Supplementary Material (ESI) for Chemical Communications


SUPPORTING INFORMATION

# Negative Differential Resistance (NDR) in similar molecules with distinct redox behaviour

Núria Crivillers, Markos Paradinas, Marta Mas-Torrent, Stefan T. Bromley, Concepció Rovira, Carmen Ocal and Jaume Veciana

Conducting Scanning Force Microscopy (C-SFM) measurements were performed using a commercial head and software from Nanotec[1] under a $N_2$ environment (RH≈ 2%) to diminish any possible humidity effect. We used commercial conductive B-doped diamond-coated tips with k= 2.8 N/m (Nanosensors). In our setup, the sample was always grounded and the voltage was applied to the tip. The same tip has been used in all the C-SFM experiments for both **1H** and **1rad** SAMs. Therefore, prior to and after each conductivity experiment, we verified measuring conditions by: i) testing the tip conductivity by measuring the contact resistance on a freshly cleaved highly oriented pirolitic graphite (HOPG) surface (Fig. S1) and ii) checking the tip–sample conditions by systematically determining the adhesion force from force versus distance curves.

The current–voltage (I–V) characteristics of the contact where obtained as a function of the bias voltage applied between tip and sample by means of the so called 3D modes.[2] In this mode, we simultaneous measure the normal force ($F_n$) and the current (I) as a function of the bias voltage (V) and the sample displacement distance towards the tip (z). The $F_n(V,z)$ and I(V,z) images, obtained at a given position on the sample, permit knowing the I-V characteristics at different applied loads while separating and controlling the mechanical response of the organic layer. Each 3D image (nxn points) was obtained with either n=512 or n=1024 depending on the dynamic range (resolution) needed to analyze a specific z region as to obtain reliable statistics. Only a part of the total acquired lines (n) corresponds to elastic deformation of the SAM before film penetration and eventually reach the metallic substrate. Horizontal profiles taken in the I(V,z) image are the I-V curves corresponding to each piezo displacement value, which combined with the F-z, permits knowing the applied load at which each I-V curve was obtained. Straightforward comparison between I-V characteristics at different applied loads for both PTM SAMs is therefore possible.

The resistance, defined as the inverse slope of the linear region around V=0 of the I-V curves of the tip-SAM-substrate junction was calculated to be in the GΩ range for both **1H** and **1rad** SAMs (Fig. 3 of the manuscript). Because all measurements have been performed with the same tip and maintaining the setup unchanged except for the sample, establishing comparative values for both SAMs as presented is possible. However, we note that absolute values of the junction resistance must be taken with care since might be influenced by tip conditions. These conditions were systematically checked and resulted in a tip-HOPG resistance of about 170kΩ (Fig. S1), well within the supplier specifications.

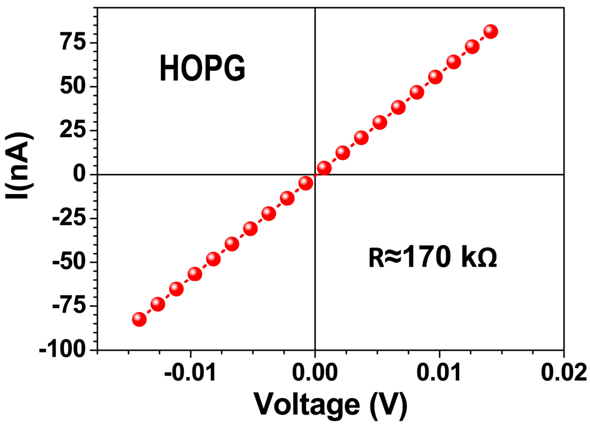


**Figure S1.** Linear fit of a typical *I-V* curve obtained for the tip used in the presented experiments on a freshly cleaved HOPG surface. The tip-surface contact resistance (R) is estimated to be ≈170kΩ.

## References

1 I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, A. M. Baro, *Rev. Sci. Instrum.,* 2007**,** ***78***, 013705.

2 C. Munuera, E. Barrena, C. Ocal, *Nanotechnology,* 2007, ***18***, 125505.