

Photovoltaics at the nanoscale

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ABSTRACT

Nanoscale thin film morphology has been identified as an important factor in organic solar cell device functionality and efficiency. To better understand the limiting factors, it is important to work at the length scale of these processes. A study of thin films of organic molecules with Kelvin probe force microscopy (KPFM) to observe charge distribution and non-contact atomic force microscopy (NC-AFM) to simultaneously obtain structural information is presented. This allows investigation of the structure-function relationships in molecular photovoltaics at the nanometer scale. PTCDI (3,4,9,10-perylenetetracarboxylic diimide) and CuPc (copper phthalocyanine) are used as organic molecules and are precisely grown on alkali halide substrates.

Keywords: PTCDI, CuPc, KPFM, AFM, local contact potential difference, photovoltaics

1. INTRODUCTION

The power conversion efficiency (PCE) of organic solar cells rapidly increased over recent decades. The world record recently passed the 10% mark, a long claimed milestone to compete with inorganic solar cells on the market.¹ In order to further improve organic solar cell performance, efficiency-limiting effects must be understood in detail. In particular, film morphology, electron traps and charge transport properties have been identified as important factors in organic solar cell device functionality and efficiency.² The understanding of loss mechanisms and structure-function relationships are key components on the way to more efficient organic solar cells. Due to the nature of organic solar cells, it is difficult to study film morphology on the necessary length scale in bulk heterojunction devices. Therefore, one has to work on a model sample where the effect of the molecular length scale can be observed. This can be achieved with small molecule systems and submonolayers, resulting in heterojunctions in nanometer scale.

An ideal tool to study film morphology of small molecule photovoltaic systems at the nanoscale is the Atomic Force Microscopy (AFM). With NC-AFM,³ molecular resolution can be achieved, revealing the structure of the molecular film. To obtain information about structure-function relationships of different film morphologies at the same time, Kelvin Probe Force Microscopy (KPFM) can be acquired simultaneously with an nc-AFM topography image. KPFM measures the local contact potential difference (LCPD) between the tip and the sample at every point of the image, effectively mapping out the LCPD over the size of the AFM image. This gives information about the work function of the measured sample and therefore about the electronic structure of the molecules.⁴ For such measurements, it is important to operate under ultra high vacuum (UHV) conditions since any surface contamination can change the local contact potential.⁵

Illuminating the sample while measuring KPFM gives insights into the changes of the electronic configuration of the molecules during charge generation.^{6,7} It has been previously shown that an overall change in local contact potential occurs under illumination on MDMOPPV/PCBM blends.⁵ However, to gain access to individual heterojunctions should be easier on structurally less complex model samples, where high resolution KPFM can be obtained.

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The powerful combination of optical excitation, high resolution topography and local contact potential mapping could help to solve some of the most urgent questions in organic photovoltaics. In this work we present preliminary results on a CuPc/PTCDI donor/acceptor system.

2. MEASUREMENT INSTRUMENTATION

A JEOL JSPM 4500A UHV AFM system / Scanning Tunneling Microscope (STM) / Scanning Electron Microscope (SEM) is used for all experiments. The system features two separate chambers, one dedicated to sample preparation and one for characterization. The sample preparation chamber includes a cleaving station for alkali halide crystals, a three source molecule evaporator (Kentax TCE-BSC) and a quartz crystal deposition monitor (Inficon), a four source electron-beam metal evaporator (Oxford Applied Research), as well as a sputtering gun and a low energy electron diffraction (LEED) system. The base pressure of the system is in the low 10^{-8} Pa.

KBr single crystals (Korth Kristalle, Germany) are used as substrates, which can be easily cleaved to expose their {001} surfaces. After cleaving in vacuum, the crystal is heated at $150\text{ }^{\circ}\text{C}$ for at least one hour to dissipate surface charges. The substrate is then characterized using NC-AFM to ensure good quality of the cleaved surface. Molecular thin films are thermally evaporated onto room temperature substrates. For PTCDI (Alfa Aesar, 98% purity), an evaporation temperature of approximately $300\text{ }^{\circ}\text{C}$, and for CuPc (Acros Organics, 95% dye content, further sublimated) a temperature of approximately $350\text{ }^{\circ}\text{C}$ is used. Nanosensors PPP-NCLR cantilevers are used for high resolution topography and KPFM imaging. A blue laser (473 nm , 50 mW max Melles Griot) is used to illuminate the sample at a grazing incidence angle to prevent shadowing of the sample by the cantilever. The AFM stage under illumination by the laser can be seen in Figure 1.

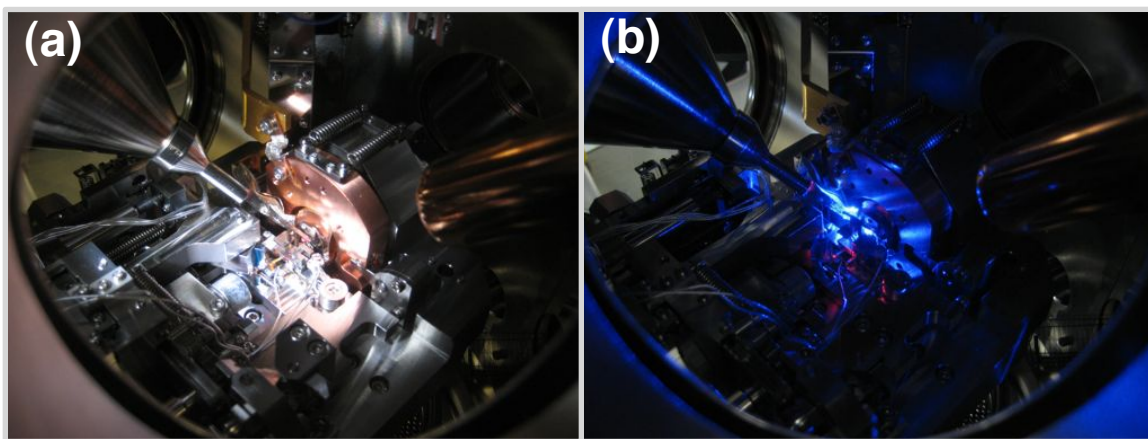


Figure 1. AFM stage with the sample shown (a) illuminated with white light for better visibility. (b) under illumination by a blue laser located outside the vacuum system.

3. RESULTS

3.1 KBr cleaving in vacuum

KBr cleaves easily along {001} planes. Figure 2 shows a freshly cleaved KBr(001) surface before the evaporation of molecules with large atomic terraces that are a few hundred nanometers wide. The sample was previously annealed to reduce surface charges.

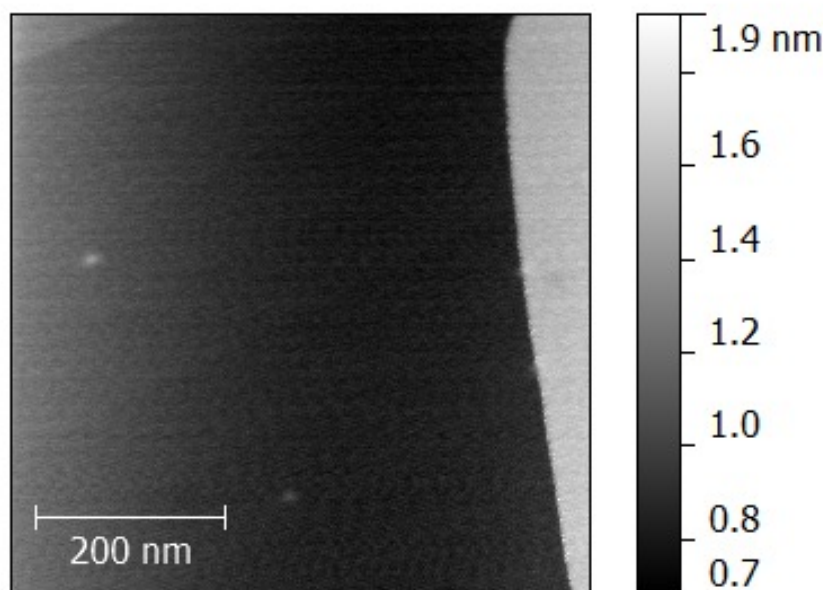


Figure 2. Cleaved KBr surface with large atomic terraces of a few hundred nanometer. The step on the right hand side is a multi layer step edge. The curved appearance in the upper part of the image is due to piezo creep.

3.2 PTCDI and CuPc on KBr (001)

PTCDI and CuPc form islands without a wetting layer (Volmer-Weber growth). However, PTCIDI islands appear as flat, needle shaped islands, whereas CuPc forms taller pyramid structures. This helps to clearly distinguish the two species. The molecules are separately deposited, CuPc is first deposited on the clean substrate followed by PTCIDI. An NC-AFM image of PTCIDI and CuPc on KBr can be seen in figure 3. The growth of PTCIDI on alkali-halides has been extensively characterized in previous works.^{8,9} Figure 3 (a) shows molecular resolution on CuPc. In figure 3 (c) molecular resolution on PTCIDI and on KBr can be seen.

KPFM images are recorded simultaneously with NC-AFM topography images and for better illustration they are overlaid on 3D rendered topography images with the color map corresponding to the KPFM signal. As shown in Figure 4, CuPc islands have a lower LCPD (blue) than to PTCIDI islands (red). This relates to a lower work function in CuPc (electron donor) than in PTCIDI (electron acceptor). The clear difference in the Kelvin signal is expected due to the different work function of the molecules.

Figure 5 shows the same sample area, on which the KPFM was recorded with and without illumination. PTCIDI islands that are connected with CuPc islands appear darker under illumination, indicating a change in the LCPD. On the other hand, the LCPD of the PTCIDI islands which are not in contact with CuPc remains almost unchanged. Figure 5 (c) and (d) show a cross section taken across a heterojunction (indicated by the arrows and dashed lines in 5 (a) and (b)) of the topography and KPFM signal of 4 consecutive images (2 dark, 2 illuminated). A change in LCPD can be clearly seen for the PTCIDI island between the dark and illumination measurements. No obvious change in the KPFM signal is observed on the CuPc island although they are in contact with PTCIDI. The observed height change during the first image under illumination is due to the thermal drift induced by the laser illumination.

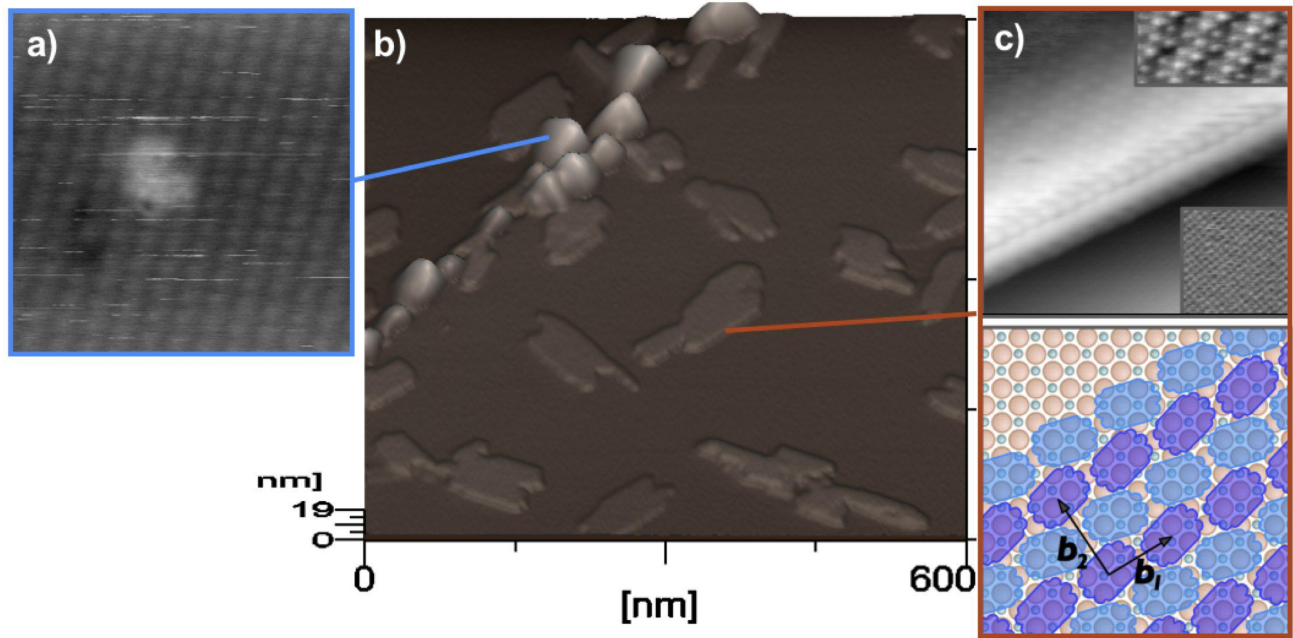


Figure 3. PTCDI and CuPc on the KBr(001) surface. PTCDI is growing in flat islands, whereas CuPc is growing in taller structures. (a) molecular resolution on CuPc, *image credit Sarah Burke* (c) molecular resolution on PTCDI and KBr substrate. Imaging parameters: (a) $f = -26 \text{ Hz} = -3.8 \text{ fNm}$ (b) $f = -3.1 \text{ Hz} = -0.4 \text{ fNm}$; (c) $f = -20.1 \text{ Hz} = -3.0 \text{ fNm}$

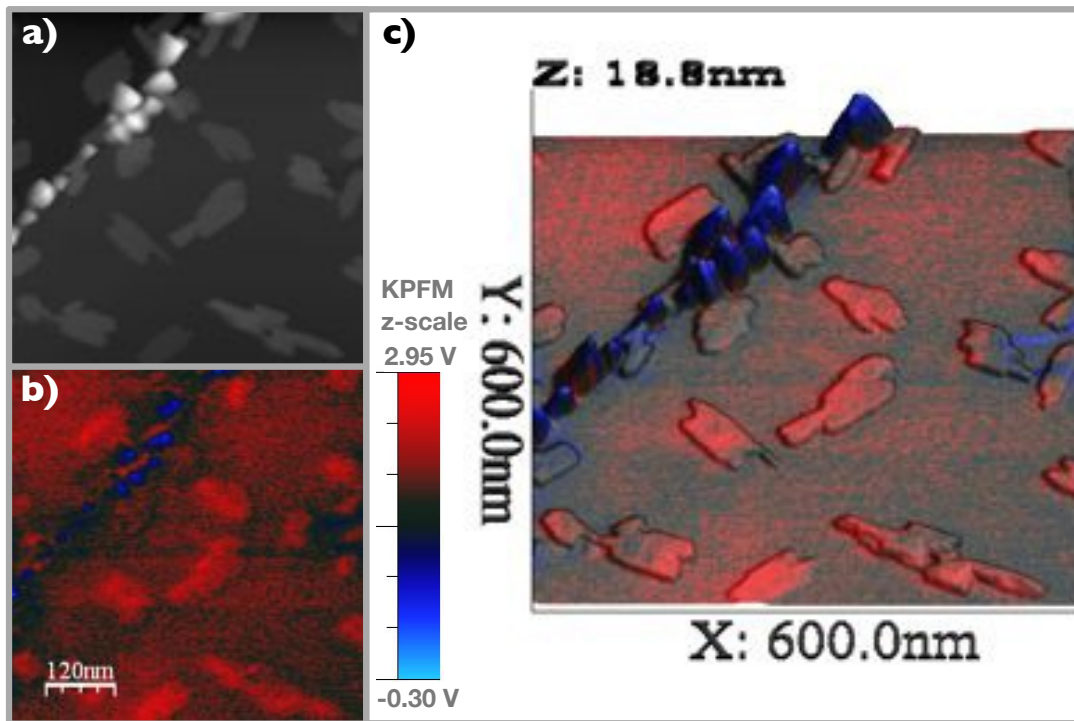


Figure 4. PTCDI and CuPc on KBr. (a) nc-AFM topography, (b) KPFM image, (c) 3D rendered topography with KPFM color overlay, KPFM scale bar included.

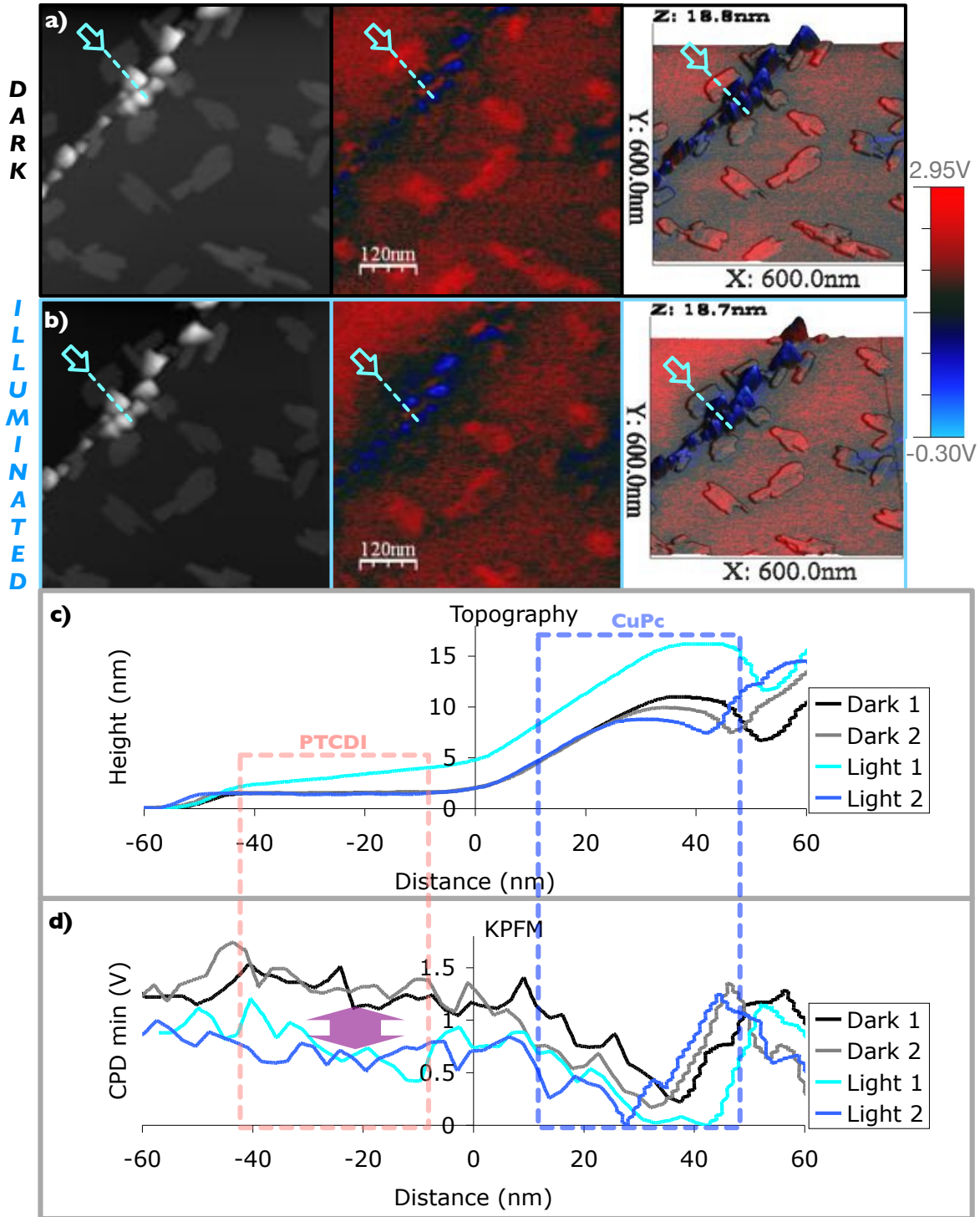


Figure 5. PTCDI and CuPc on KBr(001). From left to right: nc-AFM topography, KPFM and KPFM color overlay on 3D rendered topography images with KPFM colorbar included. (a) upper row images recorded in dark, (b) lower row recorded under illumination with a blue laser (473 nm). PTCDI island which changes KPFM contrast is indicated by blue arrows. Line profiles of (c) topography and (d) KPFM along dashed line in 4 consecutive images (2 dark, 2 illuminated). KPFM contrast change is indicated by purple arrow and only visible above the PTCDI island. Drift in height due to thermal drift immediately after laser illumination is visible in Light 1.

4. DISCUSSION CONCLUSION

PTCDI and CuPc show different structures in NC-AFM topography, therefore being easily distinguishable by this. We also observed a contrast in LCPD for thin films of PTCDI and CuPC on a KBr substrate. The lower LCPD of CuPc compared to PTCDI, and therefore lower work function, are in agreement with CuPc acting as the electron donor. We have shown that it is possible to observe a change in LCPD at organic heterojunctions upon illumination with laser light. Interestingly, the change can only be seen in the acceptor island (PTCDI) which is connected to CuPc and therefore builds a heterojunction. PTCDI molecules which are not in contact with CuPc showed no change in LCPD. This might indicate a charge transfer from the electron donor across the heterojunction to the electron acceptor. However, more data is needed to verify this observation.

Due to the clear distinguishability of PTCDI and CuPc in topography and Kelvin probe, it is a favorable system for studying photovoltaic effects with scanning probe microscopy. However, the relatively tall growth of CuPc makes high resolution imaging difficult leading to slow scan speeds. A different molecular acceptor/donor pair with a flatter growth on alkali-halides would be preferable for higher speed measurements. Even though first measurements indicate an exciting future for this type of measurement, an additional increase in spatial KPFM resolution is needed.

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