

## Supporting Information

# Electrochemically Surface-Grafted PVK Polymer Brushes as Hole Transport Layer for Organic Photovoltaics

*Maria Celeste Tria, Kang-Shyang Liao, Nigel Alley, Seamus Curran, and*

*Rigoberto Advincula*

### Experimental Section

**Materials.** All chemicals were purchased from Aldrich and were used without further purification unless otherwise indicated. Tetrahydrofuran (THF) and toluene used in the synthesis and polymerization reactions, respectively, were distilled from sodium/benzophenone ketyl.

#### *Syntheses of PVK Hole Transport Layer*

*a. Synthesis of Cbz-CTA.* The synthesis of 3,5-bis(4-(9*H*-carbazol-9-yl)butoxy)benzyl 4-cyano-4-(phenylcarbonothioylthio)pentanoate (Cbz-CTA) was prepared as previously reported by Patton et al.<sup>1</sup>

*b. Electro-deposition of the CTA on ITO or Au surface.* Electrochemical deposition of Cbz-CTA was performed using a Parstat 2263 (Princeton Applied Research) instrument equipped with PowerSuite software. All experiments were carried out using a three-electrode set-up where the ITO or Au substrate was used as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode. A solution of the CTA (0.5 mM) and the supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAH) (0.1 M) in THF was used for preparing the electro-generated CTA film. A constant potential of 1.2 V was applied on the surface for 3 minutes to deposit the CTA on the surface.

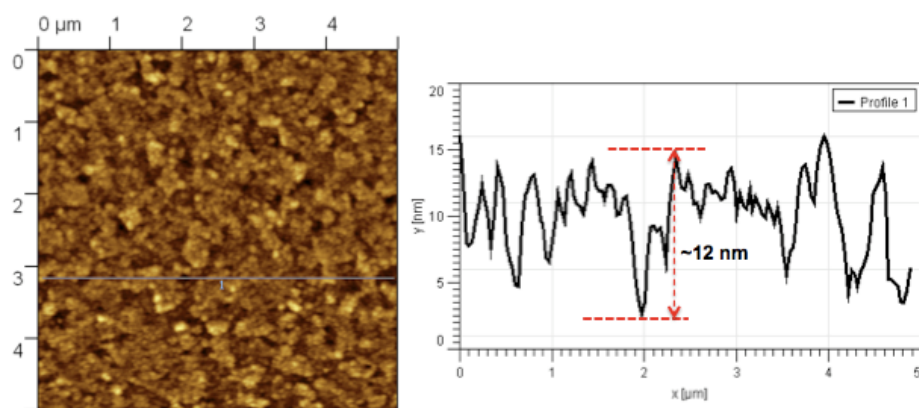
*c. Surface-initiated RAFT polymerization of vinyl carbazole.* A solution of the 9-vinylcarbazole (VK), azobisisobutyronitrile (AIBN) (VK:AIBN = 2500:1), and dry toluene was degassed in a Schlenk tube by bubbling with N<sub>2</sub> for 30-45 minutes. The degassed solution was transferred to another Schlenk tube backfilled with N<sub>2</sub> containing the CTA-modified ITO or Au through a cannula. The tube was placed in a preheated oil bath at 90 °C for 24 hours. The modified slides were then subjected to Soxhlet extraction overnight to remove any unbound polymers.

***Surface Characterization of PVK Hole Transport Layer.*** Null ellipsometry was used to determine the thickness of the films after each surface functionalization. All measurements were conducted using a null ellipsometer (Multiskop, Optrel Berlin) with a He-Ne laser ( $\lambda = 632.8$  nm) as a light source. The angle of incidence was set to 60° on all measurements. A multilayer flat film model was used to calculate the thicknesses from the experimentally measured ellipsometric values  $\Delta$  and  $\psi$ , assuming a refractive index of 1.60 for the electrochemically grafted CTA film<sup>2</sup> and 1.68 for the PVK film.<sup>3</sup> The film thickness was calculated using a fitting program (Elli, Optrel). Static contact angle goniometry was conducted using a KSV CAM-200 instrument (KSV Ltd.) using the bubble drop method with water. Atomic force microscopy (AFM) images were recorded in air under ambient conditions on PicoScan 2500 (Agilent Technologies formerly Molecular Imaging, Corp.) equipped with an 8 × 8 μm scanner using a silicon-nitride AFM probe (Ted Pella Inc.). Intermittent contact mode was used for all imaging.

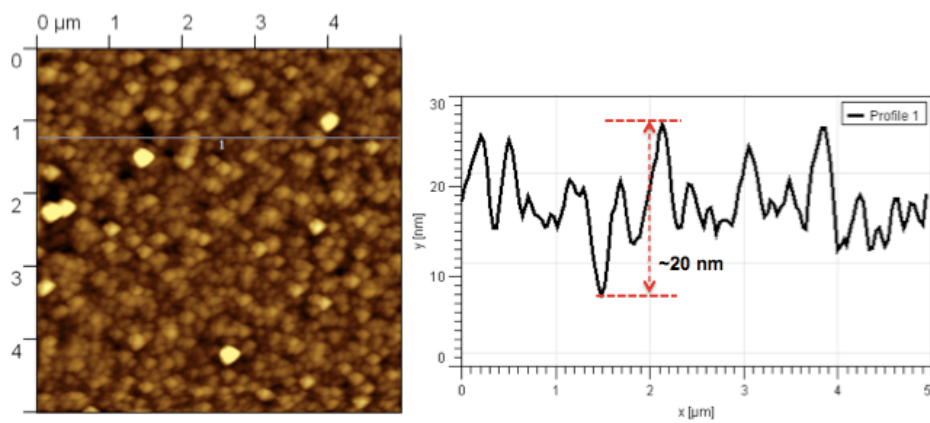
***Fabrications and Characterizations of P3HT:PCBM Based OPVs.*** All devices were fabricated on ITO coated substrates (ITO-coated glass slides with 8-12 Ω/□ surface resistivity, Aldrich). Depending on the configuration either the pristine ITO substrate or

the PVK-grafted ITO substrate was dusted with Zinc powder and etched under a 18%  $\text{HCl}_{(\text{aq})}$  for 10 seconds to form the desired anode layout. It was then cleaned in a heated ultrasonic bath with 1.5 % Micro 90 (15 minutes), deionized water (15 min x 2 cycles) and isopropanol (15 minutes).

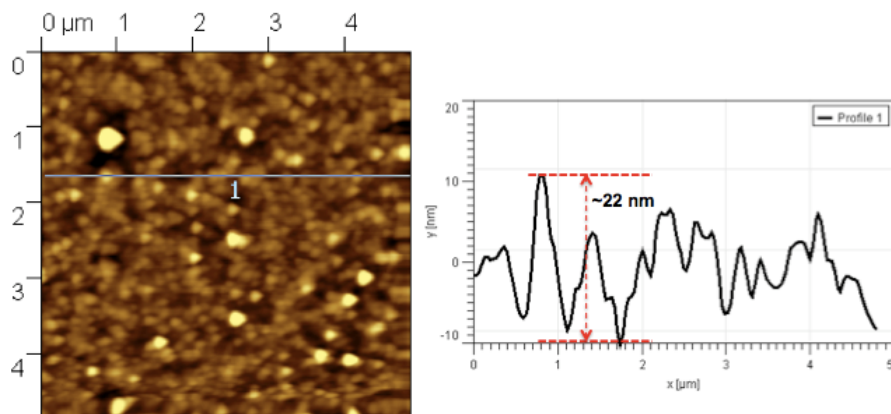
The ITO substrates to be coated with PEDOT:PSS for comparison to the PVK HTL devices were subsequently treated with ozone plasma for five minutes. The PEDOT:PSS (Clevios PH-1000, H. C. Starck) layer was spin-coated at 3000 rpm for 2 minutes. All substrates were dried in an 80°C oven for 1 hour before a P3HT:PCBM (12 g/L in anhydrous chlorobenzene with 1:0.66 ratio by weight, Aldrich) photoactive layer was spin-coated at 1500 rpm for 2 minutes. The resulting substrates were solvent-annealed in an environment saturated with chlorobenzene vapor at room temperature for 30 minutes and dried in an 80°C oven for 1 hour. Patterned Al electrodes were thermally evaporated (at a pressure of  $8 \times 10^{-6}$  mbar) on top of the P3HT:PCBM layer using a custom made shadow mask to determine the cell areas. All devices were encapsulated with glass slides using epoxy resin under a nitrogen atmosphere (~10% relative humidity) before characterization. An Abet LS 150 Xenon Arc Lamp Source coupled with an AM 1.5G filter (calibrated with Oriel 91150V Solar Reference Si Cell certified by NREL) was used as the light source. All measurements were performed in a nitrogen-filled glove box (~10% relative humidity). The light source was adjusted to illuminate the devices with 1 sun ( $100 \text{ mW/cm}^2$ ). Current-Voltage characteristics were determined using a Keithley 2400 SourceMeter. The dimension of the cell areas was determined by a Leitz ERGOLUX microscope with a micrometer scale in 0.05 mm divisions.



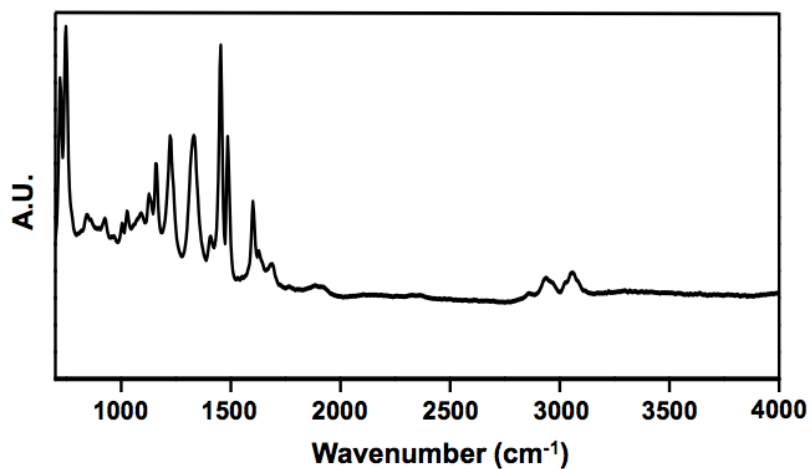
**Figure S1.** AFM line profile of the electrodeposited G1-CTA macroprecursor.



**Figure S2.** AFM line profile of the PVK brush after SI-RAFT polymerization.



**Figure S3.** AFM line profile of the electrochemically crosslinked PVK brush.



**Figure S4.** ATR-IR of the PVK brush.

**References:**

1. D.L. Patton, P. Taranekar, T. Fulghum, R. Advincula, *Macromolecules*, 2008, **41**, 6703.
2. R. Ravindranath, P.K. Ajikumar, S. Bahulayan, N.B.M. Hanafiah, A. Baba, R.C. Advincula, W. Knoll, S. Valiyaveetil, *J. Phys. Chem. B* 2007, **111**, 6336.
3. T. Komikado, S. Yoshida, S. Umegaki, *Appl. Phys. Lett.* 2006, **89**, 061123.