуется сильное экситон-решеточное взаимодействие. Оно обуславливает автолокализацию экситонов, что приводит к малому квантовому выходу люминесценции J-агрегатов. Обнаружено, что при комнатных температурах автолокализованные экситоны релаксируют безызлучательно. Обсуждается возможность воздействия на экситон-решеточное взаимодействие в J-агрегатах.

1. Introduction

The electron-lattice interaction (ELI), as a ubiquitous fundamental phenomenon of solid-state physics, is transformed to a potentially useful instrument in development of modern materials with important functional properties, for example, the GeSbTe phasechange materials, high-superconductors, etc. [1, 2]. The intensive discussion on the new ELI aspects is stimulated by the high interest to the nanodispersed materials and the design of nanomachines like single photon sources, quantum information devices, etc. [3, 4]. The ELI could be varied for semiconductors and metals by the charge density varying at the Fermi level using the chemical doping [5] or electric field effects [6]. This does not work for the bulk dielectric crystals but certain possibility appears to control the ELI in their nanosized version [7]. The short-range ELI was demonstrated to be an anomalously strong for the localized electron states which could be produced by a static disorder or spatial confinement of electron wave functions as well [8]. As to the long-range (Froehlich type) polar interaction which is

realized for nanoparticles dispersed into a medium with dielectric constant ε_{med} , the ELI was shown to depend on ε_{med}^{-1} , in addition to the Pekar factor ($\varepsilon_0^{-1} - \varepsilon_\infty^{-1}$, and polaron energy being a complex function of the nanoparticle size [9].

J-Aggregates are self-assembled molecular nanoparticles composed by the linear or ring-like arrangement chains of the polymethine or phtalocyanine dyes [10–12]. J-Aggregates belong to the large family of so-called non-covalent structures like micelles, proteins, liposomes, amyloids, etc., but their specific feature is a narrow absorption band (J-band) red-shifted with respect to the monomer one [10–12]. The major experimental finding for J-aggregates formed in aqueous solutions, like the unusual sharpness of the J-band and exciton superradiance [13, 14] were interpreted successfully in the frame of 1D Frenkel exciton model [15]. A certain type of J-aggregates was considered as supramolecular quantum wires which demonstrate the dependence of exciton energy on the lateral confinement [16]. Though the long history [10–12], J-aggregates are connected by the

wide bridge with the up-to-date science: some types of J-aggregates exhibit an effective exciton migration [17] similar to the ballistic electron propagation in the carbon nanotubes [18]; J-aggregates can undergo strong coupling (Rabi splitting ~ 250 meV) with the surface plasmon-polariton modes that favors the development of new plasmon-based technologies [19]; due to the possibility to turn the exciton localization, J-aggregates are promising systems for the quantum computing technology [20]; the specific interaction between J-aggregates and important biological objects like mitochondria, DNA and RNA [21, 22] allows to consider J-aggregates as the perspective luminescent markers with the spatial resolution.

In spite of numerous and comprehensive efforts undertaken to understand the optical and luminescence properties of J-aggregates, there is no clear conception relative to the ELI in such nanoscale objects. The weak ELI is generally accepted and the short-range interaction is considered to be realized through the deformation potential similarly to the molecular crystals [15]. This means both the energy changing of static interaction of n -th excited molecule D_n (diagonal ELI) and the resonant integral transfer β (off-diagonal ELI) are functions of the intermolecular distance. The critical parameters governing the exciton-phonon dynamics have been introduced by E.Rashba [23, 24] to be as follows: β ; ε_{LR} is the energy of lattice relaxation; ω_{ph} is the frequency of phonon mode coupling with exciton. The ELI is usually presented by the dimensionless parameter $g = \varepsilon_{LR}/2\beta$ (2β is the half of exciton band). Depending on the g value, the weak ELI ($g < 1$) or the strong ELI ($g \geq 1$) could be realized. The weak ELI resulting in an intraband exciton relaxation was used to analyze the destruction of superradiant decay and the thermal line broadening in J-aggregates [14]. The off-diagonal ELI strength was estimated to be about 26 meV from the temperature dependence of superradiant decay in PIC J-aggregates [25]. There is no univocal concept of the phonon mode providing the ELI in J-aggregates. Both the low frequency matrix phonons and the high frequency optic phonons of J-aggregates have been accepted [10, 11, 14, 15, 25]. The strong diagonal ELI has been involved into consideration to explain the significant polaron effect causing the exciton self-trapping in the amphipic J-aggregates [26–28]. Direct estimation

of ε_{LR} and β for amphipic J-aggregates gives $g \sim 1$, indicating the strong ELI [27, 28]. For the 2D J-aggregates in the form of LB films, both the weak ($g < 1$) and strong ($g > 1$) ELI were evaluated [29]. So, it is of interest to ascertain the ELI origin for the self-assembled J-aggregates in solutions.

In this work, we present for the first time the set of important deeply interconnected findings concerning the ELI manifestation in the J-aggregates. The ELI could be controlled by changing of the J-aggregate solvate shell using surfactants. The strong correlation between the J-aggregates luminescence quantum yield and the ELI strength has been revealed that allows us to consider the exciton self-trapping as the main mechanism of the J-aggregate luminescence loss. The anomalous enhancement (twenty-fold in some cases) of J-aggregate luminescence under ELI suppression will be demonstrated. This mechanism is general and works for different types of J-aggregates.

2. Experimental part

The dye 3,3'-dimethyl-9-thienyl-thiacarbocyanine iodide (L-21) was obtained from the dye collection of the Department of Combinatorial Chemistry (Institute for Molecular Biology and Genetics, NAS of Ukraine). The dyes 5,5,6,6'-tetrachloro-1,1,3,3'-tetraethylbenzimidazolylcarbocyanine iodide (JC-1 or TTBC) and 1-methyl-1'-octadecyl-2,2'-cyanine perchlorate (amphipic) were synthesized by Dr.I.Borovoy (Institute for Scintillation Materials, NAS of Ukraine). The purity of the dyes was controlled by thin layer chromatography. 1,1'-Diethyl-2,2'-cyanine iodide (PIC) dye and cationic surfactant cetylpyridinium (hexadecylpyridinium) bromide (CPB) were purchased from Sigma Aldrich and used as received.

J-Aggregates of L-21 were prepared by the adding an appropriate amount of the surfactant CPB to a stock solution of L-21 in dimethylformamide (DMF). Then the solution was diluted with aqueous buffer Tris-HCl ($C = 0.05$ M, pH = 8) in the ratio 1:19. The L-21 concentration in the solution was $1 \cdot 10^{-4}$ M. The JC-1 aggregates were prepared in a similar way from a stock solution of JC-1 dye and CPB surfactant in DMF. Then the solution was diluted with a aqueous borate buffer ($\text{Na}_2\text{B}_4\text{O}_7\text{-HCl}$, pH = 8.5) in the ratio 1:9. The JC-1 concentration in the solution was $1 \cdot 10^{-5}$ M. PIC J-aggregates were prepared by dissolving the PIC dye and

CPB surfactant in aqueous NaCl (0.2 M) solution under moderate heating ($< 80^{\circ}\text{C}$). Then the solution was cooled down to room temperature. The PIC concentration in the solution was $5 \cdot 10^{-4}$ M. To prepare amphi-PIC J-aggregates with CPB, the dye and the surfactant were dissolved in DMF, then doubly distilled water was added to obtain a binary solution DMF/water with 90 % water content. The amphi-PIC concentration in the solution was $5 \cdot 10^{-5}$ M. The CPB concentration in all the solutions was 10^{-3} M (critical micelle concentration for CPB is $6.2 \cdot 10^{-4}$ M [30]).

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 measurements, the spectrofluorimeter was supplied with an incandescent lamp.

Absolute quantum yields of photoluminescence for all the solutions were measured using a home-made integrating sphere (100 mm in diameter), 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 in [31] and successfully applied for solutions in [32]. The experimental setup was adjusted and tested for a standard dye (rhodamine 6G in ethanol, $C = 10^{-6}$ M) as described in [31]. To measure the time-resolved luminescence spectra, a mode-locked Nd^{3+} :YAG laser (second harmonics, $\lambda_{exc} = 532$ 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, USA) was used to process the experimental luminescence decay curves.

3. Results and discussion

It is well known that in real J-aggregates, we deal with disorder-induced spatially compact excitons which extension is usually described by the number of coherently coupled monomers N_{del} [15]. We can control the N_{del} through the solvate shell which is the main source of the J-aggregate disorder [10–12, 15]. For example, the solvate shell heterogeneity promotes an increasing J-band width [10–12] while in con-

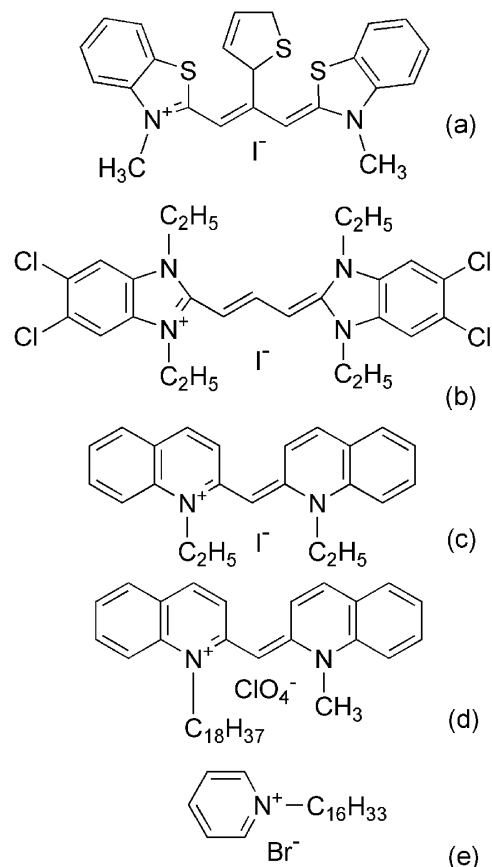


Fig. 1. Molecular structures of the dyes and surfactant investigated: a) L-21, b) JC-1, c) PIC, d) amphi-PIC and e) CPB.

trast, in surfactant solutions, J-band was shown to tend narrowing that was interpreted by an increasing N_{del} [33, 34]. The N_{del} variation could cause the ELI changing in J-aggregates, since the ELI strength was declared by Drabold [35] to increase for the localized electronic states. To verify this idea, the different surfactant molecules aiming to locate on the interface have been looked over to control the solvate shell of J-aggregates. We developed a technology free from the specific surfactant-dye interaction noted in [33]. A number of extensive polymethine dyes (Fig. 1) was selected to create J-aggregates.

In what follows, we shall focus on the most remarkable effect achieved with the CPB molecules (Fig. 1). For all J-aggregates tested, the J-band narrowing has been observed in the surfactant solution as compared to that in the aqueous solution (Table). The CPB concentration corresponded to condition $n_{CPB}/n_{dye} > 1$. The electrostatic repulsion of the identical charged surfactant molecules and dyes (Fig. 1) and the invari-

ance of the maximum of J-bands confirm that the direct CPB intercalation into J-aggregates body is impossible. CPB molecules are believed to gather around J-aggregates making a dynamical coat that is confirmed by the increasing of the J-aggregates anisotropy luminescence decay [34]. The J-band narrowing demonstrates the surfactant CPB to affect the J-aggregates structure which becomes more perfect [10–12, 15, 34]. But we have revealed the dynamical processes to give a considerable contribution to the J-band width at room temperature. In particular, the ELI strength was estimated to be reduced by the CPB molecules. So, using the absorption band parameter of monomers Δ_{FWHM}^{mon} and J-aggregates Δ_{FWHM}^J , one can obtain only a rough estimate (lower limit) of the N_{del} [34].

To single out the ELI strength from the J-band, we have used the Urbach-Martienssen (U-M) rule [36, 37]:

$$\alpha(E) = \alpha_0 \exp[-\sigma(T) \cdot (E_0 - E)/k_B T], \quad (1)$$

$$\sigma(T) = \sigma_0 (2k_B T / \hbar \omega_{ph}) \tanh(\hbar \omega_{ph} / 2k_B T), \quad (2)$$

where E is photon energy; $\sigma(T)$, the steepness parameter; k_B , the Boltzmann constant and ω_{ph} , the phonon mode frequency.

The correctness of U-M rule (1) has been firstly examined for the J-aggregates tested in solutions. For example, we have observed a typical slope variation of the low-frequency J-band edge (Fig. 2) as it was shown for J-aggregates in form of LB films [29]. Of course, the slope changing is insignificant at room temperature (Fig. 2) because the temperature dependence of steepness parameter (2) tends to saturation due to the $\hbar \omega_{ph} \leq k_B T$ criterion. The ω_{ph} value was obtained for certain J-aggregate types by Mukamel ($\omega_{ph} \sim 220 \text{ cm}^{-1}$) [14] and Inoue ($\omega_{ph} \sim 210 \text{ cm}^{-1}$) [38]. Hence, the condition $\sigma(T) \sim \sigma_0$ is acceptable and we can get the

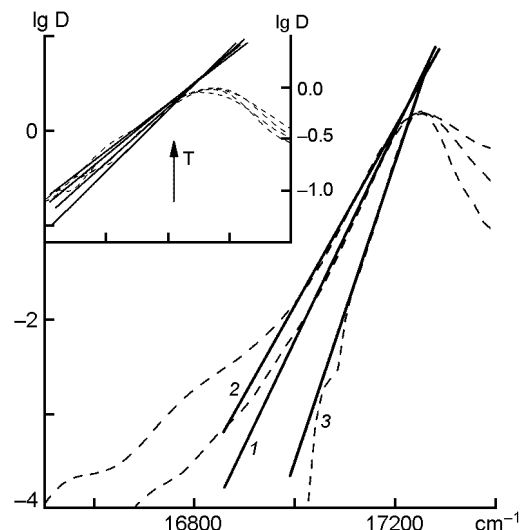


Fig. 2. Low energy edge of PIC J-aggregate J-band (dashed lines) at temperatures (K): 290 (1), 315 (2), 290 in the CPB presence (3). Solid lines represent approximation according U-M rule. Inset: application of U-M rule for PIC J-aggregates in frozen matrix: $T = 77 \text{ K}$, 180 K , 212 K , 252 K . The arrow shows the direction of J-band slope changing at temperature elevation.

ELI constant from the expression $g = s \cdot \sigma_0^{-1}$ (where s is dimensionless parameter defined by the lattice geometry) [36, 37]. For 1D system, s is known to be a function of temperature and we used the data presented in [37] to estimate its value. The set of the g values obtained shows the surfactant molecules that provoke the ELI strength reduction that correlates with J-band narrowing (Table). The weak ELI is realized only for PIC aggregates both in the aqueous and surfactant solutions. Others J-aggregates demonstrate the ELI change from the strong interaction ($g > 1$) to the weak one ($g < 1$) in the surfactant solutions.

We have ascertained the evident anticorrelation between the ELI strength and the

Table. Spectroscopic data for different J-aggregates in the absence and presence of CPB: J-band width (Δv_{FWHM}), luminescence quantum yield (ϕ) and exciton-phonon coupling constant (g).

	Δv_{FWHM} , cm^{-1}		ϕ , %		g	
	No CPB	CPB	No CPB	CPB	No CPB	CPB
L-21	800	175	2.5	17.5	1.95	0.55
JC-1	380	265	1.5	19	1.25	0.75
PIC	130	125	2.5	38	0.65	0.5
amphi-PIC	650	410	0.3	0.5	0.95	0.8

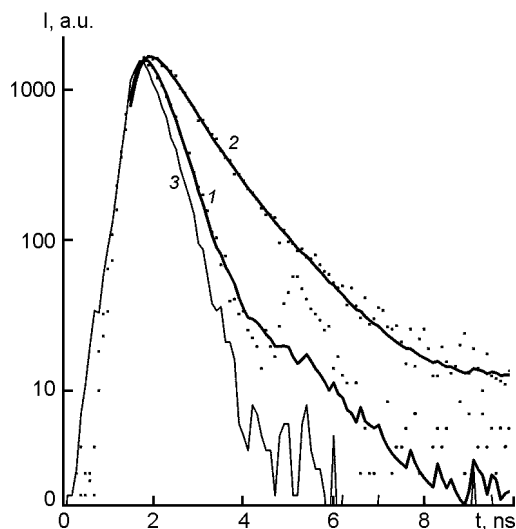


Fig. 3. Luminescence decay curves for JC-1 J-aggregates in the absence (1) and the presence (2) of CPB. 3, the instrument function.

J-aggregate luminescence absolute quantum yield (Table). The considerable increase of the J-aggregate luminescence is observed as the ELI decreases. Simultaneously, the luminescence decay of all J-aggregates becomes longer (Fig. 3) due to the inhibition of photonless relaxation of excited J-aggregates. This means the excitons suffer from the quenching provided by the strong ELI. As it follows from Table, the luminescence lack of J-aggregates is observed when the polaron formation criterion, $g \geq 1$ is realizable. The liquid solvate shell does not prevent J-aggregates deformation and the self-trapped state could be deactivated due to the monotonous lowering of the total energy and consequent photonless relaxation. That is why the quantum yield of the J-aggregate luminescence in solutions is low. But in the frozen solution, the relaxation of the self-trapped state could be stabilized by the elastic deformation of molecular chain and matrix and the free excitons and self-trapped excitons simultaneously are manifested in the luminescence spectrum (Fig. 4). At room temperature, the band of self-trapped excitons vanishes at all reflecting the 63 % loss of J-aggregate luminescence (according to the band area ratio of free and self-trapped excitons).

The control of polaron formation through N_{del} is corroborated by the microscopic model of polaron state as well. This model was partially developed in [27, 28] and accounts a specific of polymethine

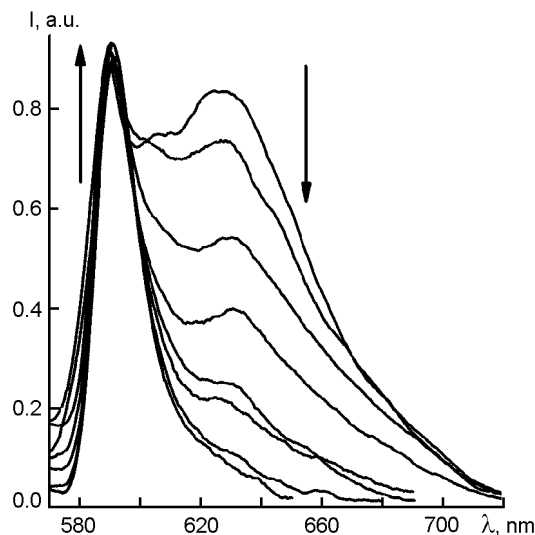


Fig. 4. Spectra of amphi-PIC J-aggregates luminescence at different temperature (from $T = 77$ K up to $T = 290$ K). Arrows show direction of band intensity changing at the temperature growth.

dyes electronic structure. The polymethine state of these dyes was shown by S.Daehne [39] to be the charge modulation along the polymethine chain consisting always of odd atoms (see Fig. 5a). Within the chromophore chain which is the main block of the real J-aggregate, there is a "plane-to-plane" interaction, typical of molecular crystals but the minimum Coulomb coupling stipulated by the charges of polymethine chains in the nearest-neighbor molecule is provided by its shift (see Fig. 5). The charge alternation becomes the opposite when the dye has been excited into the first singlet level (see Fig. 5b) that results in a substantial change of the Coulomb coupling between the nearest-neighbor molecules. The interaction energy becomes negative within the deep minimum, when the shift between two polymethine chains is absent (see Fig. 5b). Hence, the chromophore chain deformation, when the displacements of sequentially positioned molecules, δ_n , and δ_{n+1} , have opposite signs (the successive molecules shift transversely to opposite sides from the chain axis which retains a fixed position) is very important for the polaron formation, because in this case, the lattice deformation involves the small volume of the order of $l_{ex} \cdot a^2 = N_{del} \cdot a^3$ producing a low elastic energy being of the order of $k \cdot N_{del} \cdot a \cdot \delta^2$. As it is much more energ-favourable compared to the contraction of the chain segments. The

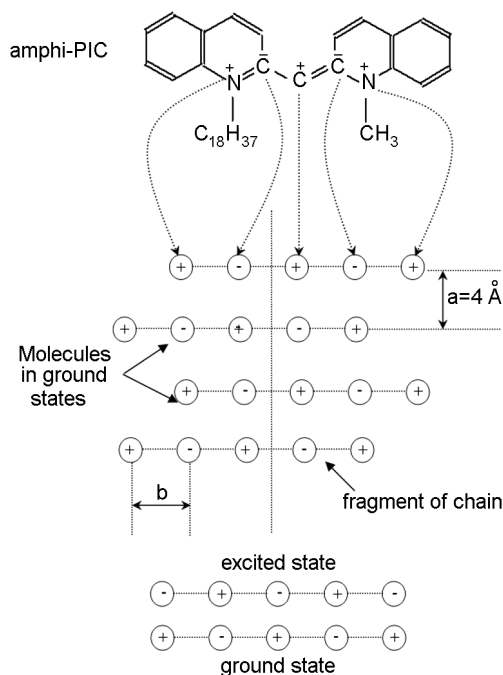


Fig. 5. (a) Amphi-PIC dye structure; (b) fragment of amphi-PIC J-aggregate chain (two types of monomer displacements are shown).

alternate-sign displacements of molecules numbered in the chain by subscript n , can be written down in the form $\delta_n = (-1)^n u(na)$, where $u(x)$ is a function slowly varying on the distance l_{ex} (x is a coordinate counted along the chain). Since the positive and negative directions of transverse displacements are physically equivalent, the ELI energy will not change when the function $u(x)$ changes its sign. Hence, the $u(x)$ — expansion of the ELI energy starts with $u(x)^2$ item instead of generally accepted linear one. The total energy of the chromophore chains containing an exciton is

$$\varepsilon_{tot} = \int_0^{a \cdot N_{del}} \{ (2m_{eff})^{-1} \cdot (d\psi(x)/dx)^2 - C \cdot u(x)^2 \cdot \psi(x)^2 + \dots + K \cdot u(x)^2 + \dots \}. \quad (3)$$

The relation (3) shows that a self-trapped state can exist under the condition $\psi(x)^2 \cdot C > K$, which could be met in the case of a large exciton density $\psi(x)^2$ or of a strong ELI described by a large constant C . Both characteristics $\psi(x)^2$ and C (according to Drabold [8, 35]) tend to increase at small N_{del} , that makes N_{del} to be the main drive parameter to control the polaron formation in J-aggregates polymethine dyes.

4. Conclusions

The strong ELI ($g \geq 1$) is shown to be realized for numerous J-aggregates and to cause the lack of J-aggregate luminescence. At room temperature, the STS of excitons which is formed under the strong ELI relaxes via a photonless process. The ELI in J-aggregates could be changed by way of N_{del} control.

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Контроль утворення поляронів в J-агрегатах

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Показано, що для J-агрегатів різних барвників реалізується сильна екситон-граткова взаємодія. Вона спричиняє автолокалізацію екситонів, що приводить до малого квантового виходу люмінесценції J-агрегатів. Виявлено, що при кімнатних температурах автолокалізовані екситони релаксують безвипромінювально. Обговорюється можливість впливу на екситон-граткову взаємодію в J-агрегатах.