

Improved Cooperativity of Spin-Labile Iron(III) Centers by Self-Assembly in Solution

Claudio Gandolfi,[†] Christian Moitzi,[‡] Peter Schurtenberger,[‡] Grace G. Morgan,[§] and Martin Albrecht^{*,†}

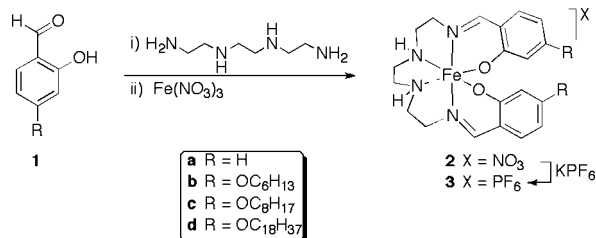
Department of Chemistry and Adolphe Merkle Institute, University of Fribourg, CH-1700 Fribourg, Switzerland, and UCD School of Chemistry & Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland

We report on the markedly increased spin crossover activity of materials when self-assembled in solution. Spin crossover is directly related to long-range elastic interactions, typically observed in the solid state, and the transition may be gradual over a large temperature range.¹ Effects such as solvent cocrystallization often modify the transition in an unpredictable way. This is predominantly because spin transitions are crucially affected by intermolecular interactions beyond crystal packing effects, such as elastic strain.² Such intermolecular interactions are the classical domain to be engineered by supramolecular chemistry.³ Specifically, the promotion of close metal–metal interactions may stimulate cooperative behavior, which is expected to result in more abrupt spin transitions. This concept has been implemented for engineering of spin crossover active materials in the solid state⁴ and recently also in soluble nanoparticles.⁵ Here, we have used a hydrophilic/lipophilic bias⁶ for inducing a favorable arrangement of potentially spin-labile iron(III) centers. Supramolecular organization in solution leads, most remarkably, to a new type of magnetically active material for liquid-phase processing.

The Fe(sal₂trien) complex **2a** is known to undergo a gradual spin transition in the solid state.⁷ Ligand functionalization and introduction of a lipophilic side chain was accomplished by selective alkylation of 4-hydroxysalicylaldehyde. Condensation of the aldehyde **1** with triethylenetetramine and subsequent metalation with iron(III) nitrate, either in situ or after isolation of the hexadentate ligand precursor, afforded the alkyl-tailed complexes **2b–d** (Scheme 1). Metathesis of the noncoordinating anion was straightforward because of the different solubility properties of KPF₆ and the alkyl-tailed iron(III) complexes and gave, after extraction, complexes **3**. A single crystal structure determination of complex **3c** unambiguously confirmed the connectivity pattern (Figure 1a). The bond lengths around the two crystallographically independent iron centers are diagnostic for high spin Fe^{III} at 173 K.^{1c} The mutual cis coordination of the phenolate moieties arranges the alkyl chains in the same direction and maximizes intermolecular van der Waals interactions. As a consequence, the crystal packing displays apolar and polar layers consisting of the lipophilic side chains, and the charged metal coordination site and the PF₆[−] anions, respectively (Figure 1b).

Despite the layered crystal packing, complex **3c** does not exhibit thermochromic behavior in the solid state. Magnetic measurements indicate the absence of thermally induced spin crossover in the 30–300 K range and antiferromagnetism or zero-field splitting below 30 K.^{1c} Similar results have been obtained for complexes **2b–d**. This suggests that alkyl functionalization in **2** generates spin-stable Fe^{III} centers. The spin stability of **2d** in the solid state may

Scheme 1. Synthesis of Functionalized Fe(sal₂trien) Complexes



also originate from the absence of favorable metal–metal interactions, as powder diffraction showed this complex to be amorphous.

In contrast to the spin stability in the solid state, complex **2d** undergoes spin crossover in solution. The spin transition is indicated by thermochromic behavior with a color change from red at room temperature to dark blue when cooled below 230 K (CH₂Cl₂). A similar color change was reported for **2a** at 193 K.⁷ The thermochromism was associated with a spin transition from high spin (HS; $S = 5/2$) to low spin (LS; $S = 1/2$). The new absorption band of **2d** in the LS state at $\lambda_{\text{max}} = 650$ nm (inset Figure 2) reflects an energetically easier metal-to-ligand charge transfer, presumably due to a contraction of the M–L bonds upon spin crossover.

Temperature-dependent monitoring of the extinction at 650 nm indicated a relatively abrupt transition around 230–240 K for **2d** (Figure 2). Superimposition of the UV–vis spectra at different temperatures revealed an isosbestic point at $\lambda = 558$ nm ($\epsilon = 3700$ M^{−1} cm^{−1}), thus providing evidence for an equilibrium between the HS and the LS states. Hence, the two spin states of **2d** are distinctly

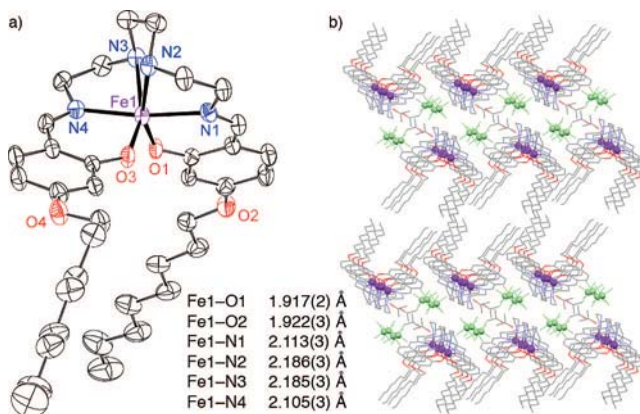


Figure 1. (a) ORTEP plot (50% probability) and pertinent bond lengths of one of the two crystallographically independent cations of **3c** at 173 K (hydrogen atoms omitted for clarity); (b) packing diagram of crystals of **3c** illustrating the polar and apolar layers of **3c** in the solid state (Fe, purple; N, blue; O, red; PF₆, green).

[†] Department of Chemistry, University of Fribourg.

[‡] Adolphe Merkle Institute, University of Fribourg.

[§] University College Dublin.

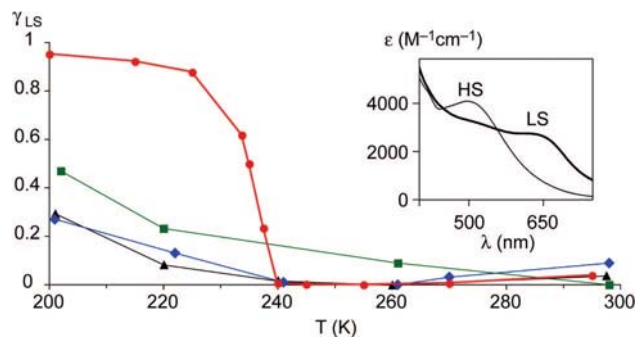


Figure 2. Fraction of LS complex (γ_{LS}) deduced from temperature-dependent UV–vis absorption at 650 nm for **2a** (■), **2b** (◆), **2c** (▲), **2d** (●); all 0.2 mM CH_2Cl_2 solutions. Inset: UV–vis spectra of **2d** at 220 K (LS, bold line) and 298 K (HS).

separated on the UV–vis time scale. No significant hysteresis has been observed upon repetitive heating–cooling cycles. Notably, the parent $\text{Fe}(\text{salt}_2\text{trien})$ complex **2a**, displays a gradual spin transition in solution over a 100 K temperature range. Similarly, no thermochromism was observed until 180 K for complexes **2b** or **2c** comprising shorter alkyl tails, suggesting that the alkyl chain length is crucial for promoting an abrupt spin transition.

Magnetic measurements confirmed the correlation between the color change and a spin crossover event. While the HS Fe^{III} signal could not be detected by EPR, the increasing isotropic resonance at $g = 2.16$ (CH_2Cl_2) upon cooling is diagnostic for the population of a LS Fe^{III} species.⁸ The high-spin nature of complex **2d** at room temperature was evidenced by determining the magnetic susceptibility using Evans' method.⁹ At 298 K, $\mu_{\text{eff}} = 5.47 \pm 0.16 \mu_{\text{B}}$ as expected for an $S = 5/2$ configuration of spin crossover Fe^{III} . Unfortunately, the limited solubility of **2d** in CH_2Cl_2 precluded ^1H NMR measurements at low temperature, and saturated solutions of **2d** at 230 K were too dilute to induce an accurately defined paramagnetic shift of the solvent signal.¹⁰

The abrupt spin transition of **2d** within 10 K suggests strongly cooperative behavior of the metal centers, which may be induced for example by self-organization of the molecules into supramolecular assemblies. Indeed, DLS measurements of solutions of **2d** revealed the presence of particles with hydrodynamic radius $R_{\text{H}} \approx 550$ nm and a large polydispersity. Analyses by cryogenic scanning electron microscopy (SEM) showed two major types of spherical particles, characterized by an average diameter of ca. 1 and 3 μm , respectively (Figure 3). While these results corroborate the DLS measurements, the SEM plots further suggest the particles to be superstructures composed of rodlike assemblies with a diameter of about 30 nm (inset Figure 3). High intensity SAXS experiments using synchrotron irradiation of **2d** are consistent with elongated objects featuring a cross-section diameter of 42 nm. Supercoils similar to DNA superstructures rather than simple micelle-type aggregates may account for the observed size of these nanorods (calculated length of **2d** in a fully stretched conformation is 30 Å).

No such distinct structures were observed with complexes **2b** and **2c** comprising shorter alkyl tails. This suggests that the abrupt spin crossover, exclusively observed with **2d**, is correlated with the supramolecular assembly of this compound in solution to form discrete aggregates. Such a structural model may rationalize the intermolecular cooperativity required for the observed abrupt spin transition in solution.

In conclusion, our results demonstrate that supramolecular principles can be successfully applied to engineer metal-centered function, as illustrated by the enhanced cooperativity and higher transition temperature induced in an originally poorly cooperating spin crossover

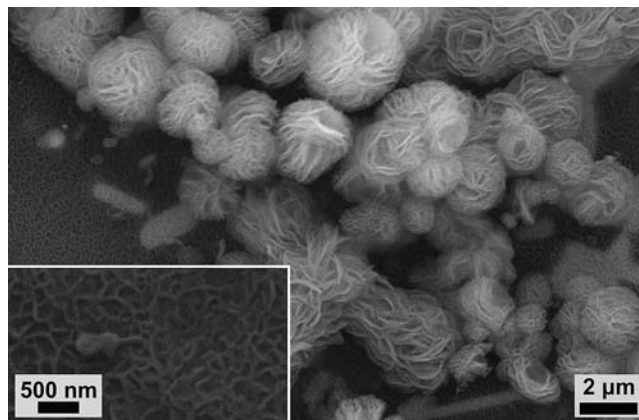


Figure 3. Cryo-SEM images of a representative section of self-assembled **2d**; two types of spherical particles are distinguishable featuring diameters of ca. 1 and 3 μm , respectively. Inset: nanosize rods as subcomponents of spherical microparticles.

iron(III) complex by self-assembly. Control and improvement of such function in solution is achieved through careful chemical modulation. We are currently investigating the generality of this approach for fabricating magnetically active materials for solution processing, ideally operating near room temperature.

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Supporting Information Available: Synthetic details and analytical data of complexes **2b–2d**, CIF for **3c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) Complex **2c**, which is more soluble, undergoes a gradual spin transition over a broad temperature range, from $\mu_{\text{eff}} = 5.44 \mu_{\text{B}}$ at room temp to the low spin state ($\mu_{\text{eff}} = 2.47 \mu_{\text{B}}$) at 180 K. A plot of μ_{eff} vs T correlates with the increase of the absorbance at 650 nm and indicates that the spectroscopic changes indeed reflect a spin transition.