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Photovoltaic properties of organic heterojunctions formed from tetracene and zinc hexadecafluorophthalocyanine[*]

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Experimental results obtained for the systems with a planar heterojunction of tetracene (Tc)/zinc perfluorophthalocyanine ($F_{16}ZnPc$) are presented in this work. The systems were prepared by vacuum evaporation of the following materials: MoO_3, Tc, $F_{16}ZnPc$, bathocuproine (BCP) and Ag, onto glass/ITO substrates. Dark current–voltage and photocurrent–voltage relationships as well as spectral and light intensity dependences of short-circuit current are presented. The favourable effect of a buffer layer of BCP at the Ag electrode was observed.

Key words: *photovoltaic effect; organic heterojunction; tetracene; zinc perfluorophthalocyanine*

1. Introduction

Organic heterojunctions have been the subject of intensive investigations for twenty years due to their possible application in electronic devices, particularly in organic solar cells. Planar or bulk heterojunctions are most often formed from such materials as polymers, fullerenes, phthalocyanines and perylene dyes [1].

The preliminary investigations into photovoltaic properties of planar heterojunction formed from tetracene (Tc) and zinc hexadecafluorophthalocyanine ($F_{16}ZnPc$) have been presented in this work. Electric and photoelectric properties of monocrystals and polycrystalline layers of tetracene have been the subject of numerous analyses [2–11], however, there are only a few reports on heterostructures based on Tc [12–14]. Perfluorophthalocyanines and, in particular, $F_{16}ZnPc$, have also been intensively investigated, since they exhibit good chemical and thermal stability, strong light absorp-

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tion (up to 900 nm) and they transport electrons relatively well [15,16]. It is worth noting that the range of strong absorption of Tc (400–550 nm) covers the range of weak absorption of F_{16}ZnPc existing between the Soret and Q bands. This means that the range of strong absorption of the Tc/F_{16}ZnPc bilayer system is quite wide.

This work presents experimental results obtained on the ITO/MoO_3/tetracene (Tc)/zinc hexadecafluorophthalocyanine (F_{16}ZnPc)/bathocuproine (BCP)/Ag systems, which were prepared by vacuum evaporation of successive layers onto glass/ITO substrates. A thin layer of MoO_3 has been applied in order to improve the injection properties of ITO [17,18]. The absorption of light by this layer is negligibly small. The layer of BCP should prevent the F_{16}ZnPc layer from being damaged during Ag deposition [19, 20].

2. Experimental

The samples were obtained in vacuum (3×10^{-4} Pa, Auto 306 Turbo, Edwards) by evaporation of the following materials: MoO_3, Tc, F_{16}ZnPc, BCP, Ag, onto glass/ITO substrates (100 Ω/square, AWAT). All materials for evaporation were purchased from Aldrich. Tc and F_{16}ZnPc were purified in advance by sublimation. The thicknesses of layers are given in Fig. 1. The active surfaces of electrodes were 6–8 mm^2 and the average deposition rate was 0.1 nm/s. The samples were illuminated through ITO. The apparatus used for measurements has been described elsewhere [21].

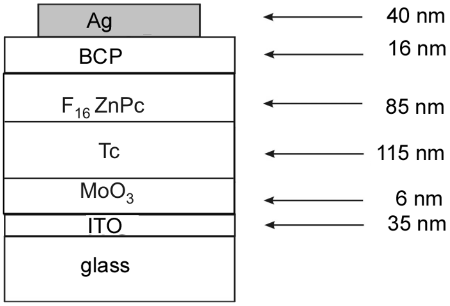

Fig. 1. The structure of the device

3. Results and discussion

Figure 2 presents the spectral dependence of short-circuit current of ITO/MoO_3/Tc /F_{16}ZnPc/Ag and the absorption spectrum of the Tc/F_{16}ZnPc system. The short-circuit current flows through the system from Ag to ITO, which is in agreement with the inner electric field resulting from the difference between work functions of electrodes ($W_{\mathrm{ITO/MoO_3}} > W_{\mathrm{Ag}}$). Within the absorption range of Tc (400–550 nm), the short-circuit current curve exhibits antibatic behaviour to absorbance, while outside this range we observe rather a symbatic behaviour. This means that, similarly as in many other bilayer planar heterojunctions, charge carriers are generated as a result of exciton dissociation at the interface of organic layers [1]. It can also be added that results obtained on the systems with other electrodes, namely on Al/F_{16}ZnPc/Tc/CuI, which are not discussed here, confirmed the above conclusion about the mechanism of charge carrier photogeneration.

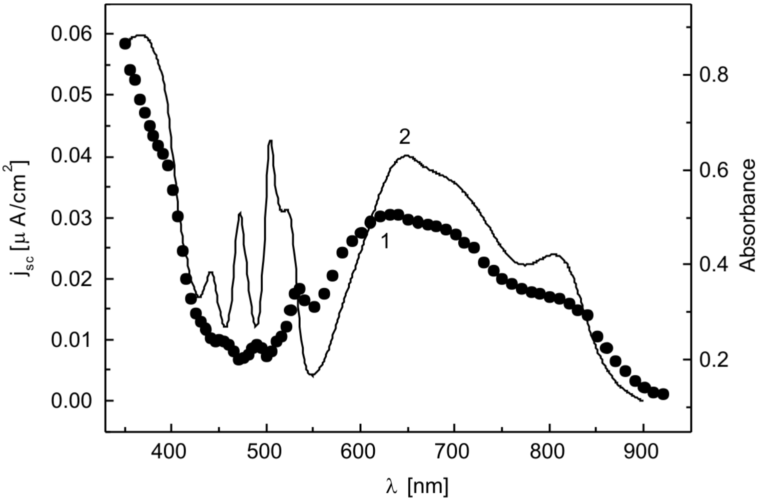

Fig. 2. Spectral dependence of the short-circuit current of the ITO/MoO_3/Tc/F_{16}ZnPc/Ag system (curve 1) illuminated with light of 10^{14} photons/(cm^2·s) and the absorbance spectrum of the Tc/F_{16}ZnPc bilayer (curve 2)

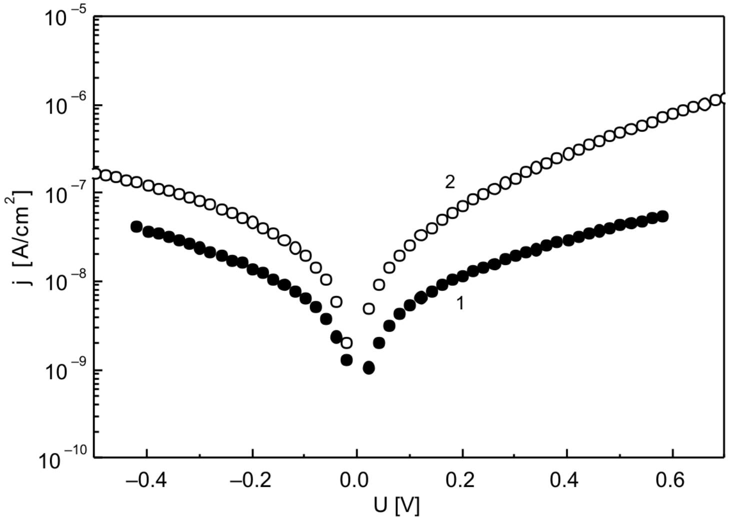

Fig. 3. Dark current–voltage curves of the investigated systems:
1 – ITO/MoO_3/Tc/F_{16}ZnPc/Ag, 2 – ITO/MoO_3/Tc/F_{16}ZnPc/BCP/Ag.
Positive values of voltage refer to the higher potential on ITO

The specific role of the Tc/F_{16}ZnPc interface is not observed in the measurement of dark current–voltage dependence (Fig. 3). Characteristic of the system without BCP (curve 1) is that it does not depend on the voltage polarization. In the case of the system including BCP (curve 2), we observed currents several time higher and the occurrence of a small rectification effect: at U = 0.4 V, the rectification ratio equals 2. These results indicate that Ag/F_{16}ZnPc is not an ohmic contact and the incorporation of the BCP layer reduces resistance of the contact (and the whole system as well).

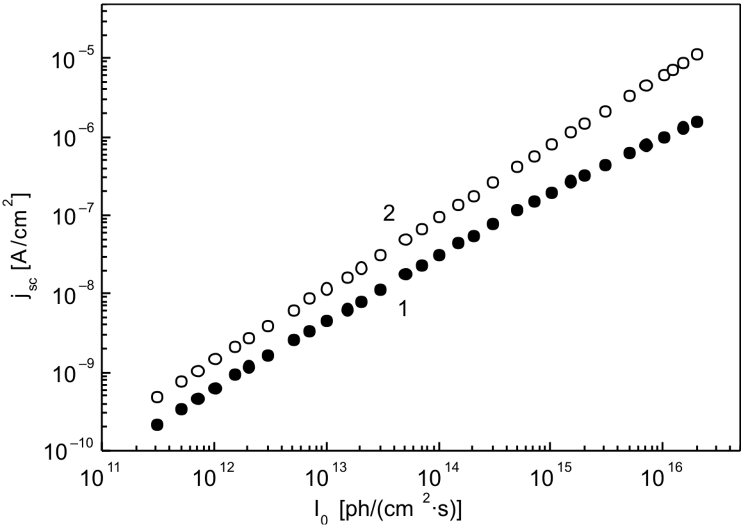

Fig. 4. Light intensity dependence of the short-circuit current of the investigated systems illuminated with light of 630 nm: 1 – ITO/MoO_3/Tc/F_{16}ZnPc/Ag, 2 – ITO/MoO_3/Tc/F_{16}ZnPc/BCP/Ag

Such a role of the BCP layer is also noticed in the relationship between short-circuit current and light intensity, as presented in Fig. 4. In both systems, with BCP or without BCP, photogeneration currents result from the same process (exciton dissociation at the Tc/F_{16}ZnPc interface), however the short-circuit current in the system with BCP is higher and almost proportional to light intensity, $j_{sc} \propto I_0^{0.9}$. It has to be borne in mind that in bilayer photovoltaic systems [1], the short-circuit current is a hole current in one layer (here it is Tc), while an electron current in the other one (here it is F_{16}ZnPc). Lower values of short-circuit current for the system without BCP, as well as sublinear dependence of $j_{sc}(I_0)$, indicate that the Ag/F_{16}ZnPc contact limits the transport of electrons through the system. A thin layer of BCP incorporated between Ag and F_{16}ZnPc can lead to the reduction in this limitation. Therefore, we suppose that the BCP prevents the F_{16}ZnPc layer from being damaged during Ag deposition and reduces the contact barrier.

Current–voltage relationship of the system with BCP illuminated with white light (Xe lamp, AMO Oriel filter) of 20 mW/cm^2 is presented in Fig. 5. The system exhibits a photovoltaic effect with the following parameters: short-circuit current j_{sc} = 18.1 μA/cm^2, open-circuit voltage U_{oc} = 0.41 V, fill factor FF = 0.25. Small values of j_{sc} and FF as well as the shape of the curve (see inset) are indicative of high series resistance R_s and relatively small parallel resistance R_p of the systems [22, 23]. Their values can be estimated as R_s = 21 kΩ·cm^2 and R_p = 24 kΩ·cm^2. The main reason for high R_s is a too large thickness of the Tc and F_{16}ZnPc layers. Moreover, oxygen from the air adversely affects the electric conductivity of F_{16}ZnPc [16].

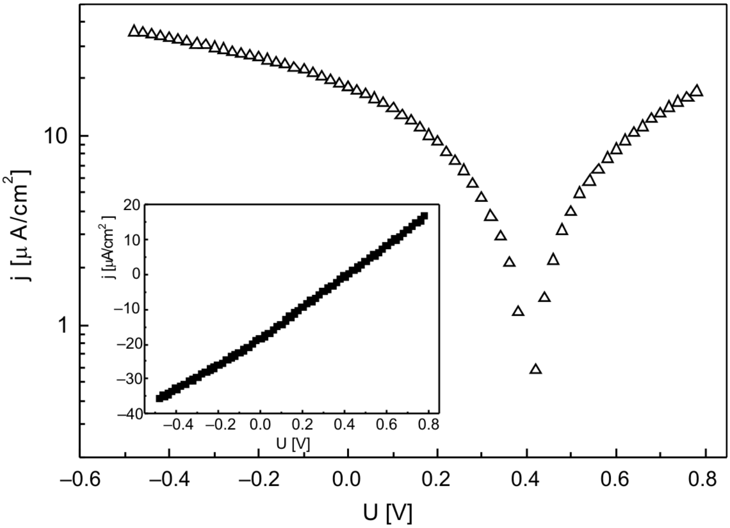

Fig. 5. Photocurrent–voltage curve of the ITO/MoO_3/Tc/F_{16}ZnPc/BCP/Ag system illuminated with white light of 20 mW/cm^2. Inset: the same curve in linear plot. Positive values of voltage refer to higher potential on ITO

The main factor limiting the value of the open-circuit voltage, U_{oc}, in organic heterojunctions is the difference Δ between the ionization energy I_h of a layer transporting holes and electron affinity energy A_e of the layer transporting electrons [24]. For Tc/F_{16}ZnPc, the value of Δ can be estimated as ca. 0.8 eV [3, 15], which means that the maximum value of U_{oc} should not exceed 0.8 V. The obtained value, U_{oc}= 0.41 V, fulfils this condition, even though it is not the maximum value. Measurements of U_{oc} indicate also that the value of U_{oc} does not depend on the presence of the BCP layer.

4. Summary

The systems with planar heterojunction of Tc/F_{16}ZnPc exhibit strong absorption of light within a wide range of wavelengths, from 350 nm up to 900 nm. The process of charge carrier photogeneration occurs at the Tc/F_{16}ZnPc interface as a result of dissociation of excitons excited in the Tc or F_{16}ZnPc layers, and diffusing towards this interface. Incorporation of the buffer layer of BCP improves the transport of electrons through the Ag/F_{16}ZnPc contact. The analysis of the current–voltage curve leads us to the conclusion that it is strongly determined by parasite resistances, and in particular by high series resistance.

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