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Evidencing size-dependent cooperative effects on spin cross-over nanoparticles of Hofmann-type [Fe(pz)Pt(CN)₄] coordination polymers.

Laure Guenee¹, Teresa Delgado², Cristian Enachescu³, Antoine Tissot⁴, Andreas Hauser², Céline Besnard⁵

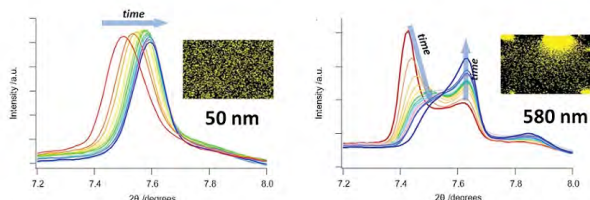
1. University of Geneva, Geneva, Switzerland
2. Department of physical chemistry, University of Geneva, Geneva, Switzerland
3. Department of physics, University of Alexandre Ioan Cuza, Iasi, Romania
4. Institut des matériaux poreux de Paris, ENS, Paris, France
5. Laboratory of crystallography, university of Geneva, Geneva, Switzerland

email: laure.guenee@unige.ch

Photo-induced processes are of paradigmatic importance in many fields, ranging from biology where light harvesting is the basic process of photosynthesis, to solid-state physics where light can be applied to control the electronic properties of solids. In this context, spin crossover compounds are fascinating photoswitchable materials, with possible applications in sensing or memory devices. However, such materials need to be synthesized as nanoparticles or thin films in order to be incorporated into functional devices. Therefore, the effect of size reduction on the thermo- and photo-switching properties has been abundantly described and modelled within the past few years [1]. However, no direct experimental evidence was made so far on the microscopic origin of the size reduction effects.

Following a previous structural study of the high spin to low spin relaxation dynamics of the porous coordination network [Fe(pz)Pt(CN)₄]·2.6H₂O in the bulk state [2], nanoparticles of [Fe(pz)Pt(CN)₄] were synthesised and the HS to LS relaxation through the light-induced excited spin-state trapping (LIESST) effect is investigated using synchrotron X-ray powder diffraction.

We evidence a clear limiting particle size below which the HS to LS relaxation adopts a different mechanism, indicating a drastic change in cooperative processes. We also provide a qualitative explanation of this observed change in cooperativity upon size reduction within the framework of a mechanoelastic model.



References:

- [1] Bousseksou, A.; Molnar, G.; Salmon, L.; Nicolazzi, W., (2011) *Chemical Society Reviews*, 40 (6), 3313-3335.
- [2] Delgado, T.; Tissot, A.; Besnard, C.; Guénée, L.; Pattison, P.; Hauser, (2015). A., *Chemistry – A European Journal*, 21 (9), 3664-3670.

Keywords: Spin crossover, LIESST, relaxation dynamics

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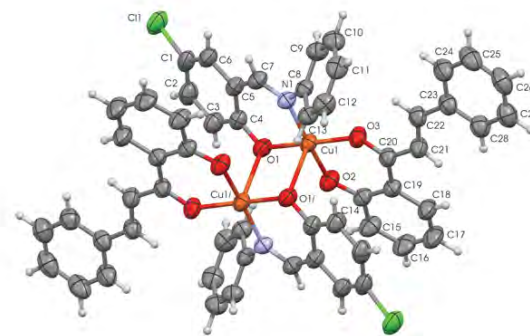
Crystal structures and bioactivity studies of four novel chalcone and flavonol copper(II) complexes containing Schiff base co-ligand

Aleksandar Višnjevac¹, Adnan Zahirović², Irma Osmanković², Emir Turkušić², Emira Kahrović²

1. Zavod za fizičku kemiju, Institut Ruđer Bošković, Zagreb, Croatia
2. Department of Chemistry, Faculty of Science, University of Sarajevo, Sarajevo, Bosnia & Herzegovina

email: aleksandar.visnjevac@irb.hr

Four new heteroleptic copper(II) complexes having chalcone or flavonol ligands and Schiff base (*N*-phenyl-5-chlorosalicylideneimine) as co-ligand were prepared, chemically and structurally characterized and investigated as functional biomimetic catecholase models. The complexes were prepared by the solution synthesis and crystal and molecular structures were determined by X-ray diffraction. Complexes were chemically characterized by elemental analysis, infrared and electron spectroscopy as well as by electrochemical measurements. Copper(II) chalcone complexes, with square-pyramidal CuO₄N core, are binuclear, featuring phenolate oxygen from the Schiff base as a bridging ligand, while copper (II) flavonol complexes are mononuclear, and reveal a square planar CuO₃N coordination core. Catalytic activity of the complexes in 3,5-di-*tert*-butylcatechol oxidation was confirmed by spectrophotometric and electrochemical measurements. Kinetic measurements revealed that the binuclear (chalcone-containing) complexes have enhanced catalytic activity as compared to the mononuclear Cu(II) flavonol complexes. Relatively high *k*_{cat} values (300 – 750 h⁻¹) confirmed their respectable biomimetic catecholase-like activity.



Keywords: copper, Schiff base, chalcone, flavonol, catecholase activity