Synthesis of SCO Fe^{II} complexes with novel π-extended 2,2'-biimidazole ligands

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Spin crossover (SCO) is a phenomenon observed for certain transition metal complexes with electronic configuration $3d^4$-$3d^7$. The conversion between the low-spin (LS) and high-spin (HS) states is usually driven by a variety of external perturbations, such as temperature, pressure, or light. The switching between the enthalpically preferred LS state and entropically favorable HS state is accompanied by dramatic changes in the metal-ligand bond lengths, unit cell volume, optical absorption spectrum, and magnetic susceptibility.[1] These changes make SCO materials suitable for applications in sensors, memory, and display devices.

One of the central challenges in the SCO research is to initiate strongly cooperative interactions known to lead to abrupt spin transitions and thermal hysteresis that can be harvested as a memory effect. One of the strategies to enhance the cooperativity is to design SCO complexes with supramolecular interactions such as π-stacking of aromatic fragments or hydrogen bonding.[2]

In this work, we report syntheses and characterization of heteroleptic complexes of $[Fe(tpma)(L)](ClO_4)_2$ (tpma = tris(pyridin-2-ylmethyl)amine) with novel π-extended biimidazole-type ligands (L) bearing 2,3-dimethyl-naphthalene-, 6,7-dimethyl-2,3-diphenyl-quinoxaline, and 2,3-dimethyl-anthracene pendant fragments. Solvent-free naphthalene-functionalized complex $[Fe(tpma)(xnap\text{-}bim)](ClO_4)_2$ exhibits abrupt spin transition at $T_{1/2}$ = 127K with a narrow 1 K hysteresis loop. In contrast, polymorph of this complex that contains one interstitial molecules of pyridine exhibits gradual SCO. Anthracene-functionalized complex $[Fe(tpma)(anthra\text{-}bim)](ClO_4)_2$ also crystallizes as two polymorphs. Structural studies at 100, 230, and 300 K revealed dramatic changes in the N-Fe-N biting angles and Fe-N distances, indicating the occurrence of temperature-induced SCO. Complex $[Fe(tpma)(quin\text{-}bim)](ClO_4)_2$ (quin-bim = 6,7-dimethyl-2,3-diphenyl-quinoxaline-2,2'-biimidazole) showed only HS state at 100 and 230 K. In the crystal packing the mononuclear cations form stacks along b axis. We discuss how the observed magnetic behavior correlates with changes in the crystal packing and interactions between the pendant aromatic substituents on the aforementioned complexes.

1. Brooker, S. Spin crossover with thermal hysteresis: practicalities and lessons learnt. *Chem. Soc. Rev.* **2015,** *44*, 2880-2892.
2. Zhang, X.; Xie, H.; Ballesteros-Rivas, M.; Wang, Z.-X.; Dunbar, K. R. Structural distortions of the spin-crossover material $[Co(pyterpy)_2](TCNQ)_2$ mediated by supramolecular interactions. *J. Mat. Chem. C* **2015,** *3*, 9292-9298.