

## MS36-P25

## Structures and physical properties of some derivatives of 2,2',6',2''-terpyridine chelating Fe/Co metal complexes

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The multi-functional metal complex with magnetic, luminescence, or conductivity properties is one of the directions to design new modern materials. Spin crossover (SCO) compound is one kind of these complexes due to its potential applications to sensors, information storage, cantilever and so on. In this work, we modify terpyridine to 4'-(2-Furyl)-2,2',6',2''-terpyridine (ftpy) and 1-methyl-1H-Pyrrol-2-yl-2,2',6',2''-terpyridine (mtpy), and successfully obtained metal complexes  $M(II)L_2(BF_4)_2$  ( $M = Fe(II), Co(II)$ ;  $L = ftpy, mtpy$ ). In these metal complexes,  $Co(II)(ftpy)_2(BF_4)_2 \cdot 1.5H_2O$  (complex **1**) exhibits SCO behavior from high spin (HS) state with  $\mu_{eff} = 4.10$  B.M. at 350K to low spin (LS) state with  $\mu_{eff} = 2.14$  B.M. at 100K, but  $Co(mtpy)_2(BF_4)_2$  (complex **2**) only displays HS state. The other Fe(II) complexes both exhibit diamagnetism. To resolve how structure variation leads to the SCO phenomenon so that we can realize why complex **1** exhibits SCO character, the temperature dependent powder x-ray diffraction (PXRD) measurements are carried out at TPS09A beamline and the high resolution PXRD data are analyzed by Rietveld refinement to obtain detailed structural information. The results indicate that the crystal structures are still in triclinic system from 90K (LS) to 350K (HS) with averaged Co-N distance varied from 2.02(3) Å to 2.10(1) Å. Taking insight into crystal packing structure, one H<sub>2</sub>O is located at ~ 2.41 Å away from one of furan in complex **1**, but no solvent molecule in complex **2**. This short distance may indicate intermolecular interaction plays a critical role in tuning SCO phenomenon. In addition, the temperature dependent of x-ray absorption spectroscopy (XAS) is applied to study the electronic structures of complex **1**. Moreover, the UV absorption and photoluminescence characters of ftpy and mtpy are also discussed in this study.

Keywords: PXRD, XAS, spin crossover

## MS36-P26

## Unexpected long-lived photogenerated High-Spin phase investigated by X-ray diffraction

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Spin crossover compounds are interesting photoswitchable materials, with possible applications in sensing or memory devices. At low temperature the Low-Spin state can be excited into the photoexcited High-Spin state through the Light-Induced Excited Spin-State Trapping (LIESST) effect. The relaxation time is however usually short at higher temperatures.

The spin-crossover compound  $[Fe(n-Bu-im)_3(tren)](PF_6)_2$ <sup>1</sup> shows an unusual long relaxation time at 80K of 20 hours after Light-Induced Excited Spin-State Trapping when irradiated at 80 K. This is more than 40 times longer than the 80K relaxation time when irradiated at 10 K. To explain this unusual behavior single crystal structures were determined after irradiation at low temperature and at 80K. The structures of the two excited High-Spin states differ in the configuration of the side alkyl chains of the compound. Using synchrotron radiation, the long relaxation at 80K could be monitored by single-crystal X-ray diffraction. We showed that the rearrangements of the alkyl chains, which undergo order-disorder transitions, are responsible for the unexpected long relaxation time.

These results highlight the importance of structural studies to better understand and control the LIESST photoexcited states. Multimetastability can be exploited to tune the properties of the system.

