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Semitransparent organic photovoltaics using a near-infrared absorbing cyanine dye

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ABSTRACT

A selective near-infrared absorbing heptamethine cyanine dye (Cy7-P) electron donor was used for the fabrication of bilayer solar cells with the acceptor C₆₀. Using a reflective metal top electrode, solar cell optimization resulted in an external power conversion efficiency (η) of 1.5% for layer thicknesses of ~20 nm for Cy7-P and of ~40 nm for C₆₀, with using either PEDOT:PSS or MoO₃ as anode and Alq₃ as cathode buffer layers. Highly transparent devices were then fabricated by using silver/Alq₃ cathodes. Average visible transmittance (450–670 nm) values of, for example, 67.2% ($\eta=0.7\%$), 62.1% ($\eta=0.9\%$) or 50% ($\eta=1\%$) were obtained for different thickness combinations of silver and Alq₃. Optimized solar cells had a maximum transparency of 79.8% at 568 nm. The operational stability under 1 sun illumination was $T_{80}=30$ h, after which 80% of the initial cell performance was reached.

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1. Introduction

Solution-processed, small molecule-based organic photovoltaic (SM-OPV) cells are attracting interest in research and industrial laboratories due to their potential as low-cost, flexible and light-weight devices for solar energy conversion [1,2]. Power conversion efficiencies (η) of SM-OPV devices are rapidly increasing. For simple bilayer cells and using C₆₀ as electron acceptor, $\eta=1.5\%$ (using subnaphthalocyanine [3]), $\eta=2.6\%$ (using azadipyrromethenes [4]), $\eta=3.3\%$ (using diketopyrrolopyrrole derivatives [5]) or $\eta=5.7\%$ (using squaraine dyes [6]) have been reported. Bulk heterojunction SM-OPV cells with soluble fullerenes as acceptors performed even better, and η ranging between 4.4% and 6.7% were achieved, with donors based on diketopyrrolopyrrole [7], thiophenes end-capped with alkyl cyanoacetate [8] or rhodanine groups [9], such as a push–pull thiophene–thiadiazolopyrrolo chromophore [10].

As for polymeric systems [11], high-performing SM-OPV cells require tailored redox energy levels of the donor–acceptor components, high and balanced charge-carrier mobilities and a film morphology that allows for loss-free charge transport pathways to the electrodes. In addition, a broad optical absorption around the

peak (~700 nm) of the solar spectral photon irradiance is prerequisite for efficient light capture and a high resulting photocurrent. Therefore, small molecule dyes for OPV applications have primarily been developed so far that absorb over the whole wavelength region of visible light and into the near-infrared (NIR) region [3–10].

By making the organic layer thin enough, not all of the incoming light is absorbed and the active film becomes semitransparent. Combined with transparent, non-reflecting electrodes, this has allowed for the fabrication of semitransparent (SM and polymeric) OPV cells that have been proposed for applications such as power-generating windows that provide sun shading at the same time. For example, by using the poly(3-hexylthiophene)/soluble fullerenes material combination, which absorbs in the visible wavelength range between ~400 and 650 nm, semitransparent solar cells with η between 1.5% and 3% were manufactured [12–15].

Clearly, for many window-integrated applications OPV cells that do not absorb visible light at all would be advantageous. Visible photopic light corresponds to the wavelength range of ~450–670 nm, where the relative spectral sensitivity of the human eye is above 5% [16,17]. Not many organic materials with selective NIR absorption are available [18] and important steps towards transparent OPV cells were reported only recently [19]. Using chloroaluminum phthalocyanine as electron donor and C₆₀ as acceptor, SM-OPV cells were designed with $\eta=1.7\%$ and a visible

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transparency of $> 55\%$ [17]. In another example, a SM-OPV solar cell with the Ph₂-benz-bodipy/C₆₀ combination resulted in $\eta=2.4\%$ with an average transmittance in the 400–750 nm wavelength range of 47.9% [20]. Finally, by using a NIR light-sensitive polymer (PBDTT-DPP) as electron donor and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as electron acceptor, promising solution-processed polymer OPV cells with $\eta\sim 4\%$, an average visible transmittance (AVT) of 61% and a maximum transmittance of 66% at 550 nm were fabricated [21].

Cyanine dyes are charged polymethine colorants where a usually positive charge is delocalized over an odd number of sp² carbon atoms forming the π -conjugated bridge between electron-donating or -accepting groups [22,23]. Cyanine dyes are characterized by a sharp, very intense absorption band. The absorption maximum is shifted to longer wavelength with increasing number of double bonds (~ 100 nm per additional methine group) [24]; therefore, a desired absorption throughout the visible and into the NIR region (with absorption peak maxima > 1000 nm [25]) can be adjusted by synthesizing cyanine dyes with the appropriate number of methine units. Similarly, a conjugated polymer that absorbs solely in the NIR wavelength region with an absorption maximum of 1000 nm was obtained by connecting cyanine dyes in a head-to-tail fashion [26].

Cyanine dyes were also studied for photovoltaics. As an important advantage, cyanine dyes are relatively cheap and commercially available in large quantities or they can be synthesized by straightforward chemistry. The best performance ($\eta=3.7\%$ [27]) for a purely organic solar cell was achieved for a bilayer heterojunction when using a trimethine cyanine dye with a film absorption maximum in the visible at 578 nm as electron donor and C₆₀ as acceptor. An organic salt consisting of a heptamethine cyanine cation and a cyanine anion was used with PCBM in organic bulk heterojunction cells ($\eta\sim 0.4\%$ [28]). Thin films of this cyanine-cyanine salt displayed pronounced light-harvesting properties in the NIR range with peak absorptions at ~ 820 nm and ~ 940 nm. In both cases, a non-transparent metal cathode was used as top contact for solar cells [27,28]. A heptamethine cyanine dye was synthesized for use in dye-sensitized solar cells with a maximum spectral response at 800 nm [29].

Here, we report on bilayer solar cells using a commercially available heptamethine dye with terminal benzindol moieties as electron donor and C₆₀ as electron acceptor. Solar cell performance was first optimized using a reflective aluminum back contact. In a second step, semitransparent devices were fabricated by using thin silver/Alq₃ top electrodes. The feasibility of cells with an average visible transmittance of over 65% and a performance of 1% was demonstrated. For any semitransparent solar cell application, a compromise must then be made between maximized transparency and performance.

2. Experimental

3-Butyl-2-(2-[3-[2-(3-butyl-1,1-dimethyl-1,3-dihydro-benzo[e]indol-2-ylidene)-ethylidene]-2-chloro-cyclohex-1-enyl]-vinyl)-1,1-dimethyl-1H-benzo[e]indolium hexafluorophosphate (Cy7-P, FEW Chemicals), poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), (PEDOT:PSS, Sigma-Aldrich, conductivity 1 S cm⁻¹), 2,2,3,3-tetrafluoropropanol (TFP) and chlorobenzene (CB, Sigma-Aldrich) were used as received.

Indium tin oxide-coated glass substrates (ITO, Thin Film Devices, 140 nm, resistivity 20 Ω sq⁻¹) were sequentially cleaned in acetone, ethanol, detergent and de-ionized water. As hole-extracting layer, PEDOT:PSS (75 \pm 10 nm) was spin coated onto ITO followed by heating to 120 °C for 15 min. Alternatively, thin anode films of MoO₃ (Alfa Aesar, 99.9995%) were deposited by

thermal evaporation from a tungsten boat at a base pressure of $< 10^{-6}$ mbar onto unheated ITO substrates which were rotated during deposition. Although we designate MoO₃ throughout, Rutherford backscattering spectroscopy on silicon substrates showed that the material was actually slightly oxygen deficient (O/Mo=2.94).

Cy7-P layers were spin coated from CB solutions inside a nitrogen-filled glove box (< 5 ppm H₂O, < 6 ppm O₂). Layers with different thicknesses of the C₆₀ fullerene (SES Research, 99.9%) and of the exciton blocking layers tris-(8-hydroxyquinoline) aluminum (Alq₃, Sigma-Aldrich, 99.995%) or bathocuproine (BCP, Sigma-Aldrich, 96%) were then deposited by thermal sublimation under vacuum at a pressure of 3×10^{-6} mbar. As cathodes, either a 35 nm thick film of Al (Cerac, 99.999%) or Ag (Cerac, 99.99%, different thicknesses) were evaporated through a shadow mask to define eight solar cells on each substrate with active areas of 3.1 mm² or 7.1 mm².

Film thicknesses were determined by profilometry (Ambios XP1), AFM measurements were performed on a Nanosurf Mobile S in tapping mode at a resonance frequency of 170 kHz using silicon cantilevers. Current–voltage (J – V) characteristics were measured using 100 mW cm⁻² simulated AM 1.5 G solar irradiation on a calibrated solar simulator from Spectra-Nova. The incident photon-to-current conversion efficiency (IPCE) was measured using a monochromator and the light from a 300 W Xe lamp together with an AM1.5G filter set. The monochromatic light intensity was determined using a calibrated Si-diode. Absorption spectra for solutions and thin films were measured on a Varian Cary 50 UV–vis spectrophotometer using a quartz cuvette or a glass substrate as baseline. Thin films and solar cells were characterized via illumination through the anode side (glass/ITO) only.

To study the intrinsic lifetime, cells were stored in the glove box in the dark. A homemade airtight transfer box was used to measure cell J – V characteristics outside the glove box. The degradation over a period of 100 h was measured under N₂ at 1 sun illumination intensity. For TEM measurements (CM 30 Philips, 300 kV operating voltage), amorphous carbon coated TEM grids (Agar Scientific) were dip-coated in CB (6.5 mg mL⁻¹) Cy7-P solutions and were then dried overnight. Optical constants for Cy7-P and Ag were determined by spectroscopic ellipsometry (M-2000, J.A. Woolam Co., Inc.). For the ellipsometry measurement, a 23.1 nm thick Cy7-P film was spin coated from CB onto a silicon wafer, and 12 nm Ag were evaporated onto an ITO/glass substrate. Optical constants were taken from the literature for glass, ITO and PEDOT:PSS [30], for C₆₀ [31], for Al [32], for Alq₃ [33] and for the 8 nm Ag layer [34]. For thicker Ag layers (12–100 nm) the measured values from ellipsometry were taken.

Cyclic voltammetry measurements were recorded on a PGStat μ 30 potentiostat (Autolab) using a standard three electrodes cell system with a glassy carbon rotating disc (3 mm in diameter) as the working electrode, a platinum counter electrode and a water-free double junction Ag/AgCl reference electrode system separated by a ceramic and a sleeve diaphragm, respectively (Metrohm). Electrolyte of the inner couple system was 0.1 M tetrabutyl ammonium chloride in acetonitrile, whereas the outer bridging system was 0.1 M tetrabutyl ammonium perchlorate in acetonitrile. Cy7-P (100 mg) and C₆₀ (140 mg) were measured in degassed *ortho*-dichlorobenzene (ODCB) solutions (~ 40 mL) in an argon atmosphere using 0.1 M tetrabutyl ammonium hexafluorophosphate as supporting electrolyte. The ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as internal reference. As an approximation of the formal potential of the redox couples, half-wave potentials $E_{1/2}=1/2(E_{pc}+E_{pa})$ were evaluated, with the cathodic and anodic peak potentials, E_{pc} and E_{pa} . $E_{1/2}$ for Fc/Fc⁺ was 1.17 V against the Ag/AgCl reference electrode.

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