

The Structure of Pseudoisocyanine Decahydro-*closo*-decaborate and Its Nonlinear Optical Properties in Thin Films

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Abstract

The presence of decahydro-*closo*-decaborate anion ($B_{10}H_{10}^{2-}$) in the solution of pseudoisocyanine iodide ($(C_{23}H_{23}N_2)^+I^-$) is demonstrated to lead to the efficient formation of J-aggregates on the surface of a glass substrate which allows to obtain stable thin-film samples of high optical quality. Spectral and X-ray diffraction studies prove that the dianion $B_{10}H_{10}^{2-}$ forms a complex $(C_{23}H_{23}N_2)^+_{1/2}B_{10}H_{10}^{2-}$ which is more efficient in forming J-aggregates than $(C_{23}H_{23}N_2)^+I^-$. The organizing role of the $B_{10}H_{10}^{2-}$ anion in the formation of the structure by means of close contacts $B-H \cdots H-C$ is thus confirmed. By means of spectral ellipsometry, we measured the coefficients of the complex refractive index of film samples composed of J-aggregates of pseudoisocyanine iodide and pseudoisocyanine doped with the $B_{10}H_{10}^{2-}$ anions. Dispersion of the cubic susceptibility $\chi^{(3)}$ of thin films formed by J-aggregates was measured near the J-band of absorption. The films exhibit large $|\chi^{(3)}| \approx 10^{-5}$ esu units at the thickness much less than the light wavelength.

INTRODUCTION

Much effort has been made in the recent years to obtain and investigate molecular nanostructures including conjugated polymers, fullerenes, molecular aggregates and others [1]. These species also include the so-called J-aggregates of organic dyes which are self-organized quasi-one-dimensional structures [2, 3]. Aggregated molecular structures are composed of tens thousand initial molecules [4, 5] bound by the van der Waals interaction. Excited states of J-aggregates are the Frenkel excitons. Coherent exciton length in these molecular aggregates is ten to twenty monomeric molecules [6–8]; it is due to the resonance dipole-dipole interaction between the molecules. These species are characterized by unusual optical and nonlinear optical properties, first of all due to their topology. A characteristic feature of J-aggre-

gates is a narrow absorption band (J-band) shifted towards lower frequencies with respect to the monomer absorption band. The absorption of light in the J-band followed by energy transfer between the aggregates plays an important part, for example, in light-harvesting photosynthesis systems [9]. J-aggregates are also used as efficient stabilizers in AgHal photography [10].

After high nonlinear-optical susceptibility was discovered in the J-band region, the interest to these species increased [6, 11–13]. For example, the cubic susceptibility of thin films composed of pseudoisocyanine (PIC) was measured in [14] to be about 10^{-5} esu units. However, one of the tasks is the preparation of reproducible stable samples of J-aggregates. Several methods of the preparation of J-aggregates are known. For example, J-aggregates were obtained by cooling the heated (to 70 °C)

solution of dye with 0.2 mol/l NaCl added [4, 13], according to the Langmuir – Blodgett technique [15], by using the interaction between the charged polymer and the dye [7], vertical spincoating [16], formation of liquid crystals in concentrated aqueous solutions [17], as well as by using the aggregation in thin films [18].

In the present study we report the preparation of stable film samples of J-aggregates by means of spin-coating of the PIC dye solution in the presence of the anion of decahydro-*closo*-decaborate $B_{10}H_{10}^{2-}$ on a glass substrate and the investigation of their optical and nonlinear optical properties.

EXPERIMENTAL

Preparation of the thin films composed of J-aggregates of PIC and investigation of their properties

Important factors that affect the formation of J-aggregates are temperature, humidity of the medium, concentration of the initial dye solution. Besides, the nature of anion incorporated in the dye has an effect on the formation of J-aggregates. We used PIC iodide ($C_{23}H_{23}N_2$) I^+ (1) obtained according to [19]. The $K_2B_{10}H_{10}$ salt (2) was prepared according to the technique [20]. The films with J-aggregates were prepared by spin-coating the dye 1 solution on the surface of a glass substrate (with the dimensions of 2.5×2.5 cm) at room temperature. The concentration of dye 1 in solution was $5 \cdot 10^{-3}$ mol/l. Film thickness was varied within 15–40 nm by changing the initial dye concentration. Optical density in the absorption maximum was 0.1 to 0.5. Maximum absorption of the films for the J-aggregates of compound 1 was observed at 583 nm. The degradation of J-aggregates due to the crystallization of the dye in these films occurs within one–two weeks.

We discovered that the addition of low-concentration ($\sim 10^{-4}$ mol/l) solution of salt 2 to the initially prepared solution of dye 1 allows to obtain stable films of J-aggregates with a good reproducibility. At present more than twenty hydroborate anions are known, from $B_2H_7^-$ to $B_{20}H_{18}^{2-}$. We studied the effect of the anions

$B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, $B_{10}Cl_{10}^{2-}$ on the formation of J-aggregates. Absorption spectra of the films prepared using different ratios of molar concentrations of borate anions and dye 1 show that the addition of the salt 2 solution starting from the the concentration of $8 \cdot 10^{-5}$ mol/l till $6 \cdot 10^4$ mol/l leads to the growth of J-band. The addition of the solutions of $K_2B_{12}H_{12}$ or $K_2B_{10}Cl_{10}$ salts in concentration of 10^{-4} mol/l and above leads to the destruction of spontaneously formed J-aggregates. The obtained data allow to conclude that only under the action of $B_{10}H_{10}^{2-}$ the J-aggregates are formed with high efficiency. It is sufficient to have only one $B_{10}H_{10}^{2-}$ anion per 20 dye molecules for the formation of J-aggregates to occur.

If salt is added at a concentration above 10^{-3} mol/l, the dye gradually precipitates. The precipitate was twice recrystallized, then its IR absorption spectrum was recorded (Fig. 1, a). For comparison, Fig. 1, b shows a similar spectrum for pure $K_2B_{10}H_{10}$. According to the data of [21, 22], a strong absorption band at 2472 cm^{-1} in the $K_2B_{10}H_{10}$ spectrum (see Fig. 1, b) is attributed to the equatorial vibrations of the B—H bond. A sharp peak at 2540 cm^{-1} located at the wing to the left of this band corresponds to the contribution from vertex B—H bonds. In

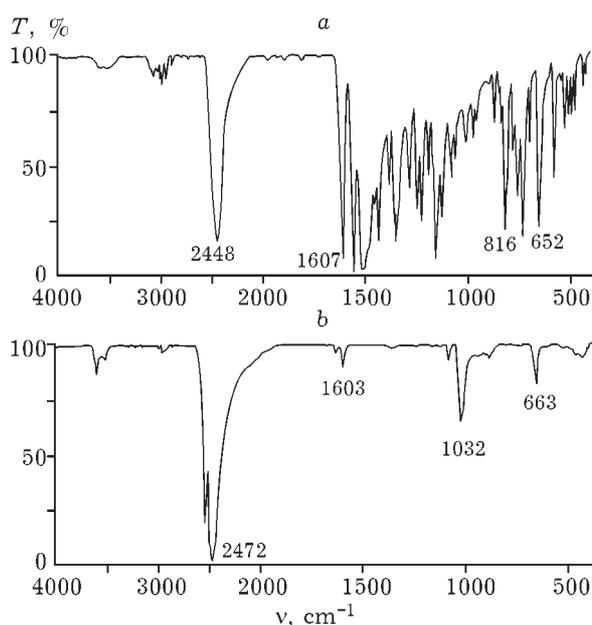


Fig. 1. IR absorption spectra of PIC iodide with the $B_{10}H_{10}^{2-}$ anion (a) and $K_2B_{10}H_{10}$ (b).

Fig. 1, *a*, for the obtained dye, a strong absorption band related to B—H bond stretching vibrations is shifted to 2448 cm^{-1} ; the peak corresponding to B—H top vibrations is absent. For pure dye 1, no absorption bands are observed at 2500 cm^{-1} . These data point that the anion $\text{B}_{10}\text{H}_{10}^{2-}$ forms the complex $(\text{C}_{23}\text{H}_{23}\text{N}_2)^+\text{B}_{10}\text{H}_{10}^{2-}$ which is more efficient in forming J-aggregates than dye 1. The disappearance of the absorption band of top B—H vibrations is the evidence that this fragment may participate in the formation of these complexes. Besides, the absence of PIC J-aggregates in the case when we add the $\text{B}_{12}\text{H}_{12}^{2-}$ anion possessing icosahedral structure, *i. e.* with symmetric B—H bonds, stresses the importance of top B—H bonds. The absence of J-aggregates under the action of the $\text{B}_{10}\text{Cl}_{10}^{2-}$ anion is likely to be due to the destructive action of chlorine atoms. Absorption spectra of the films with J-aggregates exhibit a tendency of shifting the absorption peak from 583 nm to shorter wavelengths by about 10 nm while the concentration of $\text{B}_{10}\text{H}_{10}^{2-}$ anion increases in the solution of dye 1.

The role of anion in the formation and stabilization of the aggregates was discussed by the authors of [23] who noted that the investigation of crystal structure can be useful in determi-

ning the role and mechanisms of anion ranging near the cation dye. On the other hand, the authors of [24] concluded, on the basis of transmittance spectral data on thin crystals of 1 and absorption spectra of aggregated solutions, that the aggregated solution contains microcrystals only slightly differing in structure from massive crystals.

In order to state the role of the anion $\text{B}_{10}\text{H}_{10}^{2-}$ in the formation of stable J-aggregates, we performed X-ray structural investigation of dark-red crystals $(\text{C}_{23}\text{H}_{23}\text{N}_2)_2\text{B}_{10}\text{H}_{10}$ obtained by the deposition of dye synthesized by us. The deposition was performed in pure acetonitrile by means of water vapour diffusion in tightly closed container. The experimental data for the determination of structure were obtained according to a standard technique with a CAD-4 autodiffractometer (Mo K_α radiation, graphite monochromator, $\theta/2\theta$ scanning, 978 reflections with $I > 2\sigma_I$) at room temperature using a crystal with the dimensions of $0.2 \times 0.5 \times 0.65\text{ mm}$. The compound is crystallized in monoclinic chiral space group C2. The projection of the structure on the (001) plane is shown in Fig. 2. One can see that the long axis of the pseudoisocyanine molecule is parallel to the single crystallographic axis of the structure. The configuration of the dye cation is chamfered; the $\text{B}_{10}\text{H}_{10}^{2-}$ ani-

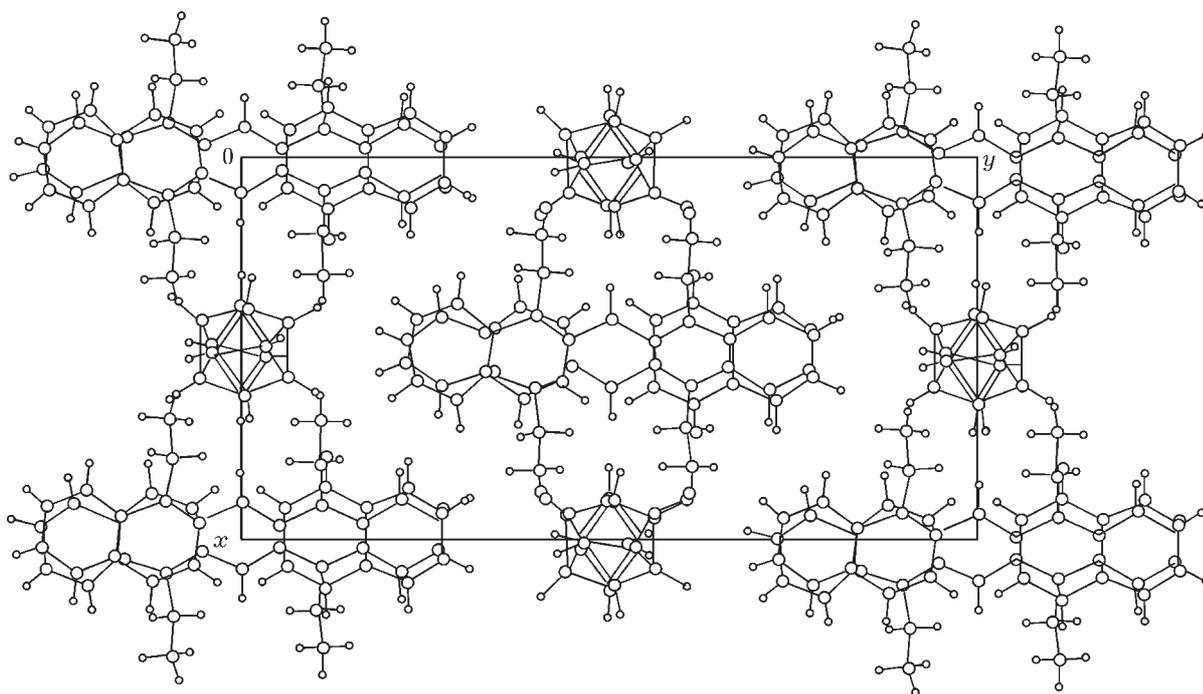


Fig. 2. A projection of the structure $(\text{C}_{23}\text{H}_{23}\text{N}_2)_2\text{B}_{10}\text{H}_{10}$ on the (001) plane.

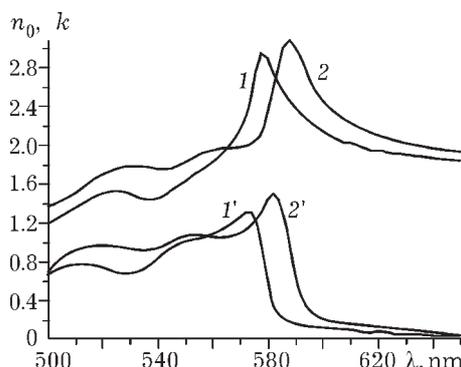


Fig. 3. Optical constants for the films of J-aggregates, PIC iodide with the $B_{10}H_{10}^{2-}$ anion (1) and PIC iodide (2): 1 and 2 – n_0 , 1' and 2' – k .

on is structurally disordered. Structural data point that the $B_{10}H_{10}^{2-}$ anion plays an organizing role in the creation of structure by means of close hydride-proton contacts $B - H \cdots H - C$.

Investigation of optical and nonlinear-optical properties of thin films composed of J-aggregates of PIC

We studied optical and nonlinear-optical properties of the films of PIC J-aggregates obtained by spin-coating of dye solutions on a glass substrate in the presence and in the absence of the $B_{10}H_{10}^{2-}$ anion. Optical constants n_0 and k of the complex refractive index $n = n_0 - ik$ of the films within the spectral range of 500–650 nm were calculated from the data obtained by means of spectral ellipsometry (Fig. 3) [25].

Nonlinear optical properties of thin films were studied by the Z-scan method [14, 26]. This method allows to measure the coefficients of nonlinear absorption $\beta(\alpha_0 = \alpha + \beta I$ where α_0 is the linear absorption index) and of nonlinear refraction γ ($n = n_0 + \gamma I$ where n_0 is the linear refractive index), as well as their signs. A pulsed dye laser (DL) pumped by the second harmonics of the YAG laser was used in the experiments. The power of DL was 5 kW at 5 ns pulse. The pulse repetition rate was 10 Hz. DL wavelength was tuned within the range of 573–595 nm.

We studied a series of samples of two types. Typical absorption spectra of these samples are shown in Fig. 4 (curves 1 and 2). The measurements of the linear absorption spectrum showed that the position of J-peak depends on the film type. The films of dye 1 with the addi-

tion of the $B_{10}H_{10}^{2-}$ anion exhibited maximum absorption of the J-aggregate at the wavelength of 574 nm (type 1) while the films of pure dye 1 – at 583 nm (type 2). Half-width at half-height $\Gamma \sim 220 \text{ cm}^{-1}$ for both types of samples. The difference in the positions of J-peaks can be explained by the effect of anions on the structural parameters of the aggregate. The change of structural parameters, for example relative positions of molecules in the aggregate, causes the change in the potential of dipole-dipole interaction which is responsible for the shift of J-peak with respect to the absorption peak of dye monomer [27].

The measurements of β and γ were performed in the range of about 600 cm^{-1} near the J-peak. The imaginary part of cubic susceptibility is proportional to the coefficient β and the real part is proportional to the coefficient γ . Characteristic dispersion curves $\text{Im}\chi^{(3)}(\Omega/\Gamma)$ for the films of types 1 and 2 are shown in Fig. 5, *a* and *b* ($\Omega = \omega - \omega_J$ is the position of J-peak). It is clear from the given dependencies $\text{Im}\chi^{(3)}(\Omega/\Gamma)$ that the absolute value of the imaginary part $\chi^{(3)}$ reaches its maximum at $\Omega = 0$. When ω changes in the vicinity of ω_J , the $|\text{Im}\chi^{(3)}|$ decreases while at the low-frequency side from the J-peak the imaginary part of the nonlinear susceptibility changes its sign (*i. e.*, $\beta > 0$). The range of the observed nonlinear darkening has the Stokes' shift 125 to 200 cm^{-1} for different samples.

For both types of film samples, β in the maximum was $\approx -6 \cdot 10^{-4} \text{ m/W}$ which corresponds to the imaginary part of cubic susceptibility $\text{Im}\chi^{(3)} \approx -2 \cdot 10^{-5} \text{ esu units}$. The minus corres-

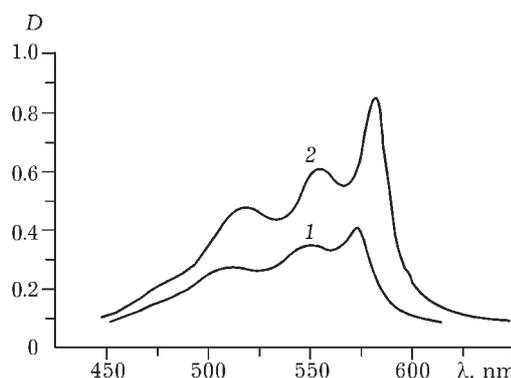


Fig. 4. Absorption spectra of the two types of films with J-aggregates: (1) PIC iodide with the $B_{10}H_{10}^{2-}$ anion (type 1) and (2) PIC iodide (type 2).

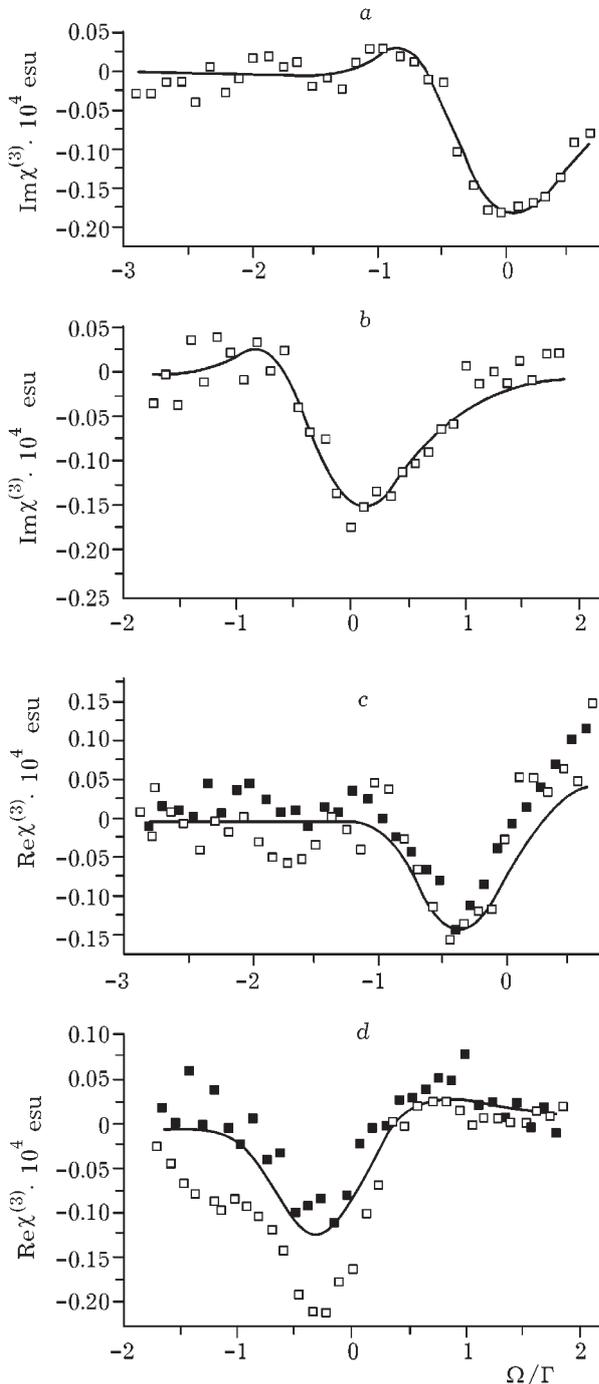


Fig. 5. Dispersion of imaginary and real constituents of the third-order nonlinear susceptibility for the films of the type 1 (a, c) and 2 (b, d), respectively.

ponds to nonlinear bleaching caused by the saturation of the exciton transition absorption.

Characteristic dispersion curves $\text{Re}\chi^{(3)}(\Omega/\Gamma)$ for the films of types 1 and 2 are shown in Fig. 5, c and d. For both types of film samples, γ at the maximum was $-3.3 \cdot 10^{-11} \text{ m}^2/\text{W}$ which corresponds to the real part of cubic susceptibility $\text{Re}\chi^{(3)} \approx -1.7 \cdot 10^{-5}$ esu units.

Unlike nonlinear absorption, the measurement of nonlinear refraction is affected by, for example, thermal refraction, scattering in the sample. In order to determine the refraction conditioned by the electron polarizability and not affected by these factors, the Kramers – Kronig relation should be used that connect $\text{Im}\chi^{(3)}$ and $\text{Re}\chi^{(3)}$ [14].

The data shown in Fig. 5, c suggest that the measured $\text{Re}\chi^{(3)}$ (light squares) well agree with those calculated according to the Kramers – Kronig relation (dark squares). For the film of type 2 (see Fig. 5, d), some negative difference is observed for the experimental $\text{Re}\chi^{(3)}$ compared to the calculated values. The reason is that the film of type 2 possessed larger optical density compared to the film of type 1 (see Fig. 4), so the former absorbed more energy and got heated more than the film of type 1. Because of this, for the film of type 2 a more substantial contribution from thermal nonlinearity should be expected.

CONCLUSION

The investigations showed that the presence of the decahydro-*closo*-decaborate anion in the dye solution leads to efficient formation of J-aggregates on the surface of a glass substrate which allows to obtain stable thin-film samples of high optical quality. Spectral and X-ray studies show that the $\text{B}_{10}\text{H}_{10}^{2-}$ anion forms a complex $(\text{C}_{23}\text{H}_{23}\text{N}_2)^+\text{B}_{10}\text{H}_{10}^{2-}$, which is more efficient in forming the J-aggregates than $(\text{C}_{23}\text{H}_{23}\text{N}_2)^+\text{I}^-$; the organizing role of the anion $\text{B}_{10}\text{H}_{10}^{2-}$ in the formation of the structure by means of close contacts $\text{B} - \text{H} \cdots \text{H} - \text{C}$ is confirmed. By means of spectral ellipsometry, the coefficients of the complex refractive index of film samples were measured both for the J-aggregates of pure dye 1 and that doped with the $\text{B}_{10}\text{H}_{10}^{2-}$ anions. Nonlinear optical properties of these films were studied. Dispersion dependencies were obtained for both the imaginary and real parts of the nonlinear cubic susceptibility $\chi^{(3)}$ in the vicinity of the J-peak of PIC aggregates. These films exhibit large $|\chi^{(3)}| \approx 10^{-5}$ esu units at thickness much smaller than the wavelength of light and are promising for quantum electronics and integrated optics.

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