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# Impact of $\pi$ -conjugated self-assembled monolayer structure on their electrical properties

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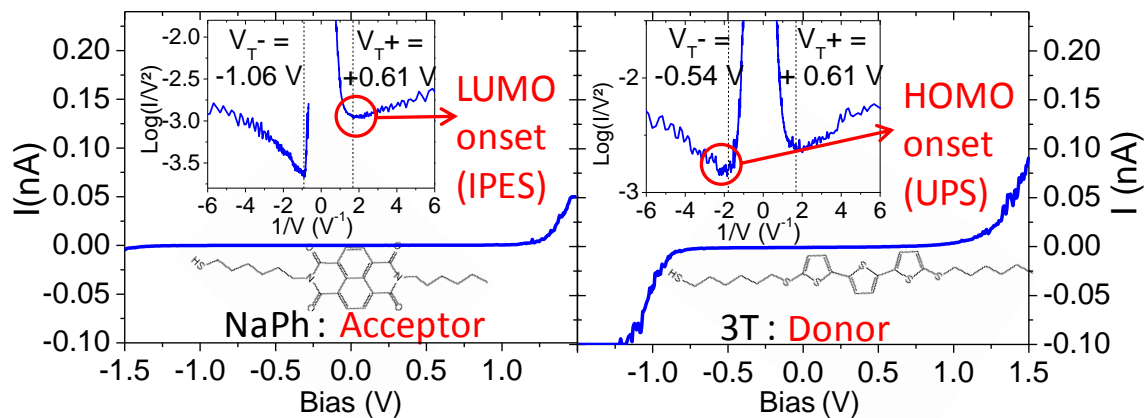
Molecular memory cells are likely to be among the most basic and important components of future molecule-based electronic devices. [1]. For instance a possible architecture for resonant tunnelling diodes consists in a self-assembled monolayer (SAM) of sigma-pi-sigma ( $\sigma$ - $\pi$ - $\sigma$ ) organic molecules composed of alkyl-chains ( $\sigma$ ) acting as tunnel barriers while a central  $\pi$ -conjugated moiety acts as a potential well [2]. In this work, we focused on SAMs of specially synthesized new organic molecules based on donor terthiophene (3T) or acceptor naphthalene tetracarboxydiimide (NaPh) central  $\pi$ -conjugated cores with carbon alkyl chains at both sides, grafted on gold through a thiolate. Water contact angles of 100-108° consistent with methyl end-groups on top of the SAM, and infrared and X-ray photoelectron spectroscopy reveal close-packed upright molecules. Scanning tunneling microscopy (STM) shows domains with typical hexagonal ordering [3] for 3T SAMs due to the flexibility given by the alkyl chain, but no NaPh molecular organization could be observed the latter being hindered by the larger NaPh core. Local current-voltage (I-V) characteristics performed under STM tip either on single 3T or NaPh SAMs, or on binary alkylthiol/3T or alkylthiol/NaPh SAMs are shown to correlate well with macroscopic I-V curves measured using eutectic GaIn contacts and to be related with the intrinsic electrical properties of molecules. Contrary to alkylthiol SAMs that exhibit symmetric I-V curve, donor or acceptor type of 3T or NaPh SAMs is revealed by opposite current rectifications. I-V curves were analyzed by Transition Voltage Spectroscopy (TVS) in which the voltage  $V_T$  at the minimum of the Fowler-Nordheim

plot ( $\ln(I/V^2)$  vs  $1/V$ ) is proportional to the energy barrier [4]. For alkylthiol SAMs we found  $V_T \sim 1.1$ - $1.4$ V, close to that reported by Beebe et al. [4]. HOMO and LUMO positions of the SAMs were extracted using UV photoelectron (UPS) and inverse photoemission spectroscopy (IPES) respectively. From measured values, we show that  $V_T$  obtained for the various molecules (0.5-1.1V) corresponds with the bias necessary to reach the tail of the HOMO or LUMO density of states closest to the Fermi level, as proposed in the literature [5]. At last, most importantly we show from the SAMs of the various studied molecules that the better structured the SAMs the narrower the distribution of their transition voltage  $V_T$  obtained by TVS, thus giving evidence of a relationship between structural and electrical properties.

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**Figure 1.** STM  $I(V)$  of NaPh & 3T SAMs on Au(111). Bias is applied to the sample. Inset shows TVS graph: the bias  $V_T$  at the minimum corresponds to the energy barrier and correlates with HOMO and LUMO onset measured by UPS and IPES respectively.