Improved bulk heterojunction organic solar cells employing C_{70} fullerenes

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We show that the fullerene C_{70} is suitable to replace fullerene C_{60}, which is commonly used as electron transporter and acceptor in small-molecule organic solar cells. It is shown that the higher absorption of C_{70} leads to high external quantum efficiencies of over 50% in the spectral range of 500–700 nm. By optimizing the energy level alignment to hole transport layers, the absorption, and the ratio of C_{70}:zinc phthalocyanine (ZnPc) in a bulk heterojunction solar cell, an efficiency of η =2.87% is achieved. This is a substantial improvement over an identical solar cell employing C_{60} having η=2.27%. The efficiency increase is due to a higher photocurrent, while fill factor and open-circuit voltage for C_{70} and C_{60}-containing organic solar cells remain comparable. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3148664]

Organic solar cells (OSCs) have attracted considerable interest as a potential cost-efficient alternative to current silicon solar cells. Oligomer (small molecule) solar cells are attractive due to better materials purification and the possibility to easily deposit multilayer devices. Since the OSC breakthrough due to a copper phthalocyanine/perylene derivative flat heterojunction by Tang,[1] new materials and concepts, e.g., bulk heterojunctions,[2,3] doping of organic molecular matrices with donor or acceptor molecules,[4] or the *p-i-n* architecture[5] have lead to efficiencies of up to 5%.[6]

To be competitive with established solar cell technologies, higher efficiencies and longer lifetime are still necessary. Possible pathways toward higher efficiency are tandem cells which utilize different absorber materials to harvest photons from a wide part of the solar spectrum with little thermal losses, or materials with high exciton diffusion length and high absorbance.[7] Currently, the buckminster fullerene C_{60}[8] is used as standard material in OSC research as absorber and electron transporter due to its high electron affinity and good availability. However, its low absorbance in most parts of the solar spectrum ultimately limits its potential.

C_{70} has also been of interest for the polymer based solar cells, e.g., $[C_{70}]$PCBM[9] and convinced with its properties.

In this letter, we investigate higher-order fullerene C_{70}[10] as replacement for C_{60}. Superior performance and higher external quantum efficiency (EQE) of C_{70}-containing OSC are demonstrated, showing a way for further optimization toward more efficient devices.

The solar cells are fabricated in custom-made multichamber ultrahigh vacuum evaporation systems (BESTEC, Germany; K. J. Lesker Co., U.K.) at base pressures of 10^{-6}–10^{-8} mbar, using shadow masks and in high vacuum B30 evaporation chambers (Oerlikon Leybold Vacuum Dresden GmbH, Germany). As substrate, tin-doped indium oxide (ITO)-coated glass (Thin Film Devices, USA) is used. The substrates are cleaned in ultra sonic bath with detergent, acetone, ethanol, and isopropanol prior to processing.

The OSC stack consists of ITO, followed by 5 nm of C_x and a blend layer of 30 nm coevaporated C_x and zinc phthalocyanine (ZnPc) (weight ratio 2:1) as absorber. C_x denotes either C_{60} or C_{70}. For optimized hole extraction, a stack of 5 nm N,N'-diphenyl-N,N'-bis(4'-(N,N-bis(naphth-1-yl)-amino)-biphenyl-4-yl)-benzidine (Di-NPD), 15 nm Di-NPD or 40 nm N,N'-di(4-(2,2-diphenyl-ethen-1-yl)-phenyl)-N,N'-di(4-methylphenylphenyl)benzidine (PV-TPD) *p*-doped by 4.4 wt% of a proprietary *p*-type dopant (Novaled AG, Dresden, Germany)[11] and 10 nm of 3.2 wt% *p*-doped ZnPc is used. Finally, an Au back contact is deposited. For processing in the Lesker system, a comparable hole transport material, PV-TPD is used instead of Di-NPD. PV-TPD has comparable optical and electrical properties as Di-NPD.[12] All organic materials had been purified by vacuum gradient sublimation to remove contaminations.[13] The C_{70} had been purified four times.

Typical solar cell areas are about 6.4 mm^2 (measured individually using a light microscope). $I(V)$-characteristics are recorded using a source measurement unit 236 SMU (Keithley) under a sun simulator (Hoenle AG). The EQE is measured employing the lock-in technique in a custom-made setup with Xe illumination and a Cornerstone 260 monochromator. All short-circuit current densities J_{SC} shown in this letter are corrected for spectral mismatch and normalized to 100 mW/cm^2.

The obtained solar cell characteristics are summarized in Table I. The current-voltage characteristics of the B30 samples are shown in Fig. 2.

The open-circuit voltage is strongly influenced by the energy level alignment to the transport layers and the distance of highest occupied molecular orbital (HOMO) of the donor (ZnPc) and the lowest unoccupied molecular orbital (LUMO) of the acceptor (fullerene). Since the LUMOs of C_{60} and C_{70} both appear at -3.9 eV,[14] no difference in V_{OC} is expected, which is confirmed by the same $V_{OC}=0.56$ V for

TABLE I. Solar cell characteristics.

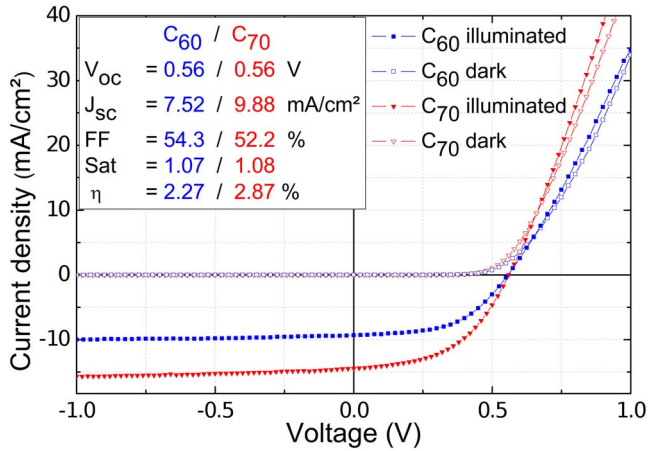| Absorber	C_x:ZnPc ratio	*p*-HTL thickness (nm)	J_{SC} mA/cm^2	V_{OC} (V)	FF (%)	η (%)
C_{60}	2:1	40	7.52	0.56	54.3	2.27
C_{70}	2:1	40	9.88	0.56	52.2	2.87
C_{70}	2:1	15	10.34	0.57	43.7	2.56
C_{70}	1:1	15	10.05	0.52	41.6	2.16

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FIG. 1. (Color online) $J(V)$-characteristics of the samples ITO/C_x(5 nm)/C_x:ZnPc(30 nm, 2:1)/Di-NPD(5 nm)/p-Di-NPD(40 nm, 4.4 wt%)/p-ZnPc(10 nm, 3.2 wt %)/Au. Shown are C_{70} device at AM 1.5 G illumination (filled squares), in the dark (empty squares), and C_{60} device at AM 1.5 G illumination (filled upside-down triangles) and in the dark (empty upside-down triangles). The currents are corrected for spectral mismatch and normalized to 100 mW/cm².

FIG. 3. (Color online) EQE measurements of solar cells with different C_{70}:ZnPc blend layer ratios 2:1 (filled squares) and 1:1 (empty circles). ITO/C_x(5 nm)/C_{70}:ZnPc(30 nm, 2:1/1:1)/Di-NPD(5 nm)/p-Di-NPD(15 nm, 4.4 wt %)/p-ZnPc(10 nm, 3.2 wt %)/Au.

C_{60} and C_{70}, respectively. The saturation $[J(-1\ \text{V})/J_{SC}]$ for both OSC is the same within experimental error, with the difference being less than 1%. This hints at high parallel resistances for both types of acceptor molecules and suggests similar blend layer morphologies and charge carrier percolation networks. A slight decrease in fill factor (FF) from 54.3% for C_{60} to 52.2% for C_{70} can be explained by the lower C_{70} electron mobility, which is determined by organic field effect transistor (OFET) measurements to be $\mu_e = 1.3 \times 10^{-3}$ cm²/V s. This differs by about two orders of magnitude of the mobility of C_{60}.

However, the decisive difference between both J-V characteristics is the short-circuit current density J_{SC}, which is 7.52 mA/cm² for the C_{60} and 9.88 mA/cm² for the C_{70}-containing cell, respectively, as shown in Fig. 1. This can be explained by the differences in absorption spectra shown in Fig. 2: the absorption of C_{70} in the range of 380–700 nm is significantly stronger over a wider range of the visible spectrum than C_{60}. This leads to increased photon harvesting and an improved EQE.
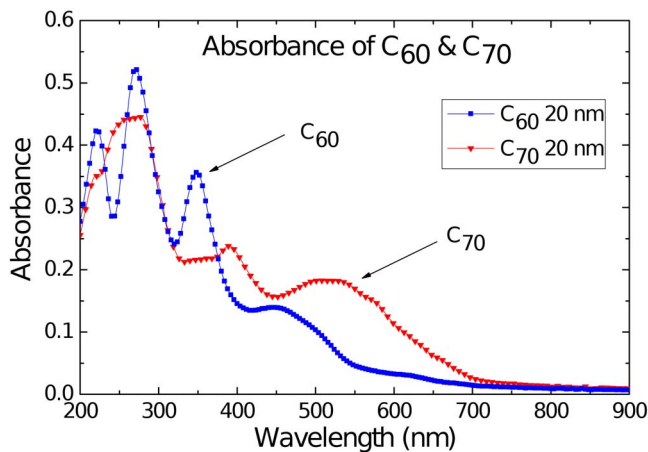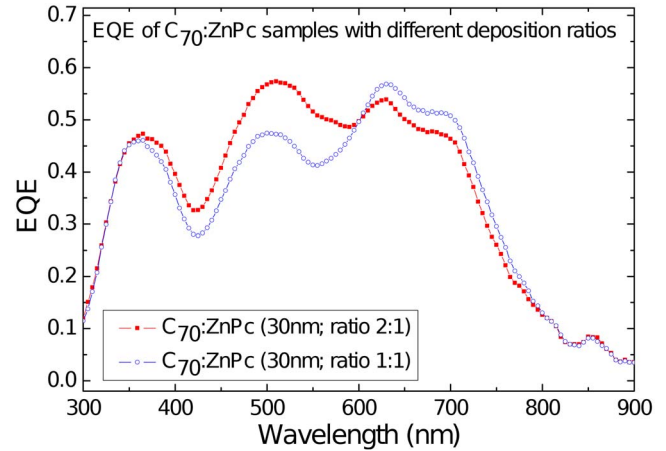

FIG. 2. (Color online) Absorbance spectra of C_{60} (filled squares) and C_{70} (filled upside-down triangles) in a range of 200–900 nm. Enhanced absorption of a wide spectral range is observed for C_{70} compared to C_{60}.

To study the influence of the blend layer ratio of C_{70}:ZnPc, different samples with ratios of 1:1 and 2:1 were fabricated. At an optimum ratio of 2:1, the OSC exhibits a combination of high photocurrent due to high absorption, and at the same time high FF owing to a favorable morphology within the blend layer. Ideally, a three-dimensional interconnected network should be formed, consisting of ZnPc and the fullerene.

The sample with a blend ratio of 2:1 exhibits improvements in J_{SC}, V_{OC}, and FF compared to the 1:1 ratio. The higher V_{OC} may be explained by an increased cluster growth of C_{70} in the blend.[15] The higher FF is evidence for lower charge carrier recombination and reduced transport problems. This correlates with improved percolation paths and interconnected transport networks. It appears that a better molecular arrangement occurs due to higher amount of C_{70}. The increase in photocurrent is caused to a stronger absorption in the blue region and is verified by EQE measurements shown in Fig. 3.

The sample with 2:1 ratio shows a high EQE of 0.55 and a much stronger absorption around 500 nm, corresponding to absorption of C_{70}. Compared to the 2:1 sample, a higher absorption in the ZnPc region (600–750 nm) occurs for the 1:1 sample due to the increased amount of ZnPc. Owing to the broad range of absorption of C_{70}, the photocurrent is higher for the 2:1 sample and leads to an enhanced power conversion efficiency of 2.56%. Due to the thinner p-doped hole transport layer (p-HTL) of 15 nm the FF decreases significantly in comparison to 40 nm. The small loss in photocurrent for the thicker device is overcompensated by the higher FF and results in higher efficiency.

In summary, we show a significant improvement of the efficiency of OSCs by replacing C_{60} by C_{70} in a bulk heterojunction device. Despite a slightly lowered FF, most likely due to lower electron mobility, the broader and enhanced absorption of C_{70} leads to an improvement of J_{SC} by about 30%. When comparing similar stacks, the use of C_{70} increases the efficiency to 2.87%, compared to 2.27% for a C_{60}-containing device. Due to the higher absorption, C_{70} is shown to be a promising material for future optoelectronic devices. Please note that Sakai *et al.*[16] have recently published work on C_{70} incorporated in OSCs. Their research was

conducted independently and was published online after submission of our manuscript.

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