

MOLECULAR WIRES OF MMX POLYMERS.

F. Zamora,^a D. Olea,^b A. Guijarro,^a S. S. Alexandre,^b M. Remuiñan,^a J. M. Soler,^b P. J. de Pablo,^b R. González-Prieto,^c R. Jiménez-Aparicio,^c J.L. Priego,^c J. Gómez-Herrero^b

^aUniversidad Autónoma de Madrid, Departamento de Química Inorgánica (C-VIII), 28049 Madrid, Spain. ^bUniversidad Autónoma de Madrid, Departamento de Física e la Materia Condensada, 28049 Madrid, Spain. ^cDepartamento de Química Inorgánica I. Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040 Madrid.

felix.zamora@uam.es

Current researches in the field of electronic applications at nanometer-scale have been focused on the development of large molecules able to conduct electricity.

Quasi-1D halogen-bridged mixed-valence compounds named as “MMX” chains or polymers have been investigated extensively in the last years because of their interesting physical properties in solid state (macroscopic scale: crystals) [1-3]. These compounds are formed by two metal ions, showing a short metal-metal distance, which are bridged by organic ligands, usually carboxylates or dithiocarboxylates, and the halides act bridging the “MMX” units, to give one-dimensional structures (Fig. 1). Halides (F, Cl, Br and I) represent the smallest and simple linkers of all bridging ligands of the Figure 1. Some of them have shown in solid state (crystals) metallic conduction and /or magnetic behaviour [2, 3]. However, the studies of these properties have been limited to a macroscopic scale.

Some of the most important features of the MMX polymers are the following: (a) easy synthesis which allows facile substitution of the fragments, (b) the design of the fragments that could increase or minimize the interaction between chains and, therefore, the architecture in one, two or three dimensions (c) the solutions of these compounds give monomers of “MMX” composition that can self-assemble to give one-dimensional chains, circles, or bidimensional nets, and finally, (d) their electronic and magnetic properties can be controlled by varying their constituents of the transition metal ions, the bridging ligands between the metal ions and the bridging halogen ions.

The morphological and electrical characterization of the polymers: $[\text{Pt}_2\text{I}(\mu\text{-S}_2\text{CCH}_3)_4]_n$ and $[\text{Ru}_2\text{Br}(\mu\text{-O}_2\text{Cet})_4]_n$ by AFM have been recently achieved. Solutions of these compounds at different concentrations and solvents have given several arrangements on a mica surface. Thus, single chains of these polymers have been characterized by AFM (Fig. 2 and 3). Preliminary experiments strongly suggest that individual chains of these polymers may behave as molecular wire with good electrical conducting properties. As an indication we are showing the topography of a molecular chain of $[\text{Ru}_2\text{Br}(\mu\text{-O}_2\text{Cet})_4]_n$ adsorbed on mica using AFM (Fig. 2i-a). Figure 2i-b shows the electrostatic signal produced by this molecule which is a good indication of the conducting nature of the chain. Other arrangements for these polymers have been observed. For instance, closed systems of single molecules (Fig. 2ii-a) and networks formed by organized nanolattice (Fig. 2ii-b) and networks (Fig. 3b) have been obtained. Direct measures of the electrical properties on these polymers are currently in progress and will be presented (Fig. 2-iii). DFT calculations carried out on $[\text{Pt}_2\text{I}(\mu\text{-S}_2\text{CCH}_3)_4]_n$ and $[\text{Ru}_2\text{Br}(\mu\text{-O}_2\text{Cet})_4]_n$ polymers indicate that single chains of these polymers should behave as a metallic conductor and semiconductor (gap of 0.6 eV), respectively.

The aim of this project is to develop a new line of action to extend the spectrum of possible candidate to molecular wires for the construction of nanocircuits. The main advantages of these polymers over CNT, are the easy synthesis and the facile chemical modifications that can be done allowing modulation of their properties.

Acknowledgements

Financial support from NISAN/IST-2001-38052 and, MAT2001-0664 is acknowledged. Research Projects MCyT-BFM2003-03372, and Grupos Precompetitivos UAM (CS13-541A-9-640).

References:

- [1] H. Kitagawa, N. Onodera, T. Sonoyama, M. Yamamoto, T. Fukawa, T. Mitani, M. Seto, Y. Maeda, J. Am. Chem. Soc., **121** (1999) 10068.
- [2] M. Mitsumi, K. Kitamura, A. Morinaga, Y. Ozawa, M. Kobayashi, K. Toriumi, Y. Iso, H. Kitagawa, T. Mitani, Angew. Chem. Int. Ed., **41** (2002) 2767.
- [3] M. Mitsumi, T. Murase, H. Kishida, T. Yoshinari, Y. Ozawa, K. Toriumi, T. Sonoyama, H. Kitagawa, T. Mitani, J. Am. Chem. Soc., **123** (2001) 11179.

Figures:

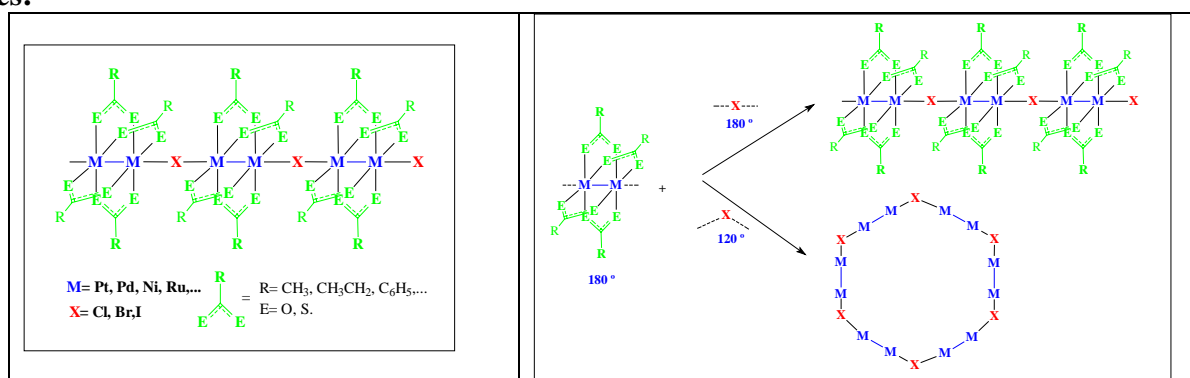


Figure 1. Schematic representation of MMX one-dimensional polymers and their process of self-assembly by molecular recognition.

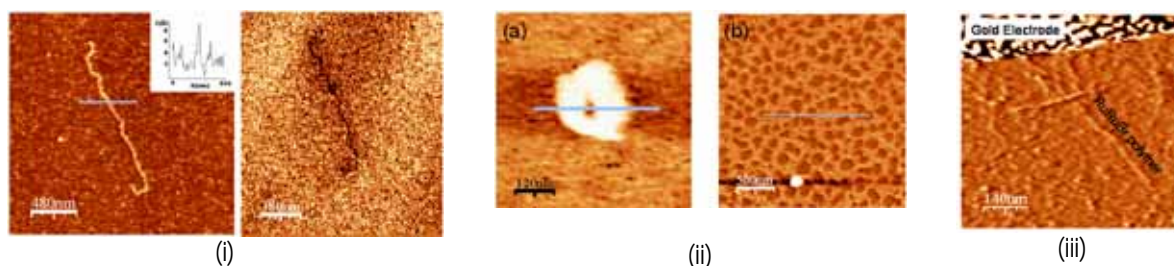


Figure 2. From left to right (i) AFM topography of single chains of the $[\text{Ru}_2\text{Br}(\mu\text{-O}_2\text{CET})_4]_n$ and contrast in the phase by applying 6000 mV. (ii) Two different arrangements of single molecules (circles-like and nanolattice). (iii) Conducting AFM measurements

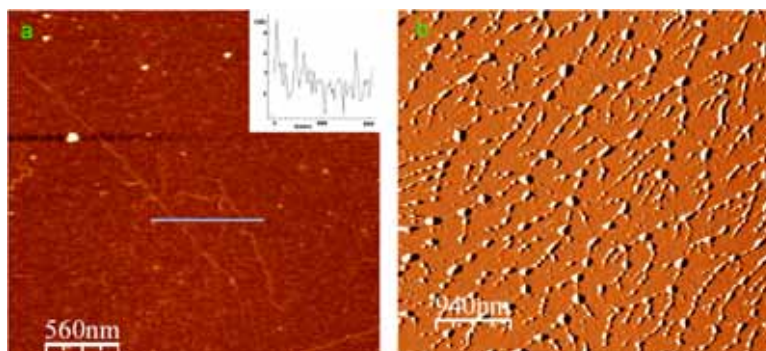


Figure 3. AFM topography of (a) individual chains and (b) networks of $[\text{Pt}_2\text{I}(\mu\text{-S}_2\text{CCH}_3)_4]_n$.