

Effect of aggregation on optical and photovoltaic properties of an metallorganic compound*

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Optical and photovoltaic properties of an metallorganic compound – nickel(II)bis(dithiobenzil) (NBDB) in various states of aggregation (solution, vacuum-deposited film, polymer composite) have been studied. Its absorption spectra are explained by the formation of sandwich aggregates in deposited films, which are absent in the solution and polymer composites. The study of photovoltage spectra showed that both deposited and composite films are photosensitive at the range of 500–1000 nm, and the quantum efficiency of the photogeneration for the direct excitation of aggregates is greater than that for the excitation of monomer molecules.

Key words: *metallorganic compound, composite, aggregation, photovoltage*

1. Introduction

Most of organic compounds have a long-wavelength edge of absorption at 600–800 nm. This is one of the reasons of relatively limited use of organic compounds for different applications in IR region, such as dye lasers, organic light-emitting diodes, photoconverters, solar cells, etc.

Therefore, our purpose was to develop organic layers, which can be used in near IR region [1, 2]. The study of optical and photovoltaic properties of metallorganic films, photosensitive at near IR region is described.

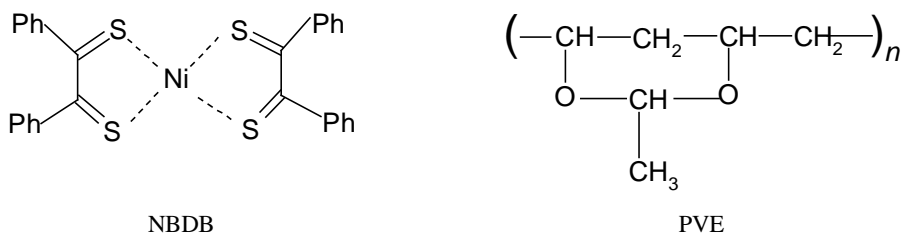
2. Experimental

Films of nickel(II)bis(dithiobenzil) (NBDB) [3] were prepared by vacuum deposition onto glass substrates coated with SnO₂ layer at room temperature.

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Films of NBDB-doped polymer composites were obtained from the solutions of both NBDB and polyvinylethylal (PVE) polymers (“Azot” plant, Severodonetsk, Ukraine) [4] in methylene chloride (CH_2Cl_2).



Absorption spectra were measured by the Specord M40 and Perkin-Elmer lambda 20 spectrophotometers. The experimental set-up and configuration of cells for the measurement of spectral characteristics of photovoltage (V) were described elsewhere [1, 2, 5]. All photovoltage dependences were measured using modulated illumination and they were corrected for the equal number of incident photons.

3. Results and discussion

Absorption spectrum of NBDB in solution can be described by two electronic transitions with maxima at 600 and 860 nm (Fig. 1). In Fig. 1 it can also be seen that absorption spectrum of NBDB-doped polymer composite film ($\sim 1 \mu\text{m}$ thickness) is similar to the spectrum of solution with a slight ($\sim 10 \text{ nm}$) red shift.

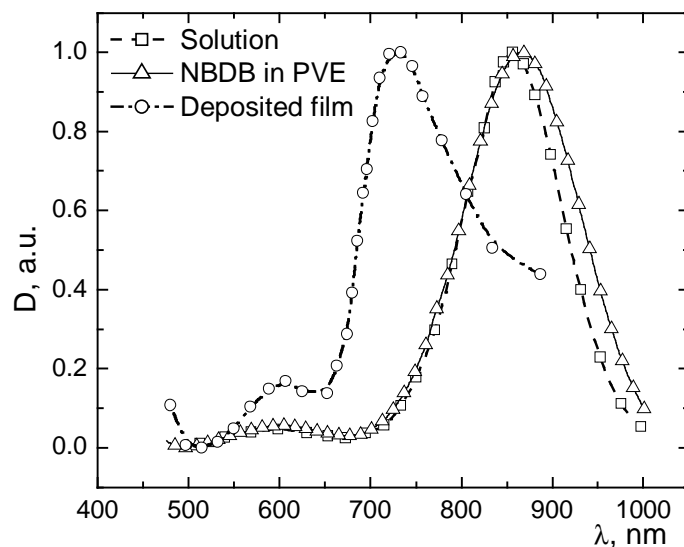


Fig. 1. Absorption spectra of NBDB

The morphology of these composite films is as follows: in a solid solution with randomly arranged crystallites most of them have a “cross-swords” shape. In Figure 2, the image of a polymer composite film made by means of a polarization microscope supplied by a digital photo-camera with high resolution (cross polarizers) is shown.

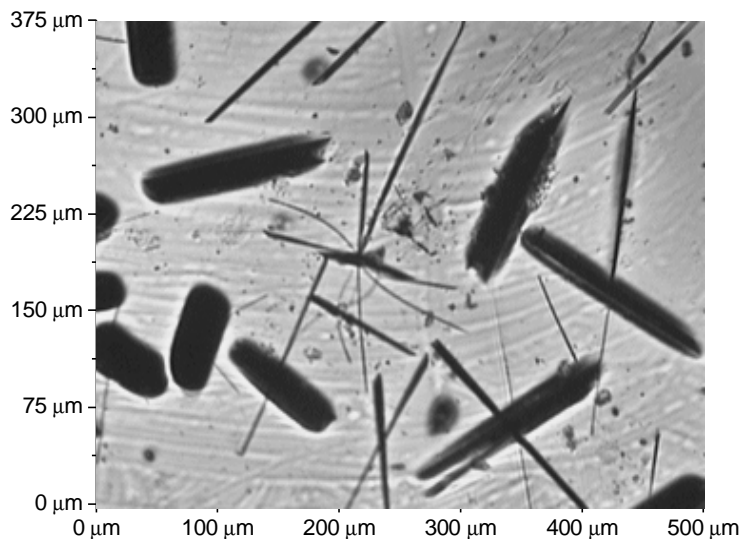


Fig. 2. Image of NBDB-PVE composite film

A strong deformation of the spectrum is observed when passing from the solution and composite to a solid deposited film. During the film formation both bands of a molecule are splitted (Fig. 3).

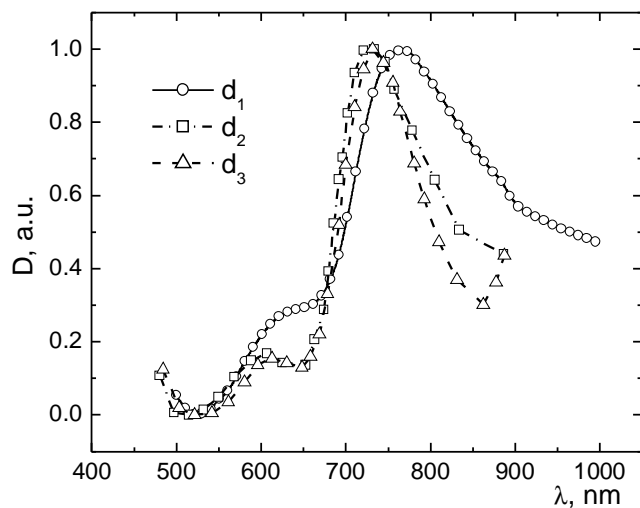


Fig. 3. Thickness dependence of the spectra of NBDB films

Figure 3 shows the absorption spectra of NBDB vacuum-deposited films of different thickness: 42 nm (d_1), 220 nm (d_2) and 410 nm (d_3). From the comparison of the spectra with those of solutions and polymer composites it is seen that due to the film formation both bands of the spectrum with the maxima at 600 nm and 860 nm are splitted. Since NBDB molecules have a planar structure, they most probably form aggregates in which planes of chromophore groups of dyes are parallel to each other – so-called sandwich-aggregates since dispersion and electrostatic interactions are maximal for such orientation of molecules [6]. Decrease of the long-wavelength absorption band intensity and appearance of new short-wavelength bands are in the agreement with the sandwich structure of aggregates [6].

According to the exciton theory, the interaction of chromophores in aggregates of dyes leads to the splitting of the first excited state S_1 into two states: S_1^h of higher energy and S_1^l of lower energy [6]. The electronic transitions $S_0 - S_1^h$ and $S_0 - S_1^l$ correspond to short-wavelength- and long-wavelength bands in the absorption spectra of aggregates, respectively.

In sandwich aggregates, the long-wavelength transition is forbidden, and short-wavelength transition has doubled intensity [6]. Therefore, the formation of sandwiches is accompanied by the decrease in intensity of a long-wavelength band and increase of intensity of a short-wavelength band which is blue-shifted. Such a situation, as was mentioned above, is observed in our case. In thick films, the number of dye molecules participating in the process of aggregation increases. This causes, as follows from the exciton theory, additional splitting of the S_1 level, and consequently, amplification of the above-described effects in absorption spectra as the thickness of the film increases (Fig. 3).

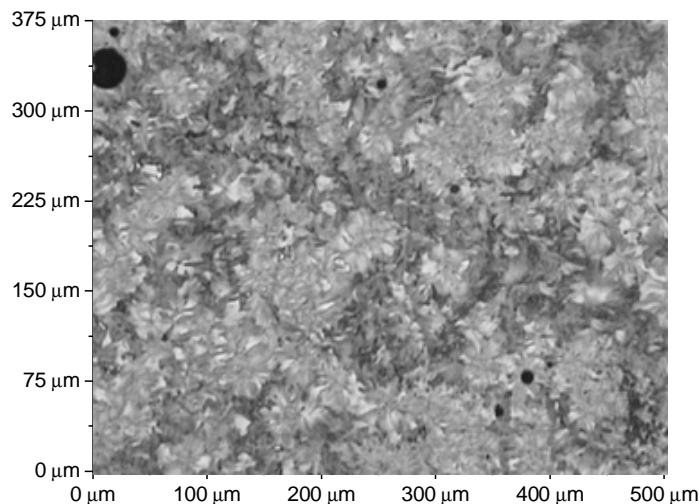


Fig. 4. Image of NBDB deposited film

Such a mosaic aggregate structure can be clearly seen in Fig. 4, where the photograph of vacuum-deposited film of 210 nm thickness (cross polarizers) is shown. The study of photovoltage spectra of deposited and composite films showed that both films are photosensitive at the range of 500–1000 nm (Fig. 5).

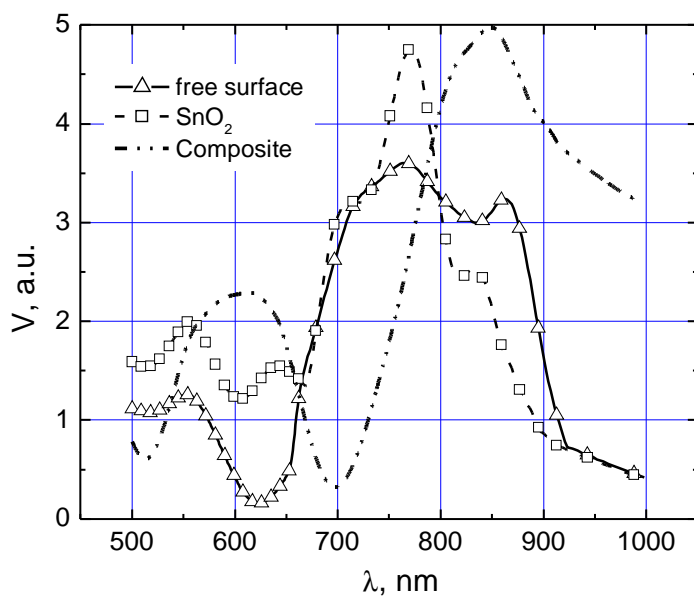


Fig. 5. Photovoltage spectra of NBDB deposited film and polymer composite

Figure 5 shows photovoltage spectra of vacuum-deposited films under the excitation from the side of the SnO₂ electrode as well as from the free-surface side, and the spectrum of photovoltage for polymer composite film which, in general, is similar to the absorption spectrum with a slight change in the ratio of bands intensity. Opposite picture is observed for deposited films.

During the film formation, the band with the maximum near 600 nm is splitted into the band at 640 nm and a weak band with the maximum at 550 nm. The more intensive band with the maximum near 860 nm in the spectra of films is splitted into bands with the maxima at about 770 and 860 nm. The shoulder at 700 nm is also observed. All these bands are clearly seen at the photovoltage spectra (Fig. 5).

Observation of photovoltage under illumination of deposited films from both sides confirms that during light absorption aggregates create carriers, which then are separated by internal electrical fields because of the formation of a potential barrier at the interface with SnO₂ electrode and at the free surface of NBDB film. Besides, it should be noted that the height of the potential barrier at the interface between NBDB and SnO₂ is higher than a bend of energetic bands at the free surface.

The higher relative intensity of additional bands in spectra of photovoltage than in absorption spectra of films testifies that the quantum efficiency of photogeneration for direct excitation of aggregates is greater than for the excitation of monomer NBDB molecules.

Conclusions

- We have shown that mosaic structure consisting of sandwich-aggregates is formed in vacuum-deposited films of NBDB contrary to NBDB-polymer films, which consist of crystallites randomly arranged in the composite.
- The study of photovoltage spectra, as well as of deposited and composite films are photosensitive at the range of 500–1000 nm. New bands due to sandwich-aggregates formation are observed for deposited films both in absorption and photovoltage spectra.
- It is found that relative quantum efficiency of photogeneration is maximal for the direct excitation of aggregates.

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