

Supplementary Data for:

High Temperature Spin Crossover in Amide-Functionalised 2,6-bis(pyrazol-1-yl)pyridine Iron(II) Complex Revealed by Variable Temperature Raman Spectroscopy.

Max Attwood^a, Hiroki Akutsu^b, Lee Martin^c, Toby J. Blundell^c, Pierre Le Maguere^d, Scott S. Turner^{a, *}

^a Department of Chemistry, University of Surrey, Guildford, GU2 7XH, UK.

^b Department of Chemistry, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan

^c School of Science and Technology, Nottingham Trent University, Clifton Lane, NG11 8NS. UK.

^d Rigaku Americas Corporation, 9009 New Trails Drive, The Woodlands, TX 77381, USA

Additional Experimental Details

Synthesis of 2,6-dichloropyridine-4-carboxylic acid

Citrazinic acid (20.0 g, 0.129 mols) and benzyltriethylammonium chloride (32.3 g, 0.142 mols) in 40 ml of POCl₃ were heated to 140°C for 24 hrs under reflux with a CaCl₂ drying tube. After being cooled to room temperature, the brown mixture was poured on ice (400 g) and stirred for 2 hrs. Initial addition of the solution to water produces a thick brown sticky solid which was manually stirred for the first 30 minutes. The resulting brown solid was filtered off, washed with water and dissolved in ethyl acetate (400 ml). The organic phase was then washed with saturated NH₄Cl, dried over MgSO₄ and evaporated to dryness yielding a light brown powder. Yield: 18.553 g (75%).

Synthesis of 2,6-bis(pyrazol-1-yl)pyridine-4-carboxylic acid (bppCOOH)

A solution of pyrazole (2.0414 g, 30 mmol) in DMF (30 ml) was slowly added to a suspension of KH (1.203 g, 30 mmol) in DMF (10 ml) all under N₂ and cooled using an ice bath. The resulting slurry was heated to 70°C for 45 min and 2,6-dichloropyridine-4-carboxylic acid (1 g, 5.2 mmol) was added in one portion. The brown mixture was then heated to 130°C under N₂ for five days. DMF was removed *in vacuo* and distilled water (100 ml) was added. The mixture was acidified with conc. HCl (5 ml, 35% w/w) and the formed light brown precipitate was filtered and washed with water. The solid was dissolved in the minimum volume of hot acetone and let to stand overnight in the freezer forming light brown needle crystals. Products were obtained after filtration and washing with cold portions of acetone (3 x 3 ml). Yield: 0.946 g (71%). ¹H NMR (400 MHz, DMSO): δ 14.1 (bs, 1H), 9.01 (d, *J* = 2.35

Hz, 2H), 8.18 (s, 2H), 7.92 (d, $J = 1.14$ Hz, 2H), 6.67 (dd, $J = 1.69$ Hz, $J = 2.58$ Hz, 2H). ^{13}C NMR (400 MHz, DMSO): δ 165.41, 150.85, 145.03, 143.66, 128.87, 109.32, 108.55.

Thermogravimetric Analysis (TGA)

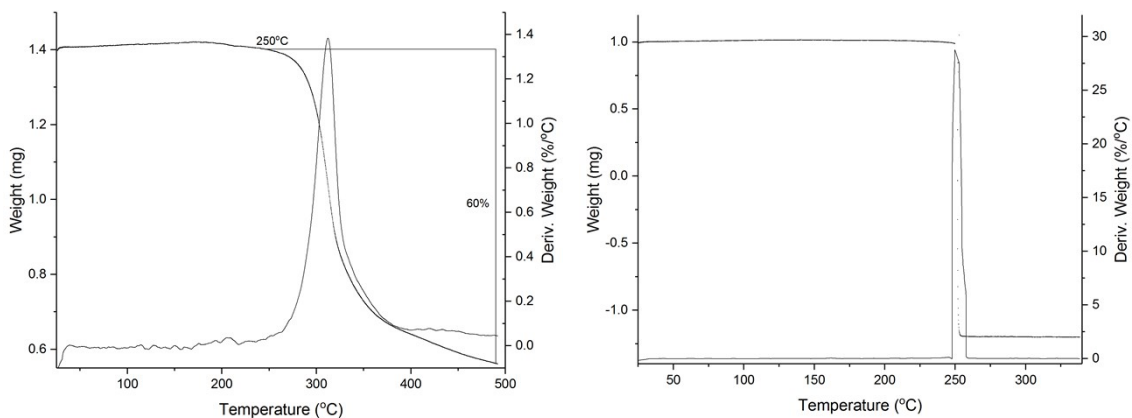


Figure S1: TGA for $[\text{Fe}(\text{bppCONH}_2)_2](\text{BF}_4)_2$ (left) and $[\text{Fe}(\text{bppCONH}_2)_2](\text{ClO}_4)_2$ (right) measured at a heating rate of 20 K/min.

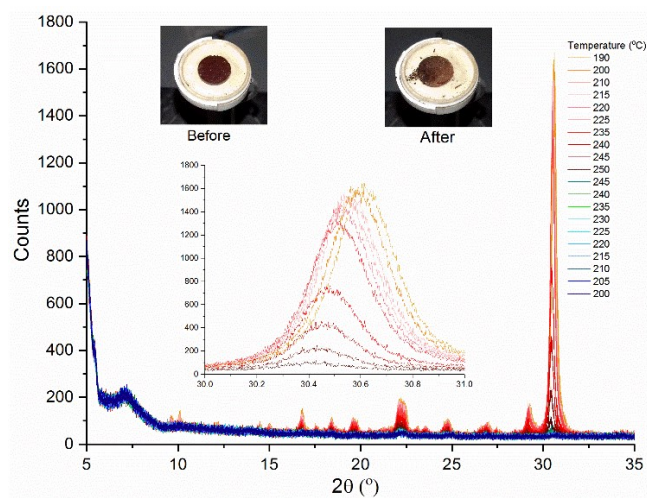


Figure S2: Variable temperature powder X-ray diffraction of a $[\text{Fe}(\text{bppCONH}_2)_2](\text{BF}_4)_2$ compressed pellet.