

Optical properties of thin merocyanine dye layers for photovoltaic applications

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Abstract. The potentiality was studied of our newly synthesized push-pull type merocyanine dye, labeled A1, for use as an electron donating component in solution-processed bulk heterojunction (BHJ) organic solar cells. For the purpose, a soluble n-type fullerene, (6,6)-phenyl C61 butyric acid methyl ester (PCBM), which is currently and in the ear future without an alternative, was chosen as an acceptor. The optical constants (n and k) of thin films obtained by spin coating from solutions in chlorobenzene of A1 and of an A1/PCBM blend were determined by spectrophotometric measurements. Further, an optical simulation of a standard BHJ cell with an active layer of an A1dye/PCMB blend was performed using a transfer-matrix formalism. Thus, the optimum thickness of the active layer was calculated to be about 80 nm, which provides overlapping of the total absorption with the solar spectrum in the broad range 400 nm – 800 nm. Finally, the maximum current density, J_{sc} , was determined to be 13 mA cm⁻² assuming that the internal quantum efficiency, IQE, is unity. Comparing the calculated J_{sc} with data on some advanced small-molecule BHJ devices, the prospects for practical applications of the new merocyanine dye are discussed.

1. Introduction

During the past several years, the organic photovoltaics (PV) have been the subject of a continuously growing interest as a promising alternative to the expensive 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 (PCBM), as an acceptor, is blended with a donor of conjugated p-type polymers to form bulk-heterojunction (BHJ) cells [1]. An advantage of these devices, which are processed from a 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 simple processing, but are easier to synthesize in many variants and to purify, are intrinsically monodisperse, and are often environmentally more stable [2]. The disadvantage of the lower solubility of this class of organic semiconductors can be overcome by functionalizing their molecular structure. This approach has been successfully applied to different dyes and very encouraging results have been

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achieved concerning the performance of devices developed on this basis [3]. However, the power conversion efficiency remains considerably lower than that of the polymeric solar cells [4]. This explains the increased scientific efforts devoted recently to developing new small-molecule electron donors for solution-processed BHJ solar cells. In this respect, the so-called “push-pull” chromophores look very promising [5]. The molecular structure of this unique class of dyes comprises electron-donating, π -conjugated bridging and electron withdrawing moieties. In the excited state, a strong intramolecular charge transfer occurs which provides an enlargement of the absorption area of the donor, increases the charge mobility and, therefore, raises the conversion efficiency [6].

The present work represents a first step in the characterization of our newly synthesized push-pull type merocyanine dye, which we labelled as A1. We determined the optical constants (refractive index n and extinction coefficient k) of spin-coated thin A1 dye and A1/PCMB films using methods developed previously based on spectrophotometric measurements. Further, optical simulation was carried out in order to predict and understand the photovoltaic performance of a bulk heterojunction cell with an active layer consisting of a solid-state blend of A1 and the fullerene C60 derivative PCBM.

2. Experimental

The new push-pull dye A1 was synthesized via the reaction between 3-nitro-7H-benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one and 1-benzyl-4-methyl-quinolinium bromide in methoxyethanol in the presence of diisopropyl-ethylamine (DIPEA) and pyridine. The target merocyanine compound (E)-3-((1-benzylquinolin-4(1H)-ylidene)methyl)-7H-benzo[de]benzo[4,5]imidazo-[2,1-a]isoquinolin-7-one was obtained with excellent yield. A detailed description of the reaction procedure and the characterization data on the molecular and electronic structure of the A1 dye will be published in a separate paper.

Single dye films were prepared from a solution of the compound in chlorobenzene by spin coating. In the preliminary experiments, the concentration of the solution, the spin rate and the duration were varied in order to obtain films with thickness suitable for optical measurements. Thus, 25 nm films were deposited from a solution containing 4 mg/ml A1 coated at 1500 rpm for 120 s. Blended films were also prepared by spin coating from chlorobenzene solutions of 1:1 (by weight) mixture of A1 and PCBM (PCBM was commercially available). In both cases, carefully cleaned BK7 optical glass plates and Si wafers were used as substrates.

The optical constants of the A1 dye and the blended A1/PCMB layers were determined on the basis of three spectrophotometric measurements at normal light incidence – transmittance T and reflectance R_f and R_m of the dye and the blended films deposited on transparent (BK7) and opaque (Si wafers) substrates. The spectrophotometric measurements were carried out by a Cary 5E spectrophotometer in the spectral region 350 nm– 800 nm. A value of the dye-film thickness derived through applying the (TR_fR_m) method [7] was used for determining n and k , as well as the (TR_m) or (TR_f) methods using the Newton Raphson iterative techniques [8]. The combination of two methods made it possible to determine the optical constants of the dye and the blended films with a high accuracy [8].

Optical simulation 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 [9, 10]. In our work, a Matlab script developed by Burkhard and Hoke was applied, which treats the case of normal light incidence [11]. The absorption distribution for each wavelength over the film thickness was calculated in the 300 nm – 800 nm wavelength range. Multiplying by the light of the AM 1.5 solar spectrum and integrating over the film thickness yielded the total number of photons absorbed at each wavelength. Finally, summation over all wavelength resulted in the total number of absorbed photons. The maximum current density J_{sc} was calculated assuming that each absorbed photons results in a collected electron, i.e. the internal quantum efficiency, IQE, was set equal to unity [11].

For the optical simulation we chose a common BHJ device structure consisting of ITO (120 nm)/MoO₃ (5 nm)/blend A1/PCBM /LiF (10 nm)/Al (100 nm). The 5-nm MoO₃ and the 10-nm

LiF films are inserted between the active layer and the ITO and Al surfaces to form ohmic contacts for hole and electron collection, correspondingly. In the numerical simulation, the thickness of the blended layer was varied in the 40 nm – 320 nm range. The optical constants of ITO, Al and LiF used in the simulation were taken from the literature [12]. The optical constants of the MoO₃ films were determined by us using the same procedure as for the Al dye and the blended films. For this purpose, 50-nm thick MoO₃ films were thermally evaporated in vacuum (10⁻⁴ Pa).

2. Results

Figure 1 shows the molecular structure of the A1 and the absorption coefficient α determined for a 25-nm thick dye film. As it is seen, there are two absorption peaks of $7,3 \times 10^4 \text{ cm}^{-1}$ and $5,5 \times 10^4 \text{ cm}^{-1}$ at $\lambda = 598 \text{ nm}$ and 402 nm , correspondingly. Besides, although the absorption of the film is moderate, the absorption area is broad and covers the 400 nm – 750 nm spectral region, where the solar photon flux is maximal. This, as well as the low intrinsic fluorescence of the new push-pull merocyanine dye, is an important prerequisite for its photovoltaic application.

To model the light propagation within the solar cell device, one needs to know the optical constants of all involved layers. The refractive indices (n) and the extinction coefficients (k) of each layer used in the simulation are plotted as a function of the wavelength in figure 2. The blended film's optical constants were determined for a film with a thickness of about 45 nm.

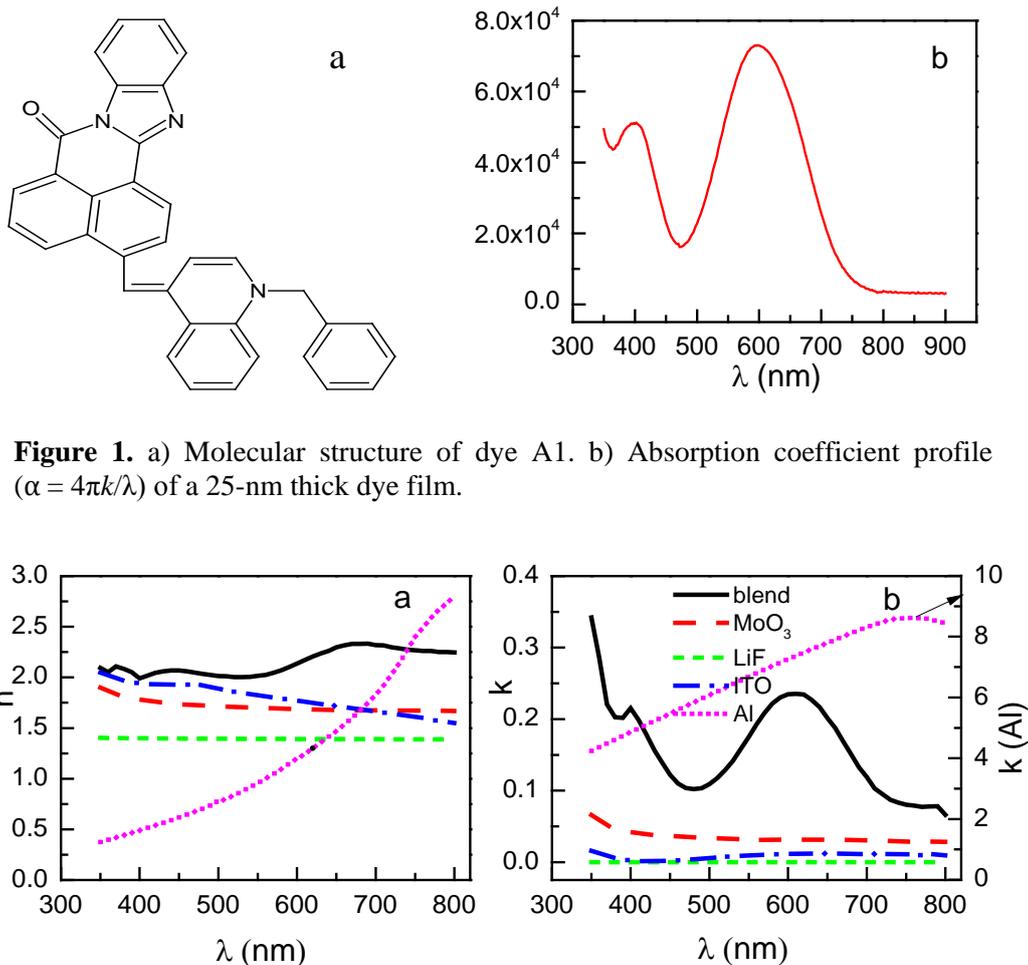


Figure 1. a) Molecular structure of dye A1. b) Absorption coefficient profile ($\alpha = 4\pi k/\lambda$) of a 25-nm thick dye film.

Figure 2. Optical constants of layers used in the simulation: a) refractive indices n ; b) extinction coefficients k .

As already mentioned, the optical simulation was performed for a standard BHJ cell structure, where the light enters through the glass substrate and sequentially passes through the ITO, MoO₃, Al/PCBM blend and LiF layers. The light is then reflected back from the Al electrode and, finally, a part of the light leaves the solar cell through the front.

Figure 3 presents the spectral dependence of the total absorption within the active layer for a set of different layer thicknesses. For comparison, the photon flux of a standard AM 1.5 solar spectrum is shown as a gray solid line. It is clear that the blue light is absorbed mainly by the PCBM, and the red and near infrared, by the Al dye. It is also seen that the blended film's absorption overlaps with the solar spectrum from 400 nm to 800 nm as required for high-efficiency solar energy conversion.

Assuming an IQE = 1, the maximum short-circuit current density J_{sc} under AM 1.5 illumination for different layer thicknesses is shown in figure 4. Due to the interference effects in the device structure, J_{sc} does not follow a straight line, but shows local maxima at about 80 nm and 230 nm. In general, the photocurrent is higher for a larger active layer thickness, but due to the limited exciton diffusion length in the organic layer, the real photocurrent decreases as the active layer thickness is increased. Therefore, we may expect an optimized overlap between the 80-nm active layer's absorption and the solar spectrum. J_{sc} of about 13 mA cm⁻² is obtained for this thickness, which is comparable to the maximum current calculated for, e.g., MDMO-PPV (poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene) and PCBM bulk heterojunction solar cells [14].

Experimental studies of a real device are in progress and are forthcoming in a separate paper.

4. Conclusions

The results of the present study show that thin films of the newly synthesized merocyanine dye Al is characterized by a moderate absorption in a broad spectral region – between 400 nm and 750 nm. Moreover, the total absorption within a Al dye/PCBM blend layer overlaps with the solar spectrum from 400 nm to 800 nm. Therefore, it could be expected that, as an active layer, the blended film prepared will provide a good sunlight harvesting and, thus, a high-efficiency solar energy conversion. This is confirmed by the estimated value of the maximum density of the short-circuit current J_{sc} under AM 1.5 illumination for the optimum thickness of the blended film. The comparability of this value to

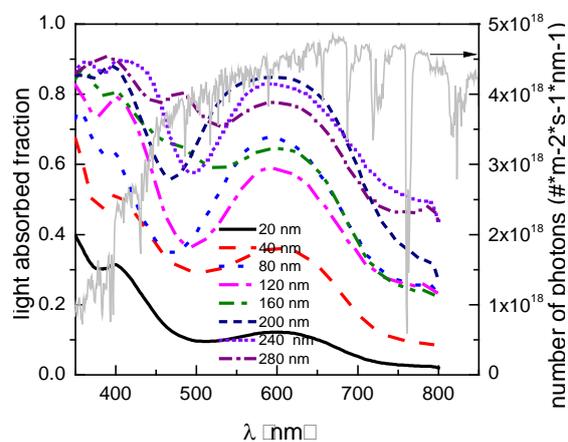


Figure 3. Fraction of incident light absorbed within the dye-PCBM layer of the solar cell for several layer thicknesses. For comparison, the photon flux of a standard AM 1.5 solar spectrum is shown as a gray solid line (right axis).

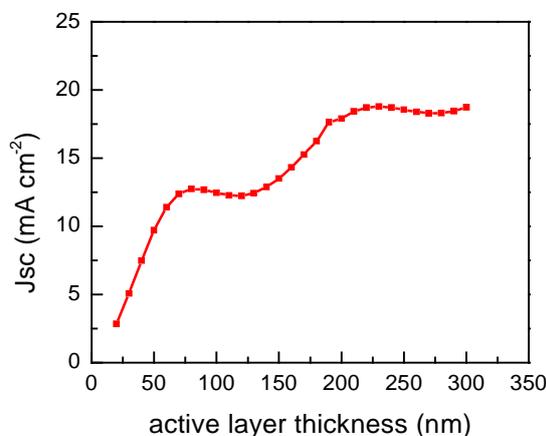


Figure 4. Calculated short-circuit current density J_{sc} under AM 1.5 spectral illumination (100 mW cm⁻²) versus the active layer thickness (IQE = 1).

literature data for some advanced solar devices demonstrates the potentiality of our new merocyanine dye for application as an electron donor in solution-processed BHJ solar cells.

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