Stability of bilayer trimethine cyanine dye/fullerene organic solar cells

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ABSTRACT

The long-term (up to 100 days) stabilities of thin films of a trimethine cyanine dye (Cy3-P) and of Cy3-P/ C_{60} bilayer solar cells with initial power conversion efficiencies of up to 3.6% in the regular and inverted device architecture were studied. For storage conditions under nitrogen at room temperature in the dark, Cy3-P films were stable and no decrease in performance was measured for inverted ITO/TiO$_2$/C$_{60}$/Cy3-P/ MoO$_3$/Ag solar cells. ITO/PEDOT:PSS and aluminum were found to be responsible for a slight inherent degradation of regular solar cells under inert storage conditions. Solar cells stressed at accelerated (80 °C) full sun simulation showed a burn-in period of ~5 days with a performance loss of 75%. This initial performance decrease might be linked to the photopolymerization reaction of C_{60}. For longer times, performances stabilized and arrived at 15% of the initial values after a test period of 17 days.

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1. Introduction

Small semiconducting molecules are attracting interest for efficient solar energy conversion in low-cost, flexible and light-weight photovoltaic devices [1–3]. Equally important from an application point of view is the lifetime of small-molecular solar cells. Durability analysis and studies on degradation mechanisms in small-molecular solar cells, especially carried out under recommended standard testing conditions [4], are relatively rare, however, as compared to their polymeric counterparts [5–8].

For pentacene/fullerene C_{60} heterojunction solar cells that were stored at a relative humidity of 33% in the dark, an operation time of about 850 h was found until 50% of the initial power conversion efficiency was lost (T_{50}) [9]. Inverted, non-encapsulated copper phthalocyanine (CuPc)/C$_{60}$ cells with a shelf lifetime of over 1500 h in air were reported [10]. Pentacene/PCBM (a soluble fullerene derivative) and CuPc/PCBM cells were studied for different atmospheric storage conditions under continuous illumination. For cells encapsulated with polydimethylsiloxane or stored

under vacuum and using UV-filtered light illumination, T_{50} of ~2000 and 2500 min (for pentacene) and of ~1450 and 1900 min (for CuPc) were measured [11]. The degradation behavior under illumination of zinc phthalocyanine (ZnPc):C$_{60}$ cells encapsulated with different barrier films was studied. It was found that water was critical for the long-term stability compared to oxygen. Lifetimes T_{50} of 4000 h were obtained for glass-encapsulated devices [12]. No sign of degradation of glass-encapsulated ZnPc:C$_{60}$ cells was observed after accelerated full sun simulation (100 mW cm^{-2}, 85 °C) for 1800 h [13].

Here, we report on the durability of bilayer cyanine dye/C$_{60}$ solar cells. Cyanine dyes are charged polymethine colorants where a usually positive charge is delocalized over an odd number of sp^2 carbons forming the π-conjugated bridge. Cyanines are notable for their exceptionally high light extinction coefficients, tunable absorption throughout the visible and into the NIR region such as the presence of specific and relatively mobile counter anions [14,15]. Cyanine/fullerene bilayer solar cells in the regular and inverted architecture with power conversion efficiencies (η) of 2.9–3.7% were demonstrated so far [16–18]. Numerous cyanine dyes are commercially available. At present, these dyes are at least a factor of ten cheaper than the most popular semiconducting polymers in the fields, which make them interesting candidates for cost-effective organic solar cell applications.

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† In memoriam of Gaetan Wicht who passed away in his beloved Swiss mountains in the spring of 2013.

Solar cells with different charge extraction layers and top metal electrodes in the regular and inverted geometry were fabricated using a trimethine cyanine dye with the counter anion PF_6^- (Cy3-P) and C_{60} as active materials. In the first step, the performance of these devices was optimized. The low photo- and thermal stability of cyanines has repeatedly been reported [19–21], especially with increasing number of methine groups. Therefore, in the second step thin cyanine films, individual layer stacks and completed solar cells were tested for their inherent stability under different atmospheric storage conditions in the dark. Finally, the durability of solar cells was measured under accelerated full sun simulation.

2. Experimental

Solar cells were fabricated on cleaned glass/ITO substrates (Thin Film Devices, resistivity 20 Ω square^{-1}, 150 nm thickness). For cells in the regular geometry, hole extraction layers consisted of thermally evaporated MoO_3 (20–40 nm, Sigma Aldrich, 99.99%) or spin-coated PEDOT:PSS films (PEDOT, 90 nm, Clevios P VP Al 4083) that were heated at 120 °C for 15 min. Between C_{60} (SES Research, 99.5%) and the metal electrodes, a 2.5 nm thick Alq_3 layer (Sigma Aldrich, 99.995%) was thermally evaporated. For inverted cells, thermally evaporated MoO_3 (30 nm) and TiO_2 (40 nm, anatase phase) thin films deposited by magnetron sputtering were used as buffer layers. Active electron donor 1-ethyl-2-[3-(1-ethyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-propenyl]-3,3-dimethyl-3H-indolium hexafluorophosphate (Cy3-P, FEW Chemicals) films were spin coated inside a nitrogen-filled glove box (<5 ppm H_2O, <6 ppm O_2) from filtered 2,2,3,3-tetrafluoropropanol (TFP, Sigma Aldrich) or chlorobenzene (CB, Sigma Aldrich) solutions, and thermally evaporated C_{60} was used as electron acceptor. Cells were completed by evaporating Al (Lesker, 99.999%) or Ag (Cerac, 99.99%) electrodes through a shadow mask defining eight cells per ITO substrate with areas of 0.031 cm^2 and 0.071 cm^2, respectively. All thermal evaporations were carried out in the same vacuum chamber (4×10^{-6} mbar) with deposition rates of 0.2 Å s^{-1} for C_{60}, Alq_3 and MoO_3, and of 0.5 Å s^{-1} for Al and Ag.

To study the intrinsic lifetime, cells were stored in the glove box in the dark. A homemade air-tight transfer box was used to measure cell $J–V$ characteristics outside the glove box on a calibrated solar simulator (Spectra Nova) using a Xe lamp with 100 mW cm^{-2} simulated AM 1.5 G solar irradiation. Accelerated cell testing over a period of 17 days was carried out in a homemade environmental chamber. Stressing took place in an N_2 atmosphere. Light was supplied by water-cooled white LEDs (Citizen Electronics, CL-L340-MC41W1-C) with a calibrated illumination intensity of 1 sun. The LED spectrum is characterized by a broad light distribution over the visible wavelength range with a maximum at ~580 nm and an additional sharp peak at 450 nm. Samples were mounted on a copper sample holder lying on a heating plate at a temperature of 80 °C. Cells were held in short-

circuit conditions and cell parameters were measured periodically without breaking the test conditions. To avoid any contact with oxygen and humidity during transfer from the glove box to the environmental chamber and during experimental setting, these cells were encapsulated using epoxy and a cover glass. To study the initial stress-induced degradation, non-encapsulated cells and individual films were treated in the glove box at 80 °C on a hot plate and with light (1 sun) from a Xe-lamp for 24 h. Scanning probe microscopy scans were performed with a Nanosurf Mobile S in tapping mode at a resonance frequency of 170 kHz with silicon cantilevers from Mikromasch, Nanosensors.

3. Results and discussion

3.1. Initial solar cell performance

Cy3-P/C_{60} bilayer solar cell architectures with five different layer sequences were fabricated (Table 1). Devices (1)–(4) from Table 1 were regular geometries with varying electrode materials to test their influence on cell lifetime, device (5) was fabricated in the inverted structure (Fig. 1a, right). For device optimization and lifetime studies, more than 1200 solar cells on over 150 glass/ITO
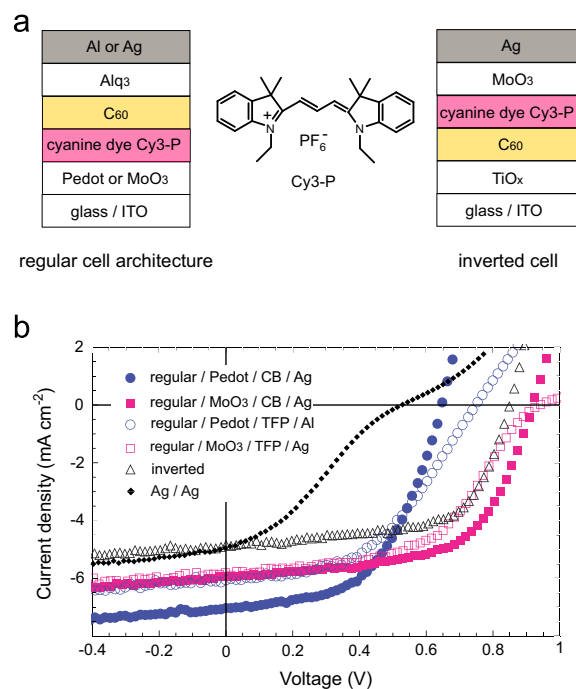

Fig. 1. (a) Schematic of regular and inverted cyanine dye/C_{60} solar cells and the molecular structure of Cy3-P. (b) Initial $J–V$ curves of the best performing cells listed in Table 1.

Table 1
Initial device performance/parameters from Cy3-P (20 nm)/C_{60} (40 nm) solar cells. V_{oc} is the open-circuit voltage, J_{sc} the short-circuit current, FF the fill factor, and η the external power conversion efficiency. Ranges of values originate from # different devices with eight cells per device. The illumination intensity was 100 mW cm^{-2}. Solvents used for dye coating were 2,2,3,3-tetrafluoropropanol (TFP) and chlorobenzene (CB).

	Device structure	Cy3-P coating solvent	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	η best (%)
(1)	ITO/PEDOT/Cy3-P/C_{60}/Alq_3/Al	TFP (#5)	0.58–0.79	6.4–6.6	34.8–43.5	2.3
		CB (#1)	0.48–0.6	5.5–6.7	48.8–54.8	2.0
(2)	ITO/PEDOT/Cy3-P/C_{60}/Alq_3/Ag	TFP (#1)	0.54–0.67	6.7–7.7	29.7–35.6	1.6
		CB (#3)	0.64–0.68	6.3–7.7	48.5–52.1	2.7
(3)	ITO/MoO_3/Cy3-P/C_{60}/Alq_3/Ag	TFP (#4)	0.86–0.95	5.9–6.5	39.9–52.4	3.2
		CB (#5)	0.67–0.92	5.9–6.6	56.5–63.8	3.6
(4)	Ag (12 nm)/PEDOT/Cy3-P/C_{60}/Alq_3/Ag	TFP (#1)	0.35–0.51	3.5–5.0	30.4–32.4	0.8
(5)	ITO/TiO_2/C_{60}/Cy3-P/MoO_3/Ag	TFP (#4)	0.82–0.84	3.6–5.4	61.1–63.3	2.9