

Supplemental information for: Band-Bending in Conjugated Polymer Layers

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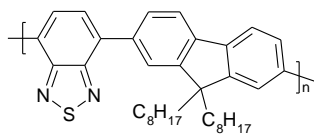
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Experimental methods

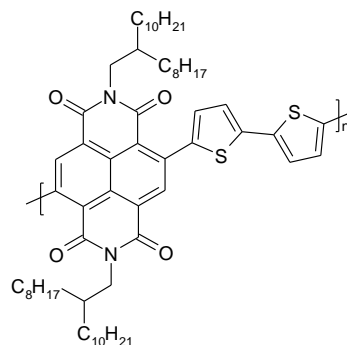
Substrates were prepared by depositing 100 nm-thick metal electrodes (Ag, Au, Cr, Al, Sm) or 70 or 100-nm-thick MoO₃ electrodes by thermal evaporation under high vacuum (<10⁻⁶ mbar) onto cleaned glass substrates (indium tin oxide (ITO) coated glass substrates for MoO₃). Also, 50 nm films of the conductive polymers Clevios™ P VP Al 4083 and Clevios™ HIL1.3 from H.C. Starck on ITO/ glass substrates were used as high work function electrodes. F8BT, PFTBTT, CN-ether-PPV and Polyera™ ActiveInk N2200 (see supplemental information for full names, chemical structures, and suppliers) were dissolved in toluene and spin-coated onto the electrodes in a N₂-filled glovebox. Work functions of all samples before and after polymer coating were measured in a N₂-filled glovebox at room temperature with an SKM KP 4.5 (KP Technology Ltd.) with 2 mm probe diameter. Calibration of the tip work function was done against highly ordered pyrolytic graphite (HOPG), for which we assumed a work function of 4.6 eV.[1]. Under these conditions, all KP measurements were highly reproducible, varying by less than ±20 meV upon repetition of the experiments (see example in Figure S2). All electrodes used in this study were pre-characterized by KP measurements under an N₂ environment, both before and after treatment of the surface by spin-coating with pure toluene. The range of these measurements is indicated by the error bars in Fig. 1. As substrate work functions can be largely affected by the adsorption of molecules, e.g., by exposure to air or to solvents, the values given here might differ substantially from work functions measured under ultrahigh vacuum conditions on atomically clean surfaces.

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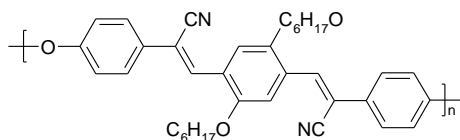
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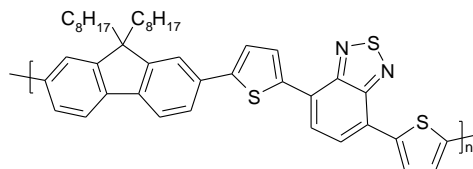
poly(9,9-dioctylfluorene-alt-benzothiadiazole) [F8BT], supplied by Dr. S. Janietz, Fraunhofer Institute IAP Potsdam. Molecular weights: M_w 46,500 g/mol; M_n 23,700 g/mol (measured by GPC).



poly{[N,N9-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,59-(2,29-bithiophene)} [p(NDI2OD-T2); Polyera ActivInk™ N2200], supplied by Z. Chen and A. Facchetti (Northwestern University and Polyera)



poly(oxa-1,4-phenylene-1,2-(1-cyano)-ethylene-2,5-dioctyloxi-1,4-phenylene-1,2-(2-cyano)-ethylene-1,4-phenylene) [CN-ether-PPV], supplied by Prof. H.-H. Hoerhold, Universität Jena.



poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-5,5-(40,70-di-2-thienyl-20,10,30-benzothiadiazole)] [PFTBTT], supplied by Dr. S. Janietz, Fraunhofer Institute IAP Potsdam. Molecular weights: M_w 11,500g/mol; M_n 5,900 g/mol (measured by GPC).

Figure S1 Chemical structures of the four semiconducting polymers

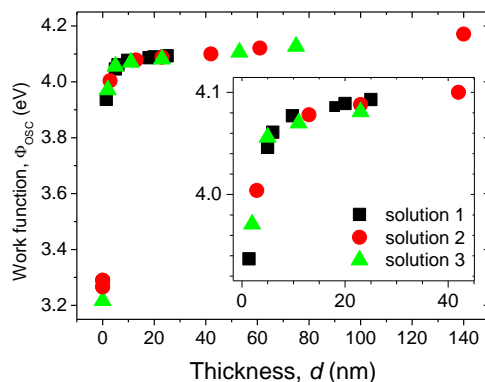


Figure S2 Work function of Polyera ActivInk N2200 as a function of thickness on Al electrode, demonstrating the high reproducibility of the experiment. Films were prepared by dilution of three different master solutions to the required concentration before spin coating. Solutions 1 and 2 (3.5 g/l and 15 g/l in toluene) were prepared on the same day and spin coated on the same batch of substrates. Solution 3 (12 g/l in toluene) was prepared on a different day and spin coated onto a separate batch of substrates. A variation of less than 20meV was seen between solutions. The inset shows the same data on a smaller scale. $d = 0$ corresponds to measured Al electrode work functions.

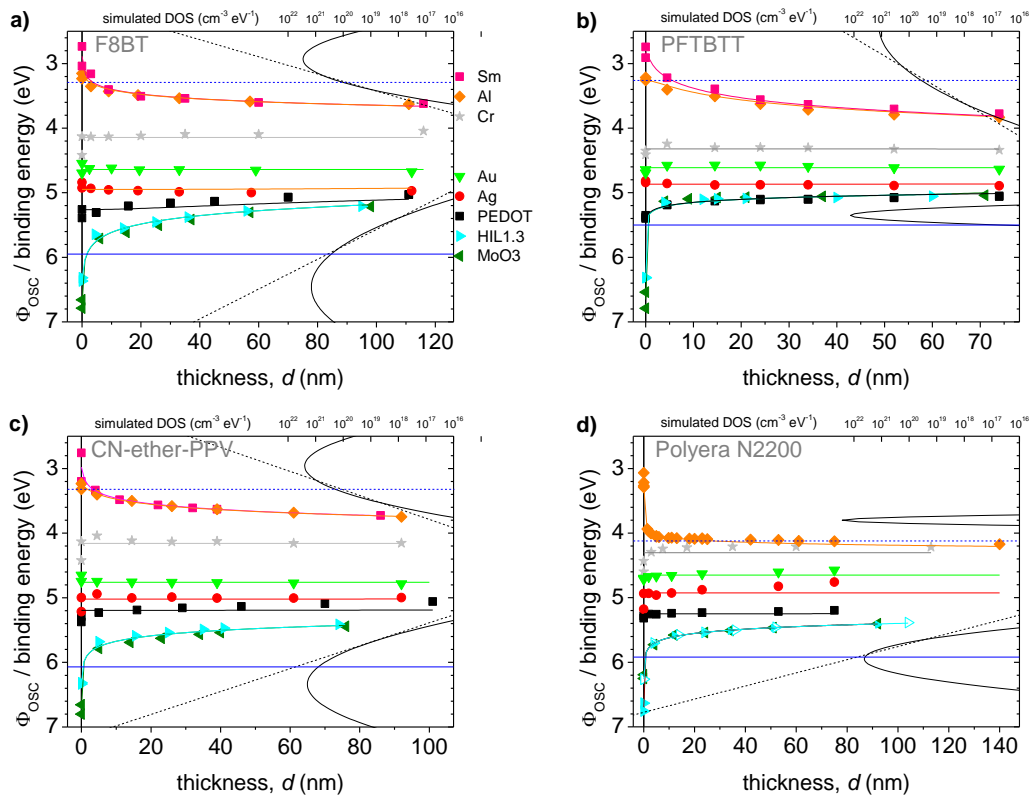


Figure S3 Polymer work functions as a function of thickness for a) F8BT, b) PFTBTT, c) CN-ether-PPV and d) N2200 (symbols) fitted using an exponential model DOS (solid curves). The solid and dashed curves on the right show the best-fitting model DOS using both Gaussian and exponential models (scale on top axis). Horizontal blue lines show the nominal HOMO onset measured by photoemission spectroscopy (solid line) and the approximate LUMO onset estimated by subtracting the visible absorption maximum from the HOMO onset (dotted line).

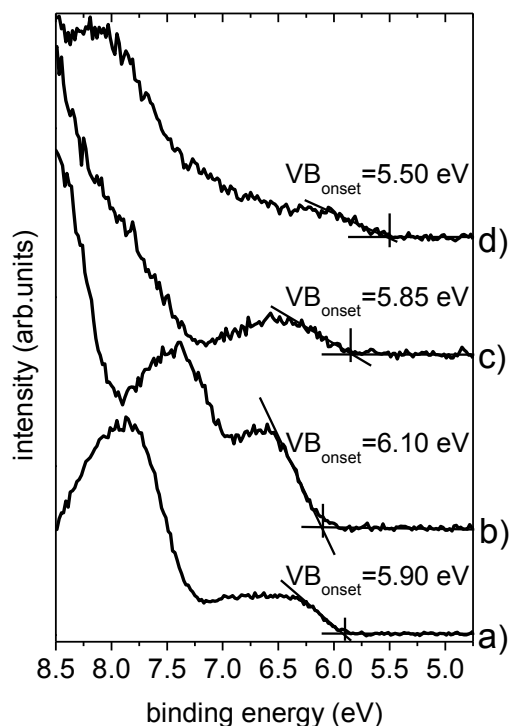


Figure S4 Valance band UPS spectra of a) F8BT, b) CN-ether-PPV, c) N2200, and d) PFTBT. The spectra are plotted with respect to the vacuum level, set to zero. The valence band onset (VB_{onset}) is indicated for each polymer.

The polymers for UPS studies were spin coated from chloroform solution on the conductive polymer (on ITO) CleviosTM P VP Al 4083. Film thicknesses were approximately 10 nm. UPS measurements were performed at the endstation SurfCat (beamline PM4) at the synchrotron light source BESSY II (Berlin, Germany). Spectra were collected with a hemispherical electron energy analyzer (Scienta SES 100) using an excitation photon energy of 30 eV. The energy resolution was 0.1 eV. Secondary electron cutoff spectra (used to determine the sample work function) were measured with the sample biased at -10 V to clear the analyzer work function. Standard procedures to ascertain the absence of sample charging were applied for every sample; these include variation of excitation photon flux and sample illumination with visible light. The error of reported binding energy is estimated to be smaller than +/- 0.05 eV.

[1] M.M. Beerbom, B. Lagel, A.J. Cascio, B.V. Doran, R. Schlaf, J. Electron Spectrosc. Relat. Phenom. **152**, 12 (2006)