The impact of active layer nanomorphology on the efficiency of organic solar cells based on a squaraine dye electron donor

D Stoyanova¹, S Kitova¹, J Dikova¹, M Kandinska², A Vasilev², I Zhivkov¹,³ and A Kovalenko³

¹Acad. J. Malinowski Institute for Optical Materials and Technologies, Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 109, 1113 Sofia, Bulgaria
²Faculty of Chemistry and Pharmacy, St. Kliment Ohridski University of Sofia, 1 James Bourchier blvd., 1164 Sofia, Bulgaria
³Brno University of Technology, Faculty of Chemistry, Materials Research Center, Purkyněova 118, 612 00 Brno, Czech Republic

E-mail: skitova@iomt.bas.bg

Abstract. The possibilities were studied of improving the photovoltaic performance of solution processed BHJ solar cells by solvent vapor annealing (SVA) of the active layers, based on a squaraine dye Sq1 as a donor and the fullerene derivative PCBM as an acceptor. For this purpose, the optical properties were determined of as-deposited and of annealed with tetrahydrofuran (THF) vapors for different duration Sq1/PCBM layers, as well as the efficiency of cells built on their basis. A considerable change was established in the absorption spectra of treated for only a few seconds films and a twofold increase of the power conversion efficiency after 6 sec SVA. The results obtained are explained in terms of solvent vapor induced phase separation and formation of squaraine dye small aggregates in the blend nanostructure. The assumption made was confirmed by morphological investigation of as-deposited and of annealed Sq1/PCBM blended layers. On this basis, the impact of the active layer nanomorphology on the efficiency of solar cells based on squaraine dye as electron donor is discussed.

1. Introduction
During the past two decades, the organic solar cells (OSCs) have drawn considerable interest due to their high potential of low-cost, light-weight and simple fabrication of roll-to-roll production on flexible substrates [1]. In the most successful implementation, a soluble n-type fullerene derivative, (6,6)-phenyl C₆₁ butyric acid methylester (P₆₁CBM) as acceptor, is blended with the donor from conjugated p-type polymers or small molecular weight organic semiconductors to form bulk-heterojunction (BHJ) cells. Although high power-conversion efficiencies (PCEs) of 10.8 % have been achieved [2], the polymeric solar cells still suffer from some shortcomings, such as batch-to-batch variation, indefinite molecular weight, polydispersity and impurity. In contrast, small molecular weight materials intrinsically do not have such drawbacks. Additionally, they have a well-defined molecular structure with a definite molecular weight, giving the advantages of high purity, tunable

¹ To whom any correspondence should be addressed.
electronic structures and better device reproducibility [3]. Even though the highest PCE of 9.96 %, obtained very recently in the solution-processed small molecule OSCs [4], in the most cases PCE is still lower than that of the polymer devices. It is considered that this is mainly due to the difficulty of controlling the nanomorphology of the active layers, where donor and acceptor components self-assemble to form bicontinuous interpenetrating networks [5]. The latter should allow the excitons to diffuse to the donor-acceptor interface and charge carriers to transport to the respective electrodes after separation. Therefore, the challenge of solution processed BHJ small molecule OSCs is to enhance the molecular order in the active layers for a better charge carriers’ mobility, and at the same time, to restrict the domain size due to the limited exciton diffusion length in these materials. Different strategies for resolving the problem have been reported, among which the solvent vapor annealing (SVA) seems very promising [6].

Recently, we studied the potentiality of a symmetrical n-hexyl substituted squaraine dye, marked as Sq1, for using as electron donating component in the active layer of solution processed BHJ organic solar cells [7]. The dye was in-house synthesized by optimizing a method proposed earlier in the literature [8]. Optical modelling was performed to predict and improve the photovoltaic performance of a BHJ device with a blended Sq1/PC61MB active layer; encouraging results were thus obtained. However, the initial experiments with constructed real cells showed a moderate PCE, not exceeding 0.7-0.8 %. Obviously, the improvement of the active layer morphology is a must for achieving an increased power conversion efficiency.

In this work, studies are presented on the influence of solvent vapor annealing treatment on the photovoltaic performance of solution processed BHJ organic solar cells based on Sq1 dye as an electron donor and PCBM as an acceptor. For the purpose, the absorption spectra of as-deposited and annealed Sq1/PCBM blended layers were investigated and the efficiencies of the solar cells were determined. The morphological changes induced by the solvent vapors were followed by TEM observations.

2. Experimental
The squaraine dye Sq1, synthesized earlier [7], is 2-((5-(((2,2-diphenylhydrazono) methyl)-1-hexyl-1H-pyrrol-2-yl)-4-(5-(2,2-diphenyl-hydrazono)-ylidenemethyl)-1-hexyl-2H-pyrrol-1-ium)-3-oxocyclobut-1-enolate. The soluble PC61BM acceptor, with a purity of more than 99 %, was supplied by Sigma-Aldrich. The blended active layers were obtained by spin casting of 20 mg/ml chloroform solution of Sq1 and PC61MB in a weight ratio 1:2, previously determined as optimal.

The annealing of the blended Sq1/PCBM films was performed by exposing the samples to vapors of anhydrous tetrahydrofuran (THF ≥ 99.9 %, Sigma-Aldrich). The choice of THF was done on the basis of literature data according to the requirements for used solvents to have high vapor pressure and medium dissolving ability of the respective donor component [9]. The SVA processing of Sq1/PCBM blend films was carried out in nitrogen atmosphere at room temperature 21°C.

The absorption spectra of as-cast and solvent-annealed Sq1/PCBM blend films were recorded using a Varian Cary 50 Probe Spectrophotometer (UV-VIS-NIR). The samples studied were spin-coated over glass substrates from a 20 mg/ml chloroform solution of Sq1 and PC61MB in a weight ratio 1:2, previously determined as optimal.

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For studying the effect of the SVA treatment on the photovoltaic performance, BHJ solar cells were built with the structure ITO/PEDOT:PSS(~60nm)/Sq1:PCBM(~100nm)/Al(~100nm), developed in the previous work [7]. The depositions of the photoactive and Al layers, as well as the encapsulation procedure, were fulfilled in a nitrogen filled glove box. The Al cathode was thermally evaporated on the top through a shadow mask giving an active device area of 4.76 mm². The thicknesses of the individual layers in the cell’s structure were controlled by using a Bruker’s DektakXT Stylus Profiler.

The current density-voltage (J-V) characteristics were obtained by a Keithley 2601B System Source Meter. The photocurrent was measured under AM 1.5G illumination at 98.8 mW cm⁻² under LOT – QuantumDesign solar simulator, as the light intensity was preliminary determined by a Si reference solar cell. From the J-V curves, the basic characteristics Jsc, Voc and FF were determined,
whose product gives the maximum power of the electrical energy $P_{\text{max}}$ generated. Here $J_{\text{sc}}$ is the short circuit current, $V_{\text{oc}}$ is the open circuit voltage and $FF$ is the fill factor [10]. The power conversion efficiency $\text{PCE}$ was determined as the ratio between the maximum power of the electrical energy generated and the power of the incident sun light energy: $\text{PCE} = \frac{P_{\text{max}}}{P_{\text{(solar in)}}} = \frac{J_{\text{sc}}V_{\text{oc}}FF}{P_{\text{(solar in)}}}$.

The investigation of the SVA impact on the morphology of the Sq1/PCBM blend films was performed by an HR STEM JEOL JEM 2100 high-resolution scanning transmission electron microscope at an accelerating voltage of 200 kV. All inspected films were spin-coated from 20 mg/ml chloroform blend solution on KBr lamellas.

3. Results and discussion

Figure 1 shows the molecular structure of the Sq1 dye and the fullerene derivative PC$_{61}$BM used in the study.

Figure 2 presents the absorption spectra of as-cast and annealed for different durations by THF vapors Sq1/PCBM films. As seen, the spectrum of the reference virgin sample shows absorption of light across a broad range of wavelengths – from UV to NIR, with a maximum at 775 nm. The absorption in the range 350 – 600 nm is due to the presence of PCBM in the blended film, whilst the main absorption peak is caused by electron excitations in the squaraine dye molecules. After solvent vapor annealing with THF, the absorption of PCBM and Sq1 changes notably. The PCBM absorption of light is enhanced, while the maximum of the main peak is reduced considerably after only 6 seconds of treatment by THF vapors. Besides, the appearance of a shoulder-type peak is seen at ~ 690 nm in the visible part of the solar spectrum. Such an absorption band splitting into two components after SVA could be due to a good packing of the squaraine molecules in the presence of THF into a manner that favors aggregation of the chromophore molecules, when they are in close contact to each other. Similar appearance of blue-shifted absorption shoulder in relation to the band of monomeric state is explained in the literature as due to the formation of small aggregates, like dimers, trimmers and tetramers [11]. Besides, it is seen from the figure that the SVA duration affects also the magnitude of the absorbance, which slightly decreases from 6 to 10 and 14 seconds treatment. The absorption bands owing to the PCBM molecules in that case appear rather unaffected. In general, the results from the optical measurements give us a reason to suppose that some rearrangements in the active layer nanomorphology occur under SVA with THF vapors, which undoubtedly will affect the photovoltaic performance of the cells studied.

Figure 3 shows the architecture and $J$$-$$V$ characteristics of BHJ cells with untreated and Sq1/PCBM active layers treated for different times by THF vapors. As seen from the figure, the photovoltaic
response increases as a result of the SVA processing, the response being maximal for the 6 sec treatment time. A further extension of the annealing duration reduces the $J_{sc}$ values.

Most probably, the structural transformations in the active layers, induced by THF vapors for the 6 sec treatment, are the most favorable with respect to photocurrent generation. This statement is confirmed by the basic electrical parameters calculated from $J$-$V$ curves and summarized in table 1. From these data, some general performance trends can be clearly discerned: i) the solvent treatment with THF vapors for only 6 seconds is enough to double the PCE; ii) the improvement of the fabricated cell’s performance is associated mainly with the increase of $J_{sc}$ as well as of $FF$ and $R_{sh}$; iii) The values of $V_{oc}$ are almost unaffected by the solvent annealing. Hence, the tendency observed of the electrical characteristic’s changing under the action of THF vapors is similar to the literature data for other small molecule donor/acceptor blended active layers [6].

Table 1. Electrical characteristics of BHJ cells with Sq1/PCBM active layers annealed in THF vapors for different duration.

| Treatment duration (s) | $J_{sc}$ (mA cm$^2$) | $V_{oc}$ (V) | $FF$ (%) | PCE (%) | $R_{shunt}$ (Ohm cm$^2$) | $R_{series}$ (Ohm cm$^2$) |
|------------------------|----------------------|-------------|----------|---------|--------------------------|--------------------------|
| 0                      | 3.66                 | 0.59        | 36.93    | 0.79    | 6670.49                  | 34.34                    |
| 6                      | 6.22                 | 0.59        | 43.10    | 1.57    | 8147.78                  | 14.61                    |
| 10                     | 6.08                 | 0.57        | 41.92    | 1.46    | 7871.89                  | 15.07                    |
| 14                     | 5.03                 | 0.55        | 42.60    | 1.18    | 8128.73                  | 15.29                    |

Figure 4 presents TEM bright field images and the corresponding SAED patterns of Sq1/PCBM blended films as-deposited (a) and treated for 6 sec (b) and 14 sec (c) by THF vapors. A slightly inhomogeneous structure of the virgin film is clearly seen (a). After only 6 sec SVA treatment, the film nanomorphology is changed visibly, most probably due to the occurrence of phase separation (b). A further increase of the treatment duration results in an enhanced contrast of the TEM images and a better developed phase separation. Simultaneously, the diffraction patterns, shown in the lower frame of figure 4, evidence the amorphous structure of all inspected specimens. As seen, the diffraction peak intensity is increased visibly after 6 seconds SVA treatment with THF, which is probably due to obtaining a more ordered network. The latter can be regarded as optimal, having in mind that the best photovoltaic performance of the cells studied is observed for this time of solvent vapor treatment.
4. Conclusions
The results of the present study demonstrate the possibilities of improving the photovoltaic performance of solution-processed BHJ solar cells by solvent vapor annealing of Sq1/PCBM blended active layers. It is established that only a few seconds processing of Sq1/PCBM films by THF vapors results in a double increase of the solar energy conversion efficiency. Simultaneously, a modification of the active layer’s nanomorphology after annealing for different duration is observed, which is most probably due to assembling of the squaraine dye monomers into small aggregates. The latter statement stems from the observed notable changes in the absorption spectra of solvent vapor treated samples, including the appearance of a shoulder-type peak, explained reasonably in the literature by aggregation of the chromophore molecules. Thus, the very important role is evidenced of a controlled active layer’s morphology for producing highly efficient small molecule OSCs.

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