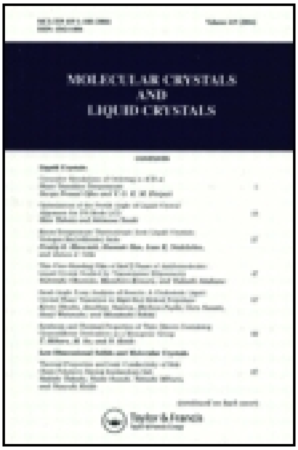

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Organic p-n Type Heterostructures Based on the Hexatiopentacene

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Organic *p-n* Type Heterostructures Based on the Hexatiopentacene

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The major task of our work was to search for new organic p-n-type heterostructures photosensitive in a wide spectral region and with a small recombination rate at the interface. We used photosensitive hexatiopentacene layers as p-type components and methyl perylene pigment, C_{60} and V_2O_5 xerogel films as n-type ones. Photovoltage spectra are well described by the Van Opdorp model, which considers the presence of surface states at the free surface and the interface. The diffusion lengths of charge carriers in hexatiopentacene (200 nm) and methyl perylene pigment (40 nm) films are determined. We have shown the perspectivity to use the hexatiopentacene/methyl perylene pigment heterostructures for manufacturing plastic solar cells.

Keywords: heterostructures; hexatiopentacene; interface; organic semiconductors; solar cells

INTRODUCTION

P-n type heterostructures (HS) from organic and inorganic semiconductors are perspective for the development of organic solar cells if a significant blocking bend of bands is formed at their interface, and the rates of trapping and recombination of charge carriers are small [1,2]. Now the great efficiency of sunlight transformation has been achieved with HS based on the p-type components, pentacene and phthalocyanines [3–9]. But this efficiency is not sufficient for the production of solar cells. The basic reasons are the small quantum

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efficiency of the photogeneration of charge carriers at their n-type component, great resistance caused by the low conductivity of their components, and the narrow absorption spectral range (in comparison with that of solar cells based on CdTe and Si [1]).

As a p-type component, we used photosensitive hexatiopentacene (HTP – Fig. 1a) films, whose conductivity by 2 orders higher than that in pentacene and phthalocyanine films [10]. The absorption spectral region was widened to the IR-region up to 1.5 eV (compared to pentacene layers [8,9]) and was close, for example, to the absorption region of CdTe films [1].

We used MPP (methyl perylene pigment or N, N′ – bismethyl – perylene 3, 4:9, 10 tetracarboxylic acid diimide) [3–7], C_{60} [4] and V_2O_5 xerogel [11,12] n-type layers for the creation of a blocking barrier. This choice was caused by the fact that MPP and C_{60} have large quantum efficiency of the photogeneration of charge carriers in

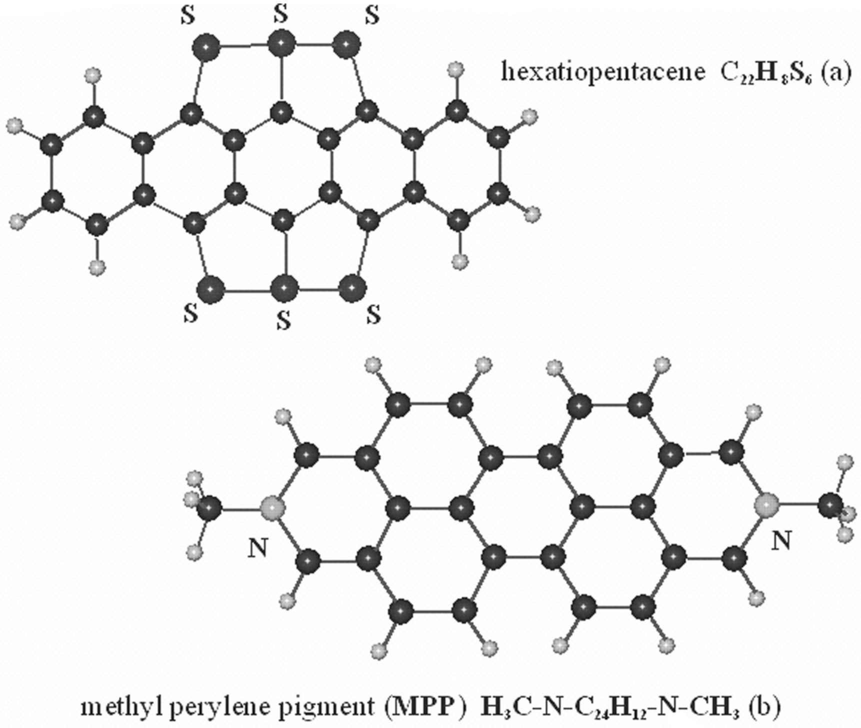

FIGURE 1 Chemical structures of molecules hexatiopentacene (HTP) – $C_{22}H_8S_6$ (a) and methyl perylene pigment (MPP) – $H_3C\text{-}N\text{-}C_{24}H_{12}\text{-}N\text{-}CH_3$ (b).

the spectral range of HTP low absorption (2.0–2.5 eV) [10]. Moreover, the conductivity of V_2O_5 xerogel films is sufficiently higher as comparing to the organic component.

EXPERIMENTAL

All organic films were prepared by the method of vacuum deposition, and V_2O_5 xerogel (the hydrated compound, vanadium pentoxide $V_2O_5 \times nH_2O$) by the sol-gel method from a colloid solution obtained with the help of the Biltz method [11,12]. The thickness of organic films was checked during evaporation and was close to the typical thickness of a space charge region in organic layers (30–50 nm), but smaller than the diffusion length of excitons in pentacene layers (200 nm) [2]. The typical thickness of V_2O_5 xerogel films was nearly 500 nm.

For the measurement of photovoltage properties, we used SnO_2 deposited on quartz substrates as transparent (transmission 80%) and conductive (specific resistance $\rho \approx 100\,\text{Ohm}\,\text{cm}^{-2}$) layers (Fig. 2).

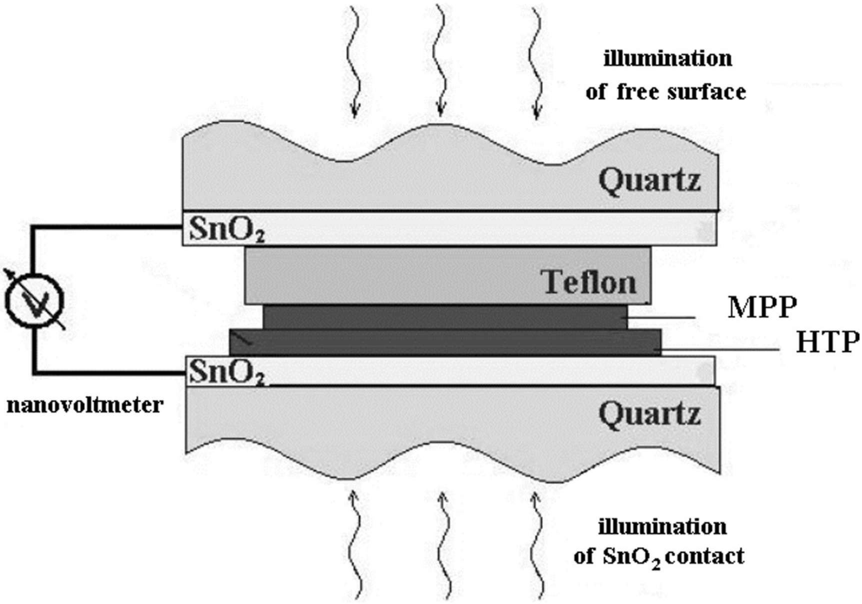

FIGURE 2 Schematic representation of the configurations of p-n heterostructures SnO_2/HTP/MPP.

Photovoltage, $\boldsymbol{\varphi}(\boldsymbol{hv})$, has been measured by the Bergman method under the illumination by a modulated light of both sides of a sample. This allowed us to check the presence of barriers at the bottom SnO_2-electrode and the free surface (Fig. 2). $\boldsymbol{\varphi}(\boldsymbol{hv})$ were measured by an "Unipan-232B" nanovoltmeter and were normalized on the same number of incident photons.

Absorption spectra were measured on a "HITACHI 356" spectrophotometer.

RESULTS AND DISCUSSION

The spectral dependences $\boldsymbol{\varphi}(\boldsymbol{hv})$ and $k(\boldsymbol{hv})$ for HTP and MPP films are shown in Figure 3. It is visible that a photovoltage of thermally deposited HTP films is approximately the same under illumination of the contact electrode SnO_2, $\boldsymbol{\varphi_c}$, and the free surface, $\boldsymbol{\varphi_s}$, in the first electronic transition range (1.45–1.75 eV). $\boldsymbol{\varphi_c} \approx \boldsymbol{\varphi_s}$ and correlates with their absorption value if $k < 4 \cdot 10^4\,\mathrm{cm}^{-1}$ (Fig. 3). It confirms the equal blocking bend of bands from both sides of a film. At the further increase of the absorption ($k > 4 \cdot 10^4\,\mathrm{cm}^{-1}$), $\boldsymbol{\varphi_s} < \boldsymbol{\varphi_c}$, and both $\boldsymbol{\varphi_s}(k)$ and $\boldsymbol{\varphi_c}(k)$ tend to a saturation (Fig. 4), which testifies to the presence of the trapping and recombination of charge carriers that is greater on the free surface of a film.

After annealing in air at temperatures 350–370 K in the range of the first electronic transition, the photovoltage $\boldsymbol{\varphi}$ correlates with their absorption value for $k < 7 \cdot 10^4\,\mathrm{cm}^{-1}$ (Fig. 4, curves 1, 2). At a temperature 390 K, $\boldsymbol{\varphi}$ correlates with $k < 3 \cdot 10^4\,\mathrm{cm}^{-1}$ only and the anticorrelation $\boldsymbol{\varphi}$ and k is observed (Fig. 4, curve 3). Since the blocking bends of bands are equal from both sides of a film, it is the argument for a decrease in the recombination and trapping at annealing temperatures $T \le 370$ K and a significant increase at the highest temperatures.

According to the theoretical model of Van Opdorp [1], which considers the presence of surface states at the free surface and the interface,

$$\begin{aligned}\boldsymbol{\varphi} = A\boldsymbol{\beta}(hv)Y_s exp(-k^*d^*)\Bigg\{ & 1 - exp(-kl) + \frac{kL}{1-(kL)^2} \\ & \times \left[\left(\frac{sh\left(\frac{d-l}{L}\right) + \frac{SL}{D}ch\left(\frac{d-l}{L}\right)}{ch\left(\frac{d-l}{L}\right) + \frac{SL}{D}sh\left(\frac{d-l}{L}\right)} - kL\right)exp(-kl)\right. \\ & \left. + \frac{kL - \frac{SL}{D}}{ch\left(\frac{d-l}{L}\right) + \frac{SL}{D}sh\left(\frac{d-l}{L}\right)}exp(-kd)\right]\Bigg\}, \end{aligned} \qquad (1)$$

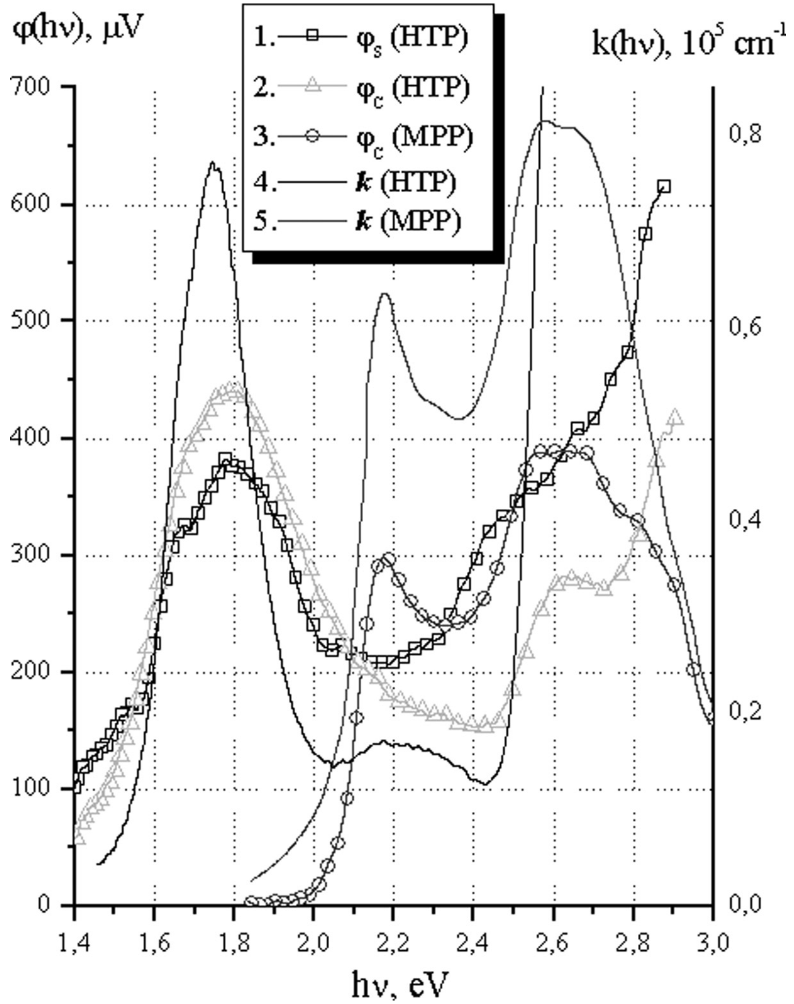

FIGURE 3 Spectral dependences of photovoltage $\varphi_s(h\nu)$ (1), $\varphi_c(h\nu)$ (2), and absorption factor $k(h\nu)$ (4) for HTP thin films and $\varphi_c(h\nu)$ (3), $k(h\nu)$ (5) for MPP thin films.

where k^*, k-absorption factors of the top and bottom layer, respectively, of the semiconductor, A-coefficient independent of k, Y_S-height of a potential barrier (bend of bands) at the interface, $\beta(h\nu)$-quantum efficiency of photogeneration, S-rate of surface recombination, D and L-diffusion coefficient and length, l-space charge region, and d-thickness of a film. We consider $\varphi(k)$ in the range of the first

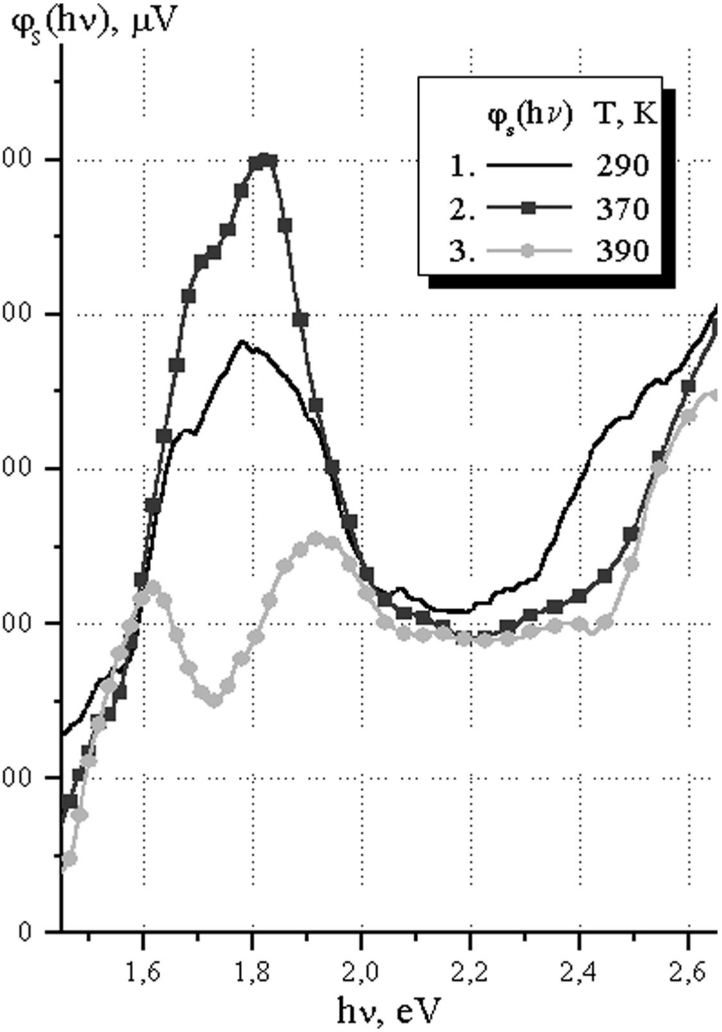

FIGURE 4 Spectral dependences of photovoltage $\varphi(h\nu)$ under illumination of the free surface – φ_s before annealing (1) and after annealing temperatures $T = 370\,K$ (2) and $T = 390\,k$ (3) for HTP thin films.

electronic transition (1.45–1.75 eV), where the absorption of an n-type layer has a insignificant contribution ($k^* \ll k$).

We specify $d \approx l$ during the preparation of researched structures. At $\beta(h\nu) = const$ (this holds within the limits of one electronic transition), and $SL \leq D$, $\varphi(k)$ can be written as:

$$\varphi = AY_S\beta\frac{kl}{(1+kL)} \tag{2}$$

$$\frac{1}{\varphi} = \frac{1}{lAY_S\beta}\left(\frac{1}{k}+L\right). \tag{3}$$

Interpolation of $\varphi^{-1}(k^{-1})$ Eq. (3) in the range of the first electronic transition for the studied HTP films allows us to estimate the diffusion length of charge carriers: $L = 200 \pm 50\,\text{nm}$ (Fig. 5) which practically was not changed after annealing up to 370 K (Fig. 5, curves 1–3). Similarly for MPP films, we get $L = 40 \pm 10\,\text{nm}$ (Fig. 5, curves 4, 5). The calculation has shown that the experimental dependence $\varphi(k)$ for the studied HTP films is described well by Eq. (1) at $S/D \sim 10^5\,\text{cm}^{-1}$ before annealing ($T = 290\,\text{K}$) and $S/D \sim 5 \cdot 10^4$ and $2 \cdot 10^5\,\text{cm}^{-1}$ after annealing at temperatures of 370 and 390 K, respectively (Fig. 6).

Whereas HTP is as a p-type component and has sunlight transmission in the range 2.0–2.5 eV and good absorption in the range 1.55–1.95 eV, n-type materials should absorb light and generate the charge carriers in the transparency range of HTP (2.0–2.5 eV). Our measurements of HS photovoltage have confirmed a significant increase of photosensitivity in the range 2.0–2.5 eV for HS HTP/MPP MPP only (Fig. 7).

It is obvious from Figure 7 that both the photovoltage HS in the transparency range of HTP, $\varphi(\boldsymbol{\nu})$, and the integrated photosensivity [the area under curves $\varphi(\boldsymbol{h\nu})$] grow in the series V_2O_5,C_{60}, MPP (Fig. 7).

Simultaneously, we observed the increase of $\varphi(\boldsymbol{h}\nu)$ HS in the range of 1.55–1.95 eV where the basic contribution to the formation of a photovoltage is given by the charge carriers photoexcited in HTP. It testifies to an increase of the barrier size at the interface in the series V_2O_5,C_{60}, MPP (Fig. 7)

It is visible also that the $\varphi(\boldsymbol{h}\nu)$ spectra of components correlate well with the spectrum of HS SnO_2/HTP/MPP (Fig. 3, curves 1, 3; Fig. 7, curve 1) in the range of their photosensivity. The estimation of the dependence $\varphi(k)$ HS HTP/MPP in the range 1.45–1.75 eV with Equation (1) gives a good coincidence with the experimental value at $S/D \leq 10^4\,\text{cm}^{-1}$. The trapping and recombination at the interface HS HTP/MPP is much less than that at the free surface of HTP films. This confirms that HS HTP/MPP is the most effective sunlight converter from all researched HS based on HTP.

Comparing HS HTP/MPP with others HS based on MPP and phthalocyanine (Pc) (Fig. 8), we have shown that the spectral ranges

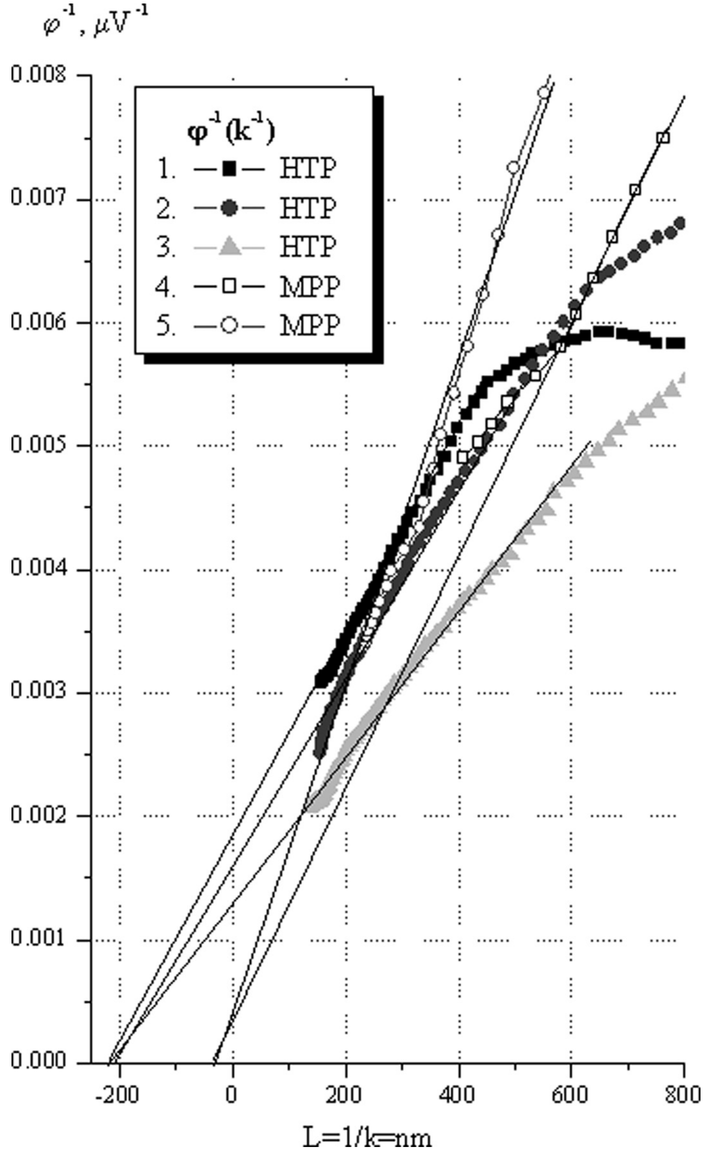

FIGURE 5 Dependences of inverse photovoltage under illumination of the free surface $-\varphi_s^{-1}$ (1) on the inverse absorption factor k^{-1} before annealing (1) and after annealing temperatures T = 350 K (2) and T = 370 K (3) for HTP thin films in the range 1.45–1.75 eV, and φ_s^{-1}(4), φ_c^{-1} (5) vs. k^{-1} in the range 1.8–2.2 eV for MPP thin films.

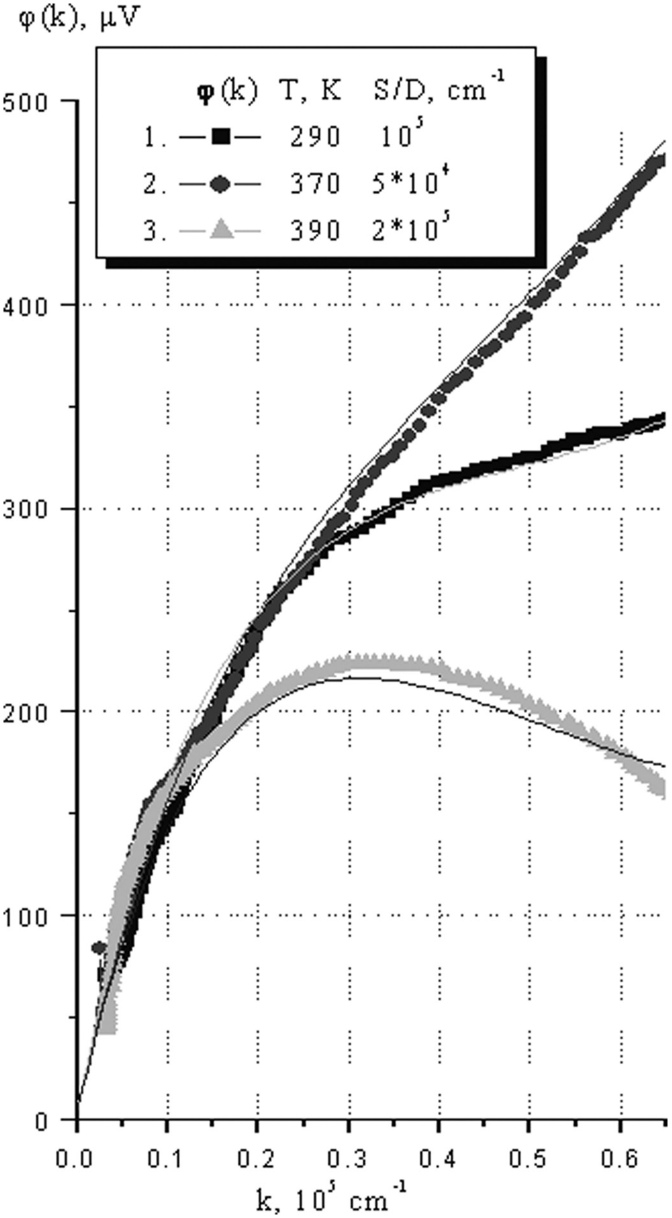

FIGURE 6 Dependences of photovoltage $\varphi(k)$ under illumination of the free surface – $\boldsymbol{\varphi}_s$ on the absorption factor k before annealing (1) and after annealing temperatures T = 370 K (2) and T = 390 K (3) for HTP thin films in the range 1.45–1.75 eV.

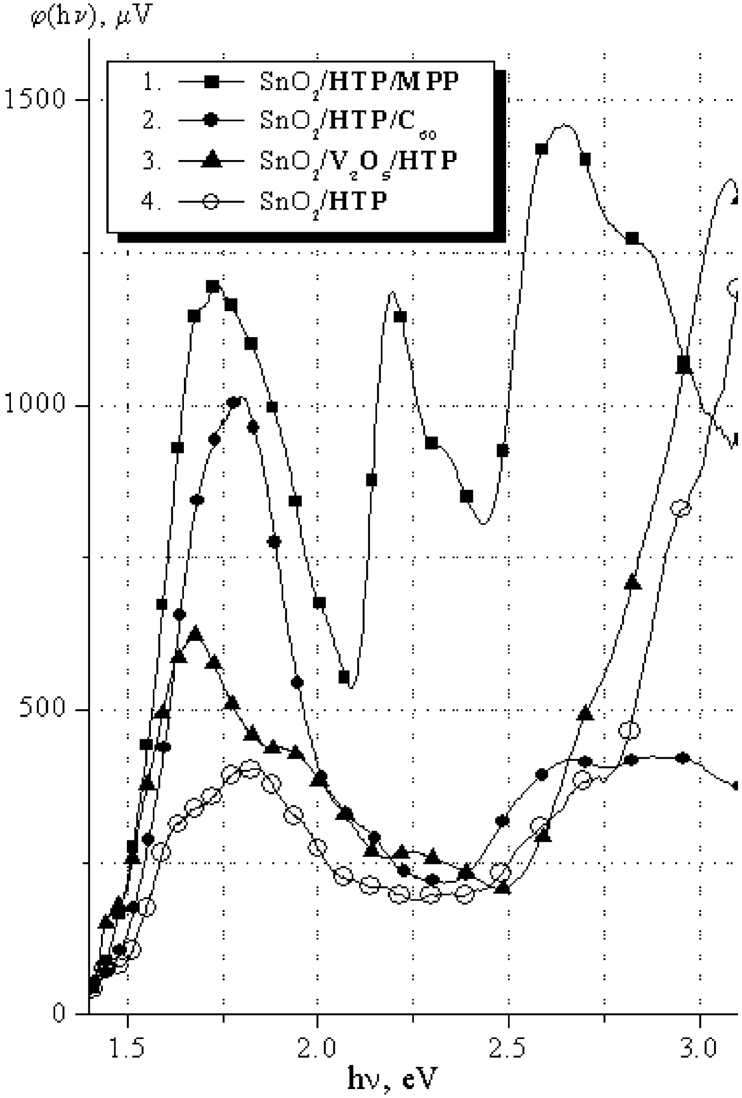

FIGURE 7 Spectral dependences of photovoltage $\varphi(h\nu)$ under illumination of the free surface – φ_s HS HTP/MPP (1), HTP/C_{60}(2), V_2O_5/HTP (3), and SnO_2/HTP (4).

of their photosensitivity are practically equal. But the photosensitivity of HS HTP/MPP is greater by 2–3 times than those of HS TiOPc/MPP [5] and ZnPc/MPP [6], for example, in the range of 1.5–2.2 eV.

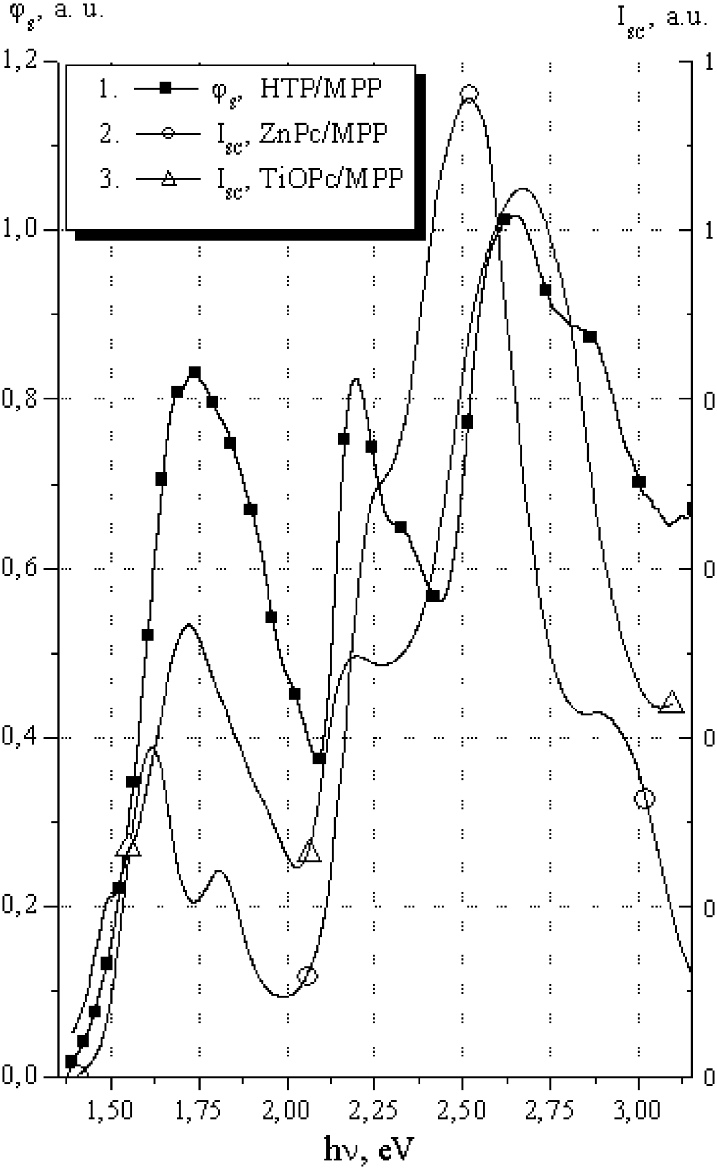

FIGURE 8 Spectral dependences of photovoltage $\varphi(h\nu)$ (1) and short circuit current – $I_{sc}(h\nu)$ (2, 3) – HS HTP/MPP (1), ZnPc/MPP (2) [6] and TiOPc/MPP(3) [5].

CONCLUSIONS

1. The diffusion length of charge carriers in vacuum deposited hexatiopentacene films is $L = 200 \pm 50\,\text{nm}$. The diffusion length of hexatiopentacene films is comparable to the diffusion length of excitons in pentacene films and more than that in phthalocyanine and methyl perylene pigment. That allows supposing their use as effective components for the creation of organic solar "heterocells".
2. The efficiency of trapping and recombination at the free surface hexatiopentacene films can be essentially decreased after annealing in air at temperatures 350–370 K.
3. In two-layered heterostructures hexatiopentacene/methyl perylene pigment, we have observed high photovoltage sensitivity in a wide spectral range, and the trapping and recombination at their interface is less than that at the free surface of hexatiopentacene films. Therefore, these heterostructures are perspective for the development of organic solar cells.

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