Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Space-charge accumulation and band bending at conductive P3HT/PDIF-CN_2 interfaces investigated by Scanning-Kelvin Probe Microscopy

Supplementary Material Section

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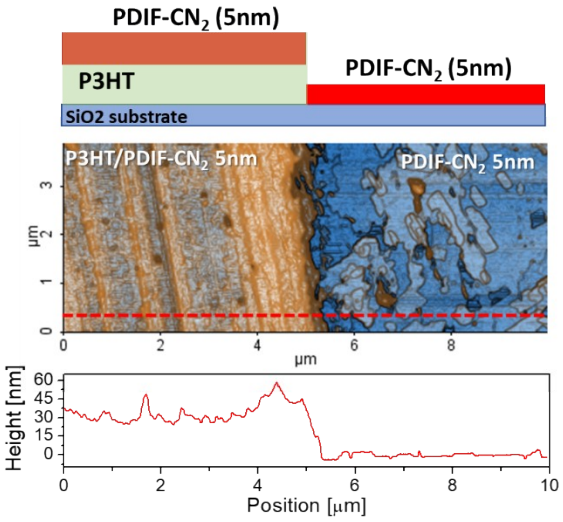
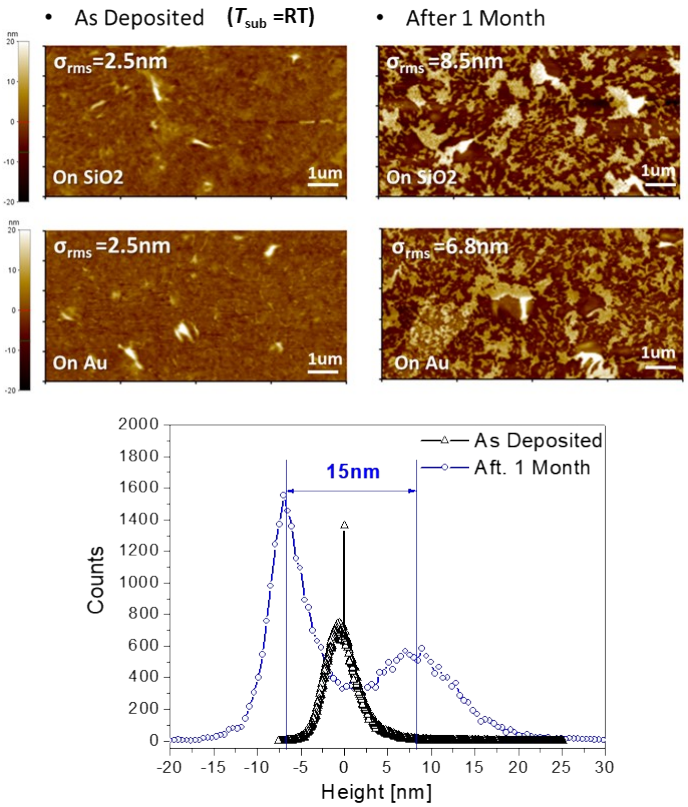


Figure S1 Enhanced color AFM topography of a bilayer/monolayer interface (schematic depiction in the upper panel). The analysis highlights the loss of molecular order when PDIF-CN_2 ultra-thin films (5nm) are deposited onto the P3HT substrate (left) with respect a bare SiO_2 substrate. The lower panel individuates a single line topography corresponding to the red dashed line.



$$\Delta h \approx 15nm \ @ \ 34\% \ cov. \rightarrow t_{eff} \approx 5nm$$

Figure S2 (Top) AFM topographies acquired immediately after the deposition with T_{sub} = RT of a 5nm PDIF-CN_2 overlayer on P3HT, and comparison after one month. Images clearly highlight the spontaneous dewetting phenomena of PDIF-CN_2 film, with a final terraced morphology. (Bottom) Height histogram representative of AFM topographies immediately after deposition and after one month. For these, an average terrace height of 15 nm is retrieved. Considering the overall coverage of the new morphology (34%), an effective deposited PDIF-CN_2 thickness of 5nm is calculated, coherently with the nominal thickness.

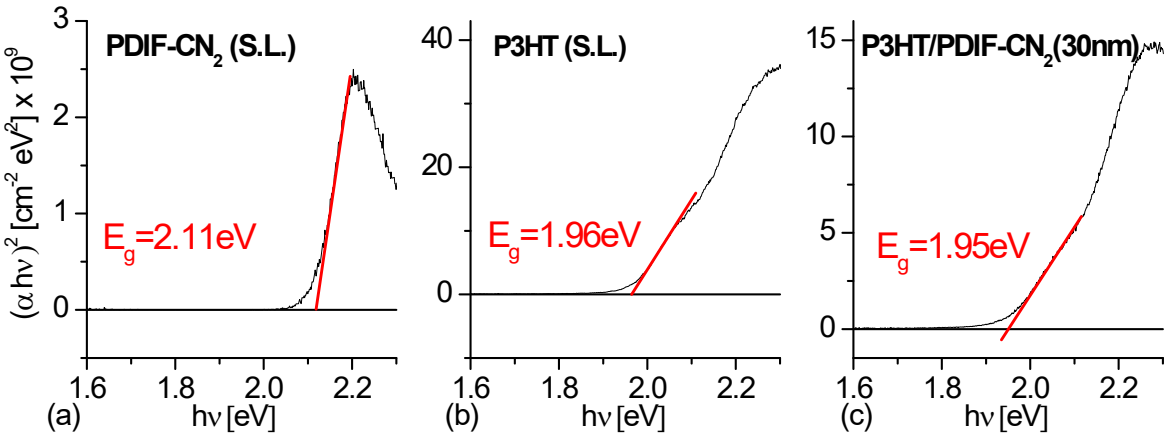


Figure S3: Tauc's plots of the (a) PDIF-CN_2 single layer, (b) P3HT single layer and (c) corresponding P3HT/PDIF-CN_2 bilayer. The plots individuate the optical bandgap of the considered organic layers as deduced from $(\alpha h\nu)^2 vs\ h\nu$ (first direct allowed transitions).

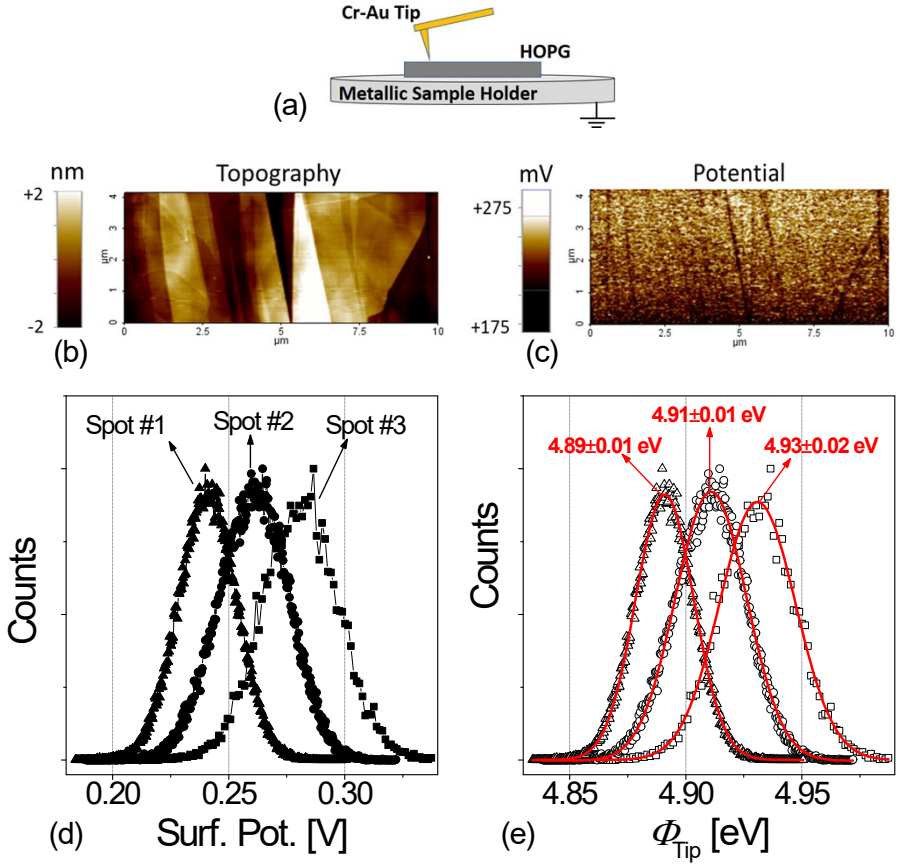


Figure S4 (a)Schematic depiction of the experimental set-up for the calibration of the conductive AFM tip on a freshly cleaved Highly Ordered Pyrolytic Graphite (HOPG) sample. (b) and (c) show a typical surface topography and corresponding surface potential map of the HOPG, respectively. (d) Statistical distribution representations of different HOPG areas. (e) Corresponding calculated work function distribution for the AFM tip, considering that $\Phi_{tip} = \Phi_{HOPG} + eV_{surf}$ and $\Phi_{HOPG} = 4.65eV$. Several HOPG areas are considered in order to compensate for possible

surface inhomogeneities over the calibrating sample. The reference value used is the resulting weighted average. In this work $\Phi_{tip} = 4.91 \pm 0.02\ eV$.

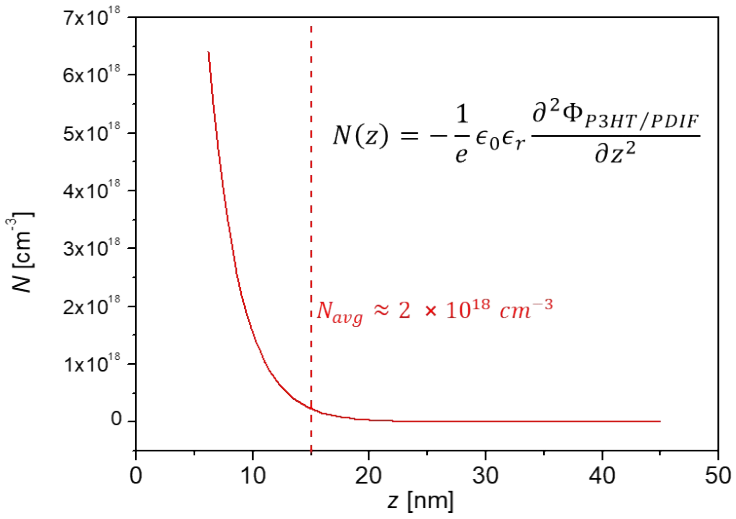


Figure S5 Charge density profile at the P3HT/PDIF-CN_2 as function of the depth z. Data were calculated considering a mono-dimensional formulation of the Poisson equation (Inset), following the arguments utilized by Rojas et al. (ref.46). Second derivative was applied to the empirical expression of the $\Phi_{P3HT/PDIF}$fit function, namely $\Phi_{P3HT/PDIF} = \Phi^{max}{}_{P3HT/PDIF}\left(1 - e^{-\gamma\left(z - z_0\right)}\right)$, considering $\epsilon_r = 2.9$ for the PDIF-CN_2 layer.