

## Galán-Mascarós Research Group



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### Abstract

Our research team is devoted to the development of new molecule-based materials for applications in the fields of Renewable Energies and Materials Sciences. On the former, we are developing efficient and stable redox catalysts from Earth abundant metals, with

special interest in water splitting catalysts for the production of solar fuels. On the later, we target the design of novel multifunctional hybrid materials with co-existence of properties of interest (magnetic, catalytic, electrical, optical,...) with control of the synergy between physical properties in the search for new phenomena

### Catalytic water oxidation with Prussian blue analogs

Transition metal hexacyanometallates (PBs) are isostructural to the original Prussian blue, the all-iron  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6] \cdot x\text{H}_2\text{O}$  derivative discovered over 300 years ago as a pigment. In the crystal structure, two octahedral metal centers are bound through cyanide bridges to construct a face-centered cubic unit cell (Fig. 1). PBs are known for many combinations of transition metal ions in multiple oxidation states. Despite of their rigid structure, these coordination polymers are usually non-stoichiometric because different non-integer ratios can be accommodated. This chemical variety makes of them a versatile type of molecule-based materials.

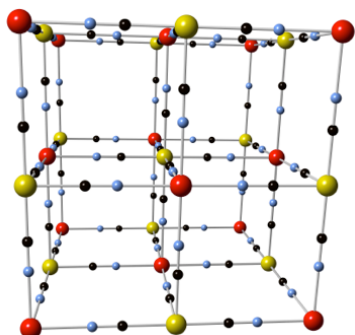


Fig. 1. Representation of a cubic Prussian blue type structure. (metal centers = red and yellow; carbon = black; nitrogen = blue)

We investigated the catalytic activity for photoinduced water oxidation in the PB derivatives  $\text{M}^{\text{II}}_3[\text{M}^{\text{III}}(\text{CN})_6]_2$  ( $\text{M}^{\text{II}} = \text{Mn}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Zn}^{\text{II}}, \text{M}^{\text{III}} = \text{Cr}^{\text{III}}, \text{Fe}^{\text{III}}, \text{Co}^{\text{III}}$ ). Oxygen evolution was monitored in suspensions of these materials, driven by a photosensitizer assay ( $[\text{Ru}^{2+}(2\text{-}2'\text{-bpy})_3]/\text{persulfate}$ ), in a potassium phosphate buffer (Fig.2).

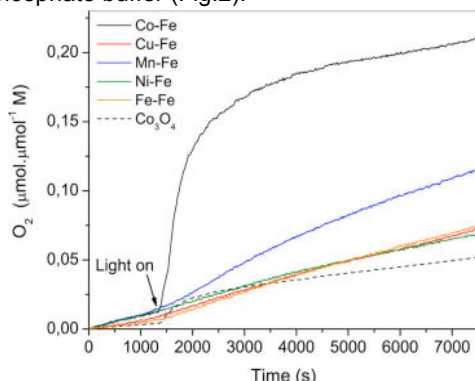


Fig. 2 - Catalytic oxygen evolution for the  $\text{M}^{\text{II}}\text{Fe}$  series. Conditions:  $[\text{Ru}(\text{bpy})_3]^{2+}$  (1.0 mM),  $\text{Na}_2\text{S}_2\text{O}_8$  (5.0 mM), and catalyst (10.0 mg) at pH 7.0. Light irradiation: 470 nm

The  $\text{Co}^{\text{II}}\text{M}^{\text{III}}$  derivatives showed a fast and maintained oxygen production, whereas  $\text{Mn}^{\text{II}}\text{M}^{\text{III}}$

showed weak but measurable activity. All other PB derivatives were inactive. We estimated initial catalytic rates based on all the Co content in the bulk materials finding turnover frequencies (TOF) as high as  $3.0 \times 10^{-4} \text{ s}^{-1}$ . Superior to those observed for  $\text{Co}_3\text{O}_4$ , a classic water oxidation catalyst (WOC) in these conditions. Thus, PB derivatives are promising candidates for the development of a novel water electrolyzer technology, with good performance when associated to solar energy.

### Catalytic water oxidation with a metal-metal bonded $\text{Ru}_2$ dimer

Ruthenium complexes are the most well-studied homogeneous WOCs, exhibiting great performance in terms of efficiency and kinetics. However, they are typically unstable in water oxidation conditions in the long term due to oxidative deactivation. In collaboration with Prof. K. R. Dunbar (Texas A&M University), we have discovered that metal-metal bonded diruthenium complexes exhibit kinetics as fast as state of the art WOCs, adding a remarkable stability conferred by the metal-metal bond.

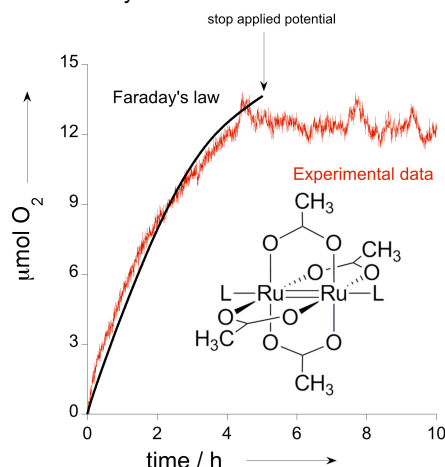


Fig. 3 - Electrocatalytic oxygen evolution with  $\text{Ru}_2(\text{acetate})_4$ . Conditions:

The  $\text{Ru}_2(\text{acetate})_4$  paddlewheel compound catalyzes water electrolysis over a wide pH range ( $1 < \text{pH} < 10$ ) and at high catalytic rates with quantitative efficiencies, reaching current densities over  $1 \text{ mA cm}^{-2}$  in dilute solutions ( $\text{TOF} = 77 \text{ s}^{-1}$ ). The advantage of this approach is that the metal-metal bond platform allows for the use of common ligands such as acetate to develop new WOCs without the need for complex organic chelating agents. Moreover, few transition metal WOCs are capable of reaching these rates, and always require strict pH conditions.

In collaboration with Prof. J. M. Poblet (URV) we carried out DFT calculations at M06-L/SMD level to investigate the intermediates involved in the plausible mechanism for water oxidation

(Fig. 4). We have found that the initial PCET event emerges as the most energetic demanding step. The presence of a direct Ru-Ru bond is responsible for the lower potentials needed in the next steps that become more and more favored in the water oxidation cycle, what supports the very fast kinetics found. The Ru<sup>V</sup>-oxo group of **S**<sub>3</sub> is prone to nucleophilic attack of an external water molecule yielding the formation of the O-O bond; the oxidation of Ru<sup>IV</sup>- to Ru<sup>V</sup>-oxo being energetically simple. It is worth mentioning that the diruthenium complex can be considered a single-site catalyst with the adjacent Ru center behaving as an auxiliary ligand that tunes reactivity providing a remarkably active catalyst. Our results pave the way for further development of an attractive new family of fast water oxidation electrocatalysts.

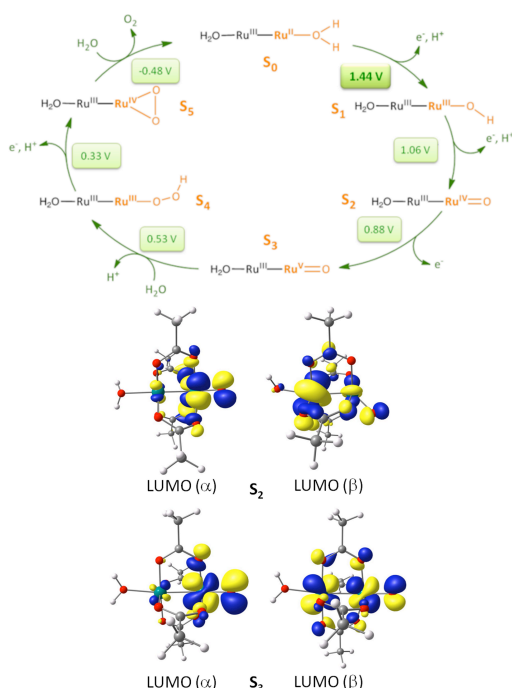


Fig. 4 - Schematic representation of the water oxidation by  $\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2^+$  catalyst based on DFT calculations, and LUMO representations for intermediates **S**<sub>2</sub> and **S**<sub>3</sub>.

### Spin crossover phenomena in Fe<sup>II</sup> complexes from sulfonate-substituted triazole ligands

Spin crossover (SCO) compounds are a paradigmatic example of bistability at the molecular level, where the electronic state of a metal complex can be switched from a low-spin (LS) to a low-lying metastable high-spin (HS) configuration through external stimuli: thermally, under light irradiation or pressure. In such compounds, cooperativity and memory effect may appear in bulk, when a structural phase transition is associated to the electronic transition.

We have obtained a neutral Fe<sup>2+</sup> trimer (Figure 3) with the anionic ligand 4-(1,2,4-triazol-4-yl)ethane-sulfonate (**L1**) that exhibits a thermally induced spin transition above room temperature once it is partially dehydrated at 80°C. The terminal Fe<sup>2+</sup> centers maintain HS configuration at all temperatures, while the central Fe<sup>2+</sup> is in its LS state at room temperature. It switches to the HS state above 345 K ( $T_{1/2}(\uparrow) = 357$  K) with appearance of hysteresis since it does not relax to the LS ground state until  $T_{1/2}(\downarrow) = 343$  K). This material exhibits spin transition with memory effect at the highest temperature reported for a molecular species.

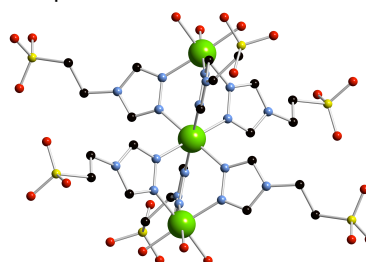


Fig. 5 - Molecular structure of the neutral  $[\text{Fe}_3(\text{H}_2\text{O})_6(\text{L1})_6]$  trimer.

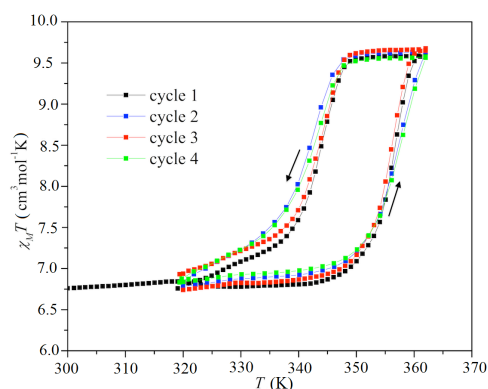


Fig. 6 - Robust thermal switching in the electronic state of the  $[\text{Fe}(\text{H}_2\text{O})_6(\text{L1})_6]$  trimer between HS and LS above room temperature.

### Switchable hybrid organic conductors

The possible exploitation of the SCO switching in electronic devices is difficult due to their intrinsic insulating character. Thus, it is a dream goal to combine SCO with a conducting network. Hypothetically, the spin transition triggered by external stimuli could induce a significant change in electrical conductivity due to the associated structural transition. We have successfully confirmed this hypothesis by the incorporation of SCO Fe<sup>II</sup> compounds into a highly conducting organic polymer matrix, such as doped polypyrrole (ppy) films.

SCO/ppy composite films can be prepared by chemical oxidation of pyrrole in a suspension containing  $[\text{Fe}(\text{trz})(\text{Htrz})_2][\text{BF}_4]$  as polycrystalline

powder. The amorphous shiny precipitate of doped ppy-covered SCO particles is sintered into a thin film under isostatic pressure.

These SCO/ppy films exhibit unprecedented phenomena showing an abrupt change in transport regime associated to the spin transition. The average difference in conductivity between the heating and cooling branches reaches over 60% (Figure 7), which is comparable, for example, to that observed in giant magnetoresistance devices although, in this case, triggered by temperature and occurring in a single composite material. Furthermore, In our SCO/ppy films, the electrical hysteresis loop is 43 K wide, defined by  $T_{1/2}(\uparrow) = 390$  K and  $T_{1/2}(\downarrow) = 347$  K. These films are robust without significant appearance of fatigue after multiple cycles. The HS and LS regimes are reliable, maintaining constant resistance at very long times.

Our results experimentally confirm the viability of using SCO complexes as building blocks for multifunctional hybrid materials to induce switching in a second physical property, in this case electrical conductivity. The performance of our hybrid films cannot be offered by any other

class of conductors, organic or inorganic, bulk or nanostructured, and opens the way for the exploitation of the unique switching abilities of SCO materials in electronic devices.

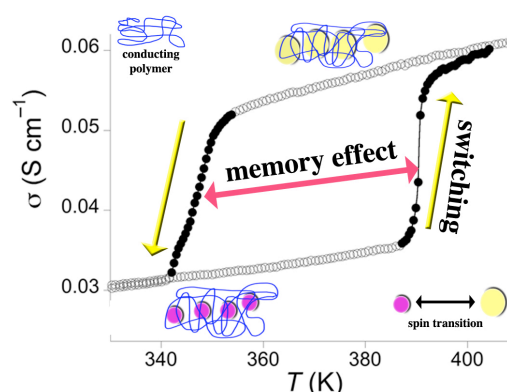


Fig. 7 - thermal hysteresis between HS and LS conductivity in a SCO/ppy conducting film.

## Articles

“Synthesis and Structural Features of Co(II) and Co(III) Complexes Supported by Aminotrisphenolate Ligand Scaffolds”

*Inorg. Chem.* (2014) 53, page 11675-11681

C. Martín, C. J. Whiteoak, E. Martín, E. C. Escudero-Adan, J. R. Galan-Mascaros, A. W. Kleij

“Spin Crossover Probes Confer Multistability to Organic Conducting Polymers”

*Adv. Mater.* (2014) 26, 6785-6789

Y. S. Koo, J. R. Galan-Mascaros

“Single-Molecule-Magnet Behavior in the Family of [Ln(OETAP)<sub>2</sub>] Double-Decker Complexes (Ln=Lanthanide, OETAP = Octa(ethyl)tetraaza-porphyrin)”

*Chem. Eur. J.* (2014) 20, page 12817-12825

N. Gimenez-Agullo, C. Saenz de Pipaon, L. Adriaenssens, M. Filibian, M. Martinez-Belmonte, E. C. Escudero-Adan, P. Carretta, P. Ballester, J. R. Galan-Mascaros

“Cation-directed dimeric versus tetrameric assemblies of lanthanide-stabilized dilacunary Keggin tungstogermanates”

*Chem. Eur. J.* (2014) 20, page 12144-12156

B. Artetxe, S. Reinoso, L. San Felices, L. Lezama, J. M. Gutierrez-Zorrilla, J. A. Garcia, J. R. Galan-Mascaros, A. Haider, U. Kortz, C. Vicent

“Transition metal complexes with oligopeptides: single crystals and crystal structures”

*Dalton Trans.* (2014) 43, page 9821–9833

V. Lillo, J. R. Galan-Mascaros

“Architectures in Copper Metal-Organic Frameworks from 4-Substituted Anionic 1,2,4-Triazoles”

*Eur. J. Inorg. Chem.* (2014) 19, page 3125–3132

V. Gómez, J. Benet-Buchholz, E. Martín, J. R. Galan-Mascaros

“A fast metal-metal bonded water oxidation catalyst”

*J. Catal.* (2014) 315, page 25–32

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“Light-Driven Water Oxidation with Metal-Hexacyanomethylate Heterogeneous Catalysts”

*ACS Catal.* (2014) 4, page 1637–1641

S. Goberna-Ferron, W. Y. Hernandez, B. Rodriguez-Garcia, J. R. Galan-Mascaros

“Hysteretic Spin Crossover above Room Temperature and Magnetic Coupling in Trinuclear Transition-Metal complexes with Anionic 1,2,4-Triazole Ligands”

*Chem. Eur. J.* (2014) 20, page 5369-5379

V. Gómez, J. Benet-Buchholz, E. Martín, J. R. Galan-Mascaros