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Optical and unique photovoltaic properties of 2-cyano-3-(4-dimethylaminophenyl)-2-propentioamide dye deposited on the gilded substrate

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Optical, dark electrical and photoelectrical properties of the organic dye 2-cyano-3-(4-dimethylaminophenyl)-2-propentioamide (solutions in different solvents and films obtained by vacuum deposition of the dye layer on quartz and gilded quartz substrates) were studied. In the case of dye films deposited on the gilded substrate new effects have been noted as compared with solutions and films deposited on glass substrates. It is argued that these effects could be related to the ordering of the dye molecule dimers with possible aggregate formation in films induced by interaction with gilded substrate. The observed effects can be used for development of a new type of solar cell as well as for design of molecular photovoltaic elements for nanoelectronics and nanophotonics.

Исследованы оптические, темновые и фотоэлектрические свойства органического красителя 2-циано-3-(4-диметиламинофенил)-2-пропентиоамид (растворы в разных растворителях и пленки, нанесенные методом вакуумного испарения как на кварцевые, так и на позолоченные кварцевые подложки). В случае пленок красителя, нанесенного на позолоченную подложку, появляются новые эффекты по сравнению с растворами красителя или пленками, нанесенными на стекло. Предполагается, что эти эффекты связаны с определенным пространственным упорядочением димеров молекул красителя и, возможно, образованием агрегатов, вызванным взаимодействием с позолоченной подложкой. Наблюдаемые эффекты могут быть использованы как для создания нового типа элементов солнечных батарей, так и для дизайна молекулярных фотовольтаических элементов для наноэлектроники и нанофотоники.

1. Introduction

One of the main problems of the creation of photovoltaic elements is the spatial separation of electric charges and the obtaining of their unbalanced distribution at the expense of the photons absorption by the system. The majority of photovoltaic elements that are used in created for solar energetics use the effect of violation of balanced distribution of electrons and holes (caused by absorption of photons) in the region of p–n-transition in semiconductors [1]. Other principles of obtaining the photocurrent in macroscopic hybrid systems were also realized (e.g., Graetzel cell [2]).

In the present paper, results are presented shown that prove the appearance of photovoltaic effect on the molecular level. To our opinion, this effect can be used on macroscopic level for the organic solar cells design and fabrication, as well as in molecular photovoltaic energy sources for nanoelectronic devices.

2. Experimental procedure

For the optical and photovoltaic investigations, organic dye (2-cyano-3-(4-dimethylaminophenyl)-2-propentioamide) samples were used (the chemical formula is shown in Fig. 1), which consisted of the dye layer deposited on both quartz substrate and gilded quartz substrate. The dye and Au layers were thermo-deposited in a vacuum chamber. The thickness of the dye film (*L*) was measured by AFM and was equal to 150÷200 nm. The optical absorption investigations of the films and solutions of the dye were performed using a Specord UV Vis spectrophotometer. The luminescence studies were carried out using a Carry Eclipse spectrometer and the experimental set made in our laboratory.

For the investigated dye film samples the changes in the value of surface electric potential (φ) were measured by Kelvin's method [3, 4] before and under irradiation by light. Also the changes in the value of surface electric potential were measured after the dye film charging in corona discharge under subsequent irradiation by light using a device that gave the possibility to change the electrical polarity of the investigated sample Au-electrode. The light-emitting diodes (LED) with wavelengths λ_{max} = 430 nm (blue), 525 nm (green), 585 nm (yellow), 660 nm (red) as well as "white" LED were used for irradiation of the dye film samples.

3. Results and discussion

Optical properties. The absorption spectra of the solutions in the region of the first electronic transition consist of two bands with maxima at 370 and 435 nm. The 370 nm maximum is manifested at low concentration $C = 2.5 \cdot 10^{-6}$ mole/l and, to our opinion, belong to the monomer molecule transition. At $C = 6 \cdot 10^{-6}$ mole/l, the second long-wave band 435 nm appeared, the intensity of which increased with concentration. This behavior of long-wave absorption bands allows us to conclude that dimers of the dye appear in solutions. So, the band with 435 nm maximum is probably related to the dimers. The short-wave band with 260 nm maximum, in our opinion, is due to the second molecular electronic transition. The absorption spectra of dyes deposited on glass are very close to the spectra of solutions. This fact proves that mainly dye molecules or their dimers are the absorption centers in the dye films on the glass substrate in the same way as in solutions.

The fluorescence spectra of solutions overlap with their long-wave absorption (435 nm maximum), and the shapes of their bands are symmetrical. It proves that in fluorescence of solutions the dimer emission dominates. Possibly, the quantum yield of monomer fluorescence is not significant. The fluorescence spectra of dye films deposited on quartz substrate are very close to the spectra of the dye solutions pointing out that the main fluorescence emitters in such type of films are single molecules (monomers). The dramatic changes in the optical properties of these dye films when they are deposited on gilded quartz substrate were observed: the short-wave molecular band of absorption related to the second electronic transition essentially decreased, which could be due to orientation along the axis of the molecule (which is roughly perpendicular to

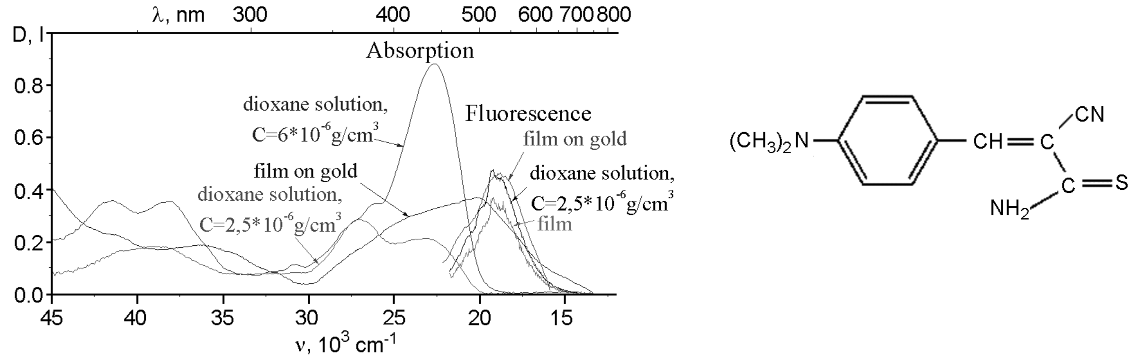

Fig. 1. The optical absorption and fluorescence spectra and the chemical formula of investigated dye.

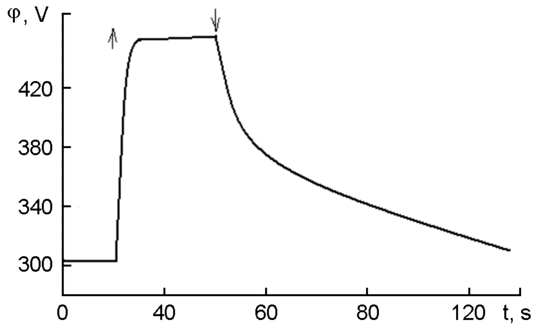

Fig. 2. Variation of surface electric potential (φ) of the deposited dye film samples with time under their illumination by the light of "white" LED. The moments of the light switching "on" and "off" are marked by the vertical arrows.

the substrate plane). Such orientation with the following self-assembling, in our opinion, is induced by the binding of the dye molecules to gold atoms by their sulfur-containing groups. Besides, in this type of films the long-wave shifted (comparing with the dimer band) absorption band (possibly, of aggregate origin) appeared.

The dark electrical and photoelectrical properties. Photovoltaic effects. The value of surface electric potential (φ) in the investigated dye samples that have been under prolonged dark storage is not equal to zero, but has positive sign with respect to Au-electrode and is equal to +(340±30) mV for $L >$ 100 nm. No increase in φ in the investigated L range was noted. Fig. 2 shows a plot of the dramatic changes of φ after illumination and turning the light off. The rate of the φ increase after the start of illumination is much larger than the relaxation rate after switching off the light. The kinetics of the φ changes does not depend on the wavelength of the irradiating light λ_{max}. The latter may be associated not only with a change in the dipole moments of the dye molecules excited by light, which should take place and relax for the time $<10^{-6}$ s, but also with the formation of long-lived charge carriers. These carriers can be formed as a result of the internal photoelectric (photovoltaic) effect.

Our additional investigations lead us to a conclusion about the hole type of the conductivity of the investigated deposited dye films.

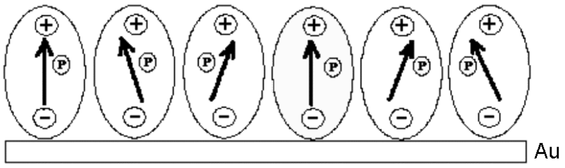

Fig. 3. The model of the arrangement of the dipole moments of dye associates on Au-layer.

The recorded electric potential φ (which was high enough) of the surface of the dye films deposited on Au-layers can be an evidence of the formation of geometrically well-ordered dipole moments (P) in these films in the ground state as it was observed in [5]. The latter proves our previous suggestions that dipole moments are oriented mainly vertically to the Au-layer plane (as it is shown in Fig. 3). The huge non-typical increase in φ under the influence of light can be attributed to the increasing of the dipole moments of the dye molecules as a result of their electron density redistribution due to light absorption.

4. Conclusions

The results obtained, to our opinion, show the following:

1. The molecular assembling induced by a gilded substrate occurs, at least in the internal molecular layers of the dye films. This assembling leads to orientation of dye molecules, their dimers and aggregates, mainly perpendicularly to the substrate plane.
2. The dominant orientation of molecules and aggregates on the gilded substrate leads to the observed photovoltaic effect and polarization of the films in the ground state. These phenomena are promising for the development of solar cells of a new type, as well for application in nanoelectronics for fabrication of the molecular photovoltaic elements.

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Оптичні та унікальні фотовольтаїчні властивості барвника 2-ціано-3-(4-диметиламінофеніл)-2-пропентіоамід, нанесеного на позолочені підкладинки методом вакуумного випаровування

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Досліджено оптичні, темнові та фотоелектричні властивості органічного барвника 2-ціано-3-(4-диметиламінофеніл)-2-пропентіоамід (розчини у різних розчинниках та плівки, нанесені методом вакуумного випаровування як на кварцові, так і позолочені кварцові підкладинки). У випадку плівок барвника, нанесеного на позолочену підкладинку, з'являються нові ефекти у порівнянні з розчинами барвника або ж плівками, нанесеними на скло. Припускається, що ці ефекти пов'язані з певним просторовим упорядкуванням димерів молекул барвника і, можливо, утворенням агрегатів, що спричинено взаємодією з позолоченою підкладинкою. Ефект, що спостерігається, може бути використаний як для створення нового типу елементів сонячних батарей, так і для дизайну молекулярних фотовольтаїчних елементів для наноелектроніки та нанофотоніки.