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JOHANNES GUTENBERG UNIVERSITÄT MAINZ

SWITCHCATALYSIS

H2020-MSCA-IF-2014 project

Project ID: 659614
From 01.06.2015 **to** 31.05.2017
EU contribution: 159 460 EUR

What is the project

Switchable catalytic activity of spin crossover materials

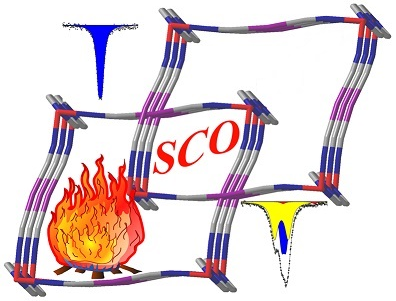
Spin crossover (SCO) is an intensively studied and highly versatile representative of molecular switches. The change of numerous physical properties during the spin transition has provoked a wide inclusion of SCO materials into various electronic, photonic and mechanical experiments. The main question asked in this project is how the drastic electronic and structural reorganizations accompanying spin transition will influence the catalytic activity of SCO complexes and composites. These studies will cover the redox catalytic activity of SCO molecular complexes, nanoparticles and composites, photocatalytic properties of SCO complexes, catalysis by conjugates with enzymes, and other switchable materials with catalytic activity. The expected results will allow the creation of switchable catalysts and will contribute to the fundamental knowledge on the spin-dependent catalytic activity of metallic centres. This project aims to combine the background of an experienced researcher that works in the domain of spin crossover materials, and the competence of a hosting group that deals with functional nanoparticles including their catalytic and photocatalytic activities. This combination of expertise supported by the facilities of Johannes Gutenberg University will create the optimal conditions for the realization of scientific purposes included in this project and will conduce to the efficient knowledge transfer between the experienced researcher and the host laboratory.

Who we are

Coordinator
Prof. Dr. Wolfgang Tremel

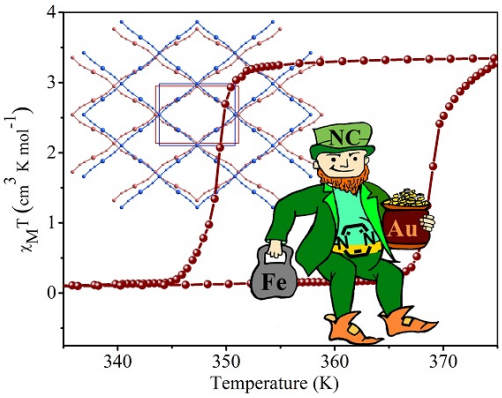
Principal investigator
Dr. Illia Guralskyi

What is done



High temperature spin crossover in [Fe(pyrazine){Ag(CN)$_2$}$_2$] and its solvate
I.A. Gural'skiy, S.I. Shylin, B.O. Golub, V. Ksenofontov, I.O. Fritsky and W. Tremel
New J. Chem. **2016**, 40, 9012-9016. DOI: 10.1039/C6NJ01472K

A high temperature spin crossover (T_{up} = 367 K) was detected in a metal–organic framework [Fe(pz){Ag(CN)$_2$}$_2$]·MeCN (pz = pyrazine). Upon heating, this solvate released acetonitrile guest molecules, which slightly shifted the transition temperature of the complex (T_{up} = 370 K and T_{down} = 356 K).

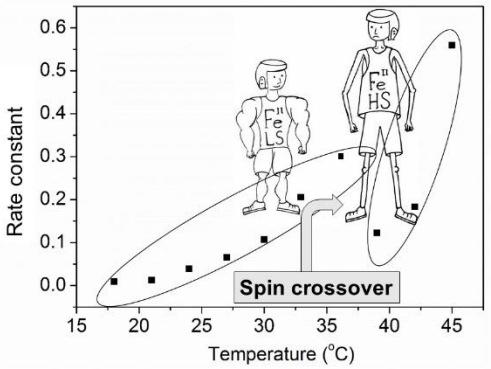


Cooperative High-Temperature Spin Crossover Accompanied by a Highly Anisotropic Structural Distortion

I.A. Gural'skiy, B.O. Golub, S.I. Shylin, V. Ksenofontov, H.J. Shepherd, P.R. Raithby, W. Tremel and I.O. Fritsky

Eur. J. Inorg. Chem. **2016**, 2016, 19, 3191-3195. DOI: 10.1002/ejic.201600406

Spin transitions are a spectacular example of molecular switching that can provoke extreme electronic and structural reorganizations in coordination compounds. A new 3D cyanoheterometallic framework, $[Fe(pz)\{Au(CN)_2\}_2]$, has been synthesized in which a highly cooperative spin crossover has been observed at 367 and 349 K in heating and cooling modes, respectively. Mössbauer spectroscopy revealed a complete transition between the diamagnetic and paramagnetic states of the iron centres. The low-spin-to-high-spin transition induced a drastic structural distortion involving a large one-directional expansion (ca. 10.6 %) and contraction (ca. 9.6 %) of the lattice. Negative thermal expansion along the c axis was detected below and above the transition temperature.



Spin-State Dependent Redox Catalytic Activity of a Switchable Iron(II) Complex

I.A. Gural'skiy, S.I. Shylin, V. Ksenofontov, W. Tremel

Eur. J. Inorg. Chem. **2017**

DOI: 10.1002/ejic.201700454

The spin state of catalytically active 3d metal centers plays a significant role for their activity in enzymatic processes and organometallic catalysis. Here we report on the catalytic activity of a Fe(II) coordination compound that can undergo a cooperative switch between low-spin (LS) and high-spin (HS) states. Catalytic measurements within 291 - 318 K temperature region reveal a drastic drop of the catalytic activity upon conversion of metallic centers from the LS to the HS form. For a thermoswitchable $[Fe(NH_2trz)_3]Br_2$ complex (T_{up} = 305 K), an activation energy is found to be considerably lower for the LS state (158 kJ mol^{-1}) comparing to the HS state (305 kJ mol^{-1}). Mössbauer analysis reveals that this is related to a higher conversion of a LS complex upon oxidation. The comparisons with another polymorph of $[Fe(NH_2trz)_3]Br_2$ (T_{up} = 301 K) and with $[Fe(NH_2trz)_3](ClO_4)_2$ (T_{up} = 240 K) are made. These results show the perspective of spin-crossover compounds to compare a catalytic activity of different spin states within the same material when other differentiations are minimized.

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