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Nanometer-Thick Bilayers by Stepwise Electrochemical Reduction of Diazonium Compounds for Molecular Junctions

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This work describes an electrochemical bottom-up approach for modification of metallic electrode to modulate the electrochemical properties of the layer. The adopted strategy is based on two successive electroreductions of diazonium salt and was successfully used in the fabrication of molecular junction with specific behavior.[1] The deposited ultrathin layers consist of an electron donating oligo (bisthienylbenzene) (BTB) and an electron acceptor namely oligo (phenyl methylbipyridium) (PMV^{2+}). The generated bilayers are studied by AFM, XPS, XPS depth analysis and electrochemical techniques. The study demonstrates the possibility to graft one layer over the initial one to create strongly coupled donor-acceptor or acceptor-donor bilayer systems with minimal interpenetration and overall thicknesses between 5 and 20 nm. The electron transfer towards redox probe in solution and electron transfer in solid state molecular junctions are studied.[2,3] The electrochemical response of several outer-sphere redox probes on such modified electrodes is close to that of a diode, thanks to the easily p-doped oligo (BTB) or easily reducible oligo (PMV) moieties. Moreover, the electron transport in solid state molecular junctions exhibits strong rectification with opposite sign depending on the order of the two layers. Our goal in this work was to control the electronic response through the structuration and the functionality of the organic layer.[4]

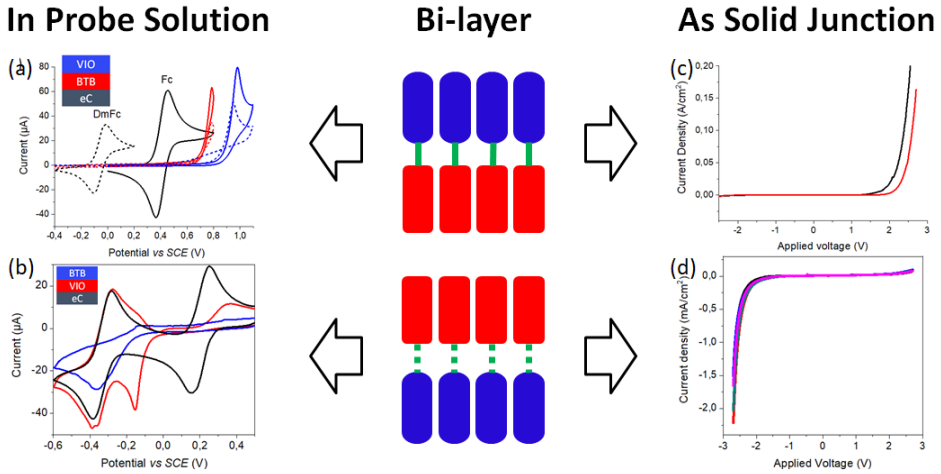

Figure 1: CVs of bare (black curve), single layer modified electrode (red curve) and bilayer modified electrode (blue curve) in Fc solution (5mM), DmFc(5mM) (a) and TCNQ(5mM)(b). Scan rate 100 $mV.s^{-1}$; *JV* curves for Au/BTB/PMV/Ti(c) and Au/PMV/BTB/Ti (d) junctions.

Références (Calibri, 11 pts, alignement à gauche)
[1] V. Stockhausen et al., ACS Appl. Mater. Interfaces 9, 610 (**2017**).
[2] C. Barraud et al., Nanoscale Adv. 1, 414 (**2019**).
[3] Q. Van Nguyen et al., J. Am. Chem. Soc. 140, 10131 (**2018**).
[4] M. Liu et al., ACS Appl. Nano Mater. 4, 13861-13870 (**2021**)