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Diffusion length of singlet excitons in copper phthalocyanine films

Ryszard Signerski, * Grażyna Jarosz

*Faculty of Applied Physics and Mathematics, Gdansk University of Technology, G. Narutowicza 11/12,
00-233 Gdańsk, Poland*

Abstract—The work presents a method of extraction of exciton diffusion length from photocurrent spectrum measurements. A copper phthalocyanine (CuPc) layer was taken into consideration as an example. Samples were made in a high vacuum system by subsequent evaporation of the following layers: N, N'-dimethyle-3,4,9,10-perylenbis(dicarboximide) (MePTCDI) and CuPc and Au onto glass/ITO substrate. The subject of our investigation was a saturation photocurrent generated by exciton dissociation at MePTCDI/CuPc interference. As a result of our analysis, the product of quantum efficiency of exciton dissociation and charge carrier collection and exciton diffusion length was estimated and it yielded 1.6nm.

Exciton diffusion length (L_D) is one of the most essential parameters characterizing energy transport in organic solid states [1]. It is hence a parameter determining the performance of organic photonic and optoelectronic devices, particularly of solar cells [2]-[5]. The value of L_D is a key quantity in designing and analysing such devices. It can be extracted via experimental methods referring to various exciton interactions. Luminescence and photocurrent are most often used here [1], [2], [4]. In particular, measurements are taken regarding the intensity of luminescence emitted by layers of different thicknesses, with one surface covered by a quenching layer. Results are fitted by an exciton diffusion model with appropriate boundary conditions. The values of L_D obtained in this manner can be charged with big uncertainty when the quenching rate is too small [6] or when the occurrence of optical interference and the possibility of energy transfer to the quencher are not taken into consideration [7], [8].

Exciton diffusion length can be also obtained from photovoltage spectra [9], analysis of photoenhanced current [10] as well as from photocurrent generated by exciton dissociation at electrodes [11], [12] or at donor-acceptor heterojunction [13]-[18]. Models of short-circuit photocurrent (J_{sc}) generated in photovoltaic devices and respecting reflection and interference of light in layers forming the system are presented in several works [14]-[18]. These models involve quite a big number of parameters and the value of L_D is obtained by fitting numerical simulation to experimental spectra of short-circuit current.

* E-mail: ryszard@mif.pg.gda.pl

In this work we focus our attention on diffusion length of singlet excitons in a copper phthalocyanine (CuPc) layer. CuPc is an organic material favorably applied in small-molecule photovoltaic devices [2]-[5], [19]. This material exhibits strong light absorption within the visible range (singlet absorption range), relatively high mobility of holes and forms layers of rather high quality in vacuum evaporation. The value of L_D for CuPc has been obviously estimated many times. We can mention here at least the following: (10 ± 3)nm [2], 8nm [13], (68 ± 20)nm [15], (20 ± 5)nm [17], 15.7nm [18].

In this work we present an attempt to estimate L_D with a method which has not been used for CuPc, yet. It was, however, used for anthracene [1] and merocyanine [11] and it resulted in quite reasonable values. In the method the flux of excitons generated by monochromatic light of intensity I_o and approaching the illuminated electrode is calculated on the basis of a diffusion equation. Excitons dissociating at an electrode lead to the following density of photocurrent:

$$J = e\,\varphi_1\Phi_o \; , \qquad (1)$$

where e is the elementary charge, Φ_o is the flux of excitons approaching the electrode, φ_1 is the quantum efficiency of exciton dissociation and charge carrier collection.

Taking into consideration the distribution of light intensity in a layer according to the Lambert-Beer law, complete quenching of excitons at electrodes and the assumption that the thickness of a layer is much bigger than exciton diffusion length ($d \gg L_D$), we come to the following relation:

$$\Phi_o = \varphi_2 I_o \left(1 + (\mu L_D)^{-1}\right)^{-1} \; , \qquad (2)$$

where μ is the linear absorption coefficient, φ_2 is the probability of generation of exciton by photon (we usually take $\varphi_2 = 1$).
We can also write down the following relation:

$$J^{-1} = \left(e\,\varphi\,I_o\right)^{-1}\left(1 + (\mu L_D)^{-1}\right) \qquad (3)$$

which for $\mu L_D \ll 1$ can be simplified to the form:

$$J = e\,\varphi\,I_o\,L_D\,\mu \; , \qquad (4)$$

where φ=φ₁φ₂ .The relations (3) and (4) will be applied to estimate L_D and φ.

Measurements of photocurrent (more experimental details can be found in [19]) were performed on systems made in high vacuum by subsequent evaporation, onto glass/ITO substrate kept at room temperature, of the following layers: 5nm-thick N, N'-dimethyle-3,4,9,10-perylenbis(dicarboximide) (MePTCDI) and 120nm-thick CuPc and 40nm-thick Au. The average evaporation rate of organic layers was 0.02nm/s. Spectra of absorbance (defined as A= −logT, where T is transmittance) were obtained with the use of spectrophotometer Shimadzu 1240. Organic materials for photocurrent measurements and for absorption were simultaneously being evaporated. As the layer of MePTCDI is very thin, we can treat the system of ITO/MePTCDI as an electrode with a quencher, at which excitons generated in the CuPc layer dissociate effectively. Such dissociation constitutes the main source of charge carriers in organic solar cells based on perylene dye/phthalocyanine heterojunction [2]-[5], [19].
The thickness of perylene dye in solar cells is obviously greater and equals tens of nm.

We performed measurements of photocurrent in a function of applied voltage and light intensity as well as measurements of photocurrent spectra. The results obtained are presented in Figs. 1−3.
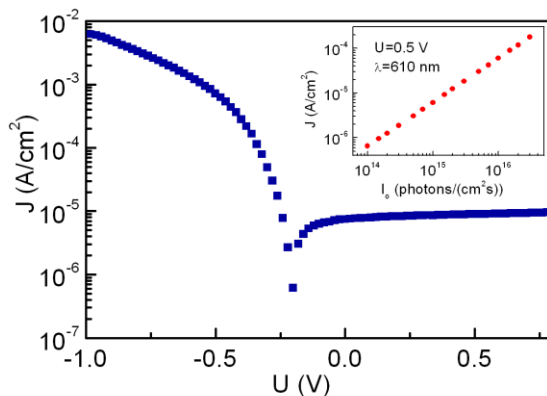

Fig. 1. Current versus voltage at λ=610nm and $I_0=10^{15}$ photons/(cm²s) and current versus light intensity (inset).

Figure 1 shows current-voltage dependence obtained on the system illuminated with a monochromatic light of λ=610nm and $I_0=10^{15}$ photons/(cm²s) and photocurrent against light intensity at U=0.5V. The positive values of applied voltage refer to higher potential at ITO. We see that the system exhibits photovoltaic effect with the following parameters: open-circuit voltage $U_{oc}= −0.2V$ and short-circuit current $J_{sc}=7.5\mu A/cm^2$. This effect originates from exciton dissociation at MePTCDI/CuPc interface and injection of holes into CuPc. We can also notice strong current rectification and occurrence of

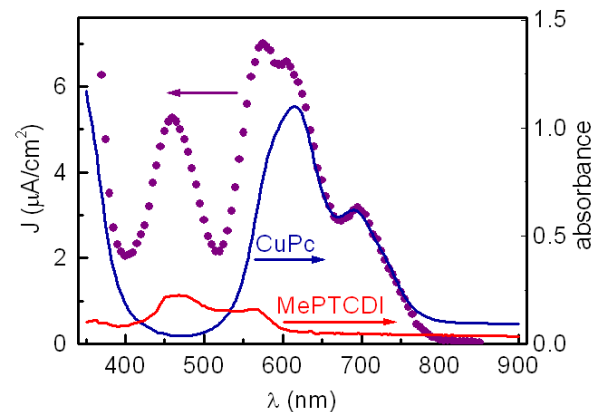saturation current flowing in the system at reverse bias

Fig. 2. Spectra of photocurrent at $I_0=10^{15}$ photons/(cm²s), absorbance of CuPc layer (blue line) and MePTCDI layer (red line). In the case of MePTCDI the absorbance was multiplied by 5 to make its structure visible.
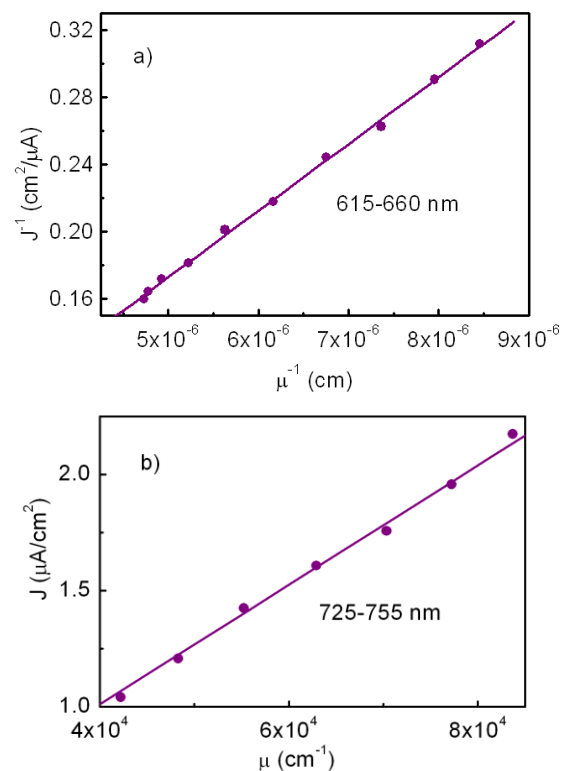

Fig. 3. Reciprocal of photocurrent versus reciprocal of linear absorption coefficient at the top and photocurrent versus linear absorption coefficient at the bottom. Points were taken from Fig. 2.

(i. e. +ITO/-Au). From the inset of Fig. 1 we notice that this photocurrent is a linear function of light intensity. So we come to the conclusion that requirements resulting from (1) and (2) and describing photocurrent limited by exciton dissociation are fulfilled.

Figure 2 shows the photocurrent spectrum at reverse bias (U=0.5V) and the absorbance spectra of MePTCDI and CuPc layers. We see that within 400–600nm the photocurrent spectrum does not follow the absorption spectrum of CuPc. It originates mainly from photogeneration of charge carriers at MePTCDI/CuPc interface and this photogeneration results from dissociation of excitons generated in an MePTCDI layer [19]. Additionally, the peak at 575nm correlates with a shoulder of CuPc absorbance. This shoulder can be related to either charge-transfer state (CT) [20], [21] or vibronic satellite of intermolecular excitation [22], [23]. These two states are probably characterized by different quantum efficiency of charge-carrier photogeneration. Due to all the facts mentioned above we notice that the extraction of φ and L_D for CuPc from a photocurrent spectrum is impossible in the whole range of CuPc absorption and therefore in a further passage we will consider only the range of $\lambda > 610$nm.

Figure 3 shows data taken from Fig. 2 within two selected ranges of wavelength and presented in coordinates suggested by (3) and (4). The values of a linear absorption coefficient were calculated according to the Lambert-Beer law:

$$\mu = 2.3\,A\,d^{-1}\ ,\tag{5}$$

where A is the absorbance of a CuPc layer. Approximation of points with straight lines led to slopes which were used for estimation of φL_D. This attitude results in the following: $\varphi L_D = 1.57$nm for Fig. 3a and $\varphi L_D = 1.61$nm for Fig. 3b. We see both results correlate quite well with each other and due to uncertainty we finally estimate $\varphi L_D = (1.6\pm0.3)$nm.

If we assume that φ is in a range of $0.1-1$, the value of L_D will be equal to $16-1.6$ nm. It is the range in which values of L_D for CuPc (and also for other organic materials) are the most often estimated. The value of 68nm reported in [15] is called in question by other authors [17].

From (3) we can also notice that parameters of φ and L_D can be extracted independently as we take into consideration an ordinate of intersection of approximation line and J^{-1} axis. In our case, however, uncertainty of the ordinate was rather big and therefore we limited ourselves only to the estimation of φL_D.

In summary, it is worth adding that thinner layers of MePTCDI will probably extend analysis of photocurrent spectra to a range of $\lambda < 600$nm. Accurate values of the absorption coefficient within a wide range of λ are also important.

In this letter a photocurrent method of estimation of exciton diffusion length in organic layers is presented. We consider a CuPc layer as an example. Simultaneously, we should keep in mind that L_D depends, in general, on the structure and morphology of a layer, which, in particular, are determined by packing geometry, disorder, impurities and grain boundaries [24]. This simple method of estimation of L_D described above can be easily employed when a question about usefulness of particular material for organic photovoltaics is put.

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