High resolution non-contact AFM and Kelvin Probe Force Microscopy investigations of self-organized photovoltaic organic architectures

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Long, conductive molecular wires have attracted Kelvin Probe Force Microscopy (KPFM) is a powerful tool of characterization in the field of organic photovoltaics. By combining KPFM with non-contact AFM (nc-AFM) under ultra-high vacuum, topography and surface contact potential (CPD) contrasts can be simultaneously mapped with an exceptional level of resolution. In the case of organic donor-acceptor (D-A) blends, KPFM has been widely used this past decade to map surface photo-voltages (SPV), paving the way for local investigations of charge generation and transport mechanisms at the nanometer scale. However, most of times, achieving a sub-10nm resolution [1] by nc-AFM/KPFM in bulk hetero-junction (BHJ) thin films remains a challenge. Moreover, carrying a quantitative analysis of the SPV contrasts is hardly achievable in the case of three-dimensional interpenetrated D-A networks with nano-phase segregated domains. Last, another issue is related to the eventuality of non-conventional effects (such as tipinduced surface polarization) in the short range regime, which can contribute to the local CPD contrasts at the sub-10nm scale [2]. In this communication, we address these issues by analyzing KPFM images acquired on new model donor-acceptor organic architectures, with better defined morphologies than the ones displayed by more conventional BHJ blends.

First, a donor-acceptor blend based on a first generation dendrimer [3] (FG1) and [70]PCBM has been used as a model system to investigate the influence of the tip-surface interaction regime on the local CPD and SPV contrasts. Thanks to the liquid crystalline properties of the electron donor FG1, the D-A phase separation can be tuned via in situ sample annealing. FG1: [70]PCBM blends can be obtained on ITO/PEDOT:PSS substrates, for which [70]PCBM clusters are buried in the sub-surface of a matrix of self-assembled pi-stacked FG1 molecular wires. These extremely flat samples constitute model photovoltaic systems for high resolution KPFM investigations, firstly thanks to the highly homogeneous nature of the surface layer, which reduces the risk of cross talk effects between the topographic and CPD channels. The photovoltaic effect is moreover completely reversible (i.e. the CPD returns completely to its initial value after switching the illumination off), which indicates the absence of charge trapping effects in these blends. Thanks to these remarkable properties, we carried out a complete analysis of the influence of the tip-surface interaction regime (from the long range to the short range) on the topographic, dissipation, in-dark CPD and SPV contrasts, with the support of electrostatic numerical simulations. Series of images were acquired on the same location by varying the nc-AFM parameters, which confirm that the optimal lateral resolution is achieved near the onset of the apparition of a contrast in the damping images. In-dark CPD contrasts over sub-surface [70] PCBM clusters are consistent with dipoles at the D-A interfaces, as predicted from integer charge transfer (ICT) models for FG1: [70]PCBM. These results also confirm that sub-10nm SPV contrasts can be achieved, and the comparison between damping, in-dark CPD and SPV images allows excluding the existence of artifacts. Last, a

remarkable dependence of the SPV magnitude with respect to the tip-surface distance is evidenced, and tentatively attributed to a local enhancement of the electromagnetic field at the tip apex.

In a second part, we apply another approach to build model D-A architectures for local SPM investigations, by using self-assembled donor-acceptor dyads. A new generation of D-A dyads based on covalently coupled perylene diimide and fluorenone-terthiophene units is studied in the form of selfassembled monolayers on highly oriented pyrolitic graphite (HOPG). By confronting nc-AFM and scanning tunneling microscopy (STM) images to the results of molecular mechanics and dynamics simulations, we show that edge-on donor-acceptor lamella grow on a buffer layer of self-assembled face-on molecules, which decouples the edge-on stack from the underlying substrate. The analysis of KPFM data recorded under different optical power and wavelength demonstrate that surface photovoltages can be detected at the scale of one monolayer. The charge photo-generation and transfer to the substrate is analyzed and a clear relationship between the molecular assembly and its photovoltaic behavior is established. This work paves the way for local investigations of the optoelectronic properties of DA dyads, triads, block copolymers and PV architectures down to the level of a single molecular layer.

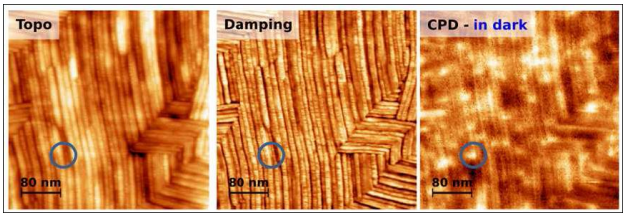

Figure: nc-AFM/FM-KPFM (UHV,300K) image of a FG1:[70]PCBM thin film blend recorded in dark. (a) Topography (b) Dissipation (c) CPD. Sub-surface [70]PCBM clusters covered by self-assembled FG1 molecular wires appear as bright spots in the CPD image, reflecting the existence of dipoles at the recessed D-A interfaces.

References

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