INFLUENCE OF THE AGGREGATE STATE OF 3,4,4-TRICIANOBUTADIENCARBAZOLE ON ITS ONE- AND TWO-PHOTON-EXCITED LUMINESCENCE

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The luminescence of monomers, dimers, and crystalline clusters depending on the aggregate state of the substance has been observed in the photoluminescence (PL) spectra of 3,4,4-tricianobutadiencarbazole (TCBC). The two-photon-excited PL intensity for crystalline and nanocrystalline structures has been shown to be several orders of magnitude higher than that for amorphous films, providing the same intensities of the exciting infrared (IR) radiation.

Introduction

In [1], it has been reported about the high efficiency of the IR laser radiation transformation into visual light by means of the PL excitation. An intense PL well visible at room temperature has been observed while exciting the crystals of a number of new organic compounds with intramolecular charge transfer by an IR pulsed laser (λ_{ex} = 1064 nm). The observed frequency elevation caused by the IR laser excitation and followed by fluorescence, was connected to a 2-photon absorption. At high laser radiation intensities, the intensity of 2-photon-excited luminescence (2PEL) becomes comparable to that of 1-photon-excited luminescence (1PEL) at double frequency. A low intensity of IR laser radiation, when the 2PEL takes place, and a high efficiency of its transformation into visual light make possible the implication of the organic compounds under investigation in opto- and molecular electronics.

To reveal the nature of the 2PEL of organic-compound crystals and films, we have studied the electronic properties of molecular solutions, crystals, and amorphous and crystalline films, which brought us to the understanding of their energy spectrum structure. In the present work, the results of investigations of the luminescence kinetics are reported and the time-resolved 1- and 2PEL spectra of crystals are shown. The investigations were carried out in the temperature interval 4.2–300 K.

1. Materials and Experimental Method

The investigated organic compound (TCBC) is composed of the heterocyclic derivatives of carbazol molecules of the form $R–CH{=}CH–C(CN){=}C(CN)_2$, R being a fragment of carbazol molecule.

To elucidate the mechanism of the organic crystal PL stimulated by 1- and 2-photon laser excitation, the TCBC compound was investigated in various aggregate states: solutions, films, and single-crystals.

TCBC single-crystals can be produced by a slow evaporation of a solvent from a supersaturated solution. The single-crystals were small plates ($3 \times 2 \times 0.5$ mm) with a well-developed ab-plane.

Due to the thermal sputtering conditions, either amorphous or crystalline films can be obtained. Amorphous films were produced by a thermal sputtering of TCBC in vacuum with a pressure of 10^{-3} Pa on quartz substrates cooled down to 77 K. The film thickness was equal to 0.1 μm. Crystalline films, comprising nanoclusters of various ordering, were produced by a thermal sputtering of TCBC on a non-cooled substrate with a rate of 0.5–1.0 nm/s, followed by annealing at a temperature of 30–40 °C below the melting point. The crystalline film thickness was 0.1–1.0 μm. For the TCBC film transformation from the amorphous into crystalline state to occur, a certain activation energy is needed. The thermal annealing of amorphous films results in producing the crystalline phase.

The emission of a nitrogen laser (λ_{ex} = 337.1 nm, the pulse length t_p = 10 ns, the emission pulse power P = 5 kW, the pulse-repetition rate f = 100 Hz) and the principle emission of a Nd:YAG laser (λ_{ex} = 1064 nm, t_p = 15 ns, P = 0.1 − 1.0 MW, f = 50 Hz) were used to excite PL. The time-resolved PL was registered by means of a stroboscopic system [1–3], which made it possible to record the time-dependence of the PL intensity, and PL spectra with various time delays t_d after the excitation to start. The time resolution of the PL spectra measuring was 0.7 ns. A fast grid
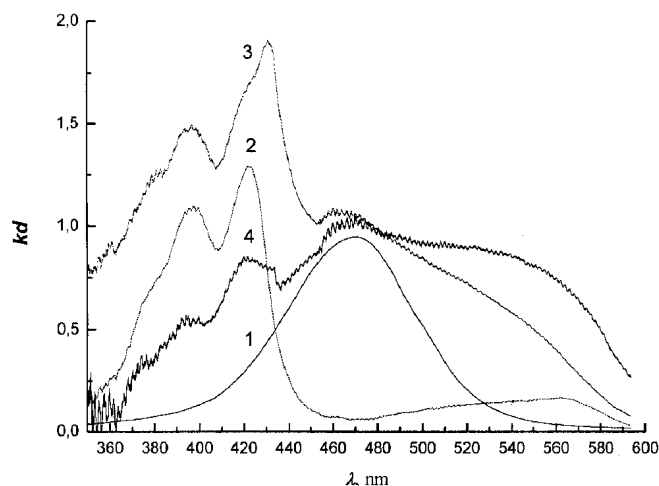
Fig. 1. Absorption spectra of TCBC solutions and films at $T = 300$ K

Fig. 2. Photoluminescence spectra of TCBC solutions at $T = 300$ K

monochromator MDR-12 was used as a spectral device to determine the PL decay time (0.1 ns). The spectral slit width for PL spectra measuring was 0.2–0.4 nm. The spectrum recording was fulfilled in automatic mode with the data supply to a computer.

2. Absorption and Photoluminescence Spectra of TCBC Solutions and Films

The absorption and photoluminescence spectra of TCBC solutions in non-polar (toluene) and polar (CH$_3$CN, acetonitrile) solvents were investigated. The absorption spectra are similar. For TCBC solutions of low concentrations, the band with a maximum at $\lambda = 470$ nm is observed in the long-wave spectrum range, which is connected to the intramolecular charge transfer from the donor carbazol fragments onto the acceptor cyanogroups (Fig. 1, curve 1). In the short-wave range, the $\lambda = 350$ nm band is observed (not depicted in Fig. 1), being connected to the carbazol fragment absorption. While the TCBC concentration increases, the $\lambda = 470$ nm band broadens to both sides, which may be due to the formation of molecular aggregates. Electron-microscopy studies of amorphous substances with a molecular structure [4] showed that the average order in them is defined by a molecule packing in pairs, whose mutual orientation changes (relaxes) at the amorphous–crystalline phase transformation. This may serve as an explanation of the fact that, in the absence of the translational symmetry features in the absorption spectra of amorphous films, the pairs of bands can be distinguished which are typical of crystals.
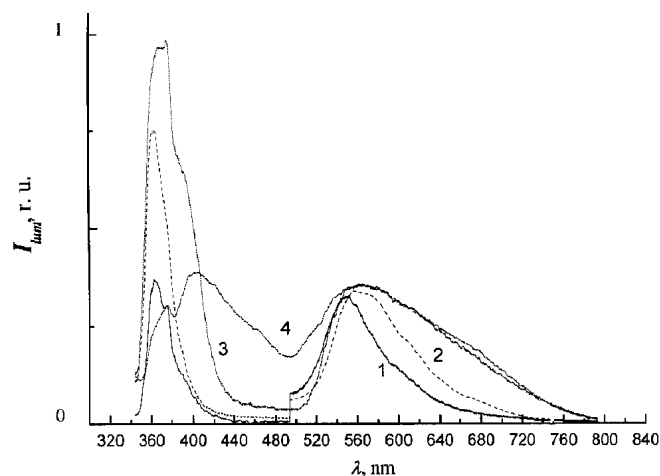
The absorption spectra of the amorphous (curve 2) and crystalline (curves 3 and 4) TCBC films are also depicted in Fig. 1. In contrast to the monomer molecular absorption spectrum (the $\lambda = 470$ nm band), a pair of bands, typical of the crystal phase, can be distinguished in the film absorption spectra. These are the $\lambda = 422$ and 560 nm bands. The first one is larger by amplitude in the amorphous film absorption spectrum. Such a distribution is characteristic of a "predimer", i.e. close to the dimer type, sandwich-like disposition of the TCBC molecules in the pair, where their electric moments are antiparallel and compensate each other [5]. For TCBC crystalline films, an increasing of absorption intensity in the long-wave spectrum range and its decreasing in the short-wave one are observed (curves 3 and 4). This corresponds to the formation of nanoclusters, possessing the translational symmetry, in TCBC crystalline films.

The structure of the PL spectra of the TCBC solutions, in contrast to the absorption ones, essentially depends on both the solvent polarity and the TCBC concentration (Fig. 2, curves 1–4). In the PL spectra of solutions, one can observe the emission of either monomers or molecular aggregates, which depends on the TCBC concentration. For low TCBC concentrations in the polar solvent, the band of molecular emission with $\lambda = 540$ nm is observed (curve 1). A substantial Stokes shift of the band is stipulated by a substantial intramolecular charge transfer in the excited state. An increasing of the TCBC concentration results in the formation of molecular aggregates and the shift of the PL band maximum to 560 nm (curve 2).
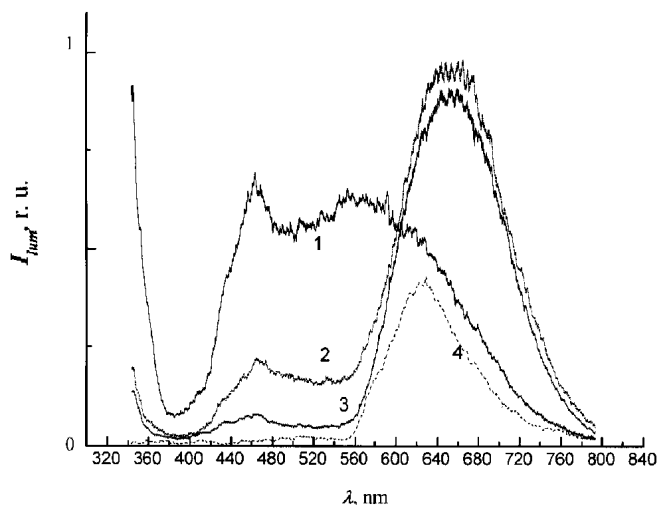
Fig. 3. Photoluminescence spectra of TCBC films and crystals at $T = 300$ K

Fig. 4. Spectra of 2-photon-excited luminescence of TCBC films and crystals at $T = 300$ K

In the toluene solutions of TCBC, molecular aggregates are formed even at low concentrations. The PL spectra at low and high TCBC concentrations are similar now (curves *3* and *4*). The long-wave PL band is strongly broadened and its maximum is at $\lambda = 570$ nm. A comparison of the PL and absorption spectra of the TCBC solutions shows that molecular aggregates are in the predimer state. Their absorption is defined by a monomer one, and the emission is of the excimer type.

The PL spectra of the amorphous (curve *1*) and crystalline (curves *2* and *3*) TCBC films, as well as of the TCBC single-crystal (curve *4*) are displayed in Fig. 3. The PL spectrum of the amorphous film (curve *1*) represents a wide non-structured band with the maximum at $\lambda = 580$ nm, which is typical of the excimer emission. The spectrum is similar to those of TCBC solutions in toluene. For amorphous films, an ensemble of predimer states is typical, with various molecular interspaces and interpair orientations. If high-energy electron states are excited, an electron excitation relaxes during the life-time to the lowest excited state, and its future realizes either in emission or in the further relaxation with a localization at structural defects.

The PL spectra of the crystalline films (curves *2* and *3*) and the single-crystal (curve *4*) are different to some extent, which may be connected to a difference in the molecule packings of a bulk TCBC crystal and nano-sized crystals in the film.
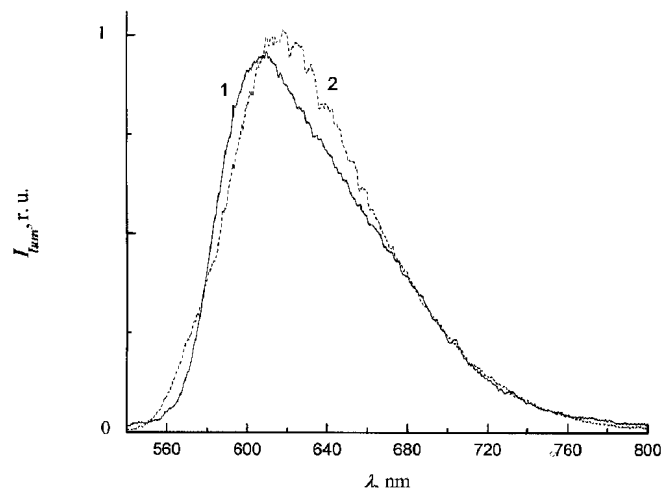
3. 2-photon-excited Photoluminescence of TCBC Films and Crystals

For thermally annealed TCBC films, an intense PL is observed (Fig. 4, curve *1*) under 2-photon excitation ($\lambda_{ex} = 1064$ nm). It can be watched in the PL spectra recorded with a nanosecond time delay, as well as in the stationary ones recorded with no delay. The stationary spectra of the 2PEL in the cases of crystalline films (curve *1*) and single-crystals (curve *2*) are similar. For amorphous TCBC films with the same IR excitation levels, the 2PEL is not observable. For thermally annealed TCBC films, the stationary and nanosecond-delayed PL spectra reveal the band with a maximum at $\lambda = 610$ nm.

In Fig. 5, the time-resolved PL spectra, with a nanosecond time delay, of the TCBC single-crystals for the 1-photon ($\lambda_{ex} = 532$ nm, curves *1* and *2*) and 2-photon ($\lambda_{ex} = 1064$ nm, curves *3* and *4*) excitations are presented. At the 1-photon excitation, the PL band maximum was at $\lambda = 615$ nm and shifted towards longer wavelengths at the 2-photon one. Its positions for short ($t_d = 0.7$ ns) and long ($t_d = 8$ ns) time delays were at $\lambda = 625$ and 635 nm, respectively. The decay time for both 1- and 2PEL is $\tau = 2$ ns. Similarly to the single-crystal case [1], the 2PEL of the crystalline TCBC films is observed at low IR laser radiation levels.

4. Discussion

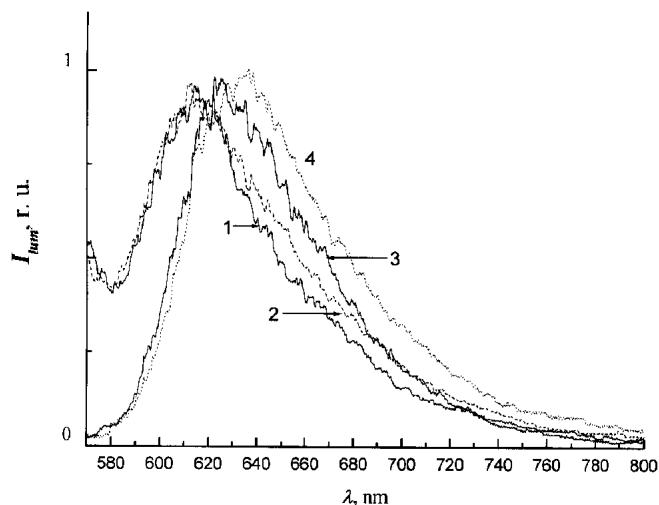The molecules, which are the heterocyclic derivatives of a carbazole molecule, are polar in the ground state due

Fig. 5. Photoluminescence spectra of TCBC crystals at $T = 300$ K for 1- (curves 1, 2) and 2-photon (3, 4) excitations

Fig. 6. Reflectance ($T = 4.2$ K, curves 1 and 2) and photoconductivity ($T = 300$ K, curve 3) spectra of TCBC crystals

to the electron transfer from the $C(CN)_2$ atom group onto the N atom of a carbazole molecule. The dipole moment of the molecules is substantially larger in the excited state. If molecular clusters are present in TCBC solutions and films, photon absorption is accompanied not only by the intramolecular charge transfer but also by the intermolecular one, i.e. excitons with charge transfer (CT-excitons) are formed [6].

The studies of the reflection spectra of TCBC single-crystals and the investigations of the photocurrent in them showed that the interaction between molecules is one-dimensional (1D) and the photoconductivity is intrinsic. In Fig. 6, the reflection spectra of TCBC crystals are depicted, which were measured in polarized light at the temperature $T = 4.2$ K (curves 1 and 2). They correspond to the reflection of the incident light with A- ($\mathbf{E} \parallel \mathbf{a}$, curve 1) or B- ($\mathbf{E} \perp \mathbf{a}$, curve 2) polarization from the ab-plane of the crystal, $\mathbf{E}$ being the E-vector of the wave. In the A-polarization curve, a narrow intense band with the peak at $\lambda = 550$ nm can be distinguished, which is due to molecular exciton excitations connected to the intramolecular charge transfer. For B-polarization, the reflection spectrum has no structure. Here, there are the $\lambda = 600$ and 650 nm bands, weak by intensity, which may be related to the intermolecular charge transfer and the formation of CT-excitons. The most intense absorption of the TCBC molecule is due to the intramolecular charge transfer along its long axis. The reflection spectra evidence for that TCBC molecules in a crystal are disposed in parallel to the a-axis. The same packing ordering takes place in
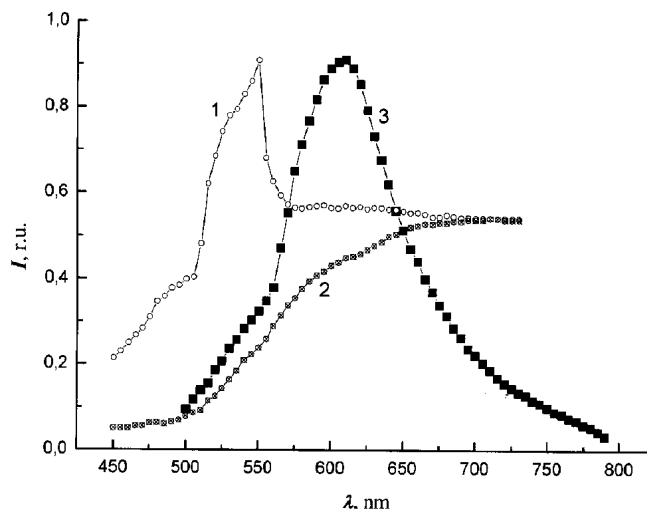
nanoaggregates emerging after the thermal annealing, since the band 550 nm is also observed in their reflection spectra. Due to the same reason, the ab-planes of the most portion of those aggregates can be assumed to be oriented in parallel to the substrate surface.

The low-temperature investigation of the reflection spectra of TCBC single-crystals and crystalline films allowed us to discover a common feature in the crystal packings typical of $1D$ structures. In both instances, the narrow intense band with a maximum at $\lambda = 550$ nm for single-crystals and $\lambda = 560$ nm for nanocrystalline films can be singled out. This band is associated with the strong light absorption with A-polarization, i.e. when $\mathbf{E} \parallel \mathbf{a}$ and is directed along the $1D$ nanoaggregates. In the absorption spectra of thin crystalline films, this band does not manifest itself, because the light absorption with B-polarization, i.e. across the $1D$ nanoaggregate, is very weak. At the same time, it is well distinguished in low-temperature PL excitation spectra.

There is no second-harmonic generation in TCBC crystals [1]. This indicates that TCBC crystals possess central symmetry. Due to this and since the TCBC nanoclusters are also central-symmetric (the static dipole moments of the molecules in a pair are mutually compensated), two different molecular packings in an elementary cell are possible. In the first case, the static dipole moments of two adjacent molecules in a linear aggregate are antiparallel to each other (a "head-to-head" molecule packing in a dimer). In the second case, the static dipole moments of molecules in a molecular chain are directed identically (a "head-

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to-tail" packing),but their directions are opposite for two adjacent chains (excimer model). Each of two antiparallel chains has the strong resonance dipole—dipole interaction of molecules and forms the J-aggregate [7]. In the excimer model, the elementary cell of a crystal (or a nanocluster) is composed of two parallel molecules with oppositely directed static dipole moments. In the ground state, the interaction between two adjacent chains in the crystal is weak and does not affect the 1-photon-absorption spectra. But when excited, two molecules in a cell may interact strongly. This results in the creation of a localized excimer state, which reveals itself in PL spectra. As was shown in [8,9], the investigations of 1- and 2-photon-absorption spectra and the related PL, allows one to single out the transitions with intermolecular charge transfer against the transitions with intramolecular one, and to determine which of two packings of polar molecules possible in a central-symmetric crystal is in action.

The intermolecular charge transfer between interacting molecules in an elementary cell was shown [8] to result in substantial dipole moments in the ground and excited molecule states, in large matrix element values corresponding to dipole transitions between the ground and excited states of an excimer, and in the resonance frequency dependence of the 2-photon-absorption coefficient. The scheme of the excimer energy levels is outlined in Fig. 7. The 2-photon-absorption coefficient is determined by the imaginary part of the third-order susceptibility and can be expressed as follows [8]:

$$\alpha_{2pa}(\omega) \propto |\Delta\mu|^2 \, |\mu|^2 \, \frac{\Gamma_{+g}}{\left[\left(\Omega_{+g} - 2\omega\right)^2 + \Gamma_{+g}^2\right]}, \qquad (1)$$

where $\mu = \langle\psi^-|\hat{\mu}|\psi_g\rangle$ is the dipole matrix element of the transition between the ground and excited molecule state at the 1-photon absorption, $\Delta\mu = \langle\psi^+|\hat{\mu}|\psi^-\rangle$ is the dipole matrix element of the transition between the excited states of the pair of interacting molecules, ψ_g is the ground state wave function of the molecular pair, ψ^+ and ψ^- are the wave functions of the excimer doublet states, Ω_{+g} is the frequency of the optical transition accompanied by the charge transfer between the ground (ψ_g) and excited (ψ^+) states of the molecular pair, which is forbidden for 1- and allowed for 2-photon-absorption, and Γ_{+g} is the decay rate of the excited state ψ^+. For the TCBC molecular aggregates under investigation, a large value of $\Delta\mu$ is related to the intermolecular charge transfer. It can be found from the Stark effect measurements.
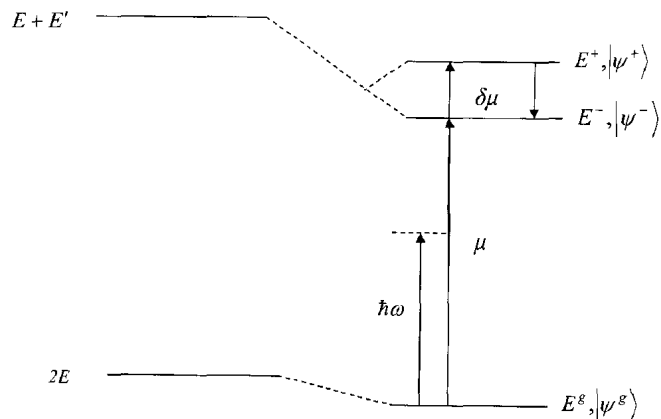

Fig. 7. Energy level scheme for a physical dimer and an excimer. E and E' are the ground and excited, respectively, state energies of physical dimer molecule, E^g is the ground state energy of an excimer, E^- and E^+ are the energies of excimer doublet states

The frequency dependence of the TCBC crystal photoconductivity is shown in Fig. 6 (curve 3). Its maximum is at $\lambda = 605$ nm. For $\lambda > 550$ nm, the photoconductivity spectra for A- and B-polarized light are identical. A comparison of the reflection and photoconductivity excitation spectra (Fig. 6) and those of 2PEL (Fig. 5, curves 3 and 4) evidences for that the CT exciton band in the TCBC crystal is situated somewhat lower than the conduction band and the band of exciton states with intramolecular charge transfer. The energy gap between the conduction and CT-exciton bands, $E_c - E_{\text{CT}} \approx 0.08$ eV, determines the activation energy of the CT-exciton thermal dissociation into electron-hole pairs. The energy gap between the electron and hole conduction bands is approximately 2.25 eV.

This energy spectrum model for TCBC crystals is typical of the crystals with charge transfer [10–13], in which the conduction and molecular exciton bands overlap, while the CT-exciton band is situated somewhat beneath.

The photoconductivity of such crystals is governed by the excitation of CT-states and a subsequent heat-activated decay of the latter into free current carriers. A numerical value of the strength of the CT-transition oscillator is proportional to $S^2 d^2$, where S is the overlapping integral of the wave functions of two adjacent molecules and d is a distance between them. It is evident that the strength of the CT-transition oscillator in TCBC crystals slightly depends on the polarization direction of the incident light and, correspondingly, the structure of the photoconductivity

spectrum is also independent of it. As was noted above, two types of molecule packing are possible for structures with central symmetry, which the linear aggregates and TCBC crystals belong to: "head-to-head" and "head-to-tail" (excimer) ones. The bipolar disposition of molecules in a cell of the crystal (nanocluster) results in disentangling the energy bands [8,9]. Due to a stronger overlapping of the wave functions of two neighbor molecules, the excimer packing is energy-gained. The probability of the thermally induced creation of such a packing is maximal in crystals at high temperatures. Therefore, the 2-photon absorption and the 2PEL are connected to the creation and deactivation of local excimer states. As a consequence, the large intensity of PL is observed for TCBC crystalline and nanocrystalline structures, being several orders of magnitude greater than that for TCBC amorphous films under the same intensities of the exciting IR radiation. The results presented in the present work show that, on the basis of the investigations of the PL of linear molecular clusters, it is possible to consider the problems of molecular packing and intermolecular charge transfer.

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ВПЛИВ АГРЕГАТНОГО СТАНУ НА ОДНО- І ДВОФОТОННУ ЗБУДЖЕНУ ФОТОЛЮМІНЕСЦЕНЦІЮ 3,4,4-ТРИЦІАНОБУТАДІЄНКАРБАЗОЛУ

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Р е з ю м е

В залежності від агрегатного стану в спектрах фотолюмінесценції спостерігалось свічення мономерів, димерів та кристалічних агрегатів. Показано, що для кристалічних і нанокристалічних структур інтенсивність двофотонної збудженої фотолюмінесценції на декілька порядків вища ніж для аморфних плівок при тих же інтенсивностях збуджуючого інфрачервоного випромінювання.