



Small molecule bulk heterojunction organic solar cells with coumarin-6 as donor material

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ABSTRACT

To leverage the potential of organic solar cells, suitable materials for the photoactive layers have to be found. Herein, we show that the well-known fluorescent dye 3-(2'-benzothiazolyl)-7-diethylaminocoumarin works as an efficient light absorber material with a sensitivity at wavelengths from 400 to 650 nm. In combination with doped transport layers and optimization of the photodiode stack, a power conversion efficiency up to 1.9% under air mass 1.5 and 100 mW/cm² illumination could be achieved.

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1. Introduction

The main reason for the widespread interest in organic semiconducting materials is the possibility to easily adjust photoelectric properties by chemical modification, the potential of low-cost processing, and the compatibility with flexible substrates [1]. Besides dye-sensitization, the heterojunction principle represents an important approach in the field of organic photovoltaics.

The most frequently investigated absorber materials for such cells based on small molecules are metal phthalocyanines and oligothiophenes with donor properties and fullerene C₆₀ as acceptor, yielding power conversion efficiencies exceeding 12% [2,3]. To broaden the still rather narrow materials basis, absorber materials with both satisfying optical and electrical properties have to be found. Also, different compounds have to be used to absorb certain regions in the visible spectrum in order to convert the sunlight in multi-stacked devices [4].

Here, we investigate the suitability of 3-(2'-benzothiazolyl)-7-diethylaminocoumarin (coumarin-6, C6) as a donor material in small molecule bulk heterojunction (BHJ) solar cells. Due to its outstanding properties, C6 has already been applied in various fields, such as in organic light emitting diodes as a strong fluorescent emitter [5,6], as laser dye because of its high stability [7,8] and it has been inserted as sensitizer in dye-sensitized solar cells [9,10]. Due to these characteristics of C6, the adoption for organic solar cell application follows as a straight conclusion. Iijima et al. investigated the photovoltaic properties

of C6 and other derivatives in the late eighties and showed their suitability as p-type semiconductor for photocells [11]. C6 has also been introduced into phototransistors, evinced higher conductivity of the host material and yielded higher spectral response close to the region where C6 strongly absorbs [12].

Bulk heterojunction solar cells are composed of an interpenetrating network of a p-type semiconducting donor material and an n-type semiconducting acceptor material. This concept ensures a large interfacial area and results in large numbers of generated charge carriers, providing an approach for high-efficiency solar cells. However, C6 used as sensitizer in polymer based BHJ polymer cells showed weak performance with efficiencies below 0.3% [13–15]. The poor performance was mainly attributed to the low charge carrier mobility of C6.

Here, we fabricate small molecule photodiodes with C6 as donor material using high vacuum thermal evaporation techniques and characterize them by J–V and spectral response measurements. In order to achieve high sensitivity in the spectral range from 450 to 480 nm, optical simulations are performed to optimize the layer thicknesses for concentrating the incident light in the absorption region. The mixture ratio of C6 and C₆₀ has been varied and different hole transport materials have been used to investigate their influence on solar cell key values.

2. Experiments

The solar cells were fabricated in a custom-made organic material beam deposition tool (Bestec, Germany) at a pressure of 10^{−6}–10^{−5} Pa. J–V measurements (Keithley 2400 source meter, Kepco power supply)

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are recorded in dark conditions and under air mass 1.5 (AM1.5) and 100 mW/cm² illumination (KHS Technical lighting) at a temperature of 25 °C. A mask is used to accurately limit the illumination area. The optical constants are determined by transmission and reflectance spectroscopy (Solid Spec, Shimadzu) and by subsequent data fitting with the software WVASE32 (J.A. Woollam Co., Inc.). Spectral response curve data are recorded with a spectrofluorometer (Horiba Jobin Yvon, Fluoromax-4 and Keithley 2400) calibrated with a Si photodiode and a Keithley 2400 source meter. Relative permittivity ϵ_r data are determined by capacitance-voltage-measurements with an impedance analyzer (Wayne Kerr 6520B) placing the organic layers between two 100 nm thick aluminum electrodes on silicon substrates. Layer thicknesses are measured by a stylus force profilometer (Kla Tencor) and confirmed with transmission and reflectance spectra. Film growth during deposition is monitored by quartz crystal microbalances (Inficon).

We have used a p-i-n device architecture in order to provide ohmic contacts to both electrodes. The active layer (35 nm C₆₀:C6, materials are twice sublimed prior to utilization) has been embedded between a p-doped transport layer (HTL) and a blocking layer (BL), followed by an n-doped electron transporting layer and a cathode. All applied materials have been described previously in the context of organic solar cells. p- and n-doping is done employing the molecular dopant NDP2, NDP9 and NDN26 (Novaled AG, Germany), respectively, which is used for processing reasons and could be replaced by 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) and Cs₂CO₃, respectively. The transport and dopant materials have been used as delivered. In order to determine the square amplitude of the optical field penetration profile into the absorptive device, the commercially available simulation software Setfos 3.2 (Fluxim) has been used. The field amplitudes and the energy fluxes for each wavelength, at each position within the stack are calculated by using a transfer matrix formalism implementing the optical constants of each layer as described in literature [16]. For optimization of the transport layer thicknesses, the absorptivity of the absorption layer has been maximized considering the AM1.5 solar spectrum. Values for the levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were taken from literature for 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB, 5.5 eV/2.2 eV) [17,18], 2,2',7,7'-tetra(m-tolyl-phenylamino)-9,9'-spiro-bifluorene (spiro-TTB, 5.2 eV/NA) [19], N,N,N',N'-tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD, 5.1 eV/2.0 eV) [17], 9,9-bis[4-[di-(p-biphenyl)aminophenyl]]fluorene (BPAPF, 5.6 eV/2.2 eV) [17,18], C6 (5.4 eV/2.9 eV) [5] and C₆₀ (6.2 eV/3.8 eV) [1]. The work functions for indium tin oxide (ITO) (~4.8 eV) and Al (~4.2 eV) were used according to literature [20]. The blend constitution is related to the thicknesses.

3. Results and discussion

3.1. The composition of the absorption layer

Fig. 1 shows the absorption coefficients α and the refractive indices n of neat C6 and C₆₀ containing thin films and their mixtures. The spectra feature bands that can clearly be related to the absorption of C₆₀ (344 nm; 1.62×10^5 cm⁻¹ and 445 nm; 4.85×10^4 cm⁻¹) and C6 (446 nm; 5.82×10^4 cm⁻¹). Increasing amounts of C6 in the layer cause stronger absorption in the region between 400 and 520 nm. It has to be noted that the neat C6 layer possessed a high roughness so that optical values might be distorted due to scattering. Although C6 is known to be a strong emitter, the photoluminescence intensity of mixed C6:C₆₀ thin films is hardly detectable. The absorption coefficients on the order of 10⁵ cm⁻¹ and the weak luminescence confirm the suitability as absorbing material. Hence, bulk heterojunction solar cells have been fabricated in dependence on the blend constitution. The J-V curves under illumination and in the darkness as well as the used stack architecture are depicted in Fig. 2. The resulting key values

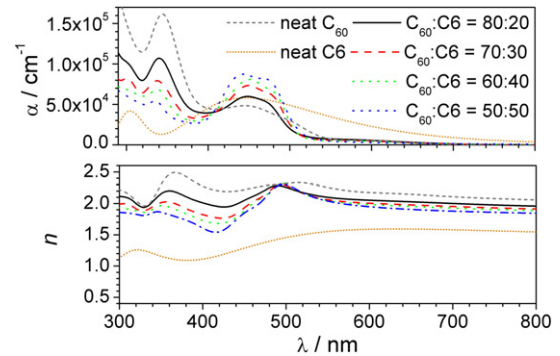


Fig. 1. Absorption coefficients α and refractive indices n of neat C6 and C₆₀ and their mixtures.

are summarized in Table 1. Clearly, all parameters are affected by the variation of the C6 content.

The open circuit voltage (V_{OC}) rises with increasing of the C6 amount. Since the origin of V_{OC} is still under debate, several approaches will be discussed in the following. A variation of the Fermi-level splitting due to a shift of the HOMO or LUMO levels could be a reason for the change in V_{OC} . Generally, V_{OC} scales with the effective gap, which is the difference between the LUMO of the acceptor and the HOMO of the donor. As discussed by Tress and co-workers for C₆₀:ZnPc blended absorption layers, the variation of the D:A ratio yielded a shift of the blend HOMO and thus, a V_{OC} adjustment [21]. Although a very similar pin-architecture has been applied, the HOMO shift resulted there in higher extraction barriers which can strongly effect the Fermi-level splitting and hence, V_{OC} of the cell. However, for our example we can exclude a LUMO shift of C₆₀ since a replacement of the neat C₆₀ showed no effect on V_{OC} , too. If lowering of the C6 HOMO level with increasing C6 content is considered, only injection barriers will be enhanced, which will not affect the V_{OC} as shown by drift-diffusion simulations [17]. Another reasonable explanation can be provided with the mobility dependent recombination given by the Langevin theory which proposes for decreasing charge carrier mobilities a drop in the fill factor (FF) and a rise of V_{OC} . However, this has never been experimentally proven so far for small molecule solar cells, although this is very good in agreement with the here presented results [22]. Finally, the correlation between the charge transfer (CT) states and V_{OC} is considered which is described by Deibel and coworkers [23]. After light absorption, a singlet exciton is formed on the donor and can diffuse towards the donor-acceptor heterojunction, where it can dissociate by performing a charge transfer, if the energy of the CT complex is lower than the energy of the singlet exciton given by the optical absorption gap. Using the equation for the Gibbs free energy of photoinduced electron transfer, it has been shown that the charge transfer energy (E_{CT}) stabilizes with higher dielectric permittivities ϵ_r and thus, V_{OC} decreases [24]. With increasing C6 amount, the relative dielectric constant

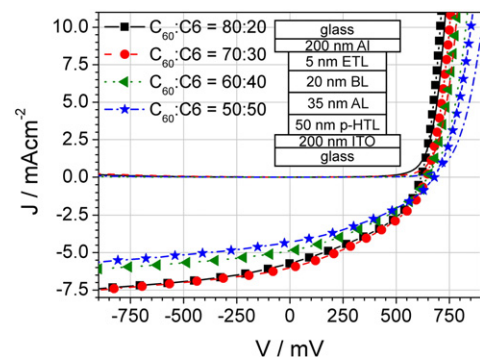


Fig. 2. J-V curves of organic solar cells with variation of the C₆₀:C6 blend composition. The inset shows the used stack architecture.

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