Fluorinated Copper Phthalocyanine Nanowires for Enhancing Interfacial Electron Transport in Organic Solar Cells

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Supporting Information

ABSTRACT: Zinc oxide is a promising candidate as an interfacial layer (IFL) in inverted organic photovoltaic (OPV) cells due to the n-type semiconducting properties as well as chemical and environmental stability. Such ZnO layers collect electrons at the transparent electrode, typically indium tin oxide (ITO). However, the significant resistivity of ZnO IFLs and an energetic mismatch between the ZnO and the ITO layers hinder optimum charge collection. Here we report that inserting nanoscopic copper hexadecafluorophthalocyanine (F16CuPc) layers, as thin films or nanowires, between the ITO anode and the ZnO IFL increases OPV performance by enhancing interfacial electron transport. In inverted P3HT:PC61BM cells, insertion of F16CuPc nanowires increases the short circuit current density (Jsc) versus cells with only ZnO layers, yielding an enhanced power conversion efficiency (PCE) of ∼3.6% vs ∼3.0% for a control without the nanowire layer. Similar effects are observed for inverted PTB7:PC70BM cells where the PCE is increased from 8.1% to 8.6%. X-ray scattering, optical, and electrical measurements indicate that the performance enhancement is ascribable to both favorable alignment of the nanowire π–π stacking axes parallel to the photocurrent flow and to the increased interfacial layer-active layer contact area. These findings identify a promising strategy to enhance inverted OPV performance by inserting anisotropic nanostructures with π–π stacking aligned in the photocurrent flow direction.

KEYWORDS: Organic solar cell, interfacial layers, copper hexadecaphthalocyanine, nanowire, zinc oxide

Solar cells are a promising renewable energy source to meet increasing world energy demands.1–5 Recently, organic photovoltaic (OPV) cells with up to ∼9% power conversion efficiencies (PCEs) have been reported in the peer-reviewed literature,6–7 and furthermore, OPVs offer the attraction of low-cost manufacture on lightweight, mechanically flexible substrates over large areas by printing techniques.8–10 Currently, the highest efficiency solar cells utilize a solution-processed bulk heterojunction (BHJ) structure in which a polymeric donor and fullerene acceptor molecules form nanoscale interpenetrating hole and electron transporting networks, respectively.11,12 The large BHJ interfacial contact area facilitates exciton separation into free carriers at the donor–acceptor interfaces, thereby enhancing charge generation. Nonetheless, charge recombination is a significant loss mechanism both at the BHJ donor–acceptor interfaces13,14 and also at the active layer-electrode interfaces.15–20 Regarding the latter, interfacial layers (IFLs) between the active layer and the electrodes have been successfully implemented to block unwanted charges from recombining at this interface while acting as selective contacts for efficient charge collection. Therefore, developing new, more effective IFLs is vital for enhancing BHJ solar cell performance.15,16,18,19

The quintessential hole transport IFL, poly(3,4-ethylenedioxythiophene:poly(styrene-sulfonate) (PEDOT:PSS), is moisture-sensitive, electrically/structurally in-homogeneous, and rapidly degrades ITO at elevated temperatures.21–23 Note that thin films of n-type semiconducting metal oxides such as ZnO24–26 and titanium oxides (TiO2)27 are effective interfacial electron transport layers due to their moderate charge mobilities, high chemical stability, and optical transparency. Furthermore, these oxide films on indium tin oxide (ITO) can be used to fabricate “inverted” BHJ solar cell architectures in which electrons are collected at the ITO electrode,24–27 while in conventional BHJ solar cells, holes are collected at the ITO electrode. Fundamentally, the develop-
Figure 1. (a) SEM image of F16CuPc nanowires grown by VCR on ITO. Cross-section SEM images of (b) F16CuPc nanowires and (c) F16CuPc nanowires after removing the ZnO layer.

Figure 2. Two-dimensional GIXD images: (a) a F16CuPc film, (b) F16CuPc nanowires, and (c) ZnO-coated F16CuPc nanowires (F16CuPc NW/ZnO) on ITO. GIXD reflections of F16CuPc nanowires (blue solid line), F16CuPc NW/ZnO (blue dashed line), F16CuPc film (red solid line), and ZnO coated F16CuPc film (F16CuPc film/ZnO, red dashed line) in (d) horizontal and (e) vertical cuts from the 2-D diffraction images (f) (010) peak (2.04 Å−1) peak intensity distribution according to angle from 2-D diffraction images of F16CuPc nanowires and F16CuPc NW/ZnO. Schematic view of molecular orientations in structures of (g) vacuum-evaporated F16CuPc film, (h) F16CuPc nanowires, and (i) F16CuPc NW/ZnO film structure on ITO.
ment of efficient inverted OPVs not only requires understanding charge selectivity at interfacial contacts but also developing diverse OPV architectures with appropriate BHJ active materials. To further improve the performance of inverted OPV cells, modified metal oxide layers have been investigated, such as embedding single-wall carbon nanotubes or polymers within the ZnO film. Such hybrid ZnO IFLs enhance charge collection28,29 and mechanical durability,28 as well as suppress leakage currents at the electrodes.30,31

We report here the implementation of copper hexadecafluorophthalocyanine (F16CuPc) nanowires as an IFL to enhance electron transport in inverted OPV cells. Importantly, F16CuPc has excellent environmental and thermal stability, and exhibits stable n-type semiconducting properties under ambient conditions.32,33 Depending on the deposition conditions, F16CuPc coatings can be grown in various morphologies, including smooth thin films,32 nanobelts,33,34 and nanowires aligned preferentially to the substrate surface.35 In this contribution, structurally well-characterized F16CuPc nanowire (NW) arrays and thin films are inserted as IFLs between the ITO and ZnO layers of archetypical inverted bulk-heterojunction OPVs. We show that the F16CuPc nanowire IFLs significantly enhance the performance of both P3HT:PC61BM and PTB7:PC71BM OPVs over that of the F16CuPc thin films and other control device structures due to more favorable electron transport arising from the face-on alignment of the π-stacked nanowires along the device current flow direction and the enhanced surface area of the F16CuPc nanowires embedded in the ZnO film.

In this study, two types of F16CuPc IFLs were explored: (1) thermally evaporated F16CuPc thin films and 2) vaporization-condensation-recrystallization (VCR)33,36,37-grown F16CuPc

Figure 3. (a) Schematic of a F16CuPc nanowire (NW) interfacial layer modified organic solar cell. (b) Schematic energy level diagram of an ITO/F16CuPc/ZnO/P3HT:PCBM/MoO3/Al inverted solar cell. (c) Representative J–V data for type A (ITO/ZnO/P3HT:PCBM/MoO3/Al, black line), type B (ITO/F16CuPc film/ZnO/P3HT:PCBM/MoO3/Al, blue line), and type C (ITO/F16CuPc NW/ZnO/P3HT:PCBM/MoO3/Al, red line) under white light illumination with 100mW/cm² and A.M. 1.5. (d) Typical external quantum efficiency (EQE) spectra of the type A (black line), type B (blue line) and type C (red line) solar cells. (e) Representative J–V data for type A’ (ITO/ZnO/PTB7:PC71BM/MoO3/Al, black line), type B’ (ITO/F16CuPc film/ZnO/PTB7:PC71BM/MoO3/Al, blue line), and type C’ (ITO/F16CuPc NW/ZnO/PTB7:PC71BM/MoO3/Al, red line) under white light illumination with 100mW/cm² and A.M. 1.5. (f) Typical external quantum efficiency (EQE) spectra of the type A’ (black line), type B’ (blue line), and type C’ (red line) solar cells.
nanowire films (Experimental Methods, Supporting Information, Figure S1). Figure 1 shows SEM images of the VCR-derived F16CuPc nanowires on ITO, which are ~15 nm in average diameter. The horizontal and vertical orientations of the nanowires reflect the random directional forces of recrystallization from the condensate.37 Thus, high Ar gas fluxes typically promote thin nanowire growth, while nanobelts or submicrometer belts grow under lower Ar flow rates of 100 sccm or 50 sccm, respectively.33

To characterize the present F16CuPc nanowire structures grown on ITO, grazing incidence X-ray diffraction (GIXD) patterns were acquired from the F16CuPc thin films (10 nm) and nanowires (Figure 2). Two features of the F16CuPc crystal structure (a = 14.61 Å, b = 3.31 Å, c = 90°)38 are assignable to the (100) (d = 14.4 ± 0.9 Å, q = 0.4 Å⁻¹) and (010) (d = 3.2 ± 0.1 Å, q = 2.0 Å⁻¹) reflections observed in the GIXD of both the F16CuPc thin films and nanowires (Figure 2d and e). Features at q = 1.6 Å⁻¹ and q = 2.2 Å⁻¹ are assigned to the ITO substrates. The (100) and (010) reflections are related to the F16CuPc molecular width and intermolecular π–π stacking distance, respectively. However, in the evaporated F16CuPc films, the (010) peak is only observed in the 2D GIXD horizontal linecut (Figure 2d) and the (010) peak is only observed in the vertical linecut (Figures 2e). The horizontal linecut corresponds to the in-plane lattice spacing of the F16CuPc crystallites on the substrate plane while the vertical linecut corresponds approximately to the out-of-plane lattice spacing. Therefore, observing the (010) peak only in the horizontal linecut indicates near-exclusive edge-on π–π F16CuPc molecular stacking in the evaporated film (Figure 2g), while the prominent (100) and (010) F16CuPc nanowire reflections in both the horizontal and vertical linecuts indicate both edge-on and face-on π–π F16CuPc molecular stacking on the ITO surface (Figure 2h). These GIXD molecular orientation results on ITO are completely consistent with the SEM images (Figure 1) showing randomly oriented nanowires.

To use the F16CuPc structures as IFLs in inverted OPV devices, a ZnO film is deposited on the structures by annealing of a spin-coated zinc acetate [Zn(CH3COO)2·2H2O] sol–gel solution film at 170 °C (See Experimental Methods in Supporting Information). Even after formation of the ZnO film, the structure of the F16CuPc nanowires is maintained (Figure 2c). However, the (010) peak intensity of F16CuPc nanowires is decreased at high angles close to 90° and increased at low angles closer to 0° (Figure 2f), which indicates the F16CuPc nanowires are somewhat more horizontally aligned and tilted after the ZnO coating (Figure 2i). The average thickness of the F16CuPc NW/ZnO films on ITO is ~36 nm since the ZnO sol–gel solution spin-coating process causes the NW to tilt slightly, while the pristine ZnO film and the F16CuPc film (~ 1 nm)/ZnO film thicknesses on ITO are approximately 23 and 24 nm, respectively, as determined by profilometry and AFM. As further confirmation that the nanowires remain intact under the ZnO film, an aqueous 1 M NH3 solution was used to etch away the ZnO film. Following the ZnO removal, the SEM micrograph clearly shows that nanowires are still in place (Figure 1c).

The F16CuPc films were next implemented as IFLs between the ITO and ZnO layers of inverted organic solar cells utilizing the structure (Figure 3a): ITO/ZnO/P3HT:PC61BM/MoO3/Ag (OPV type A), since these are n-type organic semiconductors and able to form energetically favorable contacts with the ITO surface (Figure 3b).34,39,40 Inverted solar cells were fabricated with evaporated F16CuPc films (OPV type B: ITO/F16CuPc film/ZnO/P3HT:PC61BM/MoO3/Ag) and F16CuPc nanowire films (OPV type C: ITO/F16CuPc NW/ZnO/P3HT:PC61BM/MoO3/Ag) (Figure 3a). Specifically, ZnO sol–gel films were spun-cast on the ITO glass substrates coated with F16CuPc films or F16CuPc nanowires and annealed at 170 °C for 5 min. Next, a blend of regioregular poly(3-hexylthiophene)(P3HT) and [6,6]-phenyl-C61 butyric acid methyl ester (PC61BM) was spun-cast from o-dichlorobenzene onto the ZnO film. After the P3HT:PC61BM deposition, the resulting film was slowly dried for 30 min and then annealed at 110 °C for 10 min. The P3HT:PC61BM active layer thickness in all devices was ~210 nm. Finally, a 10 nm MoO3 film and 100 nm of Ag were deposited on the P3HT:PC61BM blend film by thermal evaporation in vacuum. Here, the MoO3 and Ag act as a hole transport layer and reflective anode, respectively. OPV response data were recorded on 25 separate specimens for each type of cell.

Figure 3c shows representative OPV J–V measurements under white light illumination (100mW/cm², AM 1.5). The power conversion efficiency (PCE) of the type A cell without F16CuPc is 3.09%, with an open circuit voltage (Voc) of 0.571 V, a short circuit current (Jsc) of 9.044 mA/cm², and a fill factor (FF) of 59.90%. The most enhanced PCE, 3.59%, is measured for the F16CuPc NW-based type C cell (Voc = 0.571 V, Jsc = 10.74 mA/cm², FF = 60.48%), exhibiting a 16% increase in PCE over the type A cells. Note in contrast that the type C cell (Voc = 0.572 V, Jsc = 9.441 mA/cm², FF = 61.20%) incorporating a 1 nm thick vacuum-evaporated F16CuPc film marginally increases the PCE by 7% over the type A cell. Performance characteristics of the types A, B, and C inverted OPV cell type PCE (%)

<table>
<thead>
<tr>
<th>inverted OPV cell type</th>
<th>PCE (%)</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>type A: ITO/ZnO/P3HT:PC61BM/MoO3/Al</td>
<td>3.09</td>
<td>0.571</td>
<td>9.04</td>
<td>59.90</td>
</tr>
<tr>
<td>type B: ITO/F16CuPc film/ZnO/P3HT:PC61BM/MoO3/Al</td>
<td>3.31</td>
<td>0.572</td>
<td>9.44</td>
<td>61.20</td>
</tr>
<tr>
<td>type C: ITO/F16CuPc NW/ZnO/P3HT:PC61BM/MoO3/Al</td>
<td>3.59</td>
<td>0.571</td>
<td>10.74</td>
<td>60.48</td>
</tr>
</tbody>
</table>

Data and statistics based on 25 cells of each type. Numbers in bold are the maximum recorded values.
Table 2. Photovoltaic Properties of Optimized PTB7:PC71BM Inverted Organic Solar Cells\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>inverted OPV cell type</th>
<th>PCE (%)</th>
<th>(V_{OC}) (V)</th>
<th>(J_{SC}) (cm(^2)/mA)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>type A: ITO/ZnO/PTB7:PC71BM/MoO(_3)/Al</td>
<td>8.07</td>
<td>0.744</td>
<td>15.06</td>
<td>72.04</td>
</tr>
<tr>
<td>type B: ITO/F(_{16})CuPc film/ZnO/PTB7:PC71BM/MoO(_3)/Al</td>
<td>7.64 (±0.24)</td>
<td>0.735 (±0.005)</td>
<td>14.42 (±0.32)</td>
<td>71.95 (±1.26)</td>
</tr>
<tr>
<td>type C: ITO/F(_{16})CuPc NWs/ZnO/PTB7:PC71BM/MoO(_3)/Al</td>
<td>8.26</td>
<td>0.738</td>
<td>15.23</td>
<td>73.55</td>
</tr>
<tr>
<td></td>
<td>7.99 (±0.25)</td>
<td>0.737 (±0.003)</td>
<td>14.52 (±0.34)</td>
<td>72.07 (±0.85)</td>
</tr>
<tr>
<td></td>
<td>8.57</td>
<td>0.736</td>
<td>15.83</td>
<td>73.85</td>
</tr>
<tr>
<td></td>
<td>8.15 (±0.30)</td>
<td>0.735 (±0.004)</td>
<td>15.23 (±0.39)</td>
<td>72.39 (±0.76)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Data and statistics based on 25 cells of each type. \textsuperscript{b}Numbers in bold are the maximum recorded values.

nm F\(_{16}\)CuPc films do not reduce the optical transparency as significantly (Figure S3, Supporting Information). In addition, when the deposition order of the F\(_{16}\)CuPc NW and ZnO IFLs is reversed, yielding the device structure: ITO/ZnO/F\(_{16}\)CuPc NW/P3HT:PCBM/MoO\(_3\)/Al, the cells exhibit decreased PCEs versus the type A cell (Figure S4, Supporting Information), because electron flow from the active layer to ITO is now energetically unfavorable.

To determine whether the beneficial effects of the F\(_{16}\)CuPc NW/ZnO IFLs can be applied to enhance other highly efficient OPV systems, devices utilizing a PTB7:PC\(_{71}\)BM BHJ blend\textsuperscript{6} were also fabricated. Three kinds of OPV devices were again made: type A' (ITO/ZnO/PTB7:PC\(_{71}\)BM/MoO\(_3\)/Ag), type B' (ITO/F\(_{16}\)CuPc film/ZnO/PTB7:PC\(_{71}\)BM/MoO\(_3\)/Ag), and type C' (ITO/F\(_{16}\)CuPc NW/ZnO/PTB7:PC\(_{71}\)BM/MoO\(_3\)/Ag) (Figure 3e). The PTB7:PC\(_{71}\)BM BHJ blend films were ∼95 nm in thickness for all types of cells. Similar to P3HT:PC\(_{61}\)BM cells, the inverted OPV devices using PTB7:PC\(_{71}\)BM also show impressive improvements in device metrics, including PCE and \(J_{SC}\) enhancement, due to insertion of F\(_{16}\)CuPc structures. In fact, type C' shows the highest PCE (8.57%), whereas type B' (PCE = 8.26%) and type A' (PCE = 8.07%), exhibit lower device performance (Figure 3e and Table 2). The percentage increase in \(J_{SC}\) for these devices (∼6%) is somewhat lower than for the P3HT-based cells (∼16%) probably because the PTB7:PC\(_{71}\)BM photocurrent is also generated at longer wavelengths where there is significant nanowires absorption. The \(J_{SC}\) increase is supported by the EQE enhancement data, and the F\(_{16}\)CuPc/ZnO IFL based PTB7:PC\(_{71}\)BM inverted solar cells show the highest EQE (76% at 620 nm, Figure 3f). Note that the PCE demonstrated here for the F\(_{16}\)CuPc NW/ZnO IFL-based PTB7:PC\(_{71}\)BM OPVs is among the highest values reported to date in the peer-reviewed literature for a single-junction cell.

The increased \(J_{SC}\) observed for both active layer materials makes a significant contribution to the enhanced PCE and indicates that the F\(_{16}\)CuPc structures promote more favorable electron transport within the device. Moreover, the F\(_{16}\)CuPc nanowire IFL OPVs exhibit significantly greater \(J_{SC}\) values than the vacuum-evaporated F\(_{16}\)CuPc film OPVs. This is plausible considering the difference in F\(_{16}\)CuPc molecular orientations, with the face-on π−π F\(_{16}\)CuPc molecular stacking in the standing nanowires transporting the dissociated electrons from the active layer to the ITO electrode more efficiently than in edge-on π−π stacking.\textsuperscript{41,42} Because there is exclusively edge-on π−π stacking in the vacuum-evaporated F\(_{16}\)CuPc films, electron transport to the ITO anode is less efficient. Furthermore, the nanowires can provide increased interfacial contact between the BHJ active layer and the electron transport layer by increasing the IFL surface roughness (Figure S5, Supporting Information). Optical reflectance measurements of the completed OPV devices using the PTB7:PC\(_{71}\)BM active layer were next obtained for all the IFL types (Figure S6, Supporting Information) in order to determine whether the observed performance differences result from optical field effect variations due to the different interlayers.\textsuperscript{43} From the reflectance measurements, it is determined that the F\(_{16}\)CuPc NW IFL-based and the vacuum-evaporated F\(_{16}\)CuPc film-based OPVs have nearly identical absorption characteristics. There are small differences when compared to the ZnO-only device, however, integrating the total absorbed light within the device and calculating an ideal \(J_{SC}\) leads to identical current densities (Figure S6, Supporting Information). Thus, these data demonstrate that the enhanced \(J_{SC}\) of the F\(_{16}\)CuPc NW-based OPVs is primarily the result of favorable orientation and more efficient electron transport through the F\(_{16}\)CuPc NW IFL.

To further clarify the electron transport enhancement by the insertion of F\(_{16}\)CuPc structures, zero-field vertical conductivities of the ZnO film, the ZnO film on the F\(_{16}\)CuPc thin-film (F\(_{16}\)CuPc film/ZnO), and the ZnO film on the F\(_{16}\)CuPc NWs (F\(_{16}\)CuPc NWs/ZnO) were measured (Figure 4). After fitting the current density–electric field (\(J−E\)) plot of ZnO (black circles), F\(_{16}\)CuPc film/ZnO (blue circles), and F\(_{16}\)CuPc NW/ZnO (red circles). Inset image is the electrical device structure for vertical conductivity measurement.
between the ZnO layer and ITO electrode of inverted BHJ OPVs to reduce the energetic loss associated with unfavorable electron transport continuity and to increase the interfacial area. Among the types of inverted organic solar cells investigated, type A or A’ (ITO/ZnO/Active layer/MoOx/Al), type B or B’ (ITO/F16CuPc layer/ZnO/Active layer/MoOx/Al) and type C or C’ (ITO/F16CuPc NW/ZnO/Active layer/MoOx/Al), the F16CuPc NW/ZnO based cells (type C or C’) consistently exhibit the highest performance metrics of this study with PCE = 3.59% and EQE = 67% for P3HT:PC61BM, and PCE = 8.57% and EQE = 76% for PTB7:PC71BM. The F16CuPc NWs IFLs are proposed to more efficiently collect and transport electrons from the ZnO layer due to their face-on π−π stacking orientation parallel to the current flow and the increased surface area of the ZnO film. These n-type semiconducting organic structures can therefore be applied as buffer layers to reduce OPV energy losses, illustrating how organic materials can take advantage of controlled molecular structure and morphology to efficiently collect electrons.

**ASSOCIATED CONTENT**

Supporting Information Description of the synthesis of materials, characterization of F16CuPc structures and device fabrication, and vertical conductivity measurement on ZnO films. This material is available free of charge via the Internet at http://pubs.acs.org

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**Notes**

The authors declare no competing financial interest.

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