

Aryl Substituent Modulated Spin-Crossover Behavior in Fe(II) Complexes: Interplay of Symmetry Breaking, Structural Disorder, and Lattice Effects

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We report the design and systematic investigation of three Fe(II) spin-crossover (SCO) complexes of the type [Fe(H₂Bpz₂)₂(bipy-R)] (R = phenyl (**1**), 1-naphthyl (**2**), and 2-naphthyl (**3**)), aimed at elucidating the role of aryl substituents in tuning SCO behavior. Variable-temperature magnetic measurements reveal that all three complexes exhibit gradual and incomplete SCO, with distinct transition pathways ranging from weakly resolved two-step behavior to well-defined stepwise transitions. Single-crystal X-ray diffraction studies demonstrate that these differences originate from variations in molecular packing, symmetry, and local coordination environments. Complex **2** undergoes a symmetry-breaking transition from *Pbcn* to *Pna*2₁ upon cooling, generating two inequivalent Fe(II) sites. Persistent coordination disorder in coordination anions further gives rise to locally mixed high-spin (HS) and low-spin (LS) geometries and lead to a stepwise SCO process. In contrast, complexes **1** and **3** contain inequivalent Fe sites across the entire temperature range, resulting in site-selective spin conversion and incomplete transitions. Complementary ⁵⁷Fe Mössbauer, UV-vis, and Raman spectroscopic analyses support the coexistence of spin states and reveal that ligand vibrations and MLCT transitions are sensitive to spin-state changes. The combined results highlight that SCO behavior in these systems is governed primarily by structural factors, including symmetry breaking, lattice constraints, and intermolecular interactions (π⋯π and C-H⋯π), rather than purely electronic substituent effects (Figure 1). This study demonstrates that subtle modification of aryl substituents provides an effective strategy to modulate SCO pathways through control of lattice cooperativity and local structural heterogeneity.



Figure 1. Schematic representation of magneto-structural correlations in complexes **1-3**.

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