Optical modeling of bulk-heterojunction organic solar cells based on squarine dye as electron donor

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Abstract. The potentiality of a squarine dye (Sq1) for using as electron donor component in bulk heterojunction organic solar cells (BHJ) has been studied from the optical point of view. The soluble n-type fullerene, (6,6)-phenyl C₆₁ butyric acid methyl ester (PC₆₁MB) was chosen as acceptor. Optical modelling based on transfer matrix method was carried out to predict and improve photovoltaic performance of a BHJ device with blended Sq1/PC₆₁MB active layer. The dependence of the absorption and the calculated maximum short circuit photocurrent (Jsc max) on the thickness of the active layer (dact), was investigated for two weight ratios of Sq1 and PC₆₁MB. Thus, the optimal dact was calculated to be about 100 nm, which provides an efficient overlapping of the total absorption with solar spectrum in the range between 580 and 900 nm. Besides, it is found that the insertion of ZnO or C₆₀ spacer layer shifts Jsc max peak to lower dact and significantly enhances Jsc max for active layers with dact < 50 nm, which is mainly due to improved light absorption by a factor of 5 to 10. Simultaneously, for dact <100 nm the optical effect of inserted PEDOT:PSS hole transporting layer is negligible.

1. Introduction
During the past years the organic photovoltaics (OPVs) are subject of continuously growing interest as promising alternative for high cost crystalline silicon cells (c-Si), which still dominate the market. In the most successful devices, a soluble n-type fullerene, (6,6)-phenyl C₆₁ butyric acid methyl ester (PC₆₁MB) as acceptor, is blended with the donor from conjugated p-type polymers to form bulk-heterojunction (BHJ) cells [1]. An attraction of these devices, which are processed from solution, is the ability to deposit active layer precursors over large areas in a single step, using techniques ranging from inkjet printing to spin-coating. Small molecule donors offer the same facile processing however are easier to synthesize in many variants and purify, are intrinsically monodisperse, and are often environmentally more stable [2]. The disadvantage of lower solubility of this class of organic semiconductors can be overcome by functionalizing of their molecular structure. This approach has been successfully applied to different dyes and very encouraging results about the performance of devices developed on this base has been achieved [3].

Squarine dyes have been the subject of many recent investigations owing to their unique photochemical and photophysical properties [4]. Principal attractions of this dye class include facile synthetic access, a wide variety of possible structural motifs and high thermal and chemical stabilities.
Squaraines are the products of condensations of electron-rich molecules with squaric acid [6-7]. Their structure can be either symmetric or nonsymmetric. The nonsymmetry depends on the synthetic route employed and has enabled the preparation of a wide variety of functional structures, which have been exploited in, for example, photoconductive materials, light emitting field-effect transistors, IR absorber in optical disks, and dye-sensitized solar cells [4-8]. Squaraine dyes are promising molecular donor active materials for BHJ solar cells due to their strong absorption coefficients up to $3 \times 10^5 \text{ cm}^{-1}$ that can be extended from the green to the near infrared region [4]. The application of symmetric squaraine dyes in BHJ cells was recently reported by Pagani, Facchetti and co-workers [4, 5]. The authors demonstrated the fabrication and initial characterization of BHJ solar cells based on alkyl- and alkenyl-functionalized squaraine dyes as donors, with PC$_{61}$BM and PC$_{71}$BM as acceptors. The results are promising regarding power conversion efficiencies (PCEs) reported to date for ambient solution-processed small molecular OPVs. Based on that, we choose this approach to develop new squarine dyes suitable for application as electron donors in BHJ organic solar cells.

As a first step in our investigations, in the present work a symmetrical n-hexyl substituted squarine dye 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 was synthesized by a modified by us method, cited above. The structure and electronic properties of the dye, which we labeled as Sq1, were studied by means of density functional theory (DFT) calculations. Further, optical modeling based on transfer matrix method (TMM) was performed to predict and improve photovoltaic performance of a bulk heterojunction cell with active layer from a solid-state blend of Sq1 and the fullerene derivative PC$_{61}$BM. The influence of PEDOT:PSS hole transporting layer as well as optical spacers from ZnO and C$_{60}$ layers on the optical performance of the model OPVs was also studied.

2. Experimental

The synthesis of the target squarine dye Sq1 (indicated as 7 in figure 1) was performed via a modified by us previously reported procedure [4, 5]. The use of the sterically hindered base DIPEA instead of imidazole [4] increased the reaction yield probably due to avoid of possible side reactions. Another improvement is the addition of catalytic amounts of 4-(dimethylamino)pyridine. Double decrease of the reaction time and increase of the reaction yield have been observed. Following the purification procedure by recrystallization from iso-propanol we obtained the target dyeSq1 as golden needles as was described in [4]. The dye was purified by flash column chromatography with subsequent recrystallization and its structure was elucidated by elemental analysis and Nuclear magnetic resonance (NMR) spectroscopy.

![Figure 1](image_url)
The molecular ground-state geometry of Sq1 compound was optimized using Becke’s three-parameter hybrid exchange-correlation functional B3LYP [9] with double-ζ polarized basis set, 6-31+G(d,p). Local minima were verified by establishing that all vibrational frequencies are real. All calculations were performed using Gaussian 09 [10].

Single dye films were prepared from solution of the compound in chlorobenzene by spin coating. In the preliminary experiments the concentration of the solution, the spin rate and duration were varied in order to obtain films with thickness, suitable for optical measurements. Thus, 45 nm films were deposited on substrates from solution containing 12 mg ml⁻¹ Sq1, spin coated at 1200 rpm for 180 s. Blended films were prepared also by spin coating from chlorobenzene solutions of 1:1 and 1:3 (weight ratios) mixture of Sq1 and PC₆₁MB. 80 nm thick PEDOT:PSS films were also obtained by spin-coating on the substrates at 5000 rpm and heated at 120ºC for 20 min. under argon atmosphere. PC₆₁BM and PEDOT:PSS were commercially available. In all cases preliminary carefully cleaned BK7 optical glass plates and Si wafers were used as substrates.

Optical constants of the Sq1 dye and blended Sq1/PC₆₁MB films were determined with high accuracy on the basis of three spectrophotometric measurements at normal incidence of light - transmittance T and reflectances Rᵣ and Rᵣₗ of the both kinds of films, deposited on transparent (BK7) and opaque (Si wafers) substrates, respectively [11].

Optical modeling of a BHJ device stack was carried out using the transfer matrix formalism, based on the Fresnel formulas for the several interfaces occurring in the cell. This approach has been explained in great detail in the literature [12, 13]. In our work a Matlab script developed by Burkhard and Hoke, which treats the case of normal incidence of light, was applied [14]. The absorption distribution for each wavelength over the film thickness has been calculated in the wavelength range 350 – 900 nm. Multiplying with the light of the AM 1.5 sun spectrum and integration over the film thickness results in the total number of photons, absorbed for each wavelength. Lastly, a summation over all wavelength results in the total number of absorbed photons. The possible maximum current density Jₘₐₓ was calculated assuming that each absorbed photon results in a collected electron i.e. the internal quantum efficiency, IQE, equals one [14].

For optical modeling we have chosen a BHJ device structure, used in [5], for studying the same squarine dye. The architecture of our model cell is presented in figure 2. As seen, the cell consists of ITO (120 nm)/PEDOT:PSS (x nm)/blend Sq1/PC₆₁MB (1:1 or 1:3 wt:wt) (y nm)/LiF (0.6 nm)/Al (120 nm). The anode represented glass substrates, pre-coated with indium tin oxide (ITO), modified by spin-coated polyethylenedioxythiophene/polystyrenesulphonate (PEDOT:PSS) hole transporting layer. The cathode consisted of LiF capped with Al. Very thin LiF films were inserted between active layer and Al surface to improve the ohmic contacts for electron collection. At the next step of modeling LiF was substituted with ZnO or C₆₀ spacer layer. We have used literature data for the optical constants values of ITO, Al, LiF [15] and ZnO [16]. The optical constants of C₆₀ films were

![Figure 2. Scheme of a model BHJ organic solar cell.](image-url)
determined experimentaly by applying the same procedure as for Sq1 dye. For the purpose 25 nm thick C_{60} films were thermally evaporated in vacuum (10^{-4} Pa).

3. Results
Possible molecular structure of our Sq1 dye and the distributions of the frontier orbitals are shown in figure 3. The highest occupied molecular orbital (HOMO) is spread over the whole length of the conjugated chain, which is one of the prerequisites for achieving high power conversion efficiency. The lowest occupied molecular orbital (LUMO) is localized predominantly on the central four membered ring and the pyrrole rings. Neither HOMO nor LUMO are spread over the electronically inactive aliphatic chains, attached to the backbone. A detailed analysis of electronic transitions behavior and molecular orbital (MO) energy diagram of the dye studied under the framework of DFT and its time-dependent version is in progress.

Figure 3. B3LYP/6-31+G(d,p) optimized geometry (a) and isocontours plots (isovalue = 0.02 a.u.) of the B3LYP/6-31G(d,p) calculated frontier orbitals of Sq1 (b); Color code indicates different phases of MO.

Figure 4. Absorption coefficient profile (\(\alpha=4\pi k/\lambda\)) of 45 nm thick dye film.

Figure 4 shows the absorption coefficient \(\alpha\) determined for 45 nm thick Sq1 dye film. It is seen that the absorption area of the film covers not very broad spectral region from 590 to 840 nm with two strong typical for squarines absorption peaks of about 1.8 x 10^{5} cm^{-1} and 1.4x10^{5} cm^{-1} at \(\lambda = 766\) nm and 695 nm, correspondingly. The results obtained are in a good accordance with the data given in [5]
for the identical dye. As it was already mentioned, the optical simulation was performed for a standard BHJ cell structure, where the light enters through the glass substrate, sequentially passing the layers of ITO, PEDOT:PSS, Sq1/PC61MB blend layer and LiF (see figure 2). Then the light is reflected back from the Al electrode and finally leaves the solar cell partly at the front again. We have found that the presence of LiF film has no influence on the optical model results, probably due to its very low thickness of 0.6 nm.

Figure 5 presents the spectral dependence of total absorption within the Sq1/PC61MB (1:3 wt.ratio) active layer for a set of different layer thicknesses. For comparison, the photon flux of a standard AM1.5 solar spectrum is shown as a gray solid line. The blue light is mainly absorbed by PC61MB while red and near infrared only by Sq1 dye. It is seen that the absorption of blended film overlaps the solar spectrum in broad range from 400 to 900 nm.

**Figure 5.** Fraction of incident light absorbed within the 1:3 dye/PC61BM layer of the solar cell for several layer thickness. $d_{\text{PEDOT:PSS}} = 75$ nm. For comparison, the photon flux of a standard AM1.5 solar spectrum is shown as a gray solid line (right axis).

Assuming an IQE=1, the maximum short circuit current density $J_{sc}^{\text{max}}$ under AM 1.5 illumination in dependence of 1:3 Sq1/PC61MB layer thickness is depicted in figure 6 for several thicknesses of the hole transporting layer. Due to the interference effects in the device structure $J_{sc}^{\text{max}}$ does not follow a straight line, but shows a local maximum at about 100 and 300 nm. Further, it is established that for $d_{\text{act}} < 100$ nm the optical effect of the PEDOT:PSS hole transporting layer is negligible. In general, the photocurrent is higher for a larger $d_{\text{act}}$, but due to the limited exciton diffusion length and limited charge mobility in the organic layer the real photocurrent decreases with increasing $d_{\text{act}}$. Indeed, the experimental results obtained in [4] showed that measured $J_{sc}$ is low in a 140 nm thick layer, but by reducing its thickness down to 30 nm, OPV performance can be enhanced and $J_{sc}$ increased from 1.85 to 3.10 mA cm$^{-2}$ [4]. In particular, for the same squarine dye the best OPV performance and the highest $J_{sc}$ has been measured at 35 nm thick Sq1/PC61MB (1:3 wt. ratio) layer [5]. As can be seen from figures 5 and 6, however the fraction of incident light absorption within our active layer and the calculated $J_{sc}^{\text{max}}$ for this thickness are very low.

It is known that insertion of a transparent film between the active layer and the metal electrode can redistribute the optical electric field in the OPV stack, and then influence the device performance. This is referred to as the optical spacer effect [17]. It has been found that in polymer solar cells with conventional structure, an optical spacer of ZnO with optimal thickness leads to a significant increase of the photocurrent when the active layer thickness is below 60 nm [17]. In figure 7 the calculated $J_{sc}^{\text{max}}$ as a function of $d_{\text{act}}$ for devices with different thicknesses of ZnO spacer layer is presented.
The results demonstrate that the increasing of ZnO layer thickness shifts the $J_{sc, max}$ peak to lower $d_{act}$ and significantly enhances $J_{sc, max}$ at active layers thicknesses below 50 nm. Besides, our calculations showed that fullerene C$_{60}$ layer has analogous effect. As seen from figure 8 the presence of both spacer layers causes the increasing of the absorption in the active layer by a factor of 5 to 10. While ZnO film is completely transparent in the visible range of light, C$_{60}$ exhibits some light absorption, which explains the obtained smaller light absorption improvement.

Finally, it should be mentioned that experimental studies of a real device with Sq1/PC$_{61}$BM active layer are in progress and will be forthcoming in a separate paper.

4. Conclusions

Optical modeling based on TMM has been performed to investigate the performance of OPVs consisting of glass/ITO/PEDOT:PSS/Sq1:PC$_{61}$BM/spacer/Al. The dependence of the absorption and $J_{sc, max}$ on the active layer thickness is studied for two weight ratios of Sq1 and PCBM. The results show that the total absorption within the Sq1/PC$_{61}$MB blend active layer overlaps the solar spectrum in a broad range from 400 to 900 nm. Due to the interference effects in the device structure, $J_{sc, max}$ shows a local maximum at active layer thickness of about 100 and 300 nm. However, because of the limited exciton diffusion length and charge mobility in the organic layer of practical importance are thicknesses below 60 - 70 nm, which has been proved experimentally. For these thicknesses of the Sq1/PCBM active layer the optical effect of inserted PEDOT:PSS hole transporting layer is negligible. On the contrary, the insertion in the device stack of ZnO or C$_{60}$ spacer layer with thicknesses up to 50 nm shifts $J_{sc, max}$ peak to lower active layer thicknesses. Moreover, a significant increase of $J_{sc, max}$ for active layers thinner than 50 nm is found, due to the improved light absorption by a factor of 5 to 10.

References

[1] Dennler G, Scharber M and Brabec C 2009 Adv. Mater. 21 1323
[2] Walker B, Kim C and Nguyen T 2011 Chemistry of Materials 23 470
[3] Xin Xo, Wei G, Wang S, Zimmerman G, Renshaw Ch, Thompson M, and Forrest S 2012 Adv. Mater. 24 1956
[4] Silvestri F, Irwin M, Beverina L, Facchetti A, Pagani G and Marks T J. 2008 Am. Chem. Soc. 130 17640
[5] Bagnis D, Beverina L, Huang H, Silvestri F, Yao Y, Yan H, Pagani G, Marks T and Facchetti A 2010 J. Am. Chem. Soc. 132 4074
[6] Choi H, Baik C, Kang S, Ko J, Kang M, Nazeeruddin M and Graetzel M 2008 Angew. Chem. 120 333
[7] Li C, Yum J, Moon S, Herrmann A, Eickemeyer F, Pschirer N, Erk P, Schçneboom J, Muellen K, Graetzel M and Nazeeruddin M 2008 Chem. Sus. Chem. 1 615
[8] Chen X, Guo J, Peng X, Guo M, Xu Y, Shi L, Liang C, Wang L, Gao Y, Sun S and Cai S 2005 J. Photochem. Photobiol. A 171 231
[9] Becke A 1993 Chem. Phys 98 5648
[10] Gaussian 09 program, Revision C.01, Gaussian, Inc., Wallingford CT, 2010
[11] Babeva Tz, Kitova S and Konstantinov I 2001 Appl. Opt. 40 2682
[12] Pettersson L, Roman L and Inganä O 1999 J. Appl. Phys. 86 487
[13] Peumans P, Yakimov A and Forrest R 2003 J. Appl. Phys. 93 3693
[14] Burkhard G, Hoke E and McGehee M 2010 Adv. Mater. 22 3293
[15] Smith D, Shiles E and Inokuti M 1985 Handbook of Optical constants of Solids (New York: Academic) p 377
[16] Liu Y, Hsieh J and Tung S 2006 Thin Solid Films 510 32
[17] Gilot J, Barbu I, Wienk M and Janssen R 2007 Appl. Phys.Lett. 91 113520