Tunable charge transfer properties in metal-Phthalocyanine heterojunctions

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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Associated content includes detailed information on AFM topography characterization of the Co electrode material as well as the thin film organic materials. Also, methods for proper validation of the AFM-based electrical measurements are presented. Finally, experimental data for the so-called 'electrical breakdown' of the organic thin films is included.

CONTENTS:

S1. AFM topography characterization

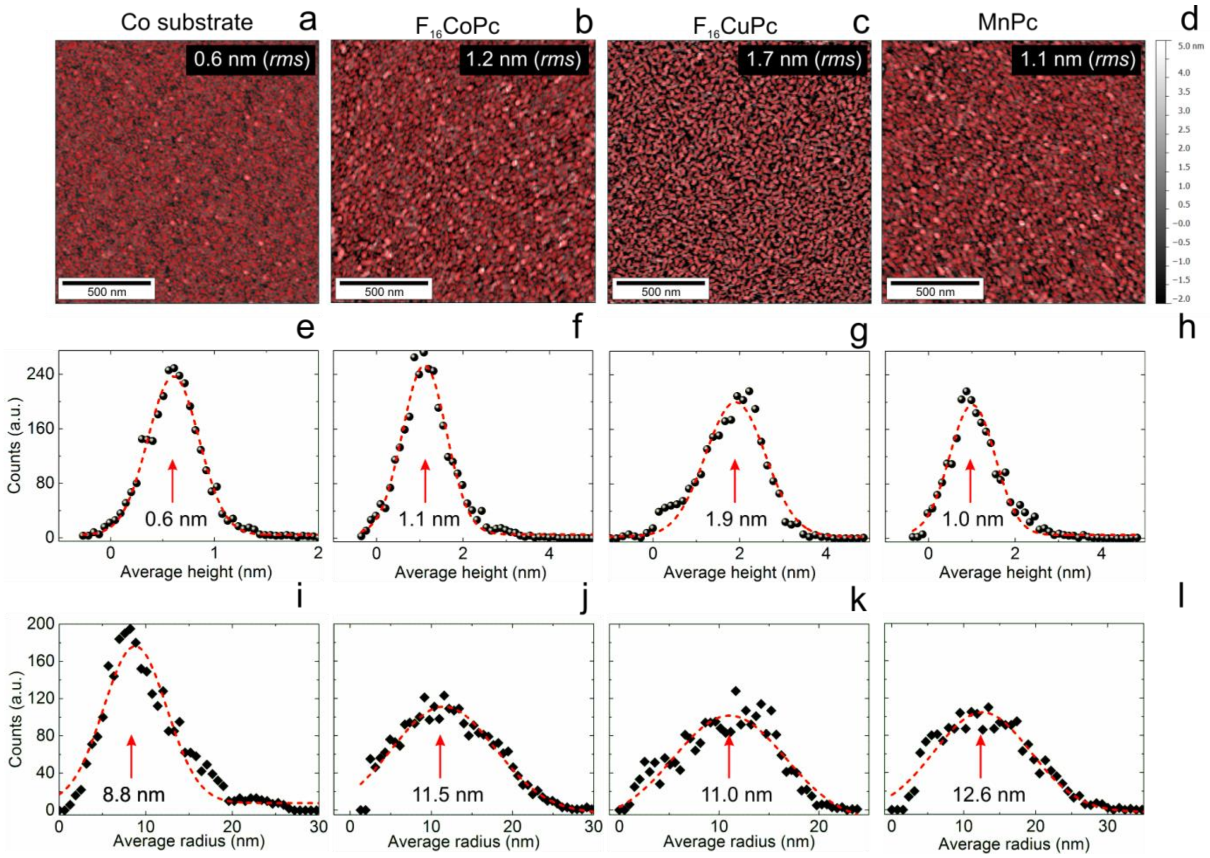

Figure S1. Topography characterization for Co substrate and metal-phthalocyanine materials. (a-d) Reference AFM images for the Co substrate, $F_{16}CoPc$, $F_{16}CuPc$ and MnPc thin films of the organic heterostructures. Red regions indicate the grain identified for the topography analysis. (e-h) Average grain heights for the films shown in (a-d). (i-l) Average grain radius for the films shown in (a-d).

S2. Validation methods for AFM electrical characterization

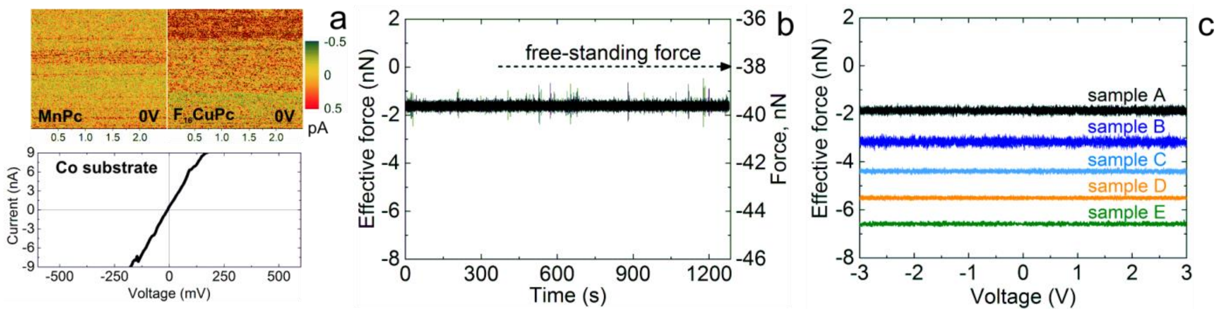

Figure S2. Validation of AFM local electrical measurements. (a) Electrical response for MnPc and $F_{16}CuPc$ organic films at 0 V and metal-metal (Co substrate - Pt AFM tip) junction. Under the absence of an applied voltage at the tip-sample interface, no electrical current is detected in the case of the current maps. Here, the small variations of electrical current observed in the maps are below the current limit of resolution of our AFM system (see color scale). These current maps at 0 V ensure that the electrical signal observed at higher voltages does not have any influence of the films topography characteristics, e.g. tip-sample friction interactions. (b) Dynamic tip-sample force interaction analysis monitored simultaneously with current maps. We observe no variation of the tip-sample force interaction during the current maps acquisition. A maximum effective force of less than 2 nN is applied over the organic films while the probe scans the sample surface. The effective force stands as the total tip-sample force minus the free standing cantilever's force (see right side axis). We observed that variations of about 10 nN on the effective force are required to influence the electrical signal obtained during the measurements. (c) Effective force as a function of the applied voltage monitored during local I-V measurements. No force variation is detected during I-V experiments, which ensures the reliability of the data obtained. All samples (**A**-**E**) presented an effective force of about 2 nN. Curves for samples **B**-**E** were intentionally shifted in the plot in order to obtain a better visualization of the data.

S3. Electrical breakdown for thin MnPc organic films

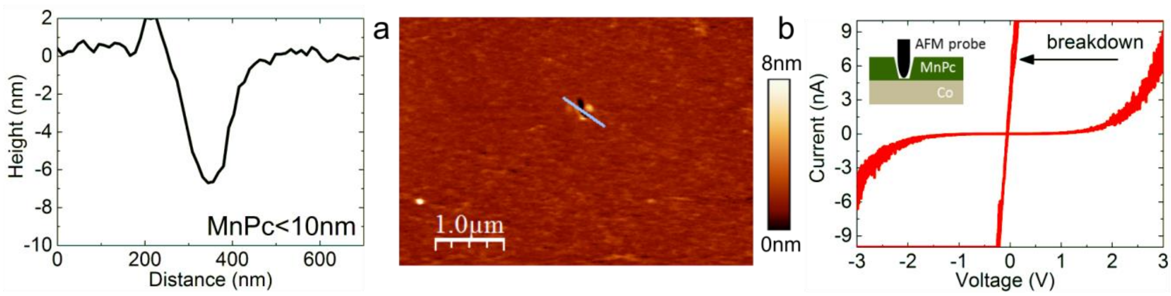

Figure S3. Electrical breakdown for MnPc organic films. (a) Scan profile of a MnPc film thinner than 10 nm on the location where local I-V measurements were performed, as indicated in (b). (b) AFM topography image. When films thinner than 10 nm are employed, a modification of the film's morphology is obtained due to variations and low control of the effective force. This may induce to variations of the electrical signal or even an electrical breakdown, as shown in (c). (c) Metal - metal (AFM probe – Co electrode) short-circuit indicates the electrical breakdown once the AFM probes modifies the organic film. Here, the ohmic-like current signal from the metallic substrate overcomes the signal from the organic film.