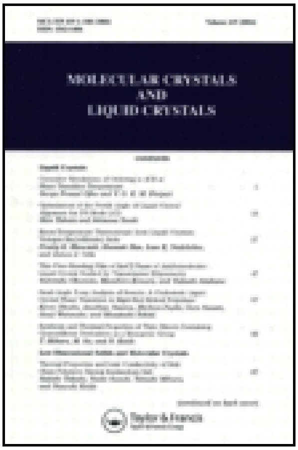

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Photovoltaic Properties of Molecular Crystal - Liquid Crystal Composites

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Photovoltaic Properties of Molecular Crystal – Liquid Crystal Composites

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A strong increase of a photovoltage has been found in composites fabricated from photosensitive semiconductors (both organic and inorganic) and nematic liquid crystals (LC) comparing corresponding powder samples of photoconductors upon illumination with light of the energy of quanta greater than the band gap of semiconductors.

The origin of observed effects has been discussed.

Keywords: composites; liquid crystals; molecular crystals; photovoltage; band gap

INTRODUCTION

An increasing attention has been given over last years to investigations of physical properties of composites, the interest resulting from emerging perspectives of their application, e.g., as materials for information recording [1,2], in displays [3], memory systems [4] components of plastic solar cells [5] etc.

It has been found that some properties of composites (including the charge carriers photogeneration efficiency) [2] are enhanced in comparison with those of pure components, and parameters of structures so obtained are improved. These studies have been focused on LC - polymer composites [1,3,4] and photosensitive molecular crystal (MC) - polymer composites [2,5].

Processes at the interface between LC and second component as well as LC interaction with other component play an important role in composite systems.

The aim of present paper is to investigate processes in MC-LC composites and inorganic semiconductor - LC composites, whose properties should be easily modified by electric and magnetic fields.

EXPERIMENTAL

As photosensitive component we used various MC including tetracene, tetratiotetracene (TTT), pentacene (Pn), phthalocyanines of lead (PbPc) and CoCl (CoClPc), as well as inorganic CdSe for the preparation of composites. The nematic LC mixture BL055 (LC Licrilite®,Merck Ltd.) with positive $\Delta\varepsilon$ (1kHz) = +13.42, $\varepsilon_{||}$ = 19.42 (analogous to E25M LC mixture) was used in the preparation of all composite samples. Samples were prepared by mixing fine powdered crystallites of MC or CdSe (33 wt. %) and LC (67 wt. %) at 300 Ê (these samples will be referred to as LC composites). The mixture was placed in a cell between two glass plates with deposited SnO_2 electrodes. Samples thickness (20 μm) and area (8x10 mm) were set by teflon spacers. Freshly prepared samples were homogeneous, as was confirmed by measurements of photovoltage (V) in the strong absorption region (~1.8 eV) under the excitation from different sides of the sample: the difference of V was inferior to 10 %.

Cells containing only fine powdered crystallites of MC or CdSe, having the same parameters (thickness, area etc.) as those made of LC composites, were also prepared for comparison.

Spectral dependences of the photovoltage were measured in all samples by illuminating them with modulated light (f_{mod}=80Hz). Iodine lamp (120 W, «Hitachi») and serial light diodes: red (E=1,772 eV) and green (E=2,195 eV) were used as light source. V was measured with a lock-in nanovoltmeter UNIPAN 232B, supplied with a 233-7 preamplifier (10^9 Ohm). The experimental setup and measurement technique have been described in more detail in [6].

RESULTS AND DISCUSSION

The photovoltage of composites (absolute value) under the illumination of red light diode decreased in the series: CdSe, PbPc, Pn, tetracene, CoClPc, TTT.

Fig.1 (solid mark curves) shows spectral dependences of the photovoltage measured on LC composites based on Pn, PbPc, CdSe and spectral dependences measured on respective powders (open mark curves). All curves have been corrected for the number of incident light quanta.

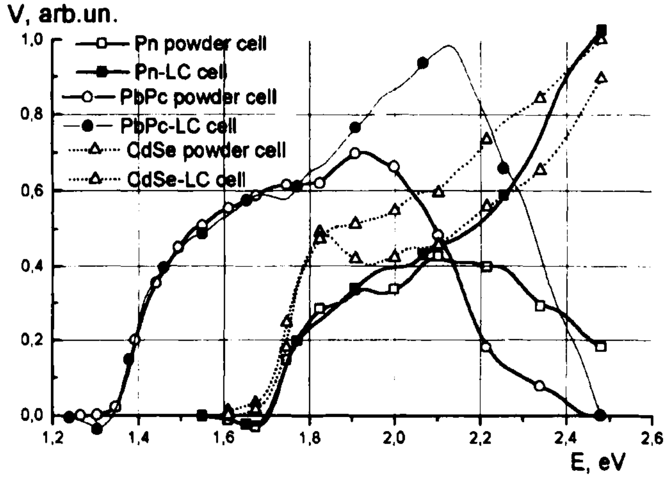

FIGURE 1 Spectral dependences of the photovoltage measured in LC composites and respective photoconductor powders.

It is obvious from Fig.1 that the main feature of the spectral performance of LC composites is their increased photosensitivity in the short wavelength region (hv>1.8 eV), significantly exceeding that of parent powders. The onsets to the increase of ΔV are located at 1.9 eV for PbPc-based composite, at 2.1 eV for Pn-based composite and

1,8 eV for CdSe one. Peak values $V_{composite} / V_{powder}$ ratio are following for these compounds: Pn - 6,8 (at 2,6 - 2,7 eV); PbPc - 5,5 (at 2,5-2,6 eV); CdSe - 1,35 (at 2,16 eV; See Fig.1).

It should be noted that phase φ of V changed on 180 degrees for CdSe contained samples with respect to V of other samples since CdSe is n-type semiconductor in spite of the fact that other investigated compounds are p-type semiconductors.

TABLE I Values of photovoltage increase and determined E_g values (see below) for investigated compounds

Compound	Averaged value of V increase, arb.units	$V_{composite}/V_{powder}$ ratio, estimated for light diodes, arb.units	E_g, eV (calculated, See Fig.2)	E_g, eV (previously published data)
Tetracene	2,1±0,05	—	2,93±0,03	2,95±0,03 [8]
Pn	1,9±0,05	—	2,22±0,03	2,2±0,02 [8]
TTT	—	1,5±0,1	—	2,0±0,03 [8]
PbPc	1,45±0,05	—	2,02±0,03	~2 [9]
CoClPc	—	1,38±0,1	—	~2 [9]
CdSe	1,16±0,05	—	1,74±0,03	1,75±0,01[10]

Table 1 shows averaged values of V increase determined as the ratio of $\int VdV$ for LC composite and $\int VdV$ of corresponding powder sample (areas under corresponding curves in Fig.1) for studied substances.

Unfortunately we could not measure with enough accuracy (noise-to-signal ratio > 10 %) photovoltage spectra of both composite and powder samples of TTT as well as of CoClPc powder sample. Because of this an relative value calculated from V ratio for the illumination of red and green light diodes and characterized V increase in LC composites is indicated in the table for these compounds. It can be seen that for acenes this value increase in series: tetracene, TTT, Pn, among phthalocyanines studied increasing value is maximal for PbPc, and for inorganic CdSe minimal V increase was observed.

The main conclusion from Table I is the correlation between E_g value and value of V increase in composites.

The photovoltage increase observed in LC composites at $h\nu \geq E_g$ can be explained assuming an increased contribution states to the charge carrier photogeneration from the autoionization of higher excited singlet [7,8]. This is caused by an enhancement of the internal electric field at the interface between MC and LC crystallites: due to a high electric permittivity of LC, the thickness of the space charge region at the interfaces should significantly decrease. The autoionization mechanism is most effective for Pn films, being clearly observed in photoconductivity spectra at $h\nu > E_g$ in strong electric field ($\cong 10^5$ V/cm) [7,8]. The effect has not been observed earlier in photovoltage spectra because internal electric fields near metal/Pn interfaces have usually been much lower ($\cong 10^4$ V/cm). The efficiency of the autoionization of higher excited states in PbPc films is smaller than in Pn, thus the contribution from the considered mechanism to the photogeneration process would be comparable with those of other

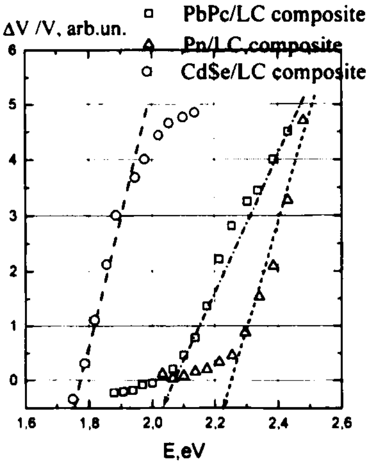

FIGURE 2 ΔV/V dependences determined for Pn- , PbPc-and CdSe-based composites. Dashed lines show the extrapolation of linear parts of dependences.

mechanisms of photogeneration, in particular with the photogenrearion via CT states.

Curves shown in Fig. 1 exhibit a decrease of ΔV around 2.4 - 2.6 eV, i.e., in the weak absorption region, due to a decrease of number of absorbed light quanta. Since both V and ΔV depend in the same way on the number of absorbed quanta, then the ratio ΔV/V ratio should not depend on absorbance, being proportional to the quantum efficiency of photogeneration (β). This feature has been used by us to interpret results obtained, as is shown in Fig. 2. According to [8] it is possible to determine E_g of MC by extrapolation of the linear section of β(hν) dependences. It can be seen that the extrapolated cutoff energies are approximately equal to E_g values determined independently for Pn, PbPc and CdSe.

It should be noted that the onset energies of ΔV/V are very close to band gap energies (E_g) for all materials that were used in experiments. It is obvious from Table 1 which shows E_g values determined by above technique for substances studied.

The band gap energy determined for crystals and films of Pn amounts to 2.2 eV [8], for tetracene and TTT this values are 2,95 and 2,0 eV [8], the value commonly accepted for phthalocyanines is equal to ca. 2.0 eV [9], for CdSe corresponding value is 1,75 eV [10] . No precise E_g value has been determined for PbPc but the value of 2.0 eV should be approximately correct since the energy of highest CT states (the process of photogeneration takes place via these centers) for films of the most stable polymorphs is 1.91 and 2.12 eV [11], and the photocurrent energy activation is 0.03 eV [11].

Our hypothesis was additionally checked on PbPc-based PM composites: we used polyurethane - a polymer whose electric permittivity exceeds that of MC and air [12]. An extrapolation of the ΔV/V(hν) curve yields the same value of E_g as for the corresponding LC composite.

CONCLUSIONS

1. A strong increase of the photovoltage (significantly exceeding than that of parent powders) was found for the first time in LC composites in the high energy region (at hν>E_g). This increase is caused by an increased contribution from the autoionization of

higher singlet states. The observed effect is explained by the enhancement of electric fields at the MC-LC interfaces, due to higher electrical permittivities of the latter components.

2. The increase of V is correlated with E_g value of compounds.
3. The release of minority charge carriers (electrons) trapped on the surface of crystallites is more effective in composites than in film and in powder samples.

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