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Strong enhancement of cyanine dye aggregation by a cationic surfactant

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Optical spectroscopy methods have been used to study the features of cyanine dye 3,3′-dimethyl-9-thienyl-thiacarbocyanine iodide (L-21) aggregation in the presence of cationic surfactant CPB at concentrations above the critical micelle concentration. It has been revealed that the addition of CPB promotes the formation of luminescent molecular aggregates. The aggregates have a complex structure that is manifested in the absorption spectrum as two new bands (hypsochromically and bathochromically shifted). The aggregates formed reveal a highly ordered structure and a significant luminescence.

При помощи методов оптической спектроскопии исследованы особенности агрегации цианинового красителя 3,3′-диметил-9-тиенил-тиакарбоцианинйодида (L-21) в присутствии катионного поверхностно-активного вещества CPB, концентрация которого выше критической концентрации мицеллообразования. Обнаружено, что добавление CPB способствует образованию люминесцирующих молекулярных агрегатов. Полученные агрегаты обладают сложной структурой, которая проявляется в спектре поглощения в виде появления двух новых полос (смещенных гипсохромно и батохромно). Полученные агрегаты обладают высоко упорядоченной структурой и значительной люминесценцией.

J-Aggregates are luminescent assemblies of non-covalently coupled molecules resulting in a narrow absorption band bathochromically shifted with respect to that of monomer. Since their discovery by Jelley and Scheibe [1–3], J-aggregates have been of fundamental interest due to their intermediate position between dissolved molecules and structurally ordered crystals. The J-aggregate size can be characterized by two different quantities: (a) the physical size n, i.e., the number of monomer units which determines the geometrical length of the aggregate and (b) the coherence (delocalization) length or number of coherently coupled molecules (N_{del}). Whereas the physical size may be in the range of several thousand molecules, the coherence domain consists of less than 20 molecules at room temperature [1–3]. Since the photophysical properties of J-aggregates are size-dependent [1–3], it is of great interest to control those by varying the size of J-aggregates, aiming for enhanced aggregation and increased coupling strength.

There are some ways to affect the aggregation of polymethine dyes in solutions: addition of salts, variation of the solution acidity, temperature, solvent ratio (for binary solutions), etc. [1–3]. Surfactants can provoke the aggregation, too [4–14]. It has been shown that the addition of surfactants at a concentration below the critical micelle concentration (CMC) enhances the aggregation [4–14] and sometime changes the J-aggregate morphology [4–6]. As a rule, at sur-

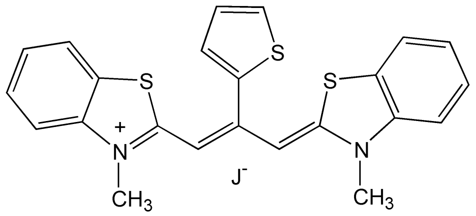

Fig. 1. The chemical structure of L-21 dye.

factant concentrations above the CMC, the dye molecules are solubilized by surfactant micelles that prevent their aggregation [4–6, 9–14]. Nevertheless, it was also shown that the addition of surfactants at concentrations above the CMC can promote polymethine dye aggregation [7–9]. For instance, in [7], the influence of a number of anionic surfactants (sulfonates, sulfates and their derivatives) on the aggregation of well-known cationic dye PIC was studied. The addition of some surfactants at concentrations below the CMC was found to cause both J- and H-aggregate formation. At the same time, one of surfactants has been revealed to cause J-aggregate formation at concentrations much above the CMC.

In contrast to anionic surfactants, the aggregation of PIC was not observed in the presence of nonionic ones [7]. In [8], the effect of a zwitterionic surfactant on TDBC J-aggregate formation was investigated. It was shown that the surfactant addition at concentrations above the CMC changes the J-aggregate spectral characteristics: the absorption J-band becomes narrower and more intense, the luminescence band of J-aggregates also becomes narrower and the fluorescence quantum yield increases. The most pronounced changes in the spectral characteristics were observed at the dye-to-surfactant ratio 1:2. In the case of cationic surfactants, the destruction of J-aggregates was observed [8]. The interaction of cationic dye amphi-PIC with anionic and cationic surfactants has been investigated in [9]. The addition of an anionic surfactant at concentrations above the CMC was found to destroy the amphi-PIC J-aggregates, while a cationic surfactant causes an increased J-band intensity and its narrowing at concentrations below and above the CMC. In this work, we have examined the features of J-aggregate formation for 3,3′-dimethyl-9-thienyl-thiacarbocyanine iodide (L-21) (Fig. 1) in aqueous solutions containing cationic surfactant, cetylpyridinium bromide (CPB).

The cyanine dye L-21 was obtained from the dye collection at the Department of Combinatorial Chemistry (Institute for Molecular Biology and Genetics NAS of Ukraine). Its purity was checked by thin layer chromatography. The surfactant CPB was purchased from Sigma Aldrich and used as received. The samples for investigations were prepared by addition of appropriate amount of the surfactant to a stock dye solution in dimethylformamide (DMF) (2 mM). Then the solution was diluted with water buffer TRIS-HCl (C = 0.05 mol/L, pH = 8) in the ratio 1:19. Thus, the dye concentration in the samples was equal to 10^{-4} mol/L and surfactant concentration was equal to 10^{-3} mol/L. The luminescence and luminescence excitation spectra were recorded using a spectrofluorimeter on the base of two grating monochromators MDR-23 and a xenon lamp. One of the monochromators was used to select the required wavelength (FWHM ~ 0.5 nm), the other one was used for luminescence collection. For absorption spectra registration, the spectrofluorimeter was supplied with an incandescent lamp. For temperature measurements, the cell with the sample was placed in a thermostat where temperature can be smoothly changed within the 20–95°C at a 1°C step.

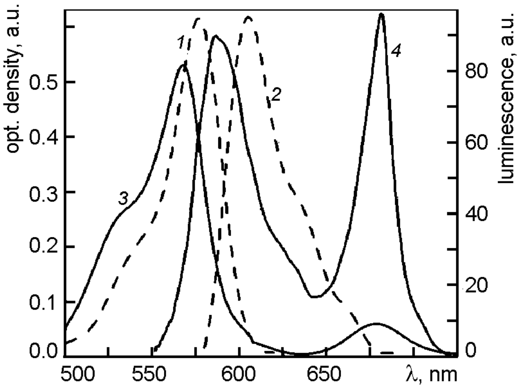

Fig. 2. Absorption (*1*, *3*) and luminescence (λ_{exc} = 530 nm) (*2*, *4*) spectra of L-21 in DMF (*1*,*2*) and in a binary solution DMF:TRIS-HCl buffer (*3*, *4*).

Due to a poor solubility of L-21 in water, its J-aggregates were prepared in a binary (polar solvent-water) solution from a stock dye solution in DMF [16, 17]. Absorption and luminescence spectra of L-21 dye in DMF are typical of cyanine dyes (Fig. 2) with absorption maximum at 576 nm (monomer band) and luminescence maximum at 605 nm, respectively. A weakly basic medium is found to be required for dye aggregation. So, to prepare the samples, an aqueous TRIS-HCl buffer (pH = 8) was used. In a DMF:TRIS-HCl buffer (1:19) binary solution, the dye absorption spectrum changes (Fig. 2): the monomer band shifts towards short wavelengths (λ_{max} = 568 nm) that is associated with an increased solvent polarity and a new low-intensity long-wavelength band with maximum at 679 nm is revealed. The new band is broad enough ($\Delta\nu_{FWHM}$ = 750 cm^{-1}). An increase of short-wavelength shoulder intensity at 532 nm in the monomer absorption band with respect to the absorption spectrum in DMF (Fig. 2) should be also noted. The luminescence spectrum of L-21 in the DMF:TRIS-HCl buffer binary solution also exhibits a new very intense band peaked at 681 nm. In the luminescence spectrum, the intensity ratio between the new band and monomer one is much larger than that in the absorption spectrum (Fig. 2). The appearance of the long-wavelength absorption band and the intense resonance luminescence one in the binary solution can be ascribed to the formation of J-aggregates of L-21 dye [1–3]. The rather broad absorption and luminescence bands of L-21 J-aggregates observed in the DMF:TRIS-HCl buffer binary solution seem to be associated with a broad dispersion of J-aggregate chain lengths [1–3].

To stimulate the aggregation of L-21 in the DMF:TRIS-HCl buffer binary solution, we have used cationic surfactant CPB, which was used to improve the amphi-PIC J-aggregation in [9]. The addition of cationic surfactant CPB at a concentration above the CMC ($6.2\cdot10^{-4}$ mol/L [18]) provokes significant changes in the absorption spectrum (Fig. 3, curve *1*). The intensity of J-aggregate band (J-band) increases and its width becomes very narrow ($\Delta\nu_{FWHM}$ = 150 cm^{-1}). The luminescence band of J-aggregates (Fig. 3, curve *2*) also becomes much narrower ($\Delta\nu_{FWHM}$ = 200 cm^{-1}) and very intense, while the intensity of the monomer luminescence band decreases. Apparently, similar to the case of amphi-PIC [9], the addition of CPB reduces the disorder degree in L-21 J-aggregates. As a result, the exciton delocalization length of L-21 J-aggregates increases that is proved by considerable J-band narrowing [1–3, 19].

The exciton delocalization length can be estimated using the equation [19]:

$$N_{\partial} = \frac{3}{2}\left(\frac{\Delta\nu_{mon}}{\Delta\nu_J}\right) - 1,$$

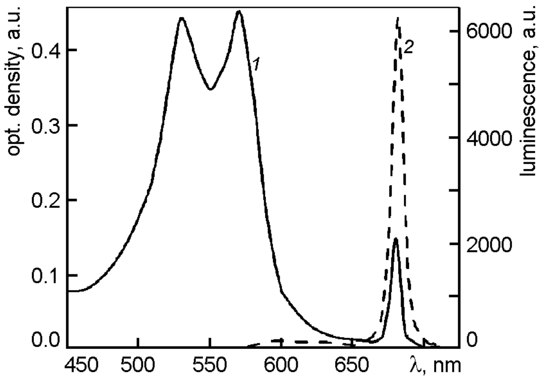

Fig. 3. Absorption (*1*) and luminescence (λ_{exc} = 530 nm) (*2*) spectra of L-21 in a binary solution DMF:TRIS-HCl buffer containing CPB.

where $\Delta\nu_{mon}$ is the full width at half maximum (FWHM) of the monomer absorption band; $\Delta\nu_J$, the J-band FWHM. Taking $\Delta\nu_{mon}$ = 700 cm^{-1} (from L-21 absorption spectrum in DMF after subtraction of the vibronic band), we obtain for J-aggregates L-21 in the presence of CPB $N_{del}\approx32$ monomer units, that is large enough value at room temperature and indicates the high ordering degree of the J-aggregates [1–3].

The next feature of L-21 J-aggregates with CPB absorption spectrum is a significant increased intensity of the short-wavelength shoulder in the monomer absorption band (Fig. 3, curve *1*) that points to the formation of so-called H-aggregates [1–3]. At the excitation in this band, only J-aggregate luminescence is observed, confirming that the blue-shifted band belongs to H-like structure [1–3]. To estimate the association degree for H-aggregates, the set of absorption spectra at different temperatures was obtained (Fig. 4). The temperature increase is seen to result in redistribution of monomer, J- and H-band intensities: H- and J-band decrease synchronously, while the monomer band increases. At *t* = 55°C, the aggregate states are completely destroyed and only the monomer band is observed. Such a low thermal stability is a characteristic feature of luminescent molecular aggregates [22]. The set of the spectra reveals a single isosbestic point at 546 nm that indicates a dynamical equilibrium in the solution between monomers and H-aggregates and as the H-aggregates are destroyed, new ones with lower association degree do not form. Moreover, the H-aggregate maximum

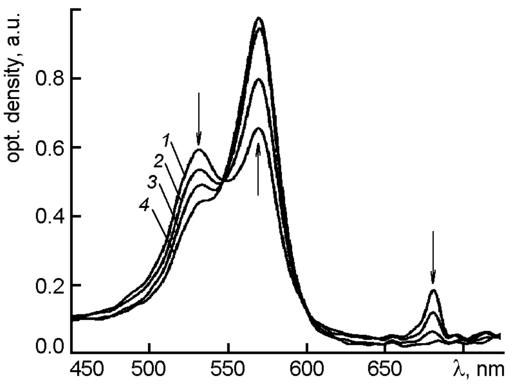

Fig. 4. Absorption spectra of L-21 in presence of CPB at different temperature: *1* — 25°C, *2* — 30°C, *3* — 35°C, *4* — 55°C.

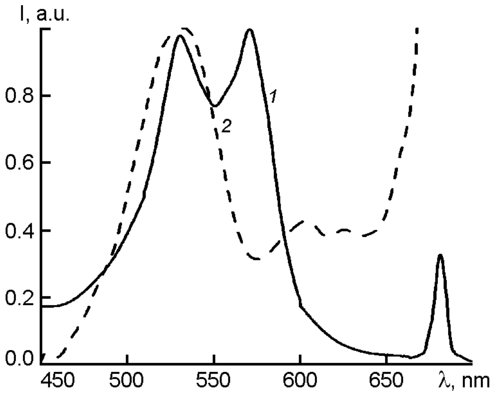

Fig. 5. Absorption (*1*) and luminescence excitation (*2*) spectra ($\lambda_{reg} = 683$ nm) of L-21 with CPB.

location is not changed at temperature increase (Fig. 4). At the same time, the J-bands reveal no isosbestic point and their maxima slightly shift towards short wavelengths, that points to the breaking of J-aggregates into smaller associates. Thus, we can conclude that the H-band belongs to the dimeric state of the dye, which is well-known for symmetrical cyanine dyes [1, 20, 21].

To find out the origin of the aggregation bands in the absorption spectrum (whether the bands belong to aggregates of different types or to one aggregate type with a complex structure), the luminescence excitation spectrum of L-21 J-aggregates in a DMF:TRIS-HCl buffer binary solution containing CPB was studied (Fig. 5). The comparison of the absorption and luminescence excitation spectra of J-aggregates has revealed that J-aggregate luminescence can be effectively excited within the H-band, so both bands can be ascribed to J-aggregates and they seem to be a result of the Davydov splitting of energy levels [1, 23–25]. The appearance of such a splitting is often ascribed to the formation of so-called "two-strap" or "herringbone" aggregate structure from the dye dimers [1, 24, 25].

Thus, we can propose the following model of the L-21 J-aggregate structure in the presence of CPB. In the solution, a "dye aggregate-surfactant" complex is formed; the dye aggregates possess a complex structure and are formed from the dye dimers with so-called "face-to-face" packing (H-dimers), such dimers are arranged in the extended J-aggregates of "head-to-tail" structure. Due to strong interaction with CPB, the J-aggregates have well-ordered structure and reveal strong luminescence. The detailed structure of the "dye aggregate-surfactant" complex obtained is still not understood and requires a further study.

To conclude, it has been shown that the dye L-21 forms extended J-aggregates in a binary solution DMF:TRIS-HCl buffer (1:19) containing surfactant CPB in concentrations above the CMC. That is an uncommon feature, because addition of surfactants at concentrations above the CMC causes as a rule the distortion of the dye aggregate state. The formation of a "dye aggregate-surfactant" complex results in the high ordering of the L-21 aggregate structure and, consequently, to the significant increase in the luminescence intensity. The main "building blocks" of the J-aggregates are "face-to-face" dimers (H-dimers). Such a structure of L-21 aggregate results in the Davydov splitting of its energy levels and the appearance of two aggregate bands in the absorption spectrum. The application of surfactants could be very useful to controlled formation of luminescent molecular aggregates and nanoclusters with specified spectral properties. So, further investigations of specific "dye aggregate-surfactant" complexes are extremely required.

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Значне посилення агрегації ціанінового барвника за допомогою катіонної поверхнево-активної речовини

Г.Я.Гуральчук, І.К.Катрунов, Р.С.Гриньов, О.В.Сорокін, С.Л.Єфімова, Ю.В.Малюкін, С.М.Ярмолюк

За допомогою методів оптичної спектроскопії досліджено особливості агрегації ціанінового барвника 3,3′-диметил-9-тієніл-тіакарбонілціанінйодиду (L-21) у присутності катіонної поверхнево-активної речовини СРВ, концентрація якої вище критичної концентрації міцелоутворення. Виявлено, що додавання СРВ сприяє утворенню люмінуючих молекулярних агрегатів. Отримані агрегати мають складну структуру, що проявляється у спектрі поглинання у вигляді появи двох нових смуг (зміщених гипсохромно та батохромно). Отримані агрегати мають високо впорядковану структуру й значну люмінесценцію.