Modular Design of Multifunctionality in TCNQ-Based Fe(II) Spin Crossover Complexes

Ökten Üngör[1], Eun Sang Choi[2], Michael Shatruk[1]

[1]*Florida State University, Department of Chemistry & Biochemistry, Tallahassee FL 32306, USA*

1800 E Paul Dirac Dr, Tallahassee, FL 32306, USA

Fe(II) coordination complexes with ligands of an intermediate field strength often show witching between the high-spin (HS) and low-spin (LS) electronic configurations, known as spin crossover (SCO). This spin-state conversion is achieved by changes in temperature, pressure, or photoexcitation, which make SCO complexes promising materials for various applications that rely on bistable systems. Multifunctional materials that exhibit both spin-state switching and conductivity can be created by combining Fe(II) SCO complexes with organic TCNQ-type electron acceptors. In such complexes, $TCNQ^{\bullet\delta-}$ radical anions are typically arranged in layers of one-dimensional stacks that provide conducting pathways (Fig. 1). The stacking distance can be affected by structural changes induced by the alteration in the electronic configuration and, thus, bond lengths at the Fe(II) center, resulting in synergy between SCO and conductivity. The synthesis of such materials can be approached in two ways: (1) by coordinating $TCNQ^{\bullet\delta-}$ ligands directly to the Fe(II) center, which is partially protected by blocking ligands that limit the growth of extended structures or (2) by co-crystallizing completely blocked Fe(II) centers with free $TCNQ^{\bullet\delta-}$ radicals. We will discuss several examples of the second approach, in which homoleptic Fe(II) cationic SCO complexes with tridentate 2,6-bispyrazolyl-pyridine (bpp) type ligands have been co-crystallized with fractionally-charged $TCNQ^{\bullet\delta-}$ radical anions. The temperature- and solvent-dependent magnetic behavior and transport properties of these materials will be discussed. We will also present new pathways to improve the design of such molecule-based conductors with spin-state switching properties. To the best of out knowledge, we report the first examples of Fe(II) based conducting molecular materials with abrupt temperature-driven spin transitions.

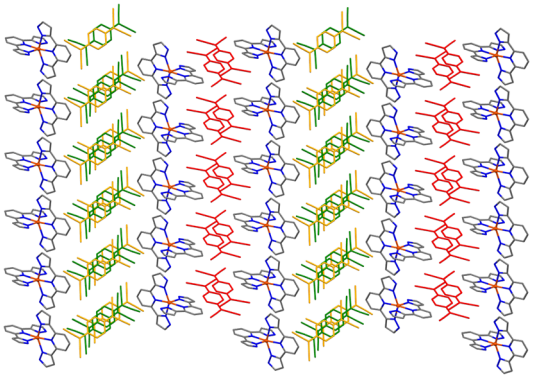

Figure 1. Crystal structure of $[Fe(3\text{-bpp})_2](TCNQ)_3 \cdot 5MeCN$ showing the segregated layers of cationic and anionic layers.