Electronic Supplementary Information

Simultaneous Cross-Linking and p-Doping of a Polymeric Semiconductor Film by Immersion into a Phosphomolybdic Acid Solution for Use in Organic Solar Cells

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1. Materials and Methods

Poly[*N*-9′-heptadecanyl-2,7-carbazole-*alt*-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) with an number-average molecular weight of 19600 and a polydispersity of 2.15 was purchased from Ossila Ltd. Phosphomolybdic acid (PMA) was purchased from Alfa Aesar. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (CLEVIOS P VP AI 4083) was purchased from Heraeus GmbH. [6,6]-Phenyl C_{71} butyric acid methyl ester ($PC_{70}BM$) was purchased from Nano-C Inc. Sheet resistances were measured by a four-probe method using a Loresta MCP-T610 (Mitsubishi Chemical Co.). UV–vis–NIR absorption spectra were recorded using a UV-3150 spectrometer (Shimadzu Co.). Work functions were determined using a Kelvin probe (Besocke Delta Phi GmbH) with a probe diameter of around 3 mm in air. These measurements were calibrated against freshly cleaved highly oriented pyrolytic graphite (HOPG) with a known work function of 4.6 eV.

2. Device Fabrication and Characterization Procedures

OSCs were fabricated on glass substrates covered with ITO (Colorado Concept Coatingssheet, sheet resistance of 15 Ω sq^{-1}). The ITO substrates were ultrasonically

cleaned with deionized water, acetone, and 2-propanol, followed by oxygen plasma treatment for two min. A dispersion of PEDOT:PSS in water (CLEVIOS P VP AI 4083) was spin-cast onto the ITO substrates and then annealed at 140 °C for 10 min in ambient conditions to yield 30 nm-thick films. A 4.0 mg mL^{-1} PCDTBT solution in chlorobenzene was spin-cast onto the ITO substrates and annealed at 70 °C on a hot plate for 10 min in a nitrogen-filled glove box to yield 30 nm-thick films. The PCDTBT films were immersed into a 0.5 M PMA solution in nitoromethane for the selected amount of time, from 10 s to 60 min. The PCDTBT films were rinsed with pure nitromethane and then annealed at 70 °C for 10 min. A 20.0 mg mL^{-1} PCDTBT:$PC_{70}BM$ (1:4 by weight) solution in chlorobenzene was spin-cast onto the modified PCDTBT layers and annealed at 70 °C for 10 min to yield 70 nm-thick photoactive layers. 20 nm-thick Ca electron-collecting layers and 100 nm-thick Al cathodes were deposited by thermal evaporation at a base pressure of 10^{-6} Torr.

Current density–voltage (*J*–*V*) characteristics were collected in the dark and under illumination using a Model 2400 SourceMeter (Keithley) in a nitrogen-filled glove box. Illumination was provided by a solar simulator (Oriel 91160) equipped with a 300 W xenon arc lamp (Newport 6258) and an Air Mass 1.5 Global filter. The illumination irradiance was calibrated to 100 mW cm^{-2} using an NREL-certified silicon photodiode (Hamamatsu S1133).