Crystal structure and magnetic properties of iron(II) and cobalt(II) complexes containing tridentate pyridine-tetrazolate ligand: A study by x-ray diffraction and x-ray absorption spectroscopy

I.-J. Hsu¹, W.-R. Lai¹, T.-J. Lin¹, C.-Y. Chen¹, C.-W. Yang¹, Y.-A. Chen¹, B.-H. Chen², Y.-C. Chuang², H.-S. Sheu², C.-W. Pao², J.-M. Chen², and M.-H. Chiang³

¹Department of Molecular Science and Engineering, National Taipei University of Technology, Taipei 10608, Taiwan, ²National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu Science Park, Hsinchu 30076, Taiwan, ³Institute of Chemistry, Academia Sinica, Nangang, Taipei 11529, Taiwan

Keywords: x-ray diffraction, x-ray absorption spectroscopy, spin transition

Materials with spin transition behavior are good candidates to prepare controllable switches for the applications of nanotechnology. To investigate the suitable compounds for such applications, Fe(II)/Co(II) complexes based on substituted 2,2′:6′,2′′-terpyridine and pyridine-2,6-ditetrazolate ligands were synthesized, and the crystal structures and electron configurations were characterized by X-ray diffraction and X-ray absorption spectroscopy (XAS), respectively. In this study, three pyridine related tridentate ligands, which are 2,2′:6′,2′′-terpyridine (tpy), 4′-(furan-2-yl)-2,2′:6′,2′′-terpyridine (ftpy), and 2-(1H-tetrazol-5-yl)-6-(2H-tetrazol-5-yl)pyridine (pydtz) were used to synthesize a series of cobalt(II) or iron(II) complexes with formula M(L₁)²(X)₂, M(L₂)(X)₂, and M(L₁)(L₂) (M=Fe or Co; L₁, L₂=ftpy, tpy or pydtz; X= BF₄⁻ or NCS⁻¹). All complexes are six-coordinate complexes with {MN₆} core. Co(ftpy)(BF₄)·1.5H₂O and Co(ftpy)(NCS)·C₇H₅O exhibit spin crossover phenomenon with T₁/₂ around 175K and 270K, respectively. A replacing Co(II) by Fe(II) yielded the complexes with low spin state at room temperature. However, two mixing ligands of Fe(pydtz)(tpy) and Fe(pydtz)(ftpy) are low spin and high spin at room temperature, respectively. Fe/Co L_II,III-edge XAS in combination with multiplets simulation were used to study these complexes, which indicate that the order of ligand filed strengths is tpy > ftpy > pydtz. More discussions will be made by comparing the experimental results with M-N bond distances and electron configurations at room temperature.