Electron Transfer through Molecular Systems in a Metal-SAM-Metal Junction.

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Electron transfer processes have been studied extensively in the last 30 years in donor-acceptor supramolecular systems¹ and in the last decade at an electrode interface through an electrochemical approach. ²

We report a series of studies of electron transfer processes carried out in an electrical systems, that is measuring the current flowing through molecules sandwiched between two electrodes. The junction (Fig 1,2,3) is based on Hg electrodes: Hg-SAM//SAM-M, where SAM is a self assembled monolayer organized at the metal surfaces and M is a metal (Au, Ag, Hg). The junctions are easy to assemble (because the mercury electrode is compliant) and they are compatible with SAMs incorporating organic groups having a range of structures.

Junction 1 where SAM(1) is formed by molecules of different length and different structure, allows for correlating electrical properties and molecular structure. ³

In junction **2**, by changing X and Y it is possible to perform different interactions connecting the two metal electrodes: it is possible to compare electron transfer rate through covalent bonds, H bonds and van der Waal s interactions.⁴

In junction 3, different redox sites have been trapped between the metal electrodes: the redox sites behave as ultimate quantum dots. 5

[1] V. Balzani, Ed., *Electron Transfer in Chemistry*, Volume I-V, Wiley, Weinheim 2001.

[2] E.D. Chidsey, Science, 1991, 251, 919..

[3] R. E. Holmlin, R. Haag, R. F. Ismagilov, M. A. Rampi, G. M. Whitesides, *J. Am. Chem. Soc.* **2001**,*123*, 5075.

[4] R. E. Holmlin, R. Haag, R. F. Ismagilov, V. Mujica, M. A. Ratner, M. A. Rampi, G. M.

Whitesides, *Angew. Chem. Int. Engl. Ed.* **2001,***40* , 2316.

[5] M. L. Chabinyc, X. Chen, R. E. Holmlin, H. Jacobs, H. Skulason, C. D. Frisbie, V. Mujica,

M. A. Ratner, M. A. Rampi, G. M. Whitesides

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