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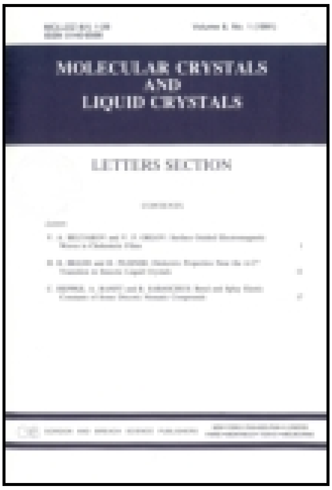

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Complexation in Composite Solutions of Melanin with 2,4,7-Trinitrofluorenone

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Complexation in Composite Solutions of Melanin with 2,4,7-Trinitrofluorenone

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A feasibility of formation of donor-acceptor charge-transfer (CT) complexes between melanin and 2,4,7-trinitrofluorenone (TNF) being good electron acceptor has been studied in solutions by means of the absorption and photoluminescence (PL) spectra. The model of electronic transitions in a melanin-TNF composite solution has been proposed.

Keywords Melanin; charge transfer complexes; time-resolved photoluminescence; excitation of photoluminescence maps; exciplexes

Introduction

Melanin as the compound possessing semiconductor properties is well known from the 1970s, when the effect of switching from a low conductive to high conductive state was observed in melanin in a comparatively low electrical field [1]. Both natural and synthetic melanins have found practical applications in different fields. Nevertheless, the molecular arrangement of natural melanins is remained vague due to their very complicate structure. It is known that melanin pigments are super-molecular compounds, which are formed at the oxidation of phenols, mainly pyrocatechin, 3,4-dioxyphenylalanine and 5,6-dioxyindole [2]. All melanins have a series of common structural features that make them similar to organic amorphous semiconductors taking their electronic properties into account. The periodic stacking structure and/or polymeric macromolecular structure with long π-conjugated parts are characteristic features of melanin [2]. Melanins also combine the structural properties of biopolymers and spectral properties of disordered inorganic semiconductors [3].

In addition, it was shown [2] that melanin has photovoltaic response in a wide spectral range. The creation of effective organic photovoltaic (PV) solar cells became possible due to the recent studies evidencing that the photovoltaic sensitivity can be enhanced, as well as the spectral range of PV responses can be widened by the addition of dyes and other compounds to different polymers resulting in a system that would be able to induce the formation of donor-acceptor (D-A) pairs. For melanin having comparatively low PV

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sensitivity, the process of enhancement of the PV response is rather more important than the spectral sensibilization.

In our earlier works [4, 5], we began the study of a natural melanin pigment absorbing light in a wide spectral range from UV to 1 μm and having semiconductor properties with the optical band gap $E_g = 1.2$ eV. Due to a great number of single and double bonds, the electrons in a melanin macromolecule can easily became free and be excited in a wide spectral range including UV and visible regions. In this case, the formation of donor-acceptor pairs or charge transfer complexes (CT complexes) in the ground state between melanin macromolecules and a good acceptor of electrons can be an important step to the enhancement of the integral PV response. Melanin macromolecules consist of indole derivatives, including both positively and negatively charged groups [6], as well as the reaction-capable tail groups C=O, OH, COOH. Thus, this complicate macromolecular compound can create complexes of different types, either electron acceptor type or electron donor type.

In this paper, we discuss a possibility of the formation of donor-acceptor (D-A) complexes between melanin macromolecules and the well-known good acceptor of electrons, 2,4,7-trinitrofluorenone (TNF). The values of the electronic affinity, A_g, and the ionization potential, I_g, are well known for TNF and amount to 0.95 and 7.4 eV, respectively. We study the absorption spectra, steady-state and time resolved PL spectra, as well as the excitation of PL (EPL) maps of a melanin water solution and two-component composite solutions of melanin and TNF in acetonitrile.

Experimental

Studied water-soluble melanin has plant origin and was obtained by an extraction [4, 5]. The chromatography and elemental analysis have shown that this melanin has a chemical structure similar to that of synthetic melanin based on 5,6-indolequinone monomer [2]. In [4, 5], it was stated that 5,6-indolequinone molecules are chemically connected and form polymers or planar two-dimensional molecular oligomers in the form of macromolecular disks, in which chromophores with different lengths of π-π conjugation can be observed. One-dimensional aggregates with stacking arrangement (H-aggregates) can be further formed from two-dimensional oligomers.

Absorbance spectra were recorded using a Shimadzu UV2450 UV-VIS spectrophotometer with a 240 nm/min scan speed and 2 nm bandpass. All spectra were collected using a 1-cm square quartz cuvette. Solvent scans obtained under identical conditions were used for background correction.

Steady state and time-resolved PL spectra were measured with a set-up based on an MDR-12 monochromator (LOMO) equipped with a photoelectric system and via an interface card connected with PC [7]. The bandpass was 0.2–0.4 nm. For spectra measurements, PL was excited by a pulsed nitrogen laser with the wavelength 337.1 nm. The duration of a laser pulse was 9 ns, the frequency of pulses was 70 Hz, and the intensity of a laser pulse was 2 kW. To register the kinetic and time-resolved PL spectra, the stroboscopic system with "time window" equal to 0.1 ns was used. It allows us to measure the PL spectra with different delay times, t_d, in respect to the laser pulse. The time resolution of the set-up at the measurement of PL spectra was 0.7 ns and was defined by the front steepness of the laser pulse. The time resolution of PL kinetics was equal to the width of an oscilloscope strobe (0.1 ns). PL spectra were measured at 77 K and room temperature (RT).

Fluorescence emission spectra at different excitation wavelengths (excitation of PL maps – EPL maps) were recorded using a Jobin Yvon system (Horiba Scientific), and

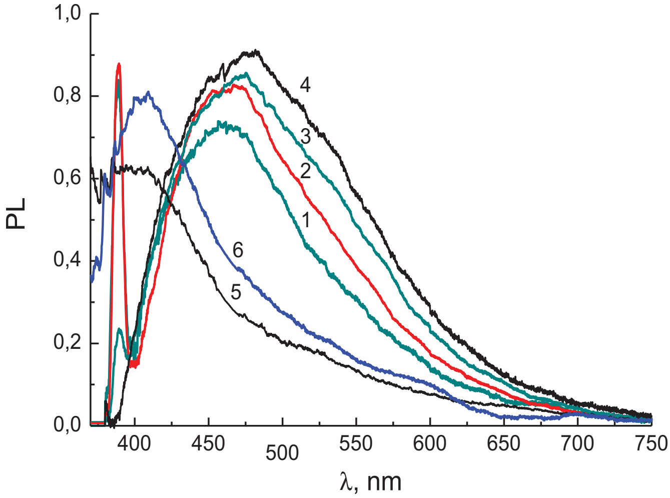

Figure 1. Steady state (1-4) and time-resolved (5-6, $t = 0$-1 ns) PL spectra of different concentrations, C, of melanin in water solutions (1-5) and indole in acetonitrile (6) at room temperature, RT, (1-4) and 77 K (5,6). The concentrations of melanin - $C = 10^{-5}$ g·cm^{-3} (1); 10^{-4} g·cm^{-3} (2); 10^{-3} g·cm^{-3} (3); $2{\cdot}10^{-2}$ g·cm^{-3} (4).

FluoroLog-3 fluorimeter using a 2-nm bandpass and an integration time of 1 s. The system has a xenon lamp as an excitation light source. Matrix scanning software allowed excitation and emission intervals of 1 nm. Solvent scans were again performed under identical instrumental conditions for the background correction. Spectra were precorrected to account for differences in the pump beam powers at different excitation wavelengths using a reference beam.

Results and Discussion

The spectra of steady-state PL for water solutions of melanin with different concentrations, C, are shown in Fig. 1 (curves 1–4). In fact, the change of C in wide range doesn't lead to any significant changes in the spectral shape of PL. PL maximum is only shifted insignificantly to the long wavelength side from 460 to 480 nm with increase of the concentration. The lifetime of melanin PL in the maxima of 480 and 460 nm are 3.2 and 2.4 ns, respectively. Time resolved PL spectrum (curve 5, $C = 2{\cdot}10^{-2}$ g·cm^{-3}), measured with $t_d = 0$-1 ns, coincides to the spectra of PL at a low concentration of melanin ($C = 10^{-5}$ g·cm^{-3}). At low temperature (77 K) the maximum of PL spectrum of a solid melanin solution is strongly displaced to the short wavelength side amounting 400 nm. Figure 1 also shows the PL spectrum (curve 6) of indole solution in acetonitrile, which is similar at whole to the low-temperature spectrum of a melanin water solution.

As for our earlier results [4, 5], the present studies of the concentration and temperature dependences of melanin PL are in good agreement with the model of the formation of melanin oligomer aggregates with stacking arrangement in a solution. Due to a weak interaction between oligomers in the ground state, they form pre-dimeric structures in the stack. At a high concentration ($C = 2{\cdot}10^{-2}$ g·cm^{-3}), melanin solutions are similar to liquid crystalline discotics. Their absorption spectrum is similar to those at low concentrations. Due to the intermolecular interaction in the ground state both molecular and excimeric

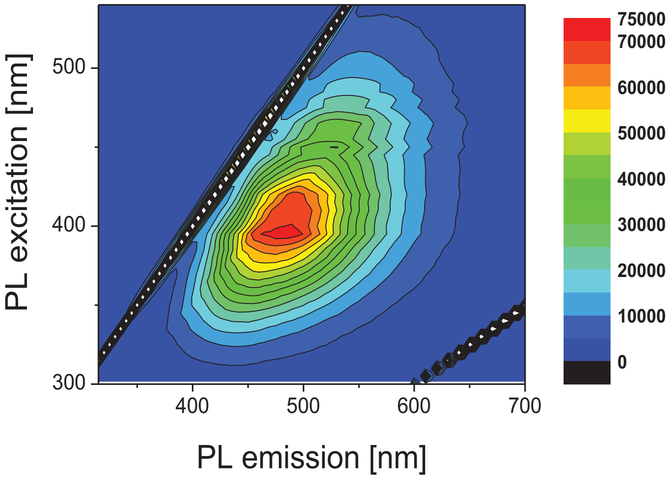

Figure 2. Excitation photoluminescence (EPL) maps at RT for a water solution of melanin.

irradiation of melanin can be observed in the PL spectra of melanin solutions. Ageing of melanin solution for longer time results in a crystallization of oligomers with the formation of water insoluble nano-aggregates consisted of a few oligomers.

In Fig. 1, it is seen that, at RT and high concentrations, PL spectra of melanin solutions are defined mainly by excimeric irradiation (480 nm band). The observed fluctuations of the PL band maximum position from 460 to 480 nm depend on oligomer sizes, the order of π-π conjugation of monomers in an oligomer, and the overlapping order of melanin fragments in the excited state.

The monomeric irradiation has a shorter lifetime compared to an excimer, being shifted to shorter wavelengths and predominated in PL spectra at low temperatures with respect to the excimeric spectrum. At low temperatures, due to structural problems, the formation of excimer states between two oligomers of melanin is difficult, and mainly the monomeric radiation of individual oligomer chromophores occurs in the PL spectra of solutions. Since melanin is composed of indole derivatives, the low-temperature PL spectrum of melanin solutions with the band at 400 nm can be identified with its monomer emission.

In Fig. 2, the EPL map displays the PL intensity for a given excitation wavelength (vertical scale) and a given emission wavelength (horizontal scale) at RT. The colour scale of the intensities is plotted on the right part of the graph. From the above map, it can be seen that the PL intensity maximum at RT is observed in the excimer part of radiation (450–520 nm), and the excitation is observed in the region of the monomer excitation of pre-dimeric structures - 380–420 nm. This confirms the above assumptions about the nature of excited states of melanin in solution. The PL maximum shift with the excitation wavelength change revealed in the EPL map is similar to that observed earlier in chemically synthesized melanin (eumelanin) [8].

Figure 3 shows the absorption spectra of an acetonitrile solution of TNF with melanin, as well as its spectra of neat solutions. The absorption spectrum of solutions and films of melanin is a structureless band starting in the UV range and decreasing in intensity to zero around 1000 nm [1]. Molecular solutions of TNF in acetonitrile mostly absorb at short wavelengths $\lambda < 450$ nm.

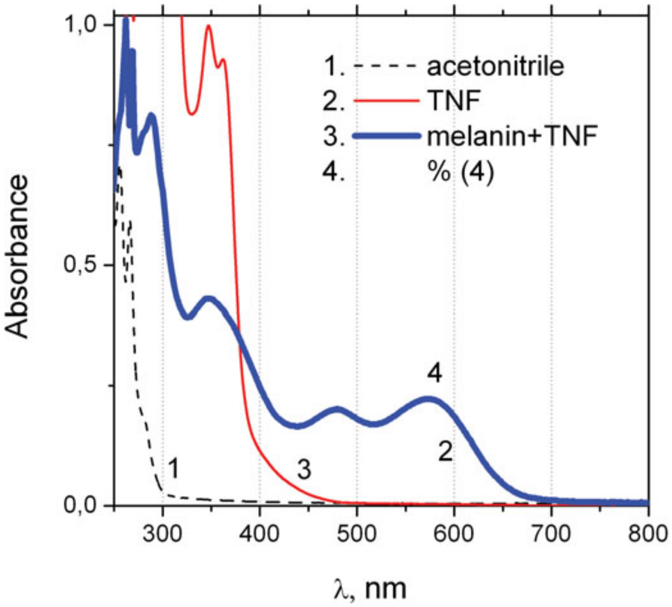

Figure 3. Absorption spectra of acetonitrile (1), solution of melanin (2), acetonitrile solution of TNF (3), and mixture of melanin with TNF (4).

In the long-wavelength range of the absorption spectra for solutions of the two-component system, two new bands at 480 and 570 nm appeared. Evidently, the bands are not present in the absorption spectra of the neat solutions of melanin and TNF. The appearance of two absorption new bands of 480 and 570 nm in the absorption spectra of the composite solutions most probably can be associated with the absorption of CT D-A complexes formed in the ground state between the oligomers of melanin and TNF. In the range of 250–320 nm, where the TNF absorbance is strong, there are blurry bands slightly shifted to shorter wavelengths relative to TNF peaks.

Figure 4 shows the PL spectra of the acetonitrile solutions of melanin, TNF, and melanin with TNF. The PL spectrum of melanin solution at room temperature is a broad band with a maximum at 465 nm. The PL band of TNF molecules in acetonitrile has a maximum near 500 nm. At high concentrations of melanin, it disappeared as a result of the complex formation. Complexation in the ground state leads to dramatic changes in the spectra of PL. In the PL spectra of melanin solutions with TNF (1:1 mass ratio), a quenching for the PL band of melanin and TNF is observed, and, on the short wavelength side, there is a new intensive band at 425 nm, the intensity of which is more than an order of magnitude superior to that of the band at 480 nm. In the long-wavelength part of the spectrum, a weak PL band at ca. 650 nm and a shoulder at 550 can be identified.

Thus, the present experimental data on the absorption and PL spectra of solutions of the natural melanin pigment with electron acceptor TNF in acetonitrile indicate the formation of weak CT complexes between the molecules of melanin and TNF both in the ground and excited (exciplex) states. Unlike an excimer, where the interplanar orientation in a pair of two interacting melanin oligomers plays an important role, in the exciplex, the intermolecular CT interaction in the excited state can proceed through the peripheral end groups.

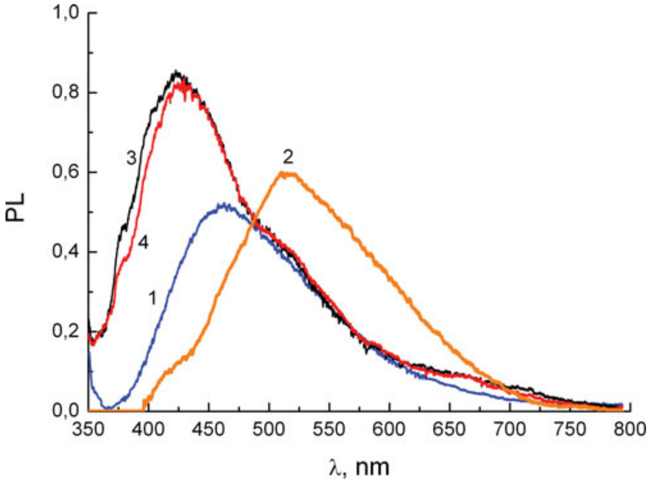

Figure 4. Steady-state (1,2,3) and time-resolved (4) [$t = (0\text{-}4)$ ns] PL spectra at RT of solutions of melanin (1), TNF (2), and the mixture of melanin with TNF (3,4) in acetonitrile. The PL intensity of curves 3 and 4 is twelvefold lowered.

The nature of the long wavelength absorption bands at 480 and 570 nm in solutions of melanin with TNF, as in the case of complexes of well-studied polymers, such as PVC, with TNF [9] can be associated with the formation of CT complexes between TNF and melanin molecules in the ground state. In the PL spectra, these CT complexes correspond to the bands at 550 and 650 nm. This assumption is confirmed by measurements of EPL maps with the excitation wavelength (vertical axis) and a given wavelength (horizontal axis), where the weak emission bands at ca. 550 and 650 nm are identified at the excitation wavelengths of ca. 480 and 570 nm, respectively (Fig. 5). The appearance of an intensive band of PL at 425 nm in the two-component systems and the quenching of the excimer band for melanin at 480 nm can also be associated with the formation of weak CT complexes or exciplexes between one of the monomeric components of the melanin oligomer and a TNF molecule. The excitation of exciplexes can go both via a macromolecule of melanin and via a TNF molecule. In the case of melanin macromolecule excitation, the active centres of PL

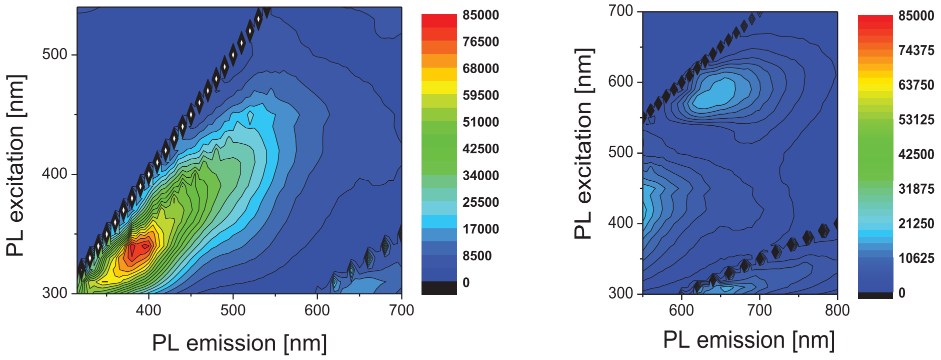

Figure 5. Excitation photoluminescence (EPL) maps at RT for a solution of melanin and TNF in acetonitrile.

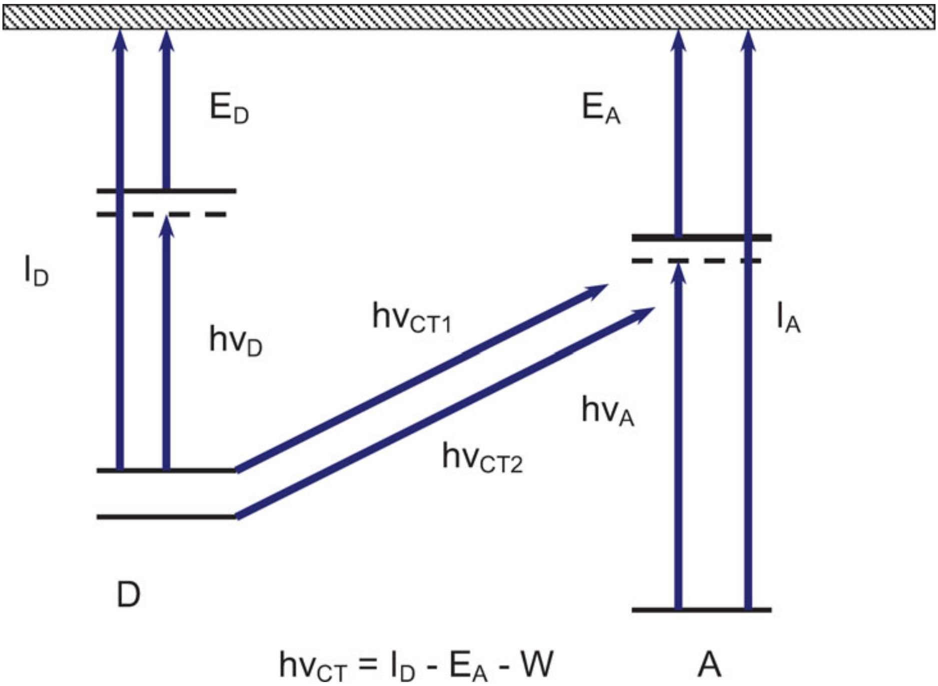

Figure 6. Scheme of electronic transitions to CT states in the melanin-TNF system.

excitation may be its structural elements (5,6-indolequinone monomers, 5,6-dioxyindole, and others), which may have properties of a donor or an acceptor with respect to TNF. The last assumptions are evidently supported by the data on EPL maps for melanin solutions with TNF (Fig. 5). As can be seen from Fig. 5, the excitation of PL for D-A complexes in the 650-nm band can be conducted in three spectral regions: 550–620, 380–470, and 300–320 nm, which can be obviously associated with the absorption of newly formed CT complexes and structural monomeric elements of melanin.

The spectral range of 550–620 nm (see Fig. 3) corresponds to the absorption of CT complexes (peak of absorbance at 570 nm). In addition, the excitation of CT complexes is occurring via the band at 470 nm, which is observed in the absorption spectra of binary solutions and is not observed in the absorption spectra of the neat solutions of melanin and TNF (Fig. 3). The absorption bands with maxima at 480 and 570 nm can be interpreted as the transitions from the two uppermost levels of the donor in the CT complex. In addition, the spectral regions of 380–470 nm and 300–320 nm, via which the excitation of 650 nm PL band takes place, can be correlated with the excitation of the monomeric fragments of melanin oligomers in pre-dimeric states. These states have a similar structure to CT complex, but with a weak interaction in the ground state. In this case, the excitation of D-A complexes (exciplexes) can go via a melanin macromolecule (the excitation region 380–420 nm) and via a TNF molecule (excitation region 300–320 nm).

The new transitions observed in the absorption spectra of CT complexes of melanin with TNF can be interpreted in accordance with the Mulliken theory [10]. The energy of the band at 570 nm can be defined by a transition from the upper occupied level of the donor (one of the monomers of melanin forming an oligomer) to the lowest unoccupied

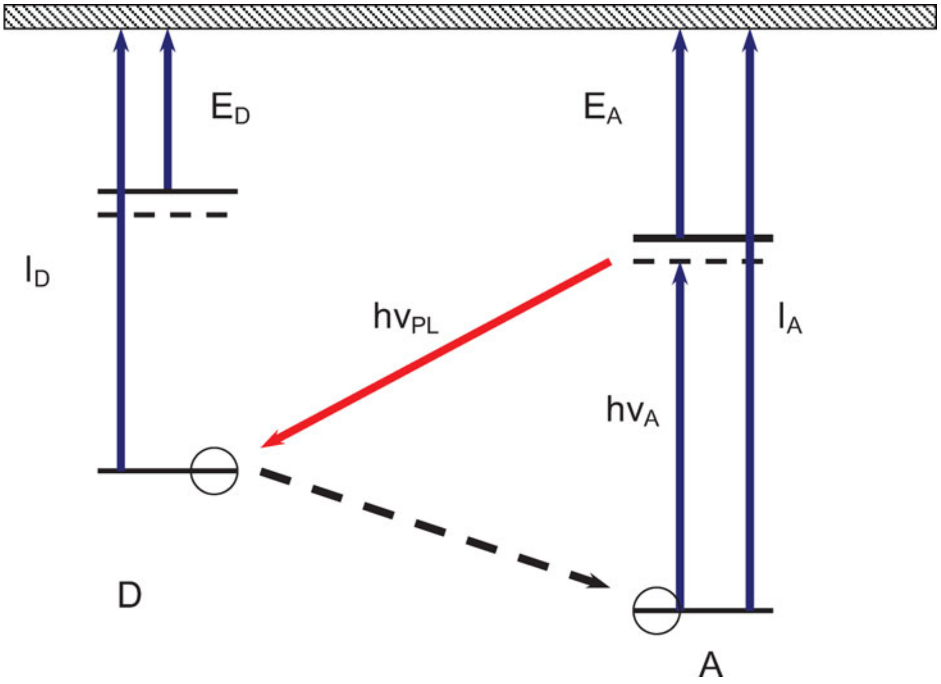

Figure 7. Scheme of the formation of exciplexes in the melanin-TNF system.

level of the acceptor. The energy $h\nu$ of such transition can be expressed as

$$h\nu = I_D - E_A - W,$$

where I_D – ionization energy of the donor, E_A – the electron affinity of the acceptor, W – energy of the excited state, $W = q^2/\varepsilon r$ – energy of Coulomb interaction of the donor and acceptor in the CT state in a medium with permittivity ε. The presence of the second CT absorption band at 480 nm can be attributed to a charge transfer from the level lying under the highest occupied level of one of the monomers of the donor or the highest occupied level of the other monomer, which is a part of the melanin oligomer and has a higher energy of ionization, to the lowest unoccupied level of the acceptor.

The model of electronic transitions in melanin-TNF composites is summarized in Figs. 6 and 7, where E_A and E_D are electron affinities of the acceptor and donor, respectively, as well as I_A and I_D are ionization energies of the acceptor and donor, respectively. The transitions to CT states are shown in Fig. 6, where $h\nu_{CT1}$ corresponds to the lower energy CT state at 570 nm (ca. 2.18 eV), and $h\nu_{CT2}$ is associated with the higher energy CT state at 480 nm (ca. 2.58 eV).

The formation and the emission of exciplexes from the point of view of molecular orbitals (excited acceptor) [11] are shown in Fig. 7. $h\nu_{PL}$ is PL emission from a lower unoccupied molecular orbital of the acceptor (TNF) to a higher occupied molecular orbital of the donor (melanin).

Conclusions

Thus, the absorption spectra, PL spectra, and excitation PL maps have been studied for solutions of the two-component system based on the natural pigment, melanin, and a good electron acceptor, 2,4,7-trinitrofluorenone (TNF). In the long-wavelength region of the absorption spectra of these solutions, there are new bands with maxima at 480 and 570 nm, which are not present in the absorption spectra of solutions of the corresponding one-component systems. In the spectral range of 250–310 nm (absorption region of TNF solutions), a broadening and a shift of the bands have been observed. The new bands at 425 and 650 nm, as well as a shoulder at 550 are appeared in the PL spectra of two-component systems.

The presented experimental data are the evidence of the donor-acceptor interaction between the macromolecules of melanin pigment and TNF, as well as the formation of weak charge-transfer complexes (CT complexes) in the ground and excited states. Thus, the model of electronic transitions in melanin-TNF composite solution has been proposed (see schemes in Figs. 6 and 7).

Acknowledgments

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