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# Photovoltaic properties of C 60 /liquid crystal composites and heterostructures

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### PHOTOVOLTAIC PROPERTIES OF $C_{60}$ /LIQUID CRYSTAL COMPOSITES AND HETEROSTRUCTURES

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An increase of the photovoltage was found in  $LC/C_{60}$  composites and heterostructures comparing  $C_{60}$  film in the 2–3 eV range, where two charge transfer states (CT-states) at 2,4 eV and 2,7 eV are present in  $C_{60}$ . A sufficient increase of an intensity and area for 2,4 eV CT-band is observed for the composite sample, while HS photovoltage rises more strongly at the region of 2,7 CT-band.

Band gap values estimated from the comparison of photovoltage spectra of  $C_{60}/LC$  composite and heterostructure with photovoltage of  $C_{60}$  film were following: 2,18 eV for the composite and 2,26 eV in the case of heterostructure.

The origin of observed effects has been discussed.

Keywords: composites; heterostructures; liquid crystals; fullerene; photovoltage and band gap

#### INTRODUCTION

An increasing attention has been given over last years to investigations of physical properties of composites and heterostructures (HS) [1–8]. These studies have been focused on LC—polymer composites [1,2], LC—colloid particles composites [3,4] and photosensitive molecular crystal—polymer composites [5,6] as well as LC HS [7,8].

The interest to the investigation of composites is the result of their possible application, e.g., as materials for information recording [2,3], in displays [1-4,8], photosensitive devices [5,6] etc.

It has been found that properties of composites and HS aren't the sum of properties of components and they are enhanced in comparison with those of pure components [1–8]. So parameters of structures obtained are improved.

The aim of present paper is to investigate processes in  $C_{60}/LC$  composites and HS.

#### **EXPERIMENTAL**

To prepare composites and HS as photosensitive component we used fullerene  $C_{60}$ . The nematic LC 5CB was used in the preparation of composite and HS samples, also nematic LC mixture BL055 (LC Licrilite<sup>®</sup>,Merck Ltd.) was used to prepare some HS samples. Composite samples were prepared by mixing fine powdered crystallites of  $C_{60}$  (33 weight %) and LC (67 weight %) at 300 K. The mixture was placed in a cell between two glass plates with deposited  $SnO_2$ -electrodes. Samples thickness (10 µm) and area (8 × 10 mm) were set by teflon spacers. Freshly prepared samples were homogeneous, as was confirmed by measurements of photovoltage (V) in the strong absorption region under the excitation from different sides of the sample: the difference of V was inferior to 10%. Photosensitive  $C_{60}$  layer of HS were prepared by vacuum deposition onto glass substrates coated with  $SnO_2$  transparent electrodes. Temperature of substrate was  $\sim 300$  K.  $C_{60}$  and LC layers thickness was set equal to 0,1–0,4 and 10 microns, respectively.

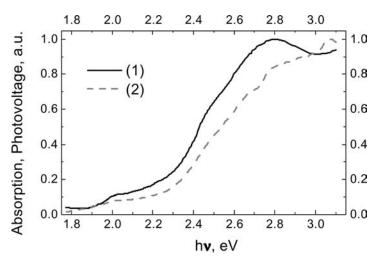
Cells containing  $C_{60}$  film only, having the same parameters (thickness, area etc.) as those made of LC heterostructures, and insulator teflon dielectric layer between film and top electrode,[9] were also prepared for comparison.

Spectral dependences of the photovoltage were measured in all samples by illuminating them with modulated light ( $f_{mod} = 80 \, Hz$ ). Iodine lamp (120 W, «Hitachi») was used as light source. Photovoltage (V) was measured with a lock-in nanovoltmeter UNIPAN 232B, supplied with a 233-7 preamplifier (10<sup>9</sup> Ohm). All photovoltage spectra were normalized to the equal number of incident photons. The experimental setup and measurement technique have been described in more detail in [10].

#### **RESULTS AND DISCUSSION**

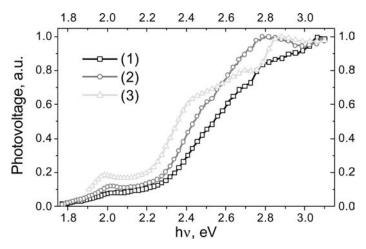
Figure 1 shows spectral dependence of absorbance (curve 1) and photovoltage (curve 2) of  $C_{60}$ . From Figure 1 it is seen that the spectrum of film photovoltage is generally similar to absorption spectrum with the change in the ratio of bands intensity.

Figure 2 shows spectra of photovoltage for  $C_{60}$  cell (curve 1),  $C_{60}/LC$  heterostructure (curve 2) and composite (curve 3). Photovoltaic response of HS and composite is sufficiently greater by an absolute and relative value comparing  $C_{60}$  film containing cell. It can be seen in Figure 2. Averaged values of V relative increase determined as the ratio of  $\int V dV$  for composite and HS and  $\int V dV$  of corresponding film (areas under curves in Fig. 2) are  $\sim 1.2$  for HS, and 1.27 for composite. It should be noted that going from



**FIGURE 1** Spectral dependence of absorption for  $C_{60}$  film (1) and photovoltaic response of  $C_{60}$  cell (2).

thinner to more thick layers, which used as components of HS, the increase of photovoltaic signal is observed. This is caused by the increase of bulk component deposit (so called Dember voltage) and by the change of surface properties with thickness. Maximal photoresponse for HS is observed



**FIGURE 2** Spectral dependence of photovoltage for  $C_{60}$  cell (1),  $C_{60}/LC$  heterostructure (2) and composite (3).

by illumination from LC side that evidences about a sufficient deposit into photovoltaic signal of a near-interface (LC/ $C_{60}$ ) region.

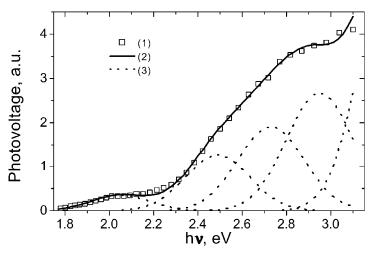
Spectral region of the increase is  $2.2 \,\mathrm{eV} - 3 \,\mathrm{eV}$  (Fig. 2). According to [11] two charge transfer states (CT – states) are observed in this region for  $C_{60}$ . The energies of CT-states estimated by electroabsorption measurement are c.a.2,4 eV and 2,7 eV.[11] Detailed analysis of an electronic scheme of  $C_{60}$  was made in.[12]

The photovoltage increase observed in LC composites and HS in this region can be explained by an enhancement of the internal electric field at the interface between MC/LC due to a high electric permittivity of LC, the thickness of the space charge region at the interfaces should significantly decrease.

To clarify the change observed in the energy position of peaks we provided detailed Gaussian deconvolution of both absorption and photovoltage spectra of  $C_{60}$ /teflon cell, HS and composite. As starting parameters we used values from energy diagram of solid  $C_{60}$  presented in [12]

Figure 3 shows the Gaussian fitting of photovoltage spectrum of  $C_{60}$  containing cell together with elementary Gaussian.

Table I summarizes the results of all deconvolutions. The main conclusion from the Table is the fact that area under elementary curve (S) for  $\sim$ 2,4 eV CT — band is maximal for composite cell while for  $\sim$ 2,7 eV band the maximal band area is observed for C<sub>60</sub>/LC HS.



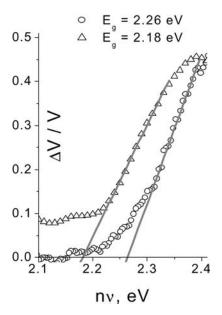
**FIGURE 3** Spectral dependence of  $C_{60}$  photovoltage (1) Gaussian fit (2) and component of fitting (3).

for investigated birdetures						
Structure		Peak position				
		2,05	2,46	2,73	2,95	3,30
Composite		5.6	17.6	16.7	21.4	39.8
C <sub>60</sub> film	S, %	2.5	9.7	15.1	21.1	51.7
Heterostructure		2.4	13.9	22.2	20.3	41.2

**TABLE 1** Values of Relative Areas of Bands (Areas under Elementary Curves - S) for Investigated Structures

Since both V and  $\Delta V$  depend in the same way on the number of absorbed quanta, then the ratio  $\Delta V/V$  ratio should not depend on absorbance, being proportional to the quantum efficiency of photogeneration ( $\beta$ ). According to [13] it is possible to determine  $E_g$  of MC by extrapolation of the linear section of  $\beta(h\nu)$  dependences.

In previous paper [14] we described the estimation of band gap  $E_g$  for organic solid films, using  $\Delta V/V$  ratio, where  $\Delta V$  is difference between V of composite (or HS) and V of film (powder) of organic photoconductor. We have shown [14] that such technique gives values of  $E_g$ , which are close to



**FIGURE 4**  $\Delta$ V/V dependence determined for C<sub>60</sub>/LC heterostructures (circles) and composite (triangles). Lines show the extrapolation of linear parts of dependences.

the values determined independently for different phthalocyanines, acenes and their derivatives.

It can be seen in Figure 4 above procedure gives following values of  $E_g$ : 2,18 eV for the composite and 2,26 eV in the case of HS.

The difference between two values can be explained by the different area of the effective interfaces. Such area in the case of composite is equal to the sum of local interfaces areas and significantly greater than area of the interface in HS. This naturally leads to some re-distribution in the deposit of different mechanisms of photogeneration to the photovoltage value.

The  $2,26\,\mathrm{eV}$  value is close to the value of  $E_g$  determined by surface photovoltage measurements, and  $2,18\,\mathrm{eV}$  is most close to the value estimated from photoemission studies [15].

#### CONCLUSIONS

- 1. An increase of the photovoltage (significantly exceeding than that of  $C_{60}$  film) was found for the first time in LC composites and HS in the region of CT-states.
- 2. This increase can be caused by the influence of LC and namely by the enhancement of an intrinsic electric fields at the  $C_{60}/LC$  interface in HS and  $C_{60}/LC$  local interfaces in the composite, due to higher electrical permittivities of the latter components.
- 3. The values of  $E_g$  estimated from photovoltage studies of  $C_{60}$  films, LC composites and heterostructures are correlated with  $E_g$  value of  $C_{60}$  determined by other methods and measurements.

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