Organic Electronics 14 (2013) 2029–2033

Contents lists available at SciVerse ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

An efficient merocyanine/zinc phthalocyanine tandem solar cell

V. Steinmann [a], T.E. Umbach [a], M. Schädel [a], J. Krumrain [a], M.R. Lenze [a], H. Bürckstümmer [b], F. Würthner [b], K. Meerholz [a,*]

[a] Department of Chemistry, University of Cologne, Luxemburger Str. 116, 50939 Cologne, Germany
[b] Institut für Organische Chemie and Röntgen Research Center for Complex Material Systems, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

ARTICLE INFO

Article history:
Available online 20 April 2013

Keywords:
Organic solar cells
Tandem cells
Small molecules
Merocyanines
Vacuum-processing
Thermal evaporation

ABSTRACT

We present a merocyanine:C_{60}/zinc phthalocyanine:C_{60} tandem solar cell, comprising two complementary absorbing bulk heterojunction subcells connected in series. High-efficiency devices were realized in a rather simple tandem setup, consisting of only three organic layers that were successively deposited in an ultrahigh-vacuum chamber. The optimized tandem solar cell features an efficiency of 4.5%, demonstrating a performance improvement by ca. 50% compared to the individual optimized single-junction solar cells. The experimental data are in excellent agreement with optical simulations, assuming an internal quantum efficiency near unity in the optimized tandem device.

1. Introduction

During the last years, organic tandem solar cells (TSC) have gained increased interest. In principle, power conversion efficiencies (PCE) up to 15% should be achievable by combining two single-junction solar cells of complementary absorption [1]. Lately, polymer based TSCs have reached PCEs up to 10.6% [2], while small-molecule TSCs revealed somewhat lower efficiencies of 6.6% [3], both in series connection. Most high-efficiency TSCs rely on rather sophisticated device architectures, comprising up to five [3], six [4], nine [5], or even 13 organic layers [6]. Therefore, reliable optimization protocols with regard to layer thickness and composition are still a great challenge and accordingly, the device optimization is mainly based on trial and error experiments, requiring a lot of laboratory time and material. Recently, Janssen et al. have successfully reported performance predictions of polymer TSCs based on optical as well as electrical simulations [7–9]. Also, Forrest et al. have used a transfer-matrix approach in order to estimate the performance of a small-molecule TSC [3].

In the past, we have introduced merocyanine (MC) dyes as electron donor compounds in single-junction bulk heterojunction (BHJ) solar cells. Our best single-junction solar cells (SSC) based on the violet-blue MC dye HB194 and the fullerene C_{60} revealed high performances with PCEs up to 6.1% despite of a relatively simple device architecture, comprising only two organic layers [10]. MC dyes show strong and easily tunable absorption from the visible to the near infrared (IR) region [11]. Therefore, they appear to be excellent candidates for TSC applications. As a proof of concept, first TSCs based on two identical MC BHJ subcells were fabricated in a series connection, resulting in respectable PCEs up to 5.0% and a high open-circuit voltage (V_{OC}) of 2.1 V [12]. However, those first TSCs showed essentially no performance improvement compared to the optimized SSCs based on the same violet-blue MC dye MD376, which covers a broad spectral range from 350 to 700 nm with a maximum at $\lambda_{max} \approx 610$ nm.

In this work, we present a highly promising small-molecule TSC based on the MC dye HB226 and zinc phthalocyanine (ZnPc; see inset of Fig. 1a for the chemical structures). The red MC dye HB226 is already known from our earlier comparison studies on solution- and vacuum-processed SSCs [13]. It was chosen due to its unique strong absorption at short wavelengths around 550 nm, thus, having

* Corresponding author.
E-mail addresses: wuerthner@chemie.uni-wuerzburg.de (F. Würthner), klaus.meerholz@uni-koeln.de (K. Meerholz).

1566-1199/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.orgel.2013.03.032

minimum spectral overlap with ZnPc, unlike other MC dyes which have shown better SSC performance, such as for example HB194 [10,13]. Furthermore, all alkyl substituents (in total five) are as short as possible, i.e. methyl groups, allowing to low sublimation temperatures and the best chance for closely packed π-systems. HB226 SSCs show one of the highest efficiencies for short-wavelength-absorbing small molecules. Therefore, HB226 appeared to us as an ideal candidate for TSC applications in combination with more abundantly available long-wavelength-absorbing compounds, such as various MC dyes or other small-molecules. ZnPc is a well-investigated small-molecule electron donor component, widely applied in OPV [14–16]. We will demonstrate that the resulting TSC is 50% more efficient than either one of the optimized SSCs it consists of.

2. Experimental

2.1. Device fabrication

Solar cells were fabricated via thermal evaporation in a custom-made ultrahigh-vacuum chamber (K.J. Lesker Co., UK) at a base pressure of 10^{-7} mbar. Commercially available indium-tin oxide (ITO) coated glass substrates were used as a transparent bottom contact. A 15 nm MoO_3 layer (99.95%, Alfa Aesar) was applied as a hole-collecting contact (HCC) on top of the ITO. The BHJ layers were fabricated by co-evaporating C_{60} (2x sublimed, CreaPhys GmbH, Dresden) and either the MC dye HB226 or ZnPc in a 1:1 donor:acceptor composition at room temperature. BPhen (1x sublimed, Sensient Imaging Technologies GmbH) was utilized as an exciton blocking layer (EBL), followed by a thick silver (99.9% Alfa Aesar) top electrode. In the TSC, a 1 nm Al (99.9%, Alfa Aesar)/15 nm MoO_3 recombination layer was sandwiched between the two subcells, which has already been successfully applied in previous TSC architectures [12,17]. Layer thickness measurements were performed with a Vecco Dektak profilometer with a measurement accuracy of ±2 nm. The device stacks are schematically shown in Fig. 2.

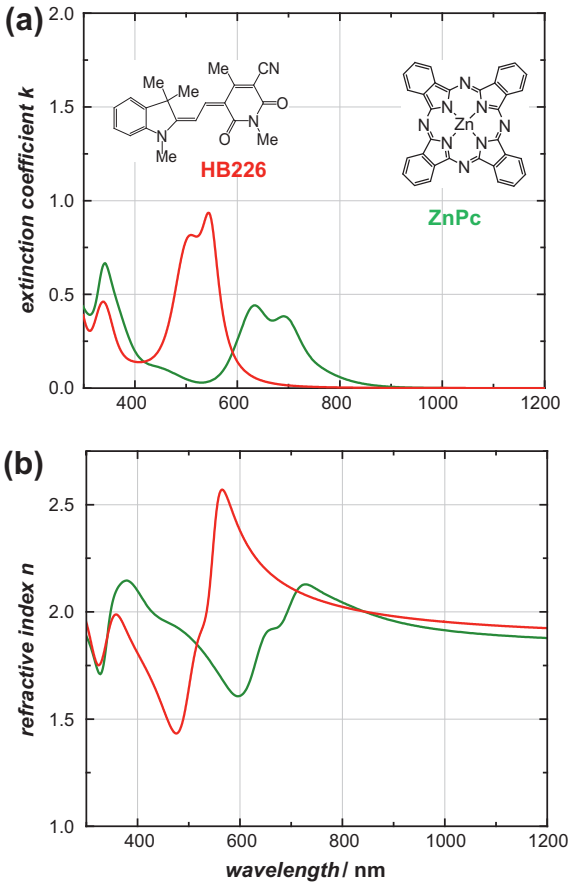

Fig. 1. Dispersion of (a) extinction coefficient k and (b) refractive index n of HB226:C_{60} (red lines) and ZnPc:C_{60} (green lines) subcells, respectively. The insets in (a) reveal the chemical structures of the electron donor compounds HB226 and ZnPc. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. Device characterization

The solar cell characteristics were measured using a Keithley 2425 source-measurement unit with a filtered Xe lamp, providing the AM 1.5 solar spectrum. The intensity of the lamp was adjusted to 100 mW/cm^2.

2.3. Optical characterization

The extinction coefficient k and the refractive index n of all layers were determined individually via variable-angle spectroscopic ellipsometry (VASE); simultaneously the transmission was detected as well. For the measurements, each layer (organic and metals) was separately deposited on glass or Si (100) substrates. In general, the measurements were performed for at least two layer thicknesses and for fifteen angles between 40.0 and 77.5°. All experimental data were fitted by the appropriate optical models assuming one consistent set of n and k values. The n and k values of the active layers HB226:C_{60} (red lines) and ZnPc:C_{60} (green lines) are presented in Fig. 1. Note, that the sample preparation was carried out under comparable conditions to the subsequent device fabrication.

2.4. Optical simulations

We carried out optical simulations with a self-developed software, and later on verified with the commercially available software SETFOS 3.2 [18]. Both programs are based on a transfer-matrix model and require the wavelength-dependent optical constants of all materials in the layer stack as input parameters.

By assuming that each photon absorbed in the active layer yields an electron and a hole, contributing to the overall external current $J_{SC,cal}$, we calculated the resulting current, which constitutes the maximum possible value. Note, that in this procedure any electrical losses, e.g. due to recombination, etc., were neglected so that essentially an internal quantum efficiency (IQE) of unity was assumed in the calculation. This can then be compared with the experimental results ($J_{SC,exp}$). The ratio $J_{SC,cal}/J_{SC,exp}$ gives