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Tetrathiafulvalene-based molecular nanowires†

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A new molecular wire suitably functionalized with sulfur atoms at terminal positions and endowed with a central redox active TTF unit has been synthesized and inserted within two atomic-sized Au electrodes; electrical transport measurements have been performed in STM and MCBJ set-ups in a liquid environment and reveal conductance values around 10^{-2} G_0 for a single molecule.

Electron transport measurements through single molecules sandwiched between metal electrodes are at the forefront of research in molecular electronics.[1] Several strategies including mechanically controllable break junctions (MCBJ)[2] and scanning tunneling microscopy (STM) techniques,[3] among others, have been employed to measure the conductance of various molecular devices based on carbon nanotubes,[4] C_{60},[5] and other organic molecules.[6]

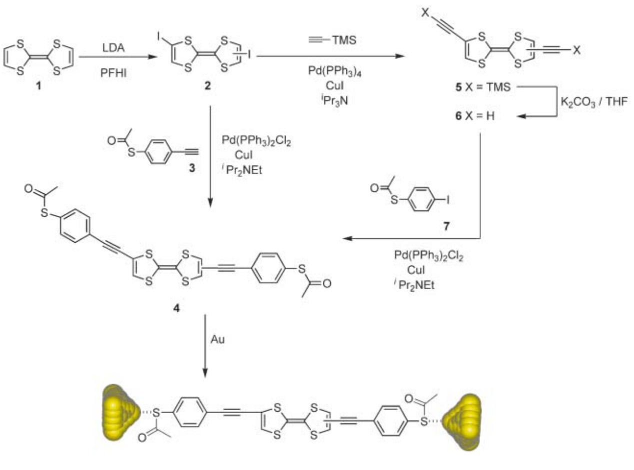
Currently, a major challenge is to make use of single molecules that function as switches on metal surfaces in response to an external trigger. In this sense, tetrathiafulvalene (TTF) is very attractive because of its three stable redox states (TTF^0, TTF^+, and TTF^{2+}).[7] Although TTF itself has been used as a bridge in different systems,[8,9] to the best of our knowledge, electrical conductance on a single molecule containing the TTF unit has not been previously studied.

In this communication we present the synthesis, solution electrochemistry and preliminary electrical transport measurements of a TTF-based molecular switch (**4**) that has thioacetyl end groups for attachment to the metal electrodes. Conductance measurements of single molecules in solution of **4** were performed using an STM, showing high conductance at low bias voltages. Additionally, stable current–voltage (*I–V*) characteristics recorded in an MCBJ immersed in a solution of **4** show indications of a gating effect.

Target TTF-based wire **4** was synthesized as shown in Scheme 1. By following modified previously reported methods, intermediates **2**,[10] **3**,[11] **5**,[12] **6**,[12] and **7**[11,13] were prepared. Further cross-coupling Sonogashira protocol for a mixture of **2** and **3** or **6** and **7** afforded the target molecule **4**‡ which was obtained in 23% or 47% yield, respectively.

In order to investigate the different variables affecting the electrical transport in a liquid environment, the solution redox properties of **4** were studied by cyclic voltammetry (CV) in different solvents (CH_3CN, CH_2Cl_2 and THF) and using tetrabutylammonium hexafluorophosphate ($TBAPF_6$) or perchlorate ($TBAClO_4$) as supporting electrolytes. Derivative **4** gives two pairs of well-defined and reversible redox couples typical of TTF, although positively shifted due to the presence of electron-withdrawing substituents (see Table S1 for detailed electrochemical data†).[7] It is evident from the results that solvent and supporting electrolyte have a notable effect on the stability of the radical species generated electrochemically. Furthermore, the redox potentials of the cation-radical or dication could be tuned as a function of the above factors (see ESI†).

To get a better understanding of the geometrical, electrical and charge-transport properties of **4**, semiempirical theoretical calculations were performed using the PM3 Hamiltonian. The optimized geometry of derivative **4**, with the TTF molecule in the neutral state, resulted in a planar D_{2h} symmetry in agreement with previous related theoretical calculations.[14] The distance for **4** measured between the two sulfur atoms was found to be 2.10 and 2.34 nm for the *cis* and *trans* isomers, respectively. In addition, the electronic distribution structure of **4** shows, in the neutral state,



Scheme 1 Synthesis of the TTF-based redox switch **4**.

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† Electronic supplementary information (ESI) available: Synthesis and structural characterization of intermediates **2**, **3**, **5**, **6**, **7** and molecular wire **4**. Electrochemical data for **4** in different solvents. See DOI: 10.1039/b710739k

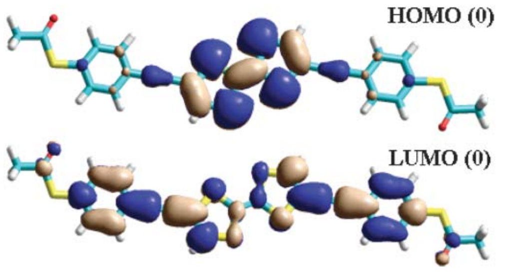

Fig. 1 Calculated HOMO and LUMO orbitals (PM3) for compound **4**.

that the HOMO is predominantly located on the TTF donor fragment (Fig. 1) and the LUMO is mainly spread on the phenylalkynyl groups. In agreement with recent results,[15] conductance is expected to change with the relative twist angle between the two dithiole rings, with the planar conformation of the neutral TTF moiety having the highest conductance.

Charge transport measurements were carried out by repeatedly forming and breaking Au point contacts in the presence of **4** using an STM at room temperature.[3c,15] The STM tip was made out of a 99.99% purity 250 μm gold wire, and the sample consisted of gold evaporated on flat quartz. Au point contacts were formed in a droplet of a dilute 1 mM solution of **4** in 1,2,4-trichlorobenzene placed on the sample. As an Au point contact is broken by pulling apart the electrodes, there is a certain probability that one or several molecules will bridge the junction giving rise to characteristic features in the conductance traces from which the average conductance of the molecules can be obtained. The observation of a conductance step at $G_0 = 2e^2/h$, the quantum of conductance, is the signature of a one-atom gold contact[16] and an indication that only a few molecules are present in the junction. We have measured 7000 conductance traces at a fixed bias of 25 mV. Most of these traces show an exponential decrease of the conductance with increasing tip–sample separation (trace a in Fig. 2A) as expected for tunneling through the solvent. Interestingly, about 1% of these traces show conductances larger than 10^{-3} G_0 for tip–sample separations in excess of 1 nm followed by an abrupt drop of conductance (traces b and c in Fig. 2A). The prominent peak in the histogram constructed with these traces suggests a conductance of about 10^{-2} G_0 for a single molecule.

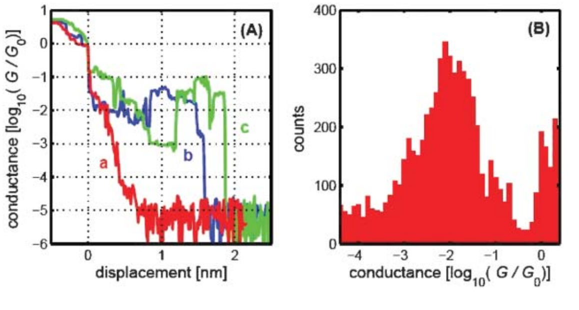

Fig. 2 (A) Conductance traces for an Au–Au junction (trace a) and two molecular junctions comprising one or a few molecules (traces b and c). (B) Conductance histogram constructed from the conductance traces that show evidence of trapped molecules.

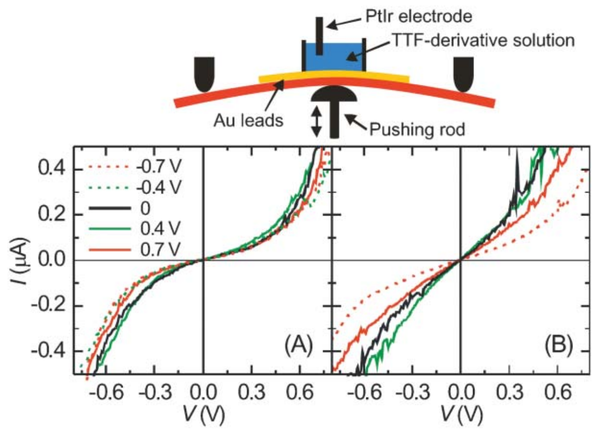

Fig. 3 *I–V* characteristics, at different gate voltages, for a wide open (A) and almost closed (B) break junction immersed in a solution of **4**. The inset shows a schematic of the break junction setup working in liquid.

Gating experiments were carried out using a MCBJ equipped with a liquid cell.[17] A schematic of the setup is shown in Fig. 3. By bending the substrate with a central pushing rod, the Au wire on its surface is elongated and finally broken. Two atomic-sized Au electrodes are then formed. The gap between the electrodes can be opened and closed repeatedly by moving the pushing rod up and down. The resolution in the gap size variation is sub-Angstrom.[17] A PtIr wire was added to the cell and operated as a gate electrode. We prepared a 0.3 mM solution of **4** in a (4 : 1) mixture of toluene–CH_3CN. The thioacetyl end groups were deprotected with tetrabutylammonium hydroxide (TBAOH) and 0.1 M Bu_4NPF_6 was added as an electrolyte. The solution with **4** was injected in the liquid cell while the junction was kept closed. The junction was then opened widely (⩾ 3 nm) for a few minutes to let the molecules assemble. Then, we performed several open/close cycles, without allowing the Au electrodes to get into contact. In this process, *I–V* characteristics were recorded at several gap openings and for different gate voltages applied. Two reproducible kinds of *I–V* characteristics were observed. These are depicted in Fig. 3. (A)-type curves were found at large gap sizes. They present a Simmons-like shape typical of tunneling, and show little sensitivity to the gate voltage. In contrast, a gate effect is observed in (B)-type curves, which present a linear profile in a larger voltage range. (B)-type curves were observed when the electrodes were brought very close together. Note that the precise gap size cannot be determined here. After the gap is opened, the gold atoms on the electrode tips will rearrange and retract.[17] The resistance in the linear regime of the (B)-type curves is approximately 2 MΩ. This value is two orders of magnitude lower than the single-molecule resistance reported for oligo(phenylene ethynylene),[18] and four orders of magnitude lower than that estimated from studies in self-assembled monolayers of a similar TTF compound.[8] These values suggest that our results do not correspond to a single molecule, but rather to a collection of confined (and not necessarily chemically bonded) molecules between the electrodes getting together. These encouraging observations emphasize the potential of TTF derivatives as molecular wires with an electrostatically adjustable conductance. Additional experiments are still needed to confirm the single-molecule response.

In summary, we have prepared a new type of molecular wire endowed with a redox active TTF unit. First liquid conductance measurements by STM and MCBJ techniques have been carried out and showed high conductance at low bias voltages. Work is currently in progress to determine how the different oxidation states of TTF influence the conductance on this molecular wire.

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Notes and references

‡ Compound **4** (see ESI† for complete structural characterization) was obtained as a mixture of two isomers depending upon the position of the alkynyl groups on the two 1,3-dithiole rings (*cis* and *trans*). This isomeric mixture is also found in compounds **2**, **5** and **6**.

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