

Mesogenic Coordination Polymers Based On Bimetallic Carboxylates: Influence of the bridging ligand on the communication between metal centers

María Ana Castro^{1,2}, Adrián Roitberg², Fabio D. Cukiernik^{1,3}

¹ Universidad de Buenos Aires, DQIAQF/INQUIMAE, Facultad de Ciencias Exactas y Naturales, Argentina.

² University of Florida, Quantum Theory Project, Gainesville, FL, 32611-8435.

³ Universidad de Gral. Sarmiento, Instituto de Ciencias, Buenos Aires, Argentina.

The design of new *molecular materials*¹ with adequate physical properties that allow them to perform specific functions (*functional materials*)², requires a deep understanding of the characteristics of the molecular fragments, their spatial organization and ways of interconnection.

Bimetallic carboxylates such as $M_2(O_2CR_{eq})_4L_{ax}$ ($M_2 = Cu_2, Rh_2, Ru_2(II,II), Ru_2(II,III)$, O_2CR_{eq} = equatorial carboxylate and L_{ax} = axial ligand) have been studied thoroughly in the last few years with the purpose of obtaining macroscopically orientable, one-dimensional structures. Depending on the nature of the metallic core, the anisotropy of their columnar LC phases and if the electron-rich bimetallic centers are bridged by adequate polymerizing axial ligands, this may result in collective properties such as high electric conductivity, ferrimagnetic behavior, ferroelectricity, or 1-D energy transport. These properties would make them good candidates as components for molecular devices such as molecular wires and columnar ferroelectrics. In this context, liquid-crystalline coordination polymers form a class of materials expected to present the properties of both coordination polymers (complexes in which the metallic centers are bridged by appropriate ligands giving extended structures) and metal containing liquid crystals (*metallomesogens*)³.

Diruthenium tetracarboxylates, $M_2 = Ru_2(II,III)$ or $Ru_2(II,II)$, are particularly interesting due to their peculiar electronic structure (metal-metal bond, partially filled HOMO and a paramagnetic ground state) and were selected as our building blocks. We have performed electronic structure calculations (Gaussian03 – DFT) in order to gain a deeper understanding of these systems. By varying the nature of the bridging axial ligand (L_{ax} = pyrazine, pyrazine derivatives, tetrazine, phenazine, acetylene, etc), we have gathered information on the influence of this bridging ligand on the electronic delocalization and the potential application as molecular wire. In this direction, the broken symmetry⁴ (BS) method was used to estimate the magnetic interactions between Ru_2 centers. The magnitude of these interactions provided us with a quantitative parameter to analyze the communication between metal centers and, together with molecular orbital analysis, estimate the electronic delocalization along the chain.

The information provided by these calculations, allowed us to discuss and decide which the most promising combinations of ligands are in order to obtain one-dimensional conductivity.

1) Simon, J.; André, J.J.; Skoulios, A. *New J. Chem.* **1986**, *10*, 295.

2) *Functional organic and polymeric materials*, Richardson, T. Ed. **2000**, John Wiley & Sons (Chechester).

3) Donnio, B.; Guillon, D.; Deschenaux, R.; Bruce, D.W. in *Compr. Coord. Chem.*, **2004**, *7*, 359. Mc Cleverty, J.; Meyer, T.J. Eds., Elsevier Pergamon, (Amsterdam).

4) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *Journal of Computational Chemistry*, **1999**, *20*, 1391.