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CONDENSED-MATTER SPECTROSCOPY

Dynamics of Optical Response of Solutions of Pseudoisocyanine *J* Aggregates upon Pico- and Subnanosecond Excitation

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Abstract—The luminescence kinetics of solutions of pseudoisocyanine iodide (PIC) *J* aggregates is studied upon excitation by pico- and subnanosecond laser pulses into the main superintense long-wavelength absorption band. The dependences of the transmission and luminescence energy on the pump energy are measured. It is found that the shape of the luminescence kinetics depends on the recording and excitation spectral regions, which is obviously related to the energy transfer between coherently coupled fragments of *J* aggregates.

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Due to their specific optical and physical properties (in particular, a giant optical nonlinearity), *J* aggregates of dyes are of great practical interest for nanophotonics, telecommunication systems, quantum electronics, etc. (see, e.g., [1–4]). Undeniably, *J* aggregate films are more promising for technical application, but the properties of *J* aggregates are more convenient to study in solutions that allow one to promptly vary the optical characteristics of chemicals under study.

In this work, we study the optical response (fluorescence, absorption) of liquid solutions of pseudoisocyanine iodide (1,1'-diethyl-2,2'-isocyanine iodide) (PIC) *J* aggregates upon excitation by subnano- and picosecond laser pulses. This study is focused on the behavior of *J* aggregates under resonance laser excitation into the main superintense long-wavelength band. Numerous works in this field (see, e.g., [5, 6]) were performed, mainly out of this transition. The laser measurements of the absorption, luminescence, and luminescence kinetics were performed on a PULS complex [7] using a combined laser source. We studied electrolyte solutions of PIC *J* aggregates with different concentrations, which were prepared from a stock solution of PIC in dimethylsulfoxide (DMSO). The formation of *J* aggregates of PIC (Ma 80 from Agfa) in water was induced, as well as in [8, 9], by the addition of high-purity-grade NaCl electrolyte with a concentration of 5 M. For this purpose, a concentrated solution of PIC in DMSO ($C = 2.25 \times 10^{-3}$ M) was added by drops to the saturated NaCl solution. When the ratio of the components was 1 : 29, the concentration of PIC monomers, from which *J* aggregates formed, was 7.5×10^{-5} M.

The spectroscopic characteristics (the luminescence, luminescence excitation, and transmission spectra) of the solutions were measured on a Fluorat-02-Panorama (Lumex) spectrofluorimeter, while the absorption spectra were recorded on a UV-3600 (Shimadzu) spectrophotometer (with a monochromator slit width of 0.5 nm).

The luminescence decay times of the solutions were measured in a thin layer between two quartz plates or in a thin 2-mm cell using a Micro Time 100 (Pico Quant) laser scanning luminescence microscope under excitation by a diode laser with a wavelength of 409 nm and a pulse repetition rate of 40 MHz.

Figure 1 shows the absorption spectra of PIC *J* aggregates measured in a freshly prepared solution. The optical density ratio of the 574- and 495-nm bands was 1 : 1.93. To record the luminescence and luminescence excitation spectra and determine the luminescence quantum yield and the luminescence decay time, we placed the solution between quartz plates. Figure 2 shows the luminescence spectrum of the same solution excited at a wavelength of 495 nm. The luminescence excitation spectrum of *J* aggregates (Fig. 3) contains all the absorption bands of the solution. Figure 4 shows the luminescence decay curve of the solution excited by a diode laser with a wavelength of 409 nm. It can be seen that, in this case, the luminescence decay curve is approximated by a biexponential dependence with the characteristic times $\tau_1 =$

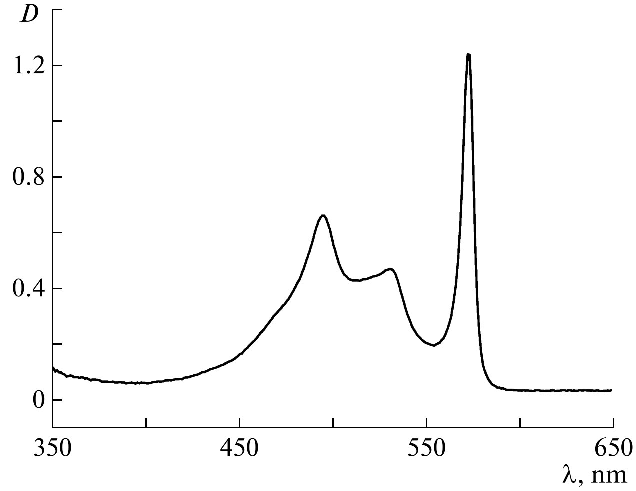

Fig. 1. Absorption spectrum of PIC *J* aggregates ($C = 7.5 \times 10^{-5}$ M); optical path length 2 mm.

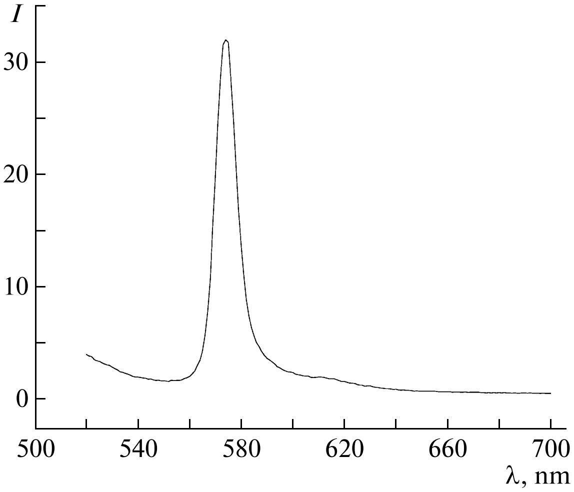

Fig. 2. Luminescence spectrum of PIC *J* aggregates excited at 495 nm.

0.71 ns and $\tau_2 = 3.64$ ns ($A_1/A_2 = 1.9$). The amplitude-weighted average luminescence decay time determined by the formula $\langle\tau\rangle = \left(\sum A_i\tau_i^2\right)/\left(\sum A_i\tau_i\right)$ is 2.8 ns.

We believe that the short-lived decay time component relates to the luminescence of PIC *J* aggregates under direct excitation, while the long-lived component is caused by indirect excitation processes. The determined time τ_1 is close to the known luminescence lifetimes of PIC chloride *J* aggregates (~600 [1] and 650 ps [5]) measured at room temperature, a high dye concentration, and a low excitation intensity. A detailed summary of other determined luminescence lifetimes of PIC *J* aggregates is given in [10].

The data obtained allow one to estimate the exciton coherence length by the formula $N = \dfrac{\tau_r^{\mathrm{PIC}}}{\tau_r^{J\,\mathrm{aggregat}}}$, where τ_r^{PIC} and $\tau_r^{J\,\mathrm{aggregat}}$ are the radiative lifetimes of the PIC monomer and its *J* aggregate, respectively, in the model of collective optical response of a molecular

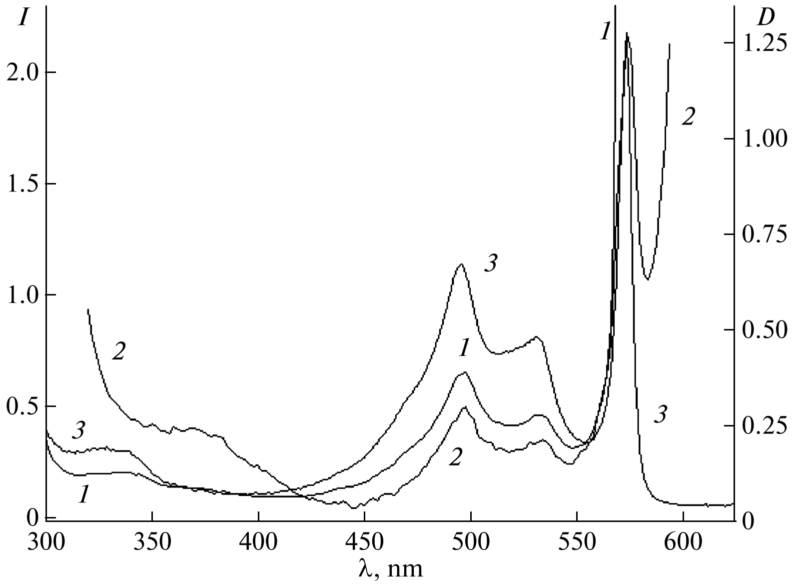

Fig. 3. (*1*, *2*) Luminescence excitation spectra of PIC *J* aggregates recorded at (*1*) 580 and (*2*) 610 nm and (*3*) absorption spectrum of the solution in a 2-mm cell.

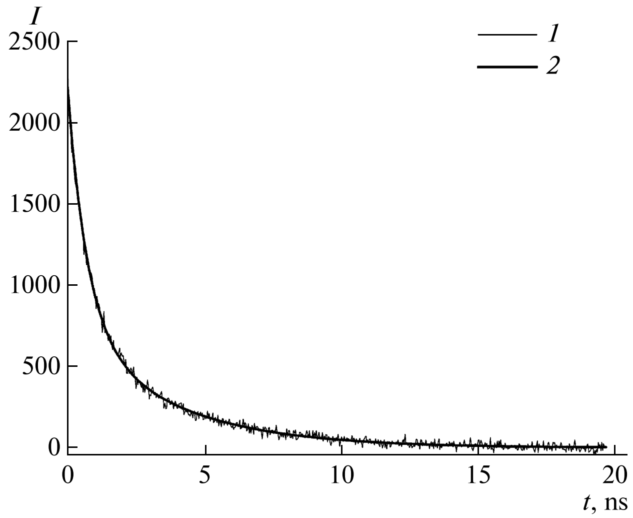

Fig. 4. Time dependence of luminescence intensity of PIC *J* aggregates: (*1*) experimental curve and (*2*) approximation by a biexponential function ($\tau_1 = 0.71$ ns and $\tau_2 = 3.64$ ns).

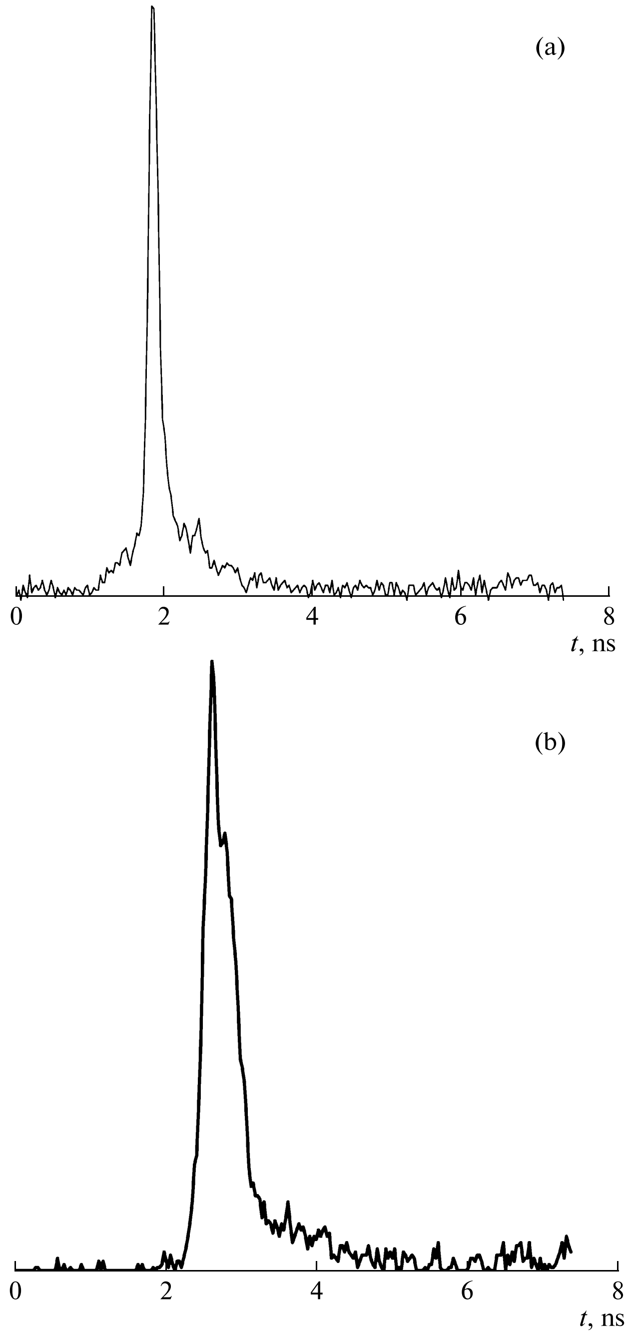

Fig. 5. Examples of excitation pulses with wavelengths near (a) 630 and (b) 352 nm.

aggregate with exciton coherence in the one-dimensional chain [11, 12].

The radiative lifetime of the PIC monomer (10 ns) was calculated by the well-known Strickler–Berg formula [13] using the measured absorption spectrum of PIC in methanol and the maximum extinction coefficient of the PIC iodide monomer in this solvent, which, according to [14], is 3.3×10^4 M^{-1} cm^{-1}. It should be noted that the lifetime τ_r^{PIC} determined by us differs from the frequently used value of 3.7 ns [11, 15, 16] taken from [17], which was obviously obtained for a concentrated solution of PIC in glycerol.

The radiative lifetime of PIC *J* aggregates was determined from the relation $\tau_r^{J\ \mathrm{aggregat}} = \tau_{\mathrm{exp}}/\Phi$, where τ_{exp} is the experimentally measured luminescence decay time of the PIC *J* aggregate (0.71 ns) and Φ is the luminescence quantum yield. The luminescence quantum yield of PIC *J* aggregates (0.44) in thin layers at room temperature was measured with respect to rhodamine 6G in ethanol ($\Phi = 0.96$ [18]). The found Φ is close to the known maximum luminescence quantum yield of PIC iodide *J* aggregates (0.38) in a water–salt solution (0.2 M NaCl) in the presence of cetylpyridinium bromide (CPB) cation surfactant [19].

The exciton coherence length (*N*) obtained based on these data is $10 \times 0.44/0.71 = 6.2$. This small value does not contradict the data on this parameter determined by other authors for PIC *J* aggregates at room temperature under the conditions of the complete or almost complete aggregation. In particular, the estimates of *N* for PIC *J* aggregates found in [1] from the data of four-wave scattering and in [5] from the data on singlet–singlet annihilation are ≈6 and ≈4, respectively. In [20], it was also reported that the formation of PIC *J* aggregates in vesicles occurs even when the average number of molecules in an aggregate is 3.2–3.5.

The laser kinetic measurements were performed using a single-pulse Nd:YAG laser with single (stimulated Brillouin scattering) or double (stimulated Brillouin scattering + stimulated Raman scattering) compression of the initial pulse by the methods of stimulated backscattering. The pulse duration was 5–7 ns for the initial pulse ($\lambda = 1.06$ μm), ~500 ps after the

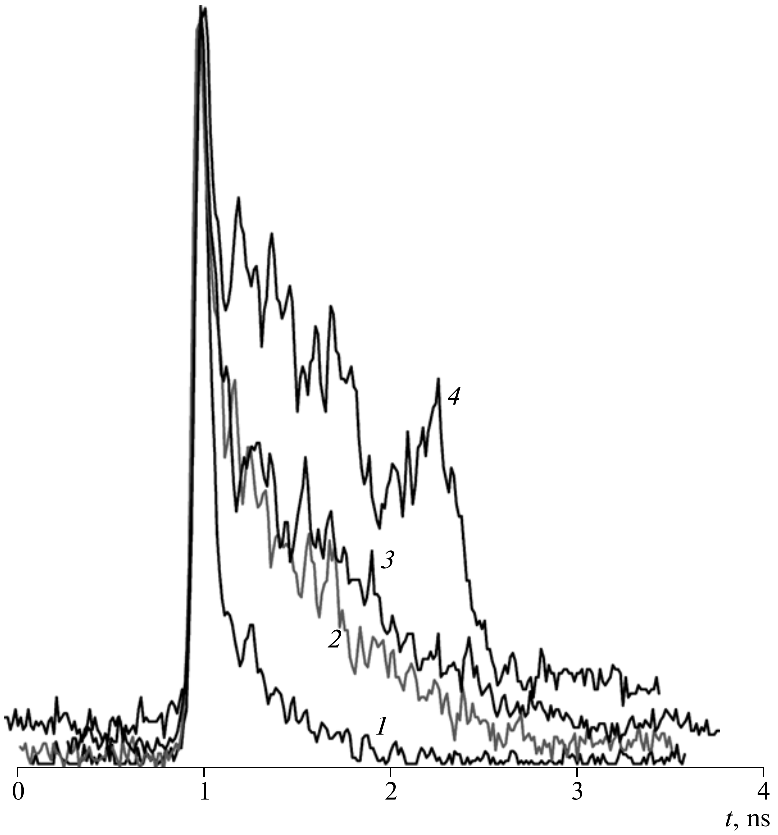

Fig. 6. (*1*) Excitation pulse and (*2*, *3*, *4*) kinetics of long-wavelength luminescence band ($\lambda \geq 570$ nm) of solution of PIC *J* aggregates at (*2*) minimum, (*3*) medium, and (*4*) maximum excitation energies.

first compression cascade ($\lambda = 1.06, 0.53, 0.35$ μm), and ~30 pc after the second cascade ($\lambda = 0.56$ μm).

For kinetic measurements, we used a Hamamatsu C-970 high-speed streak camera. The luminescence kinetics of PIC *J* aggregates was measured upon pulsed excitation near 352 ($\Delta t \sim 0.5$ ns), 532 ($\Delta t \sim 0.5$ ns), and 560 nm ($\Delta t \sim 30$ ps). The laser beam was focused into the cell, and the image of the luminescing zone in the perpendicular direction was transferred to the entrance of the recording system.

The luminescence kinetics was measured by two methods. In the first method, the luminescence beam was directly sent to the streak camera through a filter that cut off the pump radiation and the short-wavelength part of luminescence. In the second method, the beam passed through an MDR-12 monochromator with a grating (1200 line/mm) placed in front of the streak camera. The entrance and exit slits of the monochromator were 3 mm wide. The use of the monochromator allowed us to filter the pump radiation and record the luminescence kinetics in different spectral regions. The monochromator was directly connected to the entrance slit (30 μm) of the streak camera. Due to high losses in the measurement channel, the measurements were performed at the pump energy no lower than 1 mJ. The luminescence kinetics was measured by scanning a 10-nm band selected from the spectrum.

The excitation pulse shape is shown in Fig. 5. The luminescence decay character strongly depends on the pump and luminescence spectral regions. In the case of low-energy ($\sim 10^{-6}$–10^{-4} J) excitation in the region of the main absorption band of *J* aggregates near 560 nm ($\Delta t \sim 30$ ps), the luminescence in the red region ($\lambda \geq 570$ nm) decays almost exponentially with $\tau \sim 1$ ns. Note here that, in this case, the decay time is shorter than the weight average time measured using the Micro Time 100 microscope (see above). This is obviously caused by the influence of photoinduced luminescence occurring due coherent excitation, which leads to localization of luminescence in the pump field [21, 22]. At the maximum excitation energy ($\sim 2 \times 10^{-3}$ J), the luminescence decay considerably differs from the exponential law (see Fig. 6).

In contrast to the luminescence of *J* aggregates, the luminescence decay of the PIC monomer in DMSO (the concentration is the same as in the solution of *J* aggregates) under the same conditions has almost the same shape as the excitation pulse (Fig. 7).

The measurements of the luminescence kinetics in selected spectral ranges 10 nm wide (with a mono-

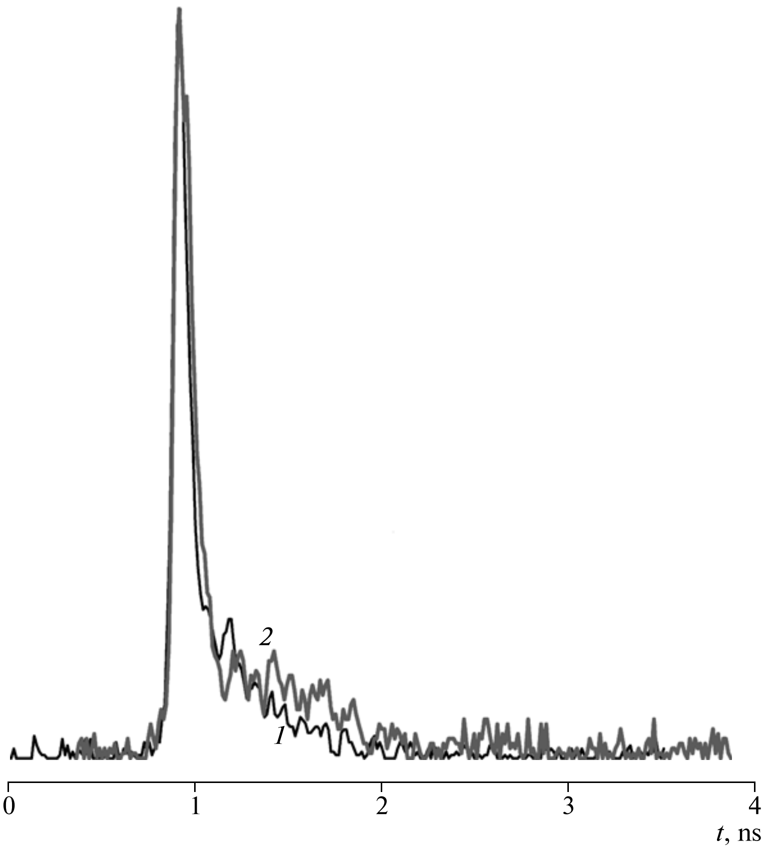

Fig. 7. (*1*) Pump pulse and (*2*) luminescence kinetics of a solution of PIC monomer in DMSO.

chromator in front of the streak camera) revealed that the kinetics strongly depends on the recording spectral region. In the region of 575–585 nm and to the red from 600 nm, the decay is close to exponential with $\tau \sim$ 1.5 ns (Fig. 8). The luminescence kinetics measured in the region of 585–600 nm is essentially different; here, switching from one type of kinetics to another is observed. The kinetics demonstrates a pronounced peak delayed with respect to the excitation instance: the longer the wavelength of the selected range, the longer the delay.

The observed dependence of the luminescence kinetics on the recording wavelength is probably related to the fact that a *J* aggregate consisting of a molecular pile, in which excitation migrates, can be represented as a set of fragments with a finite coherence length and individual PIC molecules of the nearest environment. Pumping into the aggregate absorption band selectively excites a fragment characterized by a particular coherence length (analogously to a homogeneously broadened component in an inhomogeneously broadened spectrum). This fragment of the *J* aggregate chain emits with minimum energy losses (short-wavelength region of the fluorescence band); without a delay; and with a kinetics close to the ordinary luminescence, i.e., according to a law that is close to the exponential law. As the excitation is transferred to neighboring fragments of the same *J* aggregate, which may be separated by structural defects, some energy is spent on relaxation processes, which causes a red shift in the fluorescence occurring with a time delay. This effect indicates that the size of a *J* aggregate (the number of molecules in the chain) is considerably larger than the exciton coherence length calculated from the integral fluorescence parameters (see above).

Note also that an energy transfer may occur between structurally different PIC *J* aggregates that exist in an equilibrium state in the same chain or in different chains or that they may undergo phototransformation in the excited state. Indeed, as was previously shown by one of the authors of this work [23] (independently of [24]), the long-wavelength band of the PIC *J* aggregate belongs to two structural types, which were later called blue and red *J* aggregates [25, 26]. The separation of PIC *J* aggregates into groups in aqueous solution was also confirmed in experiments on two-photon fluorescence spectroscopy in combination with optical trapping [27].

Despite the fact that chloride ions in aqueous solutions induce the formation of mainly blue, i.e., short-wavelength *J* aggregates [9, 23], some amount of red *J* aggregates still remains. The possibility of existing of red and blue *J* aggregates in one and the same chain

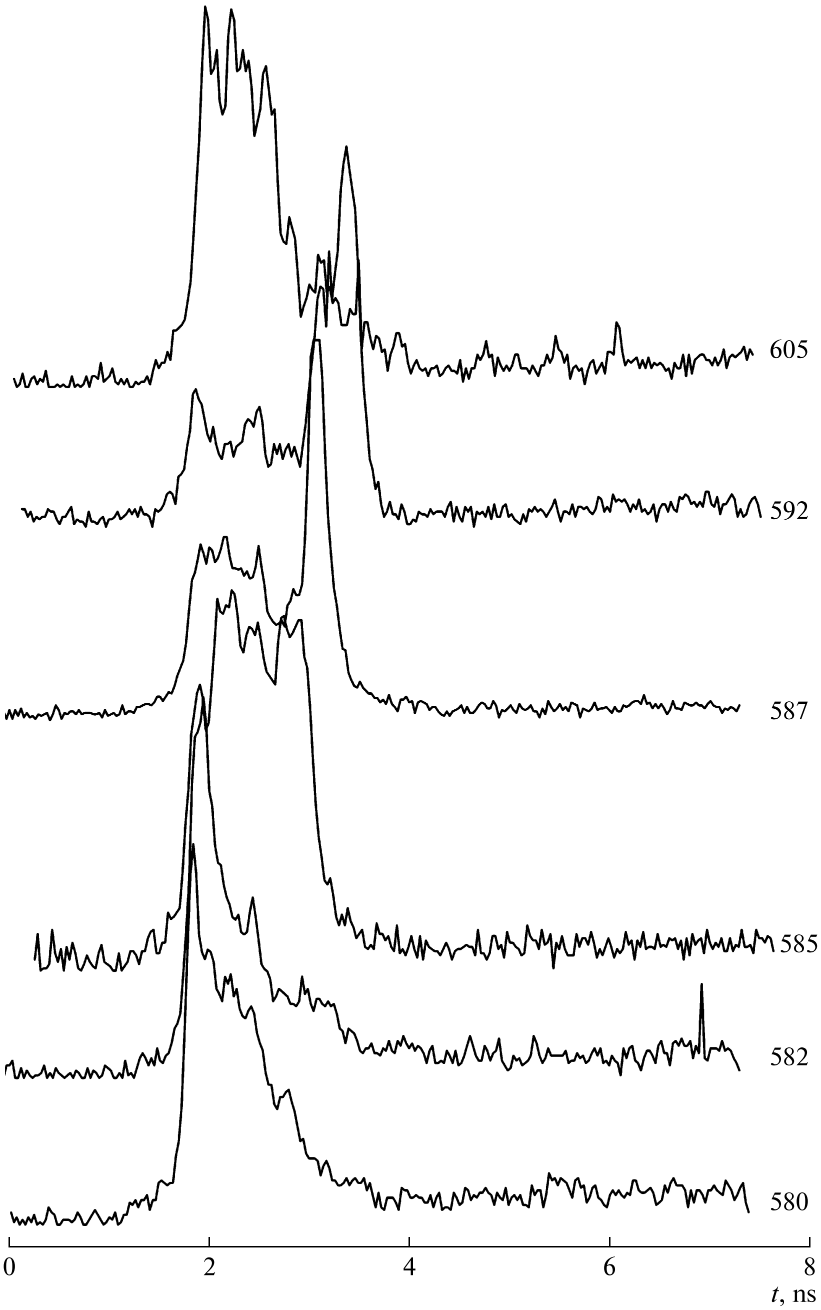

Fig. 8. Luminescence kinetics of solution of PIC *J* aggregates excited near 560 nm. Figures to the right of the curves indicate the central wavelength of spectral range separated by monochromator (in nm).

was discussed in [26, 28]. In these works, the band of blue PIC *J* aggregates was recorded in the excitation spectra of red *J* aggregates, which testifies to the occurrence of the above-mentioned energy transfer. It is believed that blue *J* aggregates are more stable in the ground state, while red *J* aggregates are stable in the excited state [28]. The transformation of blue *J* aggregates into red under steady-state photoexcitation was observed in [29]. The existence of the band of blue PIC *J* aggregates in the excitation spectrum of the red *J* aggregates, which indicates their equilibrium in the excited state, was also recorded in [25, 28].

The reversion of the luminescence kinetics of PIC *J* aggregates to the normal shape when recording wavelengths above 600 nm (Fig. 8) can be explained by approaching the second phonon peak of the luminescence of blue *J* aggregates.

The hypothesis of the energy transfer form the initial fragment to a neighboring one is confirmed by experiments in which *J* aggregates were pumped into

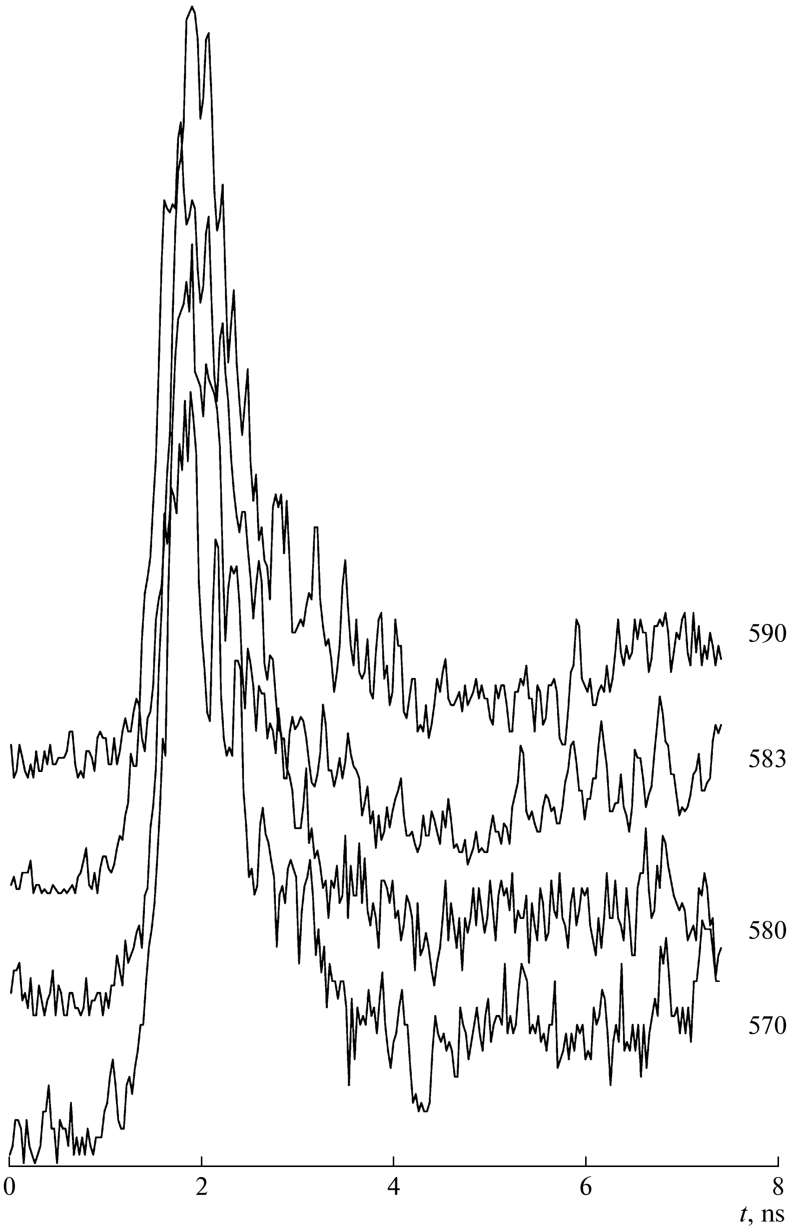

Fig. 9. Luminescence kinetics of solution of PIC J aggregates excited near 352 nm. Figures to the right of the curves indicate central wavelength of spectral range separated by monochromator (in nm).

the first absorption band out of the region of the narrow peak and into the second absorption band by UV pulses. In the case of excitation out of the narrow band of J aggregates near 352 nm ($\Delta t \sim 0.5$ ns) and at 532 nm ($\Delta t \sim 0.5$ ns), the luminescence decay is close to exponential with a decay time on the order of 1.5 ns (Fig. 9), independently of the recording wavelength. In this case, luminescent J aggregates are nonselectively excited, either due to the energy transfer from individual PIC molecules or due to a fast relaxation from the highest excited state to the lowest one.

We also measured the dependences of the transmission and luminescence of PIC J aggregates on the excitation energy. The transmission is almost independent of the excitation energy, while the fluorescence demonstrates an approximately exponential increase without saturation (Fig. 10). The absence of absorption saturation points to the equality of the absorption cross sections from the ground and the first excited states. At the same time, the unsaturated increase in the fluorescence points to the possibility of photoinduced luminescence, which occurs upon intense coherent excitation [21, 22].

Thus, the results of a spectral study of the luminescence and luminescence kinetics of J aggregates allows us to conclude that the coherently coupled fragments

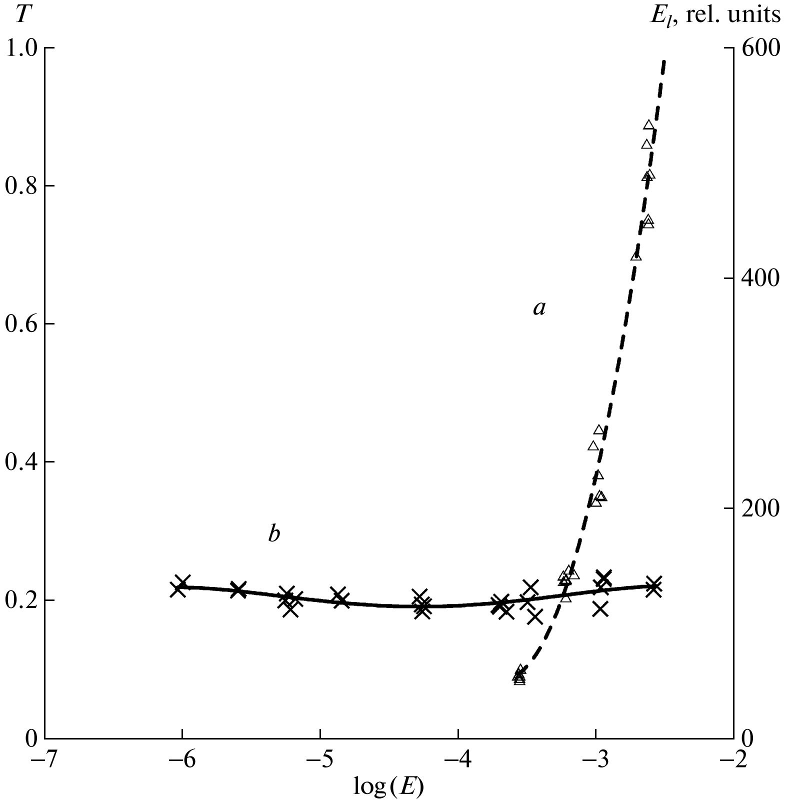

Fig. 10. Dependences of (*a*) transmission and (*b*) luminescence of solution of PIC *J* aggregates on excitation energy.

of *J* aggregates consist of six molecules. In the case of excitation directly into the *J* band, we observed for the first time the manifestations of photoinduced luminescence occurring due to the excitation by coherent radiation, which lead to the localization of luminescence in the pump field as was previously observed for molecular solutions and vapors. Under the same excitation conditions, the luminescence recorded near the long-wavelength edge of the *J* band demonstrates characteristic changes in the kinetics testifying to the possibility of energy transfer between the coherently coupled fragments of a *J* aggregate. In conclusion, we note that the rather large number of coherently coupled fragments (coherence length) in the molecular chain is necessary for the existence of dissipative solitons in the chain under resonance excitation by cw radiation (see [30] and references therein). The simulation performed in [30] also revealed a dependence of the coherence length on the cw radiation intensity.

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