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## Effects of concentrated sunlight on organic photovoltaics

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We report the effects of concentrated sunlight on key photovoltaic parameters and stability of organic photovoltaics (OPV). Sunlight collected and concentrated outdoors was focused into an optical fiber and delivered onto a 1 cm<sup>2</sup> bulk-heterojunction cell. Sunlight concentration *C* was varied gradually from 0.2 to 27 suns. Power conversion efficiency exhibited slow increase with *C* that was followed by saturation around 2% at C=0.5-2.5 suns and subsequent strong reduction. Possible OPV applications in stationary solar concentrators ( $C \le 2$  suns) are discussed. Finally, experiments at C=55-58 suns demonstrated potential of our approach for accelerated studies of light induced mechanisms in the OPV degradation. © 2010 American Institute of Physics. [doi:10.1063/1.3298742]

Organic photovoltaics (OPV) has been suggested as a low-cost, lightweight, flexible alternative to inorganic photovoltaics. In particular, intense research is directed toward the development of OPV with a bulk heterojunction (BHJ) between donor-type conjugated polymers and acceptor-type fullerenes [e.g., poly(3-hexylthiophene) (P3HT)] and fullerene derivative, phenyl-C61-butyric acid methylester (PCBM).<sup>1</sup>

OPV is known to suffer from significant degradation upon simultaneous exposure to sunlight and air (oxygen and water vapor).<sup>2,3</sup> A typical operational lifetime of encapsulated OPV under full solar illumination (1 sun =100 mW/cm<sup>2</sup>) has for a long period of time been in the range of only days or weeks.<sup>4</sup> Recently long-term-stable BHJ cells have been developed.<sup>3,5-7</sup> This achievement opens various possibilities in OPV investigations (e.g., round robin test)<sup>8</sup> and development of practical applications. On the other hand, it raises problems, e.g., need for relevant accelerated tests of operational life-time.

We suggest that stable OPV can be used with low-cost stationary concentrators of sunlight working in the low concentration regime (<3 suns).<sup>9</sup> To check this hypothesis effects of sunlight concentration on the OPV efficiency and stability should be investigated. Here we report experimental exploitation of concentrated sunlight for such study using fiber-optic/mini-dish concentrator<sup>10–12</sup> [Figs. 1(a) and 1(b)]. We also demonstrate that our experimental approach can be used for accelerated tests of the OPV degradation.

The BHJ OPV devices were prepared in the ambient at Risø DTU, using a fully roll-to-roll compatible solar cell device preparation.<sup>8,13</sup> Commercially available indium tin oxide (ITO) glass substrates with a sheet resistivity of  $5-8 \ \Omega^{-1}$  were sonicated in isopropanol followed by washing in demineralized water. Layers of ZnO nanoparticles photoactive P3HT:PCBM and poly(3,4-ethylenedioxythio-

phene): polystyrene sulfonate (PEDOT:PSS) were then subsequently spin-coated. The layered architecture of the device was thus glassIITOIZnOIP3HT:PCBMIPEDOT:PSSIAg [Fig. 1(c)]. The photoactive area is defined by the  $1 \times 1$  cm<sup>2</sup> overlap between the ITO and the Ag electrodes. The samples were encapsulated by applying an adhesive plastic foil on the Ag electrode. During illumination, the cells were masked to ensure that only 1 cm<sup>2</sup> active area contributed to the photocurrent.

Prior to the transportation to Sede Boker, Israel, the current-voltage (I-V) characterization was performed with a Steuernagel Solarkonstant KHS575 solar simulator (100 mW/cm<sup>2</sup>, AM1.5G, 25 °C).

Power conversion efficiency  $\eta$  was calculated as

$$\eta = P_{\rm m}/P_{\rm in} = I_{\rm sc} V_{\rm oc} FF/P_{\rm in} \tag{1}$$

where  $I_{sc}$  and  $V_{oc}$  and *FF* denote short-circuit current, opencircuit voltage and fill factor, respectively.  $P_{m}$  and  $P_{in}$  are the



FIG. 1. (Color online) (a) Minidish dual-axis tracking solar concentrator (20 cm in diameter). Solar radiation is concentrated outdoors into the tip of a highly transmitting optical fiber which guides the concentrated sunlight indoors onto the solar cell being tested. (b) Uniform cell irradiation via a kaleidoscope. (c) The layer sequence of the inverted P3HT:PCBM BHJ cell (through-glass illumination). The solar cell area is defined as the overlap between the ITO and the Ag electrodes.

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TABLE I. Fitting parameters for four studied solar cells. *G* and  $\alpha$  are the fitting parameters describing a power law relation between  $I_{sc}$  and  $P_{in}$  [Eq. (3)]. *n* is the diode ideality factor calculated by evaluating the semilogarithmic fit of the  $V_{oc}$  data according to Eq. (2). *G*,  $\alpha$ , and *n* were calculated for  $C \leq 10$  suns.

Solar cell	$R_{ m s}$ ( $\Omega$ )	G	α	п
A	4.06	40.83	0.96	1.27
В	2.71	44.18	0.92	1.23
С	4.12	53.33	0.95	1.22
D	5.57	55.49	0.91	1.21

maximum electrical power output and incident light power.

The cell series resistance  $R_s$  was calculated from the reciprocal slope of the *I*-*V* curve at high applied voltage (*V*=1 V).

Four different solar cells with  $\eta \sim 2\%$  and *FF*  $\sim (0.55-0.6)$ , indicating low  $R_{\rm s}$  (Table I), were delivered to Sede Boker for a study with concentrated sunlight.

In Sede Boker, sunlight collected and concentrated outdoors was focused into a transmissive (quartz-core) optical fiber of 1 mm in diameter and then delivered indoors onto the solar cell being tested [Fig. 1(a)].<sup>10–12</sup> Flux uniformity was achieved with a 3 cm long square cross-section kaleidoscope, matching the size of the cell, placed between distal fiber tip and cell [Fig. 1(b)].

Measurements were limited to clear-sky periods, two hours around solar noon. The light spectrum on the cell was nearly invariant and close to the AM1.5.<sup>8,14,15</sup> Concentration of sunlight delivered to the cell (*C*) was varied gradually from 0.2 to 27 suns with a pizza-slice iris [Fig. 1(a)], and measured pyrometrically. *I-V* measurements were made with opening a shutter above the iris and illuminating the cell during *I-V* tracing only (<3 sec) to avoid excessive degradation and temperature variations.

In addition, the cells were subjected to a long-term (3 h) illumination at C=55-58 suns in order to study effect of high concentration on OPV degradation.

For conventional inorganic solar cell,  $I_{\rm sc}$  is known to depend linearly on C. Meanwhile,  $V_{\rm oc}$  increases logarithmically with  $I_{\rm sc}$  and C

$$V_{\rm oc} \approx (nkT/q)\ln(I_{\rm sc}/I_{\rm o}) = (nkT/q)\ln(C) + \text{const},$$
(2)

where n and  $I_0$  denote the diode quality factor and the reverse saturation current, correspondingly.

Semilog plots of  $\eta$  as a function of *C* should exhibit linear behavior in the lower flux regime, with a slope proportional the effective thermal voltage nkT/q (from the contribution of  $V_{oc}$ ). These plots should also feature (a) a nonlinear decrease at sufficiently high flux due to  $R_s$  dissipation, and (b) a maximum that reflects this tradeoff. So the flux level at which  $\eta$  peaks is governed by  $R_s$ . In recent generations of inorganic concentrator cells,  $\eta$  is maximized at hundreds of suns and higher.<sup>11,12</sup>

Figure 2 summarizes our data for  $I_{sc}$ ,  $V_{oc}$ , *FF*, and  $\eta$  as functions of sunlight concentration.

For OPV the intensity dependence of the photovoltaic parameters is still under discussion. To the best of our knowledge, for BHJ OPV it was studied only for  $C \le 1 \text{ sun.}^{16,17} \text{ C}_{60}/\text{ copper phthalocyanine (CuPc) bilayer cells were characterized up to 12 suns of simulated illumination).<sup>18</sup>$ 



FIG. 2. Effect of sunlight concentration on  $I_{sc}$  (a),  $V_{oc}$  (b)  $\eta$ , (c) and *FF* [inset in (c)] of BHJ cell. Insets in (a) and (b) show the linear dependence of log  $I_{sc}$  on log *C* and the linear correlation between  $V_{oc}$  and  $\ln I_{sc}$ , respectively.

In general,  $I_{sc}$  of OPV can increase with C according to a power law

$$I_{\rm sc} = G \times P_{\rm in}^{\alpha}.$$
(3)

The deviation of  $\alpha$  from 1 is attributed to a bimolecular recombination of photogenerated carriers (for dominant bimolecular recombination  $\alpha = 0.5$ ).<sup>16</sup> For C  $\leq 10$  suns  $I_{sc}$  of our cells was found to increase with *C* according to Eq. (3) [inset in Fig. 2(a)] with  $\alpha$  very near to 1 (0.91–0.96 in Table I). This is consistent with the published characteristics of highly efficient BHJ OPV obtained for C=0-1 sun.<sup>16</sup> For  $10 < C \leq 27$  suns, a sublinear behavior of  $I_{sc}$  is in evidence [Fig. 2(a)] that can be explained either by the increased influence of the bimolecular recombination or by effect of non-ideal uniformity of illumination (see below).

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FIG. 3. (Color online) I-V curves measured before and after 3 hours of light exposure (LE) at: various C and temperature.

For C  $\leq$  10 suns,  $V_{oc}$  increases logarithmically with  $I_{sc}$  [inset in Fig. 2(b)] with a slope approximately equal to kT/q (n=1.21–1.27 in Table I) that was theoretically predicted for OPV.<sup>17</sup> Decrease in  $V_{oc}$  in h flux regime (C=10–27 suns) indicates BHJ overheating by concentrated sunlight (the thermocouple placed on the cell backside revealed a constant temperature T=27–29 °C for C < 10 suns and T increased for C > 10 suns).

*FF* [inset in Fig. 2(c)] exhibits slow increase with *C* in low flux regime reaching a maximum of ~0.55 at *C*  $\approx 1$  sun. For 1 sun  $< C \le 2$  suns, *FF* is almost independent on *C* and then starts to roll off (down to  $\approx 0.3$  at *C* =27 suns).

 $\eta$  shows a predictable slight increase followed by a saturation region with  $\eta$  around 2% (at *C*=0.5–2.5 suns) and strong reduction at high *C*. Existence of the pronounced saturation regime is very important for OPV applications in stationary solar concentrators (at *C*≤2 suns)<sup>8</sup> and benefit of possible bifacial architecture of OPV devices.<sup>13</sup>

Use of OPV at C > 1 raised challenges for the cell stability at these illumination levels and technology optimization to minimize  $R_s$ . The latter can move the efficiency peak toward high sunlight concentration. The C<sub>60</sub>/CuPc cells with a small area (from 0.007 to 0.06 cm<sup>2</sup>) and optimized  $R_s$  were demonstrated to reach the maximum  $\eta$  at 4–12 suns.<sup>18</sup>  $R_s$  is known to increase with the cell area for both inorganic cells<sup>12</sup> and OPV<sup>18</sup> that should result in the reduction in concentration for the peak  $\eta$ . Recently<sup>12</sup> it was demonstrated that  $\eta$  of 1 mm<sup>2</sup> III-V semiconductor concentrator cells is maximized at ~1000 suns while for a 1 cm<sup>2</sup> cell of the same nominal architecture it peaked at ~350 suns.

At C=10-27 suns the observed  $\eta$  behavior [Fig. 2(c)] is controlled by a strong *FF* reduction due to  $R_s$  dissipation [inset in Fig. 2(c)]. Indeed *FF* rolls off from ~0.4 at *C* = 10 suns down to ~0.3 at 27 suns. These low *FF* values together with possible nonideal uniformity of the illumination<sup>19</sup> can cause the observed sublinear behavior of  $I_{sc}$  [Fig. 2(a)].<sup>11</sup>

Figure 3 shows 1 sun outdoor *I-V* measurements of 3 similar cells (with initial  $\eta \approx 2\%$ ) before and after 3 h of light exposure at various *C* and temperatures. Details of our outdoor measurements are described elsewhere.<sup>8,14,15</sup>

Exposure of the first cell under 1 sun was performed outdoor at T=50 °C. Both *FF* and  $V_{\rm oc}$  were found to decrease slightly (by ~2% of their initial value) while  $I_{\rm sc}$  exhibited more pronounced degradation, by ~20%.

For the high *C* experiments the cells were mounted on a 6 mm thick copper heat sink and exposed indoor with the setup shown in Fig. 1. Exposure of the second cell by *C* = 58 suns resulted in T=55 °C and caused significant degradation: both  $V_{\rm oc}$  and  $I_{\rm sc}$  degraded by ~50% while *FF* reached its minimum value of 0.25.

Water cooling of the heat sink allowed to keep the thirdcell T=30 °C during the illumination by similar light concentration. The degradation was considerably slower than that revealed in the high *C*/high *T* experiment.

In summary, using the fiber-optic/mini-dish solar concentrator, we studied the effect of sunlight concentration on the key parameters of 1  $\text{cm}^2$  P3HT:PCBM BHJ cells. C was varied gradually from 0.2 to 27 suns. For C  $\leq$  10 suns  $I_{sc}$ was found to increase with C almost linearly while  $V_{\rm oc}$  increased logarithmically with  $I_{sc}$ . Decrease in  $V_{oc}$  at C =10-27 suns was attributed to the BHJ heating by concentrated sunlight. Both FF and the efficiency  $\eta$  exhibit slow increase in low flux regime that was followed by a saturation region ( $\eta$  saturated around 2% at C=0.5-2.5 suns) and subsequent strong reduction due to  $R_s$  dissipation. Existence of the saturation regime is very important for possible OPV applications in stationary solar concentrators ( $C \leq 2$  suns). Finally, the preliminary long-term experiments at high C(55–58 suns) and various temperatures proved that our setup can be used for accelerated tests of the OPV operational lifetime. Furthermore, one can propose a research strategy for future detailed experiments that may select light induced mechanisms in the OPV degradation from those (like interface diffusion, etc.)<sup>5,6</sup> controlled by the cell temperature.

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- <sup>19</sup>See supplementary material at http://dx.doi.org/10.1063/1.3298742 for description of the ray tracing in our optical system.

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