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Abstract. We present the in-depth investigation of solution-processed bulk-heterojunction solar cells based on the merocyanine dye MD304 as a donor in combination with the soluble fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as acceptor. The optimized MD304:PCBM devices exhibit an external quantum efficiency of ca. 50%, and a power conversion efficiency of up to 2.1% under standard illumination and 2.7% under reduced illumination intensities. Because of the strongly dipolar character of merocyanine dyes the bulk material features a relatively large dielectric constant, which is beneficial for charge transport and reduced carrier recombination. This somewhat compensates the limited hole mobility of the dipolar merocyanine. © *2011 Society of Photo-Optical Instrumentation Engineers*. [DOI: 10.1117/1.3528043]

1 Introduction

Bulk heterojunction (BHJ) organic solar cells are currently in the focus of interest because they offer a promising approach toward low-cost regenerative energy sources.[1,2] They are flexible, light weight, and can be deposited from solution (e.g., by a printing process using role-to-role fabrication technology) and have shown a power conversion efficiency (*PCE*) of up to 7.4%.[3–5] The active layer of BHJ solar cells consists of a bicontinous interpenetrating network of electron donor and acceptor domains, which is formed during the deposition/drying process. Currently, the favored materials for BHJ solar cells are composites of fullerenes such as [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as electron acceptor materials with semiconducting polymers, such as P3HT or PCPDTBT as electron donor materials. In order to fully exploit the potential of BHJ solar cells, the search for new donor materials is ongoing.[6] Soluble small molecules are attractive candidates for solution-processed BHJ solar cells, because they offer the same processing advantages commonly associated with polymers, but they are easier to synthesize and, above all, to purify. In addition, contrary to polymers, small molecules do not suffer from polydispersity, whereas the performance of polymeric solar cells is often affected by the molecular weight and the weight distribution of the respective material batch.[7] Recently, the first BHJ solar cells that are based entirely on small conjugated molecules (i.e., PCBM as electron acceptor and various electron donor components) have been published, indicating the increasing interest in this emerging research field.[8–20] With dendrimers or oligomers based on typical organic semiconductors derived from oligothiophenes, *PCE* values up to 2.5% could be achieved.[10–12]

Comparable values were also reported for pigment-based solar cells using acene,[13–15] squaraine,[16,17] boron dipyrromethene,[18] and merocyanine dyes.[19] Recently, outstanding *PCE* values of up to 4.4% have been reported by Tamayo et al.[20] and Walker et al.[21] for molecules composed of two subunits, a dye and a semiconductor part.

In our recent work, we have introduced traditional colorants, in particular, merocyanine (MC) dyes that are widely applied in textile coloration, printing applications, and nonlinear optics, as a new class of donor material for organic solar cells.[19] Because MCs consist of an electron-withdrawing and electron-donating subunit, connected through a π-conjugated bridge, they are rather polar compounds featuring relatively large dipole moments, which is generally considered to be disadvantageous due to limited charge-transport properties. On the other hand, in particular, if their electronic structure is in the cyanine limit (i.e., both neutral and charge-separated electronic structures contribute equally to the ground and excited state), then the optical transition dipole moment is strongly enhanced, resulting in large absorption coefficients up to 1.5×10^5 M^{-1} cm^{-1}, which is favorable for the absorption of light and thus for the efficiency of the solar cell. The absorption of MC dyes can be easily tuned from the UV to the near-infrared by attaching substituents with various electron-withdrawing and -donating strengths.[22] Therefore, the whole spectral range of the solar irradiation can be covered. Additionally, the easily tunable electrical, optical, and bulk properties of MC dyes by chemical modifications offer a new research route to a systematic study of the influences of these parameters on the solar cell performance.

In this paper, we report our efforts to improve BHJ solar cells containing the MC dye MD304 (for chemical structure, see inset in Fig. 2). With a maximal absorption at 650 nm [ultraviolet-visible (UV-vis) spectrum in Fig. 1], MD304 appears deep blue.

2 Results and Discussion

2.1 *Active Layer Thickness and Donor: Acceptor Ratio*

In line with our earlier work, a first series of devices with Al top electrode was fabricated. The MD304:PCBM ratio and the active layer thickness were varied, respectively. The largest *PCE* value of 1.74% was achieved for a PCBM content of ~70 wt% and for rather small active layer thicknesses of ca. 60 nm; a second maximum with reduced efficiency was found for thicker active layers (ca. 170 nm).[10] The optimized device features a short-circuit current (J_{SC}) of 6.3 mA cm^{-2}, an open-circuit voltage (V_{OC}) of 0.76 V, and a fill factor (*FF*) of 0.36 (Table 1). Many solution-processed small molecule BHJ solar cells appear to feature smaller *FF* values compared to polymeric solar cells mostly in the range between 0.3 and 0.5.[8–13,15–21] The highest *FF* reported for a solution-processed BHJ solar cell containing small molecule donors is 0.61,[14] while for polymer *FF* >0.7 have been reported.

As is commonly done for polymer-based devices,[23] we have tried to improve the device performance by adding a number of "secondary solvents" (anisole, nitrobenzene, or tetrahydrofuran) to the chlorobenzene:pyridine mixture; however, this did not enhance the device performance. Also, the commonly used curing protocols, such as heat treatment, solvent soaking, etc., did barely change the device performance. Thus, it can be assumed that the layer

Table 1 Performance of the investigated MD304:PCBM solar cells with varying top-electrode metals (70 wt% PCBM; $d \approx 60$ nm) for AM 1.5 light of 100 mW cm^{-2} intensity.

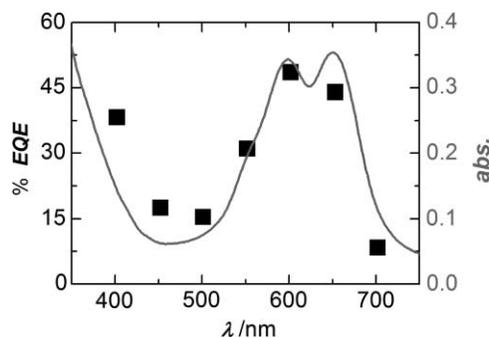| Top electrode	Φ_w (eV)	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF*	% *PCE*
Al	−4.3	0.76	6.3	0.36	1.74
Ca/Ag	−2.9	0.78	7.3	0.34	1.97
Ba/Ag	−2.7	0.77	7.8	0.34	2.08

Fig. 1 *EQE* of solar cells PEDOT/MD304:PCBM 30:70 wt% (60 nm)/Al (squares, left axis) and UV-vis spectrum of the solar cell (line, right axis).

morphology obtained from wet deposition of small-molecule inks is much closer to thermodynamic equilibrium than for polymers, where strong annealing effects are commonly observed.

2.2 *OFET Hole Mobility Measurements*

Considering the small *FF* values and the facts that the maximum efficiency is achieved for a rather high PCBM content, at a rather small active layer thickness, and that the efficiency is decreased for thicker active layers (even in the second maximum), the investigated MC:PCBM solar cells seem to suffer from a poor or unbalanced charge-carrier transport. Organic field-transister measurements reveal hole mobilities in the range of 10^{-6} cm^2 V^{-1} s^{-1} for layers of pure MD304. For mixed MD304:PCBM layers, the hole mobility decreases by roughly one order of magnitude (5×10^{-8} cm^2 V^{-1} s^{-1} at 70 wt% PCBM). These hole mobilities are considerably smaller compared to those obtained for conjugated polymers (e.g., P3HT), measured under the identical conditions and far beyond the electron mobility of PCBM.[24] This drawback might be due to the dipolar character of the dyes and could furthermore depend on unfavorable aggregation of the small molecules in the bulk.[25] However, the measured hole mobilities of the MC:PCBM devices are still in the range of those obtained for α,α-DH6TDPP:PCBM solar cells (measured in hole-only devices via space-charge-limited current), which are among the most efficient small-molecule solution-processed BHJ solar cells reported thus far.[20] Thus, obviously, a deficient carrier mobility is not necessarily detrimental for the solar cell performance.

2.3 *EQE Measurements*

This view is further supported by our measurements of the external quantum efficiency (*EQE*) in our devices (Fig. 1). The data points roughly follow the absorption spectrum of the mixture. At the wavelength of maximum absorption, *EQE* is ca. 50%, a value that exceeds the *EQE* of many other solution-processed small-molecule BHJ solar cells, which were reported to be in the range of 30–45%;[10,11,16–18,20] values up to 58% were also reported for devices containing a diketopyrrolopyrrole derivative.[21]

2.4 *Permittivity*

The origin behind this apparent discrepancy between a decent *EQE* and a rather poor carrier mobility could be the strong polarity of the MD304 (MC dyes, in general), the molecular dipole moment being ~14 D.[26] Organic materials commonly feature rather low dielectric constants ($\varepsilon_r = 2$–3), and as a result, the Coulomb interaction between charges is strong, leading to losses due to recombination. A more polar environment would stabilize charges and thus reduce
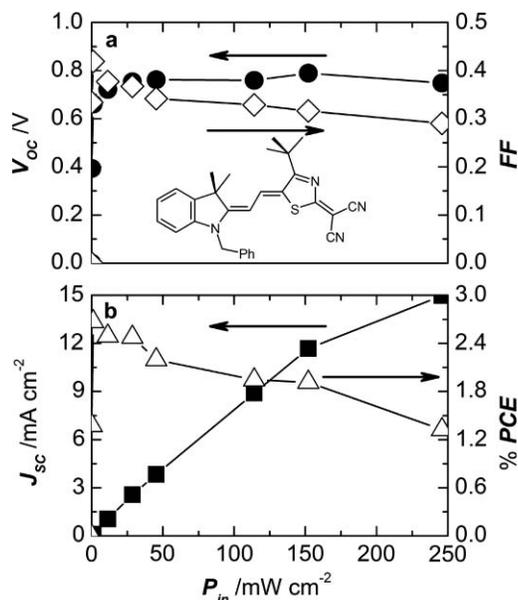
Fig. 2 Illumination intensity dependence of MD304:PCBM solar cells (70 wt% PCBM, Ba/Ag cathode). (a) V_{OC} (filled circles, left axis) and *FF* (open diamonds, right axis) and (b) J_{SC} (closed squares, left axis) and *PCE* (open triangles, right axis). The inset in (a) shows the chemical structure of MD304 (Ph = phenyl group).

recombination effects. Thus, we determined the permittivity of our materials by impedance spectroscopy (measurement of the devices' capacity). For a device PEDOT:PSS/MD304 (47 nm)/Al, an ε_r of 3.4 was obtained. This compares to $\varepsilon_r = 2.2$ for a heat-treated (i.e., fully aggregated) layer of P3HT. Because ε_r of PCBM[27] is higher than for MD304 and P3HT, the ε_r values of the actual solar cells are higher than for the neat donor compounds. For blends with optimized donor:acceptor ratios, ε_r of 4.0 for MD304 with 70 wt% PCBM and 3.6 for P3HT with 40 wt% PCBM were measured. Thus, the exciton binding energy in the MD304 layer is 0.04 eV (10%) smaller than in the P3HT blend (assuming a distance between the charges of 1 nm). It has been shown that in organic solar cells containing materials with high ε values, the charge dissociation in the active layer as well as the initial separation distance and the decay rate of the bound electron-hole pairs are improved.[28] Overall, assuming similar mobility the performance of the solar cell is enhanced.

2.5 *Variation of the Top Electrode*

In order to further optimize the devices, we investigated the influence of the nature of the top electrode (120 nm Al, 6 nm Ca/120 nm Ag, and 6 nm Ba/120 nm Ag) on the solar cell performance (see Table 1). As expected for cathode materials with work functions above the LUMO lowest accepted molecular orbital level of PCBM,[29] all cells exhibit similar values for V_{OC}, whereas J_{SC} increases with increasing work function ϕ_w of the used metal.[30] This might be attributed to a higher built-in voltage (V_{bi}) in these devices in consequence of the increasing energetic difference between the two electrodes. However, also the different reflection properties of the metals and the resulting electric field distribution inside the active layer have influences on J_{SC}. The best *PCE* value of 2.1% under AM1.5 conditions was achieved by using a Ba/Ag cathode.

2.6 *Performance at Reduced Illumination Intensity*

The dependency of V_{OC}, J_{SC}, *FF*, and *PCE* on the power of incident light (P_{in}) for the optimized MD304 devices is depicted in Fig. 2. Except for high intensities (>150 mW cm^{-2}), J_{SC} increases linearly with P_{in}. V_{OC} is nearly constant for the entire intensity range and only drops strongly for light intensities near zero, in agreement with theoretical expectations. Finally, the *FF* increases with decreasing P_{in}, which is indicative of reduced recombination effects at low charge carrier concentration (low intensity), again an outcome of the poor carrier mobility. Overall, the efficiency is increased under lower light intensity, reaching 2.7% at an intensity of $\sim$2 mW cm^{-2}.

3 Experimental

The solar cells were fabricated according to the previously reported procedure.[19] For spin-coating, the dye was dissolved in a chlorobenzene:pyridine (5:1) mixture. The *JV* characteristics of the solar cells were measured using a Keithley 2425 source measurement unit. The AM1.5 light was provided by a filtered Xe lamp. The intensity of 100 mW cm^{-2} of the AM1.5 light was determined using a calibrated inorganic solar cell from the Fraunhofer Institute for Solar Research in Freiburg (Germany) and a reference PCBM:P3HT cell measured by the same institution. No mismatch factor was included in the calculation of the efficiency. EQE measurements were performed by filtering the Xe lamp using Melles Griot interference filters with an FWHM of 10 nm. For mobility measurements, transistors were fabricated by spin-coating the materials on heavily doped p-type Si++/SiO$_x$ substrates with patterned source and drain gold contacts. The doped silicon substrate was used as the common gate contact followed by a 230-nm thick SiO$_x$ insulating layer with a capacitance of 15 nF cm^{-2}. Channel length and width were 2.5 μm and 1 cm, respectively. Devices were measured in a dry-nitrogen atmosphere with an Agilent B1500A semiconductor device analyzer. Mobilities were calculated from the transconductance in the linear regime. The dielectric constants were determined by capacity measurements using an oscillating voltage of 50 mV and a frequency between 20 Hz and 10 kHz.

4 Conclusions

MCs are very promising electron-donor compounds for organic BHJ solar cells using PCBM as the acceptor. By optimizing the cell parameters, an *EQE* of ca. 50% and a *PCE* value of 2.1% were obtained. At reduced illumination intensity (2 mW cm^{-2}), the *PCE* value further increases up to 2.7%. Our data indicate that the strongly dipolar character of the MC dyes has positive, but also some negative, effects on the solar cell performance. On the one hand, the hole mobility is quite low, which might be caused by the strong energetic disorder;[31] on the other hand however, charge generation is enhanced and recombination reduced due to the high dielectric permittivity of the material. Optimization of this trade-off by ideally packed MC dyes may accordingly open an avenue toward high-performance BHJ cells. In this regard, it is noteworthy that the active layer thicknesses of our best cells were only $\sim$60 nm (i.e., the incident light is not fully absorbed). For comparison, solar cells based on the donor polymers P3HT and OC$_1$C$_{10}$-PPV with comparable layer thickness exhibit PCE values smaller than 2%.[32] By improving the hole mobility of the MC dyes, solar cells with larger optimal layer thickness and thus higher efficiencies should be achievable.

Acknowledgments

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