SUPPORTING INFORMATION

Perylene Diimide based Organic Photovoltaics with Slot-Die Coated Active Layers from Halogen-Free Solvents in Air at Room Temperature

Francesco Tintori, Audrey Laventure, and Gregory C. Welch*

Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, AB, Canada, T2N 1N4

*gregory.welch@ucalgary.ca

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Materials and Methods

Materials: QX-3 was kindly provided from professor Yingping Zou and utilized without further purification. tPDI₂N-EH was synthetized in our laboratories following published procedures from our group.²

Solution preparation: Qx-3:tPDI₂N-EH solutions were prepared in air, from 10 mg/mL solutions of the single components, which were stirred for 2 hours before mixing in the required weight proportions. If applicable, DIO or DPE was added to the solution in the desired v/v proportion. Final solutions were stirred for at least 1 hour before deposition.

ZnO precursor solutions were prepared following the sol-gel method proposed by Sun et al.³, 1 g of zinc acetate trihydrate, 0.280 mL of ethanolamine and 10.0 mL of 2-methoxy ethanol were mixed in air and stirred overnight at room temperature before use.

Film preparation: All studied films were prepared as follow: ITO-coated glass substrates were first cleaned by surfactant/water scrubbing, followed by sequentially ultra-sonicating in de-ionized water, acetone and isopropanol (10+ minutes each) before use. ITO substrates were then dried with pressurized air and UV-Ozone treated for 30 minutes. A ZnO precursor solution was spin-coated onto the ITO substrate at a speed of 4000 rpm for 55 s and then thermally annealed at 200 °C in air for 15 min. The organic layer was then cast at room temperature, in air, by either spin-coating at 1000 rpm for 50 s or coated using a 13 mm slot-die head, at room temperature and at a rate of 30 cm/min (0.5 cm/s) with an automated solution source set at 75 μL/min (1.25 μL/s). Resulting films were measured (by AFM) to be 50-60 nm thick on average (with the exception of slot-die coated films from 10 mg/mL solutions, which resulted substantially lower at approximately 20-30 nm).
**Optical Absorption Spectroscopy (UV/vis/near-IR):** All absorption measurements were recorded using an Agilent Technologies Cary 60 UV-vis spectrometer at room temperature.

**Optical Photoluminescence Spectroscopy:** All measurements were recorded using an Agilent Technologies Cary Eclipse fluorescence spectrophotometer at room temperature.

**Atomic force microscopy (AFM):** AFM measurements were performed by using a TT-2 AFM (AFM Workshop, USA) in the tapping mode and WSxM software with a 0.01-0.025 Ohm/cm Sb (n) doped Si probe with a reflective back side aluminum coating.

**Polarized Optical Microscopy:** POM images were taken in cross-polarization (i.e. at a 90° angle) through an Olympus Optical Microscope (BX53) at 50x magnification and relative digital camera set-up.

**Fluorescence Microscopy:** FM images were taken with an Olympus Optical Microscope (BX53) at 50x magnification, equipped with a BX3-URA unit and a X-cite 120 LEDmini light source. A designated filter (Olympus U-FYW) selectively allows green light to be transmitted to the sample (545-580 nm), while red light (> 610 nm) sourced at the sample is selectively transmitted to the digital camera.

**X-Ray Diffraction:** X-ray diffraction patterns were obtained using Bruker bench top X-Ray diffractometer D8 Advance (ECO) equipped with a CuKα x-ray source.

**Solar Cells Fabrication:** Solar cells were fabricated following the initial procedure for cleaning, ZnO deposition and organic layer deposition reported above. The fabricated films were then moved to an N₂ atmosphere glovebox for 24 h before evaporating MoOₓ and Ag. The evaporations of 10 nm of MoOₓ followed by 100 nm of Ag were thermally deposited under high vacuum (10⁻⁵ torr).
**Solar Cells Testing:** Current density-voltage (J-V) characteristics were measured using a Keithley 2420 Source Measure Unit. Solar cell performance used an Air Mass 1.5 Global (AM 1.5G) Solar Simulator (Newport, Model 92251A-1000) with an irradiation intensity of 100 mWcm$^{-2}$, which was measured by a calibrated silicon solar cell and a readout meter (Newport, Model 91150V).

**ADDITIONAL RESULTS**

**Figure S1.** AFM height images of thin films of QX-3 cast from toluene with varying concentration of DIO or DPE v/v % prepared using spin-coating.
Figure S2. POM/FM images of thin films of QX-3 or tPDI$_2$N-EH cast from toluene with varying concentration of DIO or DPE v/v % prepared using spin-coating.
Figure S3. X-ray diffraction patterns of neat films of tPDI$_2$N-EH processed from toluene with 3% (v/v) DIO or DPE (left = raw, right = normalized).

Figure S4. Cross-polarized light optical microscopy and fluorescence microscopy images of films of QX-3:tPDI$_2$N-EH at 1:1, 1:2 and 1:3 w/w, spin-coated from toluene solutions at 10 mg/mL with 5% DPE (v/v).
Figure S5. POM, FM and AFM height images of films of 1:1 QX-3:tPDl2N-EH prepared with slot-die coating using 10 mg/mL, 15 mg/mL and 20 mg/mL solutions with or without 3% v/v DPE.
Figure S6. PCE vs DPE content and solution concentration of QX-3:tPDI<sub>2</sub>N-EH 1:1 devices with slot-die coated active layer. The error bars represent the standard deviation values.
REFERENCES

