RADIATION SENSITIZATION OF THE IDLE VOLTAGE SPECTRUM IN THE PHOTOACTIVE LAYERS OF THE C_{60} MOLECULES AND SQUARAINE DYES DBSQ

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Quantum-chemical calculations of geometry, charge transfer, energy states, localization of molecular orbitals, optical transitions for complexes of fullerene C_{60} molecules and DBSQ squaraine dyes were obtained. Optical absorption spectra of C_{60}-DBSQ two-layer films are investigated. It is shown that the films form J-aggregates of dye and complexes with charge transfer C_{60}-DBSQ on the interface. The presence of these complexes leads to the complex structure of the idle voltage spectra. The emergence as a result of high-energy electron irradiation ($E_e =$ 1.8 MeV) with an absorption dose of 2.0 MRad [2+2]-the cyclic connection between fullerenes and dye significantly affects the formation of complexes with charge transfer. The indicated effect results in radiation sensitization of the idle voltage spectra, which manifests itself in the hypsochromic shift of its bands and the modification of the photosensitivity of the photovoltaic cells.

INTRODUCTION

The perspective direction of the development of organic solar energy is the use in the photovoltaic cells of the fullerenes C_{60}, C_{70} or their functionalized derivatives, which belong to the semiconductors n-type. The creation of their nanocomposites with polythene polymers belonging to the p-type semiconductors already allows for an effective conversion of light energy in solar cells by about 10%.

The indicated efficiency essentially depends on the configuration of the structure of the organic photovoltaic cells, which exists in two types. The first type corresponds to a layer morphological structure in which the active photovoltaic components of n- and p-types are applied in separate layers on each other. In such cells there is a surface heterojunction with two photoactive layers formed on the interface. The second type of architecture of organic photovoltaic cells include a volumetric heterojunction. This heterojunction is formed by one photoactive layer, representing a mixture of donor and acceptor components.

Among polydrenous donors in photovoltaic cells often used dyes [1–6]. A special place is occupied by studies of photogenic properties in photovoltaic cells of squaraine dyes. The squaraine dyes include electrons rich in squaraine acid molecules. They are characterized by narrow and intense absorption bands and fluorescence in the near infrared region [7–9].

At the same time, they undergo photovoltaic processes due to singlet and triplet excitations with subsequent dissociation of charges, which significantly affect the characteristics of these dyes as donor components of organic solar cells [10].

Squaraine dyes in films tend to polymerize, in which a narrow band gap is formed. In photovoltaic cells with functionalized fullerenes C_{60} with bulk heterojunction, the photosensitivity of the active layer of the mixture of polymer, dye and C_{60} increased significantly in the wide range from 300 to 850 nm [11].

When considering the photovoltaic properties of films of solar cells, the aggregation of H- and J-types of dyes, including squaraine, which affects their structure and, as a consequence, electronic configuration of energy states, as well as the implementation of heterojunctions on the interface in two-layer cells [12–22].

It can be expected that the supramolecular reorganization of the structure of dyes in the films will affect complex formation with fullerenes C_{60}, and hence the electronic configuration of the molecular orbits of the donor and acceptor components on the interface. This, in turn, affects the photovoltaic characteristics of the interface heterojunction, including one of the important properties of the volt-ampere dependence in a two-layer system of dye – C_{60} – idle voltage. The nature of the supramolecular structure of the dye film is predominantly formed by the conditions for its synthesis.

On the other hand, it can be transformed as a result of external influences, including through radiation modification by bombing particles. Such an effect can lead to radiation sensitization of the idle voltage spectrum and, as a consequence, to optimize the efficiency of the photovoltaic layer of photovoltaic cells of organic solar cells.

In this work, mechanisms of radiation sensitization of the idle voltage of an organic photovoltaic cell made from a two-layer film squaraine dye-fullerene C_{60}, as a result of high-energy electron irradiation ($E_e =$ 1.8 MeV) will be established.

1. METHODS OF FILM'S PREPARATION AND EXPERIMENTAL

1.1. BIS [4-(N,N-DIBENZYLAMINO)-2,6-DIHYDROHYPHENYL)] FILM PREPARATION

For the preparation of a donor layer, a symmetrical squaraine dye DBSQ was used, in which, in addition to the π-conjugated organic chromophore with a four-dimensional acceptor ring on both sides, two identical

donor parts are located. Such a structure contributes to the special nonlinear properties of the dye and the intensive absorption and fluorescence in the near IR region of the spectrum. Functional capabilities of DBSQ as donors are higher than in polyhedicated polymers, since photoactivity is well suited to the spectrum of solar radiation. They have high thermal resistance, aggregation ability, with the formation of crystalline and semi-crystalline regions that contribute to exciton diffusion and transport of charges. Unlike asymmetric dyes, the DBSQ scaler is smaller than the band gap width, larger quantum yield and lifetime excited state. DBSQ refers to the dibutyl squaraine dyes. In this molecule an effective intra-molecular charge transfer is realized between the donor and acceptor fragments [23].

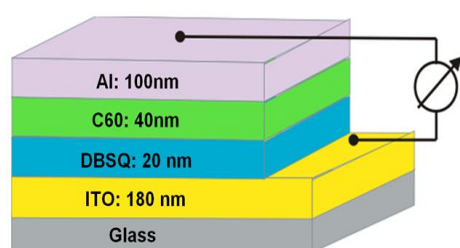Fig. 1 shows a schematic image of the photovoltaic cell structure with an interface heterojunction.

Fig. 1. The schematic image of the photovoltaic cell structure with an interface heterojunction

Layers of DBSQ and C_{60} molecules were applied by vacuum deposition, the rate of deposition was for DBSQ – 1 nm/s, for C_{60} – 0.05 nm/s, respectively. As shown, under these conditions, J-aggregates are formed in dye films, the appearance of which leads to a shift of the optical absorption band towards longer wavelengths. The thickness of the DBSQ and C_{60} films was ~ 30 nm and 80 nm, respectively.

1.2. STUDY METHODS AND APPARATURE

For these films, the optical absorption and the idle voltage spectra were studied before and after irradiation with electrons with an absorption dose of 2.0 MRad. The irradiation was carried out at room temperature. Optical absorption spectra for films were measured using a Perkin-Elmer Lambda Bio 35 spectrophotometer. The idle voltage spectra were determined using a Picotest voltmeter.

Electron irradiation was performed using linear accelerator ILU-6.

Quantum-chemical calculations are maded using the software package Gaussian 03.

2. RESULTS AND DISCUSSION

2.1. QUANTUM-CHEMICAL CALCULATIONS OF THE OPTICAL ABSORPTION SPECTRA FOR MOLECULES C_{60}-DBSQ COMPLEXES

The geometry of the complex of C_{60}-DBSQ molecules was optimized by ab-initio in the chemical model B3LIP / 6-31G (d, p) and tested for stability by analyzing the frequencies of normal oscillating modes. In Fig. 2 is represented by the geometry of the C_{60}-DBSQ complex. It is seen that the formation of a complex is accompanied by a change in the conformation of the DBSQ molecule. The dye molecule partially covers the C_{60} molecule with donor fragments, which results in the bending of the chromophore group.
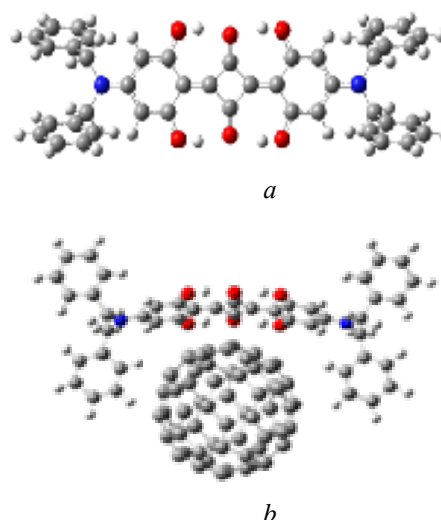

Fig. 2. The structure of the DBSQ (a) molecule and the C_{60}-DBSQ (b) complex. (Large balls of gray, red, blue, correspond to carbon atoms, oxygen and nitrogen, and small gray balls correspond to hydrogen atoms)

If the dipole moments D for both initial molecules are 0 Debai, then with the formation of the complex there is a redistribution of charges for both components and there are dipole moments. Fig. 3 shows the redistribution of charges in the C_{60}-DBSQ complex.
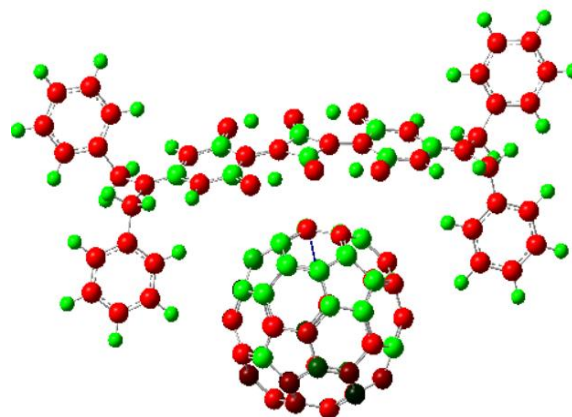

Fig. 3. Redistribution of charges on atoms of C_{60}-DBSQ molecules. (Red and green colors correspond to negative and positive charges)

The values of charges on the atoms of the chromophore fragment of the DBSQ molecule reach significant values. Thus, for a squaraine group, the charge on carbon atoms is – 0.079 a.o., 0.379 a.o., and at oxygen atoms – 0, 566 a.o. At the same time, the dipole moment is small and equals D = 1.33 Debai. Thus, the charge changes in the complex is insignificant. Similar changes of charges are observed on the molecule of fullerenes, which leads to a small dipole-dipole interaction between the components of the complex.

The calculation of the energy of the main and excited states was carried out using the model B3LIP/6-31G (d, p).

Depending on the electronic configuration of the main and excited states, the localization of molecular orbitals is very varied (Fig. 4).
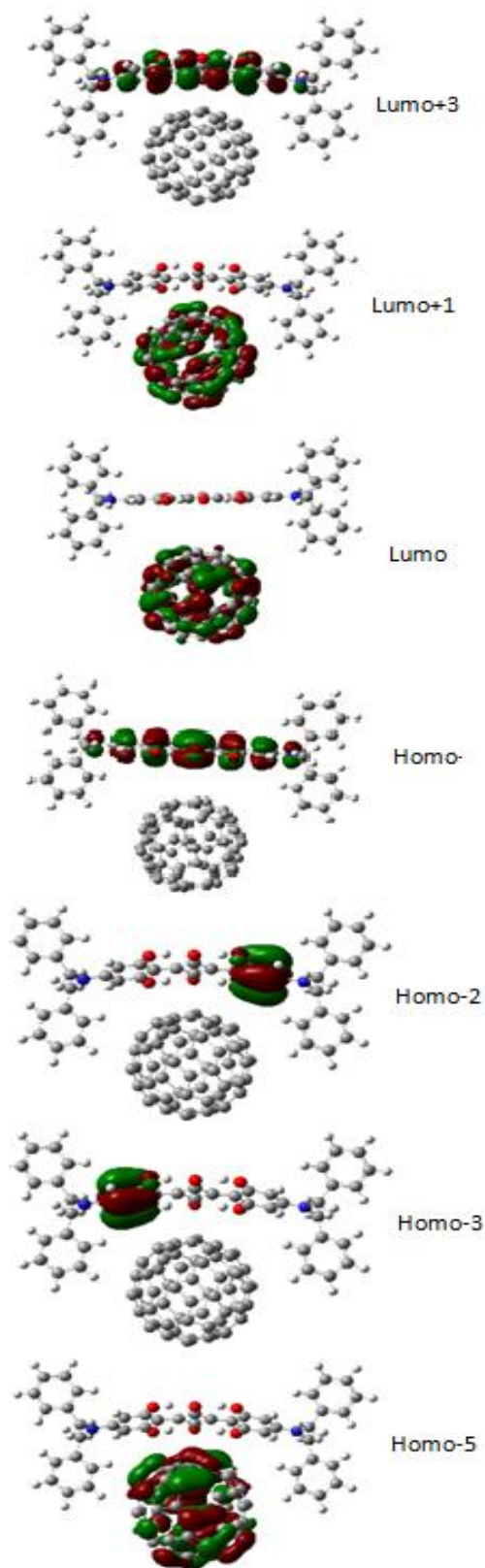

Fig. 4. The localization of molecular orbitals in the complex C_{60}-DBSQ

It is seen that for frontal molecular orbitals (MO) they are mainly concentrated on the C_{60} molecule. For other MO, the localization is concentrated on the chromophore group. At the same time, within this group of DBSQ molecules the localization varies considerably depending on the energy state of the MO. Thus, for HOMO-2, the electron density is almost homogeneously distributed over the atoms of the chromophore group. In the case of HOMO-3, the localization is shifted to one, and for HOMO-5 to another phenolic ring. Such a complex redistribution of π-localization of MO can greatly affect the values of matrix elements of transitions.

To calculate the characteristics of spectral transitions in the C_{60}-DBSQ complex the ZINDO method was used. These characteristics for the considered molecular orbitals are given in Table.

Characteristics of spectral transitions in the C_{60}-DBSQ complexes

Basic transitions	Basic configuration	Type of transition	E, eV	f	λ, nm
$S_0 \rightarrow S_1$	HOMO-5 $\rightarrow$LUMO	$\pi \rightarrow \pi$	1.9608	1.31	632.3
$S_0 \rightarrow S_2$	HOMO $\rightarrow$LUMO+3	$\pi \rightarrow \pi$	2.239	0	553.5
$S_0 \rightarrow S_3$	HOMO-3 $\rightarrow$LUMO+1	$\pi \rightarrow \pi$	2.2417	0	553.1

It can be seen that the C_{60}-DBSQ complex possesses one optical absorption band with a maximum near the wavelength λ = 632.5 nm. By the way, the optical transition with the highest force of the oscillator (f = 1.527) typical of a pure DBSQ corresponds to a band maximum of λ = 628.5 nm, that is, the formation of a complex with C_{60} leads to a shift in the maximum optical shift band of almost 5 nm.

2.2. RADIATION SENSITIZATION OF THE IDLE VOLTAGE IN THE TWO-LAYER C_{60}-DBSQ FILM

The idle voltage V_{oc} is one of the most important characteristics of heterojunctions in photovoltaic cells, which is crucial for determining its efficiency of solar energy conversion. As a rule, it is determined from the volt-ampere dependence, characteristic for the photo of the active layer of organic solar cells. Among other factors that determine the value of V_{oc}, the importance of rebuilding the electronic structure in the photovoltaic cell plays an important role, which significantly influences the interface or volume heterojunctions. The main factor influencing the change in the energy states of the MO and their localization is the degree of complexation between the donor and acceptor component of the photoactive layer, including the formation of dye aggregates in it [24].

The presence of the electronic structure rearrangement that results in displacements of the optical absorption band in the formation of the C_{60}-DBSQ complexes is confirmed by quantum-chemical calculations.

Fig. 5 shows the normalized optical absorption spectra for C_{60}, DBSQ films and two-layer C_{60}-DBSQ

film. If the absorption spectra of the separated film of the C_{60} molecules and of the two layers are almost unchanged, then the spectrum of absorption of the dye in a two-layer film differs significantly from the analogous spectrum of the separated DBSQ film.
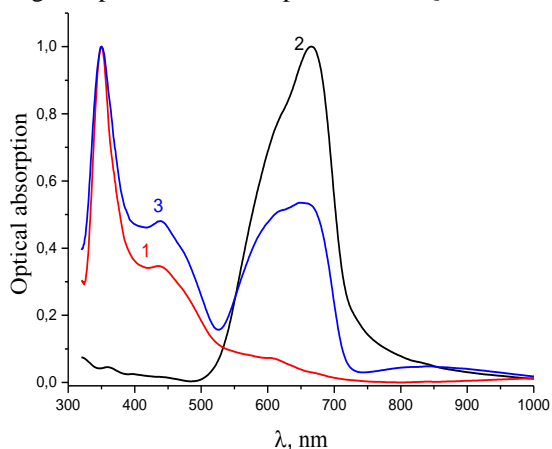

Fig. 5. Normalized optical absorption spectra for C_{60} (1), DBSQ (2) films and C_{60}-DBSQ (3) two-layer film

It can be seen that for the DBSQ film, the absorption spectrum is substantially expanded and shifted toward larger wavelengths, indicating the formation of J-aggregates in them. In a two-layer film, the extension of the band, inherent to DBSQ, becomes even larger, and hence the formation of aggregates of molecules increases. The behavior of the absorption band in the two-layer film belonging to the C_{60} molecules near 450 nm is also unusual. In this range, the absorption of C_{60} molecules increases, which suggests the emergence of an additional band in the long-wave region. This band is due to the appearance on the interface of complexes with the charge transfer between the molecules of fullerene and dye. The indicated transfer of charges is also noted in the quantum-chemical calculations of the formation of complexes C_{60}-DBSQ. Obviously, the emergence of a charge transfer band promotes the efficiency of the photogeneration of charge carriers and should manifest itself in the spectral dependence of the idle voltage.

Fig. 6 shows the normalized idle voltage spectra for a two-layer C_{60}-DBSQ film before and after electronic irradiation with an absorption dose of 2.0 MRad.

It can be seen that the V_{oc} spectrum of a two-layer film includes the presence of two lanes. The maximum intensity band is near 700 nm. This peak is shifted towards long waves in comparison with the position of absorption strips of the separated DBSQ film (650 nm) and DBSQ molecules in a two layer film (632, 660 nm). The second less intense peak has a maximum of about 530 nm, indicating a bias relative to the absorption band of the C_{60} film (440 nm). We can assume that each of the idle voltage bands corresponds to different mechanisms of the photo of the generation of charge carriers.

Thus, the band with a maximum of about 700 nm is due to the excitation of electrons in the J-aggregates DBSQ, and the less intense band is due to complexes carrying the charge of the C_{60}-DBSQ, which are formed on the interface. The appearance of a charge transfer

band indicates the significant role of each of the selected donor and acceptor components and the possibility of impact on the interface heterojunction due to the formation of complexes on the interface. This formation depends on the state of aggregation of dyes and the possibilities of creating between the two types of chemical interaction molecules, for example, by [2+2] – the cyclic connection.
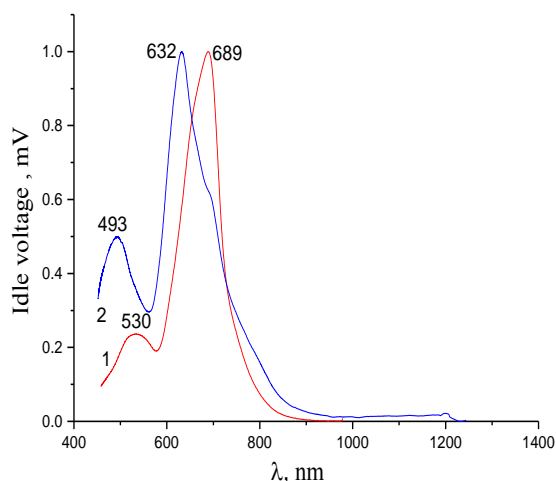

Fig. 6. Normalized idle voltage spectra before (1) and after electron irradiation ($E_e = 1.8$ MeV) with an absorption dose of 2.0 MRad (2) of a two-layer film C_{60}-DBSQ

One of the important mechanisms of influence on the aggregation of dyes and the formation of [2+2] – the cyclic connection complexes between the C_{60} and DBSQ molecules is their radiation modification when bombarded by high-energy particles, including electrons.

As can be seen from Fig. 6 as a result of electron irradiation at the low absorption dose there is a sensitization of electronic transitions, which is accompanied by the adjustment of the idle voltage spectrum. For this spectrum, there occurs a hyphenschromic shift of the main band to 632 nm, and an additional band up to 493 nm. In this case, the V_{oc} value for the charge transfer band is noticeably increased.

Thus, due to the effect on the complex formation between the molecules C_{60} and DBSQ on the interface of a two-layer film from the indicated acceptor and donor component of the heterojunction, which is realized as the emergence of charge-transfer complexes under the action of high-energy electron irradiation, radiation sensitization of the idle voltage spectrum occurs. One of the important manifestations of such an effect is the radiation modified [2+2] – the cyclic connection between molecules, which in turn determines the degree of formation of complexes with charge transfer.

CONCLUSIONS

Quantum-chemical calculations show that with the formation of complexes between fullerene molecules C_{60} and DBSQ, there is a charge transfer, a change in the energy states of molecular orbitals and their localization. The indicated changes are accompanied by

displacement of optical absorption spectra in the direction of long waves.

Optical absorption spectra for C_{60}-DBSQ two-layer films indicate their significant differences from solutions of these components. These differences indicate the formation of J-aggregates in the DBSQ film, as well as complexes with charge transfer on the interface.

An idle voltage spectrum, which is characterized by the presence of several bands, including the charge transfer bands there is the confirmation of the creation of charge transfer complexes.

The irradiation by high-energy electrons ($E_e = 1.8$ MeV) with an absorption dose of 2.0 MRad is accompanied by the appearance of [2+2] – the cyclic connection between the molecules on the interface, which in turn affects the formation of complexes with charge transfer. Changes in the creation of these complexes result in radiation sensitization of the idle voltage in photovoltaic layers of photovoltaic cells.

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РАДИАЦИОННАЯ СЕНСИБИЛИЗАЦИЯ СПЕКТРА НАПРЯЖЕНИЯ ХОЛОСТОГО ХОДА В ФОТОАКТИВНЫХ СЛОЯХ МОЛЕКУЛ C$_{60}$ И СКВАРАИНОВЫХ КРАСИТЕЛЕЙ DBSQ

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Проведены квантово-химические расчеты геометрии, переноса зарядов, энергетических состояний, локализации молекулярных орбиталей, оптических переходов для комплексов молекул фуллеренов C$_{60}$ и сквараиновых красителей DBSQ. Исследованы спектры оптического поглощения двухслойных пленок C$_{60}$–DBSQ. Показано, что в пленках формируются J-агрегаты красителя и комплексы с переносом зарядов C$_{60}$–DBSQ на интерфейсе. Наличие указанных комплексов приводит к сложному строению спектров напряжения холостого хода. Возникновение в результате высокоэнергетического электронного облучения (E_e=1,8 МэВ) с дозой поглощения 2,0 МРад [2+2]-циклоприсоединения между фуллеренами и красителем существенно влияет на формирование комплексов с переносом зарядов. Указанное воздействие приводит к радиационной сенсибилизации спектра напряжения холостого хода, которая проявляется в гибсохромном сдвиге ее полос и модификации фоточувствительности фотовольтаических ячеек.

РАДІАЦІЙНА СЕНСИБІЛІЗАЦІЯ СПЕКТРА НАПРУГИ ХОЛОСТОГО ХОДУ У ФОТОАКТИВНИХ ШАРАХ МОЛЕКУЛ C$_{60}$ І СКВАРАЇНОВИХ БАРВНИКІВ DBSQ

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Проведено квантово-хімічні розрахунки геометрії, переносу зарядів, енергетичних станів, локалізації молекулярних орбіталей, оптичних переходів для комплексів молекул фулеренів C$_{60}$ та сквараїнових барвників DBSQ. Досліджено спектри оптичного поглинання двошарових плівок C$_{60}$–DBSQ. Показано, що в плівках формуються J-агрегати барвника та комплекси з перенесенням зарядів C$_{60}$–DBSQ на інтерфейсі. Наявність вказаних комплексів призводить до складної будови спектрів напруги холостого ходу. Виникнення в результаті високоенергетичного електронного опромінення (E_e=1,8 МеВ) з дозою поглинання 2,0 МРад [2+2]-циклопід'єднання між фулеренами і барвником істотно впливає на формування комплексів з перенесенням зарядів. Вказаний вплив призводить до радіаційної сенсибілізації спектра напруги холостого ходу, яка проявляється в гіпсохромному зсуві її смуг та модифікації фоточутливості фотовольтаїчних комірок.