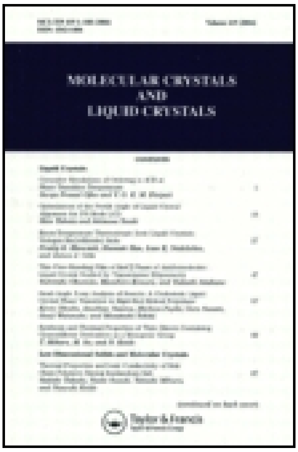

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Optical and Photoelectric Properties of Heterostructures of Fullerene C_{60} with Phthalocyanines and Tetracyanoquinodimethane (TCNQ)

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Optical and Photoelectric Properties of Heterostructures of Fullerene C_{60} with Phthalocyanines and Tetracyanoquinodimethane (TCNQ)

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The absorption spectra of thin film heterostructures XPc/C_{60} (X = Pb, ClAlCl, Pc – phthalocyanine) and TCNQ/C_{60} at the range 1.24–3.10 eV have been studied. It is found that a band of charge transfer complex (CT-complex) at 1.18 eV is observed in the absorption spectra of TCNQ/C_{60} heterostructures.

Based on the results obtained and the literature data [1–4], it is stated that that the transfer of electrons takes place on the interface of HS from the molecules of C_{60} (donors of electrons) to the molecules of TCNQ (acceptors of electrons) and from the molecules of XPc (donors of electrons) to the molecules of C_{60} (acceptors of electrons). Both components of XPc/C_{60} HS contribute to the photovoltage in the spectral region 1.24–3.10 eV.

Keywords Charge transfer; fullerene; heterostructure; photovoltage; phthalocyanine

Introduction

Thin films heterostructures (HS) XPc/C_{60} (X = Cu, Zn, Pb, $SnCl_2$, ClAlCl, VO, *etc.*), where C_{60} is the acceptor of electrons, have been intensively studied last decades [1–4]. The efficiency η, open-circuit photovoltage V_{oc}, and density of short-circuit photocurrent j_{sc} of solar cells based on these HS depend significantly on the preparation technology. The efficiency η changes from 2.0 to 2.8% depending on the angle of crystallites to the plane of a substrate and the presence or absence of the intermediate layer of molybdenum oxide (MoO_3) between a bottom electrode and HS layers under illumination of an ClAlClPC-based solar cell by AM 1.5 source with an intensity of 100 mW/cm^2 [1]. For HS CuPc/C_{60}, $\eta = 1.19\%$ for layers of CuPc and C_{60} with the only interface which are thermally deposited in vacuum. It increases to 2.15%, when components are deposited simultaneously; as a result, the

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Address correspondence to M. P. Gorishnyi, Institute of Physics of the NAS of Ukraine, 46, Prosp. Nauky, Kyiv, Ukraine. E-mail: gorishnyi@iop.kiev.ua gradient of their concentrations is created along the thickness of HS (multistepped structure) [2]. The size of the potential barrier for electrons is increased from 0.45 to 0.85 V, if a 0.5-nm layer of MoO_3 was deposited on the interface [3]. The deposition of this oxide directly on the glass or quartz substrate with a conductive layer of ITO also improves the characteristics of HS CuPc/C_{60} and ClAlClPc/C_{60} [4].

The bands of charge transfer excitons (CT-excitons) were observed in the absorption spectra of XPc films in the regions 1.1–1.6 and 2.0–2.3 eV which are located on both sides from the band of the first singlet transition [5–8]. The presence of CT – states is the necessary condition for the effective formation of CT-complexes between the molecules of XPc and C_{60}.

The purpose of our work is to study the manifestations of the donor-acceptor interaction between the molecules C_{60} with the molecules XPc and TCNQ in the absorption spectra and the open-circuit photovoltage (V_{oc}) of HS XPc/C_{60} and TCNQ/C_{60}.

Experimental

Thin film layers of XPc, C_{60}, TCNQ, XPc/C_{60}, and TCNQ/C_{60} were produced by the thermal deposition in 6.5-mPa vacuum onto quartz substrates (for studying the absorption) and onto quartz substrates coated with a conductive SnO_2 layer (for studying the photovoltage). The top Ag or Ni electrodes were deposited by the thermal vacuum or cathode deposition, respectively. The thickness of these films was measured with an interference meter MII-4. The substrates temperature has been controlled during the deposition process by thermocouple and it was c.a. 350 K. The absorption spectra of the films were obtained using a Perkin Elmer Lambda 25 UV/VIS spectrophotometer in the split mode with a spectral width of 1 nm at room temperature. The dependences of ΔD(E), where E is photons energy, were calculated as the difference between HS absorption spectra and the sum of the absorption spectra of the corresponding components. The values of absorption in the region of transparency (D_0) were also subtracted from the total absorption. The estimations of a reflectance influence shown that its deposit was respectively small especially in the region of strong absorption and indirectly was taken to the account during D_0 subtraction. The technique of V_{oc} measurements was described in [9].

Results and Discussion

Figure 1 shows the absorption spectra of HS ClAlClPc/C_{60} (curve 1), films of C_{60} (curve 2), ClAlClPc (curve 3), and difference absorption spectra of HS and the sum of its components (ΔD) (curve 4). The analysis of dependences of ΔD (E) shows that ΔD changes a sign at energies of photons (E) of 1.64 and 1.97 eV. Thus, the additional absorption ($\Delta D > 0$) is observed in the interval 1.64–1.97 eV. In all other regions of the spectrum, $\Delta D < 0$.

For the absorption spectra of HS PbPc/C_{60} and its components (Fig. 2), ΔD changes a sign at 1.82 and 2.48 eV. Thus, $\Delta D > 0$ in the regions 2.48–3.10 and 1.82–2.48 eV. In the interval 1.38–1.82 eV, $\Delta D < 0$.

More complex is the dependence of ΔD(E) for HS TCNQ/C_{60} (Fig. 3). In addition, the spectrum of HS includes a long-wave absorption band in the interval 1.13–1.24 eV which is absent in the absorption spectra components. The maximum structural band of $TCNQ^-$ at 1.52 eV (Fig. 3 curve 3) in HS is displaced bathochromically by 0.06 eV (Fig. 3, curve 1).

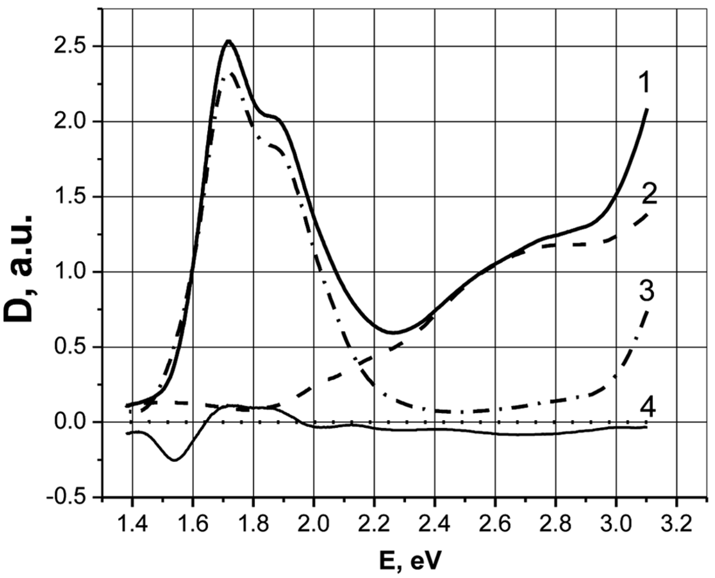

Figure 1. Absorption spectra of HS ClAlClPc/C_{60} (curve 1), films of C_{60} (curve 2), ClAlClPc (curve 3) and difference spectra of absorption of HS and the sum of their components ΔD (curve 4). The thickness of ClAlClPc and C_{60} films is 230 nm and 200 nm, respectively.

Figure 4 shows the spectrum of V_{oc} of sandwich cell: SnO_2/PbPc/C_{60}/Ag at its illumination through the SnO_2-electrode (curves 1) and the absorption spectrum of HS PbPc/C_{60} (curve 2). In V_{oc} spectra, there is long-wavelength band at c.a. 1.44 eV.

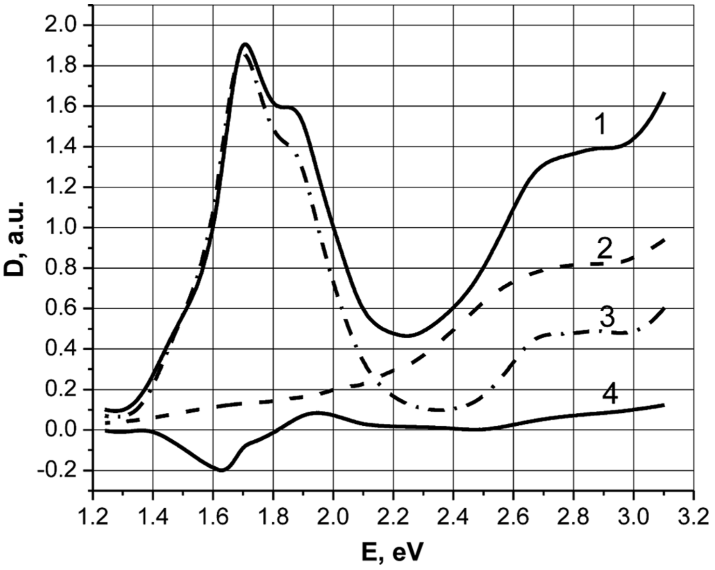

Figure 2. Absorption spectra of HS PbPc/C_{60} (curve 1) C_{60} (curve 2), PbPc (curve 3) and the difference spectra of absorption of HS and the sum of their components ΔD (curve 4). The thickness of PbPc and C_{60} films is 185 nm and 135 nm, respectively.

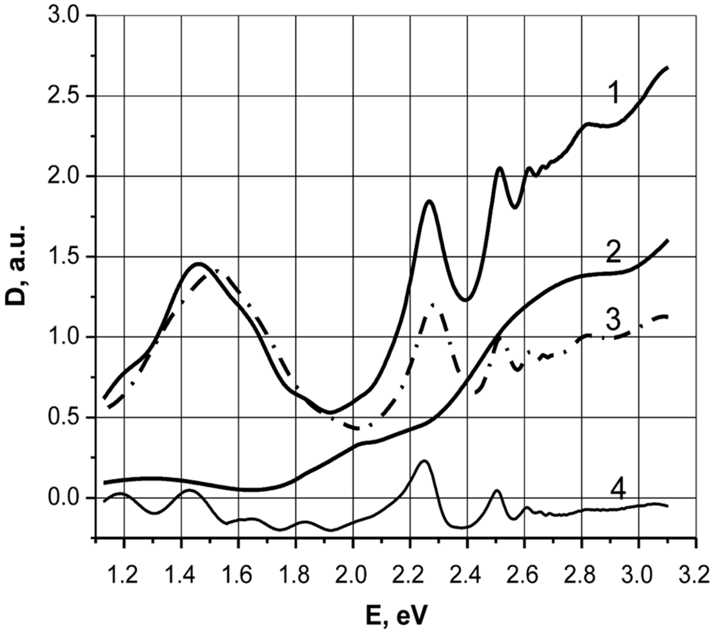

Figure 3. Absorption spectra of HS TCNQ/C_{60} (curve 1), C_{60} (curve 2), TCNQ (curve 3) and the difference spectra of absorption of HS and the sum of their components ΔD (curve 4). The thickness of TCNQ and C_{60} films is 200 nm and 220 nm, respectively.

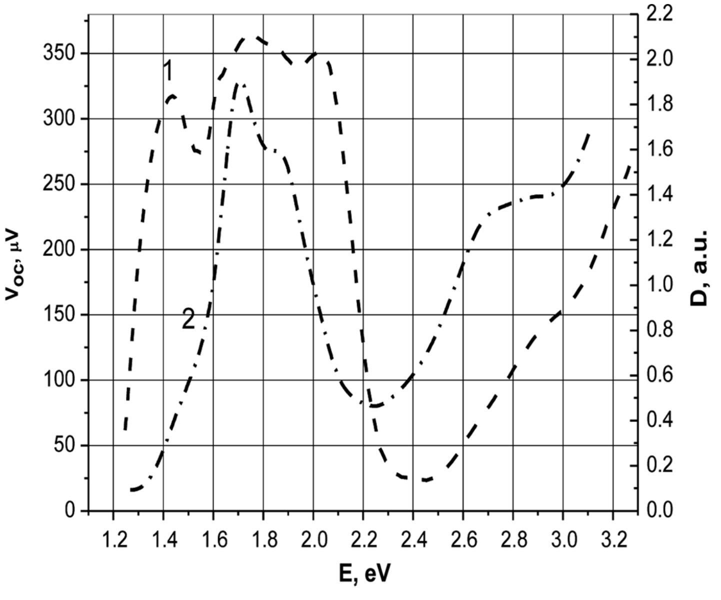

Figure 4. Spectra of V_{oc} for sandwich cells SnO_2/PbPc/C_{60}/Ag (curve 1, illumination via the SnO_2-electrode) and absorption of HS PbPc/C_{60} (curve 2). The thickness of PbPc and C_{60} films is 185 nm and 135 nm, respectively.

In the absorption spectrum of HS, this band is weak as compared with the intense band at 1.71 eV (curve 2). In the spectra of V_{oc}, the intensities of the peaks at 1.44 eV of the band at 1.71 eV (curve 1) are close. In addition, the spectra of V_{oc} contain a band at 2.05 eV which does not manifest itself in the absorption spectrum of PbPc/C_{60} (curve 2) and can be attributed to the band of the CT-state [5–8].

The spectrum of V_{oc} of a sandwich cell SnO_2/ClAlClPc/C_{60}/Ni at the illumination through the top Ni-electrode correlates with the absorption spectrum of HS ClAlClPc/C_{60} in the interval 1.31–2.26 eV, and V_{oc} changes a sign in the region 2.26–3.10 eV (Fig. 5, curves 1 and 2, respectively). The peak value of V_{oc} is by an order greater than that for HS PbPc/C_{60} (Fig. 4, curve 1). If the cell is illuminated via the SnO_2-electrode, V_{oc} is anticorrelated with the absorption spectrum of HS in the region of 1.31–2.26 eV and is correlated in the region of 2.26–3.10 eV (Fig.5, curves 3 and 2, respectively). Thus, V_{oc} changes a sign in the region 1.59–2.02 eV.

The absorption bands of C_{60} in the solid and molecular states have been classified in [10]. Thus, the weak absorption of C_{60} (Figs. 1–3, curve 2) in the region 1.85–2.26 eV can be attributed to the forbidden transitions of $h_u - t_{1u}$ (γ group) which are partly displayed as a result of the excitation of the odd vibration mode and depend on Jahn–Teller-type interaction [11]. The more intense absorption of C_{60} at 2.26–3.10 eV is attributed to the allowed electron-hole transitions of $h_u - t_{1g}$ (groups A and B) with the symmetry of T_{2u}, H_u, and G_u [12]. The energies of forbidden triplet and singlet Frenkel excitons for C_{60} molecules are 1.55 and 1.84 eV, respectively [13].

The intense structural absorption bands with maxima at 1.71 eV (ClAlClPc) and 1.70 eV (PbPc) (curve 3, Figs. 1 and 2, respectively) are identified as Q-bands [14].

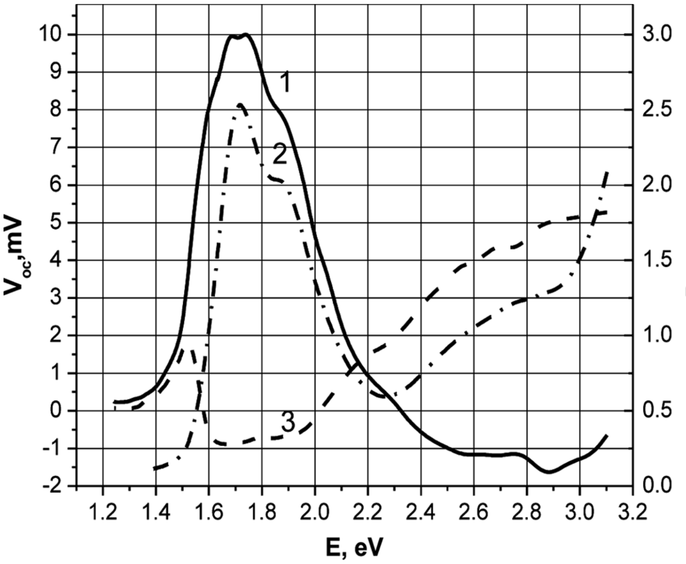

Figure 5. Spectra of V_{oc} for sandwich cells SnO_2/ClAlClPc/C_{60}/Ni (illumination via the Ni-electrode – curve 1 and SnO_2-electrode – curve 3) and absorption of HS ClAlClPc/C_{60} (curve 2). The thickness of ClAlClPc and C_{60} films is 230 nm and 200 nm, respectively.

The bands with less intensities of the peaks at 1.88 eV (ClAlClPc) and 1.87 eV (PbPc) have, probably, the electron-vibronic nature, because their energy distances to the proper bands at 1.81 and 1.80 eV are equal to 0.17 eV and are near to the energy of fully-symmetric vibrations of molecules of polyacenes [15]. On the long-wave side of Q-bands, there are the less intense bands of CT-excitons in the region of 1.46–1.55 eV [8].

In the region 1.13–3.10 eV the absorption band at 3.08 eV is characteristic for the neutral molecules $TCNQ^0$. For the molecules of anion-radical $TCNQ^-$, the bands are observed at 1.46; 1.66; 1.80, and 3.08 eV [16]. In the absorption spectra of a TCNQ film (Fig. 3, curve 3), these bands have been observed at 1.52; 1.65; 1.83, and 2.85 eV, which testifies to the presence of the $TCNQ^0$ and $TCNQ^-$ forms in this film. Thus the molecules $TCNQ^0$ and $TCNQ^-$ are formed TCNQ film. For HS $TCNQ/C_{60}$, the long-wave band of $TCNQ^-$ is displaced bathochromically, and its maximum is at 1.44 eV (Fig. 3, curve 1). In addition, in the region of 1.13–1.24 eV, there is a band, which is absent in the absorption spectra of TCNQ and C_{60} (Fig. 3, curves 3 and 2, respectively). It is possible to assume that it has the CT nature that corresponds to the data of paper [17].

The analysis shows that, among substances investigated in our work, the strongest electron acceptor is $TCNQ^0$. We suppose that this compound contains the $TCNQ^-$ form in thermally deposited TCNQ films interacting with oxygen of air or with molecules of impurities.

The formation of $TCNQ^-$ on the surface of a TCNQ film occurs during the deposition of C_{60} layer on the interface of films of TCNQ and C_{60} as a result of the interaction of molecules $TCNQ^0$ and C_{60}. This is confirmed by the bathochromic displacement of the long-wave band of TCNQ by 0.06 eV, the appearance of a new band at 1.18 eV (Fig. 3, curves 1 and 3), and and maximal values of ΔD at 1.81; 1.66, and 1.44 eV (Fig. 3, curve 4). Thus C_{60} molecules are able to create CT-complexes with different organic molecules. We assume that for the interaction of C_{60} and $TCNQ^0$ molecules the electron transfer (partial or complete) occurs in this case from T_1- or S_1- levels of C_{60} molecule to the first excited level of $TCNQ^0$ molecule.

According to [1–4], C_{60} is the acceptor of electrons in HS XPc/C_{60}. In other words, the corresponding CT-complexes appear as a result of the electron transfer from molecules of XPc onto molecules of C_{60}.

In the case of HS $PbPc/C_{60}$, the extremal values of ΔD are observed at energies of photons 1.63 eV (minimum) and 1.94 eV (maximum) (Fig. 2, curve 4). The abscissa of the minimum point of ΔD is near the CT-state energy ($E = 1.44$ eV) of PbPc molecule (Fig. 4, curves 1 and 2) and the T_1-state (1.55 eV [13]) of C_{60} molecule. The abscissa of the maximum of ΔD is in the region of energies of singlet excitons of C_{60}(1.84 eV [13]).

Dark current-voltage characteristics (I-V characteristics) of sandwich cells $SnO_2/PbPc/C_{60}/Ag$ are close to symmetric ones, i.e., the electrodes of cells are quasi-ohmic. The spectrum of V_{oc} was registered only at the illumination through the bottom SnO_2-electrode. At the illumination through the Ag-electrode, V_{oc} has a very low value close to zero, which is due to a small transparency of the electrode. The sign of V_{oc} on the illuminated electrode is positive. Since C_{60} is an n-type semiconductor, and PbPc is p-type semiconductor in air [14, 18], we can assume that, on the interface of HS $PbPc/C_{60}$, the aniso-type heterojunction appears with a positive charge on PbPc and a negative one on C_{60}.

The data obtained testify that the transfer of electrons can take place from the excited levels of the Q-band or CT-states of PbPc on the unoccupied S_1- or T_1- levels of C_{60}, respectively.

The maxima of ΔD for HS ClAlClPc/C_{60} are at 1.71 and 1.88 eV, which coincide with those of the Q-band of ClAlClPc (Fig. 1, curves 4 and 1, respectively), while the energetic position of ΔD minimum is 1.55 eV. These data testify that the formation of a CT-complex between ClAlClPc and C_{60} molecules takes place by the above-mentioned mechanism analogously as for the molecules of PbPc and C_{60}.

The dark I-V characteristics of sandwich cells SnO_2/ClAlClPc/C_{60}/Ni are asymmetric. Thus, the dependences of V_{oc} (E) change a sign at the illumination through both electrodes (Fig. 5, curves 1 and 2). These data testify that, in these cells, there are two potential barriers of opposite polarities: the electrical double layer (EDL) on the interface of ClAlClPc/C_{60} and a Schottky barrier near the Ni-electrode. The detailed study of photoelectric properties of a sandwich cell of SnO_2/ClAlClPc/C_{60}/Ni will be the subject of further studies.

Conclusions

It is stated that the band of $TCNQ^-$ at 1.52 eV in the absorption spectra of HS TCNQ/C_{60} is bathochromicaly displaced by 0.06 eV, and there is the band of a CT-complex at 1.18 eV. This information testifies that, on the interface of TCNQ/C_{60}, EDL appears as a result of the transfer of electrons from the molecules of C_{60} to the molecules of TCNQ. Thus, the abscissae of maximal values of the dependence ΔD (E) coincide with the positions of maxima of the absorption bands of $TCNQ^-$.

In a spectral region 1.24–3.10 eV, the contribution to V_{oc} of HS XPc/C_{60} is given by both components of HS. At the quasi-ohmic electrodes of V_{oc}, EDL is formed on the interface as a result of the transition of electrons from the molecules of XPc ($X = Pb$ and ClAlCl) on the molecules of C_{60}.

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