

## Nitrofluorene based donor-acceptor diads with extremely low HOMO–LUMO gap as molecular electronic devices

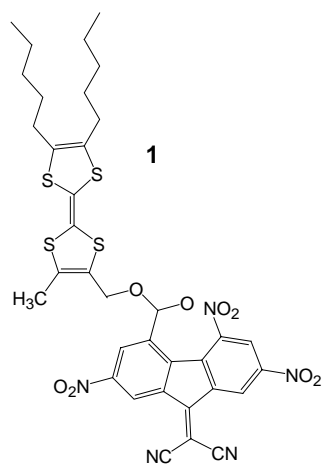
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The interest in molecular electronics began in the 1970s with the work of Aviram and Ratner, who proposed that a covalent donor-acceptor diad, specifically a single TTF– $\sigma$ –TCNQ molecule (TTF – tetrathiafulvalene,  $\sigma$  – nonconjugated bridge, TCNQ – tetracyanoquinodimethane) can resemble the electric properties of a p-n junction, acting as a unimolecular rectifier.<sup>1</sup> The reason of such behavior lies in asymmetrically distributed electronic levels and very low HOMO-LUMO gap (0.3 eV) imposed for the model molecule. Up to date, numerous donor-acceptor diads were investigated as candidates for molecular rectifiers (diodes), which included some D– $\sigma$ –A diads with weak donor moiety, numerous D– $\pi$ –A compounds 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, mostly due to synthetic unavailability of such molecules. Recently we have reported synthetic methodology for construction of D– $\sigma$ –A diads with HOMO–LUMO gap below 0.5 eV.<sup>2,3</sup>

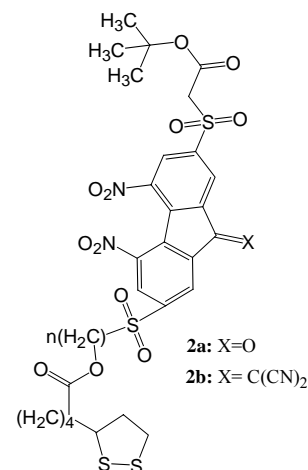


In the present work we describe synthesis of a series of donor-acceptor diads of TTF– $\sigma$ –(polynitrofluorene) of type **1**, where TTF is a strong donor moiety (with high HOMO),  $\sigma$  is a flexible nonconjugated linker, and polynitrofluorene is an acceptor moiety (with low LUMO). The compounds are fully characterized by NMR, ESR, UV-Vis-NIR, FTIR, and Raman spectroscopies. The electrochemical studies revealed a very low HOMO–LUMO gap of  $\sim 0.3$  eV, which was reproduced by DFT calculations. Having asymmetrically distributed HOMO/LUMO orbitals with so low energy gap, this compound present an ideal model for studying the original Aviram-Ratner concept of molecular electronics.

To study the electric conductivity of the molecule and possible diode behavior, we have fabricated molecular junction devices (M/D– $\sigma$ –A/M), where the D and A moieties are put in contact with metal electrodes (M). Using the amphiphilic character of molecule **1** we have prepared Langmuir-Blodgett monolayer and transferred it onto (degeneratively) *n*-doped Si substrate. Careful deposition of Ti on top of the organic monolayer afforded n-Si/D– $\sigma$ –A/Ti junction (Fig. 1). The choice of electrode materials was dictated by their work-functions, which match well the energy levels of the molecule. Also, Ti, in spite (or, may be, due) its high reactivity does not penetrate deep in the organic layer, affecting (reacting with) at most upper 1-2 carbon atoms of the aliphatic chain (which also acts as a protector of the D-A part of the molecule). The LB films were transferred at different surface pressure of 12, 17 and 25 mN/m<sup>2</sup> (Fig. 2 (top)), which correspond to decreasing molecular area and better alignment of the molecules. ATR-FTIR spectroscopy confirmed the molecular structure of the film and their alignment at increased pressure, to form at 25 mN/m<sup>2</sup> dense monolayer with molecular D–A axis being close to surface normal. A hydrophilic acceptor fragment of **1** is exposed to the polar water phase (and subsequently transferred onto Si surface), whereas the hydrophobic trialkylTTF moiety is stretched into the air (and

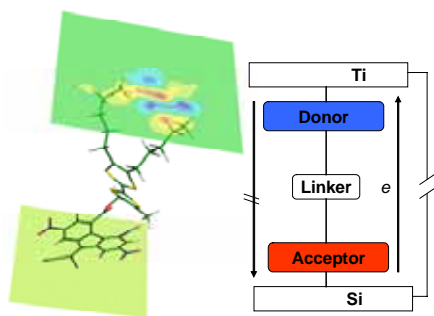
come into the contact with Ti in the device). Current-voltage curves obtained for the prepared molecular junctions (Fig. 2 (bottom)) revealed clear asymmetric behavior, with higher current in the theoretically predicted direction (A→D)[1] and the rectification ratio (RR) up to 1:18. Importantly, the RR increases as the molecules align closer to the normal. The phenomenon was not observed for electronically inactive eicosanoic acid (which showed no rectification). Also, the RR for our device does not decrease after multiple scanning ( $\pm 1.75$  V). This is in contrast to high dipole moment D- $\pi$ -A systems in which, the reorientation of molecules in the electric field results in the RR reduction by a factor of two every second scan.<sup>4</sup> Thus, due to negligible dipole moment, the device stability with molecules **1** is tremendously higher.

Our second approach towards construction of molecular rectifying devices is based self-assembly technique, in which thiol-terminated molecules are bound to the electrode surface (Au, Pt) by chemical S-Au bond. The self-assembled monolayers (SAM) of molecules of type **2** were prepared by simple dipping the metal substrates into solution of compound **2**. The properties of SAMs were vigorously characterized by grazing angle FTIR spectroscopy and cyclic voltammetry, which revealed high electron affinity of the fluorene fragment and stability of the attached molecules, both in the neutral and reduced (by electron transfer from electrode) states. A second functional ester group on the acceptor fluorene fragment was designed for attaching different electron-donor moieties (as TTFs). The construction of such molecular devices via classical solution chemistry methods as well as via solid-state modification of the preformed monolayers of **2** will be described. We will also report our studies of the electric conductivity and diode behavior in these systems via scanning probe microscopy technique (using STM tip) and via bulk molecular junction (using mercury drop contact junction). The correlation between the molecular properties, tuned by structural modifications (as HOMO-LUMO gap) and the device characteristics will be reported.



### References:

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**Fig.1** n-Si/D-σ-A/Ti molecular junction.

**Fig. 2** (Top) LB isotherm of compound 2 with indicated transfer pressures of the films that were used for device fabrication. (Bottom) The current-voltage curves obtained from the molecular tunnel junction devices made from the three films indicated in the isotherm measurement.

