

## DESIGN AND RECTIFICATION STUDY OF DIFFERENT AVIRAM-RATNER MODEL MOLECULES .

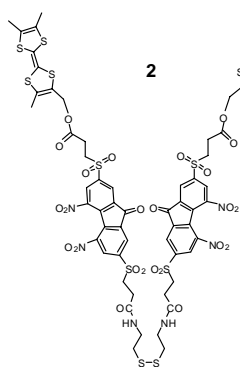
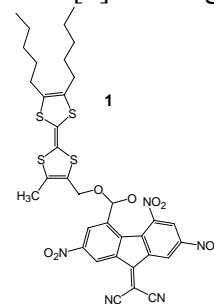
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The interest in molecular electronics began in the 1970s with the work of Aviram and Ratner. It was proposed that a covalent donor-acceptor diad, such as TTF- $\sigma$ -TCNQ molecule (TTF – tetrathiafulvalene,  $\sigma$  – nonconjugated bridge, TCNQ – tetracyanoquinodimethane) could resemble the electric properties of a p-n junction, acting as a unimolecular rectifier [1]. The reason of such behavior lies in asymmetrically distributed electronic levels, and very low HOMO-LUMO gap (0.3 eV) was imposed for the model molecule. Up to date, numerous donor-acceptor diads have been investigated as candidates for molecular rectifiers (diodes), which include some D- $\sigma$ -A diads with weak donor moiety, numerous D- $\pi$ -A and also molecules without obvious asymmetry in the structure. However, neither the original TTF- $\sigma$ -TCNQ molecule nor any other molecule with similar HOMO-LUMO gap have been studied in molecular electronics applications, which was due to synthetic unavailability of such molecules.

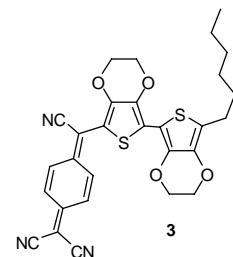
Recently we reported the synthesis and study of D- $\sigma$ -A diads, based on TTF- $\sigma$ -fluorene **1**, with HOMO-LUMO gap below 0.3 eV and unimolecular rectification ratio 1:18 [2]. Having asymmetrically distributed HOMO/LUMO orbitals with low energy gap, this compound present an ideal model for studying the original Aviram-Ratner concept of molecular electronics. The molecule **1** was specially designed with long alkyl chains for Langmuir-Blodgett type of deposition on the surface, where a polar dicyanomethylene-fluorene fragment of **1** is exposed to the polar water phase, whereas the hydrophobic trialkylTTF moiety is stretched into the air. Using such amphiphilic character of molecule **1**, monolayer can be transferred onto different surfaces such as gold, Si etc.



Furthermore, study on construction of molecular rectifying devices that based on self-assembly technique was also done, in which thiol-terminated molecules **2** could be bound to the electrode surface (Au, Pt) by chemical S-Au bond [3].

To study the rectification behavior of the molecule, molecular junction devices (M/D- $\sigma$ -A/M) were fabricated, where the D and A moieties were put in contact with metal electrodes (M). Careful contact with the organic monolayer was made by mercury drop, covered with alkyl thiol monolayer, affording Au/A- $\sigma$ -D/Hg junction. The choice of Hg and Au as electrodes was made as their work-functions match well the energy levels of the molecule and also by the fact that Hg, with alkyl thiol monolayer on the surface, does not penetrate deep in the organic layer thus preventing direct contact between two metal electrodes.

Another series of molecular rectifiers have been synthesised which are based on EDOT-3CNQ diad **3**. EDOT is a widely used nowadays in the field of molecular electronics due to its good stability. Moreover, by increasing the number of EDOT species in the chain it is possible to tune donor property of the molecule. In contrast with original Aviram-Ratner model, molecule **3** has conjugated bridge between donor and



acceptor, but geometry calculations exhibit torsion angle between EDOT and TCNQ planes, thus HOMO of donor and LUMO of acceptor are separated. Also, donor moiety has been functionalized with long alkyl chain for the purpose of Langmuir-Blodgett deposition of the molecules on the electrode surface for further rectification study.

To conclude our study of the rectification of different molecular structures we have designed diodes made of asymmetrically structured single walled carbon nanotubes [4]. SWNTs are promising materials for future nanoelectronic technologies, and chemical functionalization of CNs by attaching various substances to side walls and oxidized ends have been extensively investigated, mostly with the aim to improve the solubility and processability of SWNTs. On the other hand, an asymmetric functionalization of a highly polarizable SWNT with electron donor substituents at one end and electron acceptors at the other should yield a highly dipolar molecule for which interesting electronic properties, including current rectification, can be expected. Our synthetic strategy is based on surface-confined reaction at one end of the tubes (yielding a film of SWNTs covalently linked to the gold surface), followed by functionalization of the “top” end of the tubes via solution chemistry. To address the induced asymmetry of the SWNTs, the conductance of the prepared film was studied in mercury drop junction experiment (fig. 1, left). The typical IV characteristics of the studied junctions (fig. 1, right) exhibit highly asymmetric behavior, with rectification ratio of  $\geq 10^3$ . This work describes the first asymmetric functionalization of SWNTs and demonstrate modulation of the current rectification by the modified nanotubes, self-assembled on the gold surface.

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2. G. Ho, J. Heath, M. Kondratenko, et al, *Chem. Eur. J.* **2005**, 11, 2914–2922.
3. D.F.Perepichka, M.Kondratenko, M.R.Bryce, *Langmuir* **2005**, 21, 8824–8831.
4. Z.Wei, M.Kondratenko, D.F.Perepichka, et al, *J. Am. Chem. Soc.* **2006**, 128, 3134–3135.

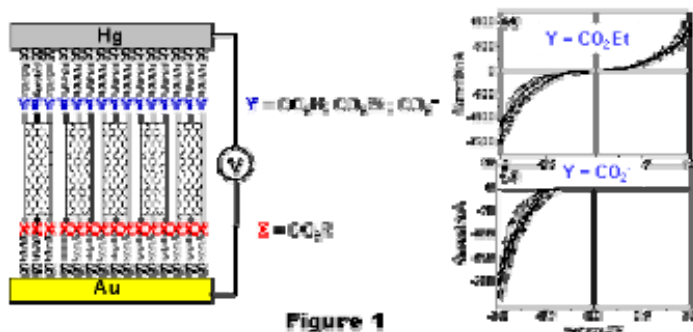


Figure 1