Photomagnetic properties of iron(II) spin crossover complexes of 2,6-dipyrazolylpyridine and 2,6-dipyrazolylpyrazine ligands

Chiara Carbonera,[a] José Sánchez Costa,[a] Victoria A. Money,[b] Jérôme Elhaïk,[c] Judith A.K. Howard,*[b] Malcolm A. Halcrow*[c] and Jean-François Létard*[a]

[a] *Institut de Chimie de la Matière Condensée de Bordeaux, UPR CNRS 9048 - Université Bordeaux 1, Groupe des Sciences Moléculaires, 87 Av. Doc. A. Schweitzer, F-33608 Pessac, France.*
Email: letard@icmcb-bordeaux.cnrs.fr
[b] *Department of Chemistry, University of Durham, South Road, Durham, U.K. DH1 3LE.*
Email: j.a.k.howard@durham.ac.uk.
[c] *School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, U.K. LS2 9JT.*
Email: m.a.halcrow@leeds.ac.uk

The photomagnetic properties of the following iron(II) complexes have been investigated: $[Fe(L^1)_2][BF_4]_2$ (**1**), $[Fe(L^2)_2][BF_4]_2$ (**2**), $[Fe(L^2)_2][ClO_4]_2$ (**3**), $[Fe(L^3)_2][BF_4]_2$ (**4**), $[Fe(L^3)_2][ClO_4]_2$ (**5**) and $[Fe(L^4)_2][ClO_4]_2$ (**6**) (L^1 = 2,6-di{pyrazol-1-yl}pyridine; L^2 = 2,6-di{pyrazol-1-yl}pyrazine; L^3 = 2,6-di{pyrazol-1-yl}-4-{hydroxymethy}pyridine; and L^4 = 2,6-di{4-methylpyrazol-1-yl}pyridine). Compounds **1**-**6** display a complete thermal spin transition centred between 200-300 K, and undergo the light-induced excited spin state trapping (LIESST) effect at low temperatures. The T(LIESST) relaxation temperature of the photoinduced high-spin state for each compound has been determined. The presence of sigmoidal kinetics in the HS→LS relaxation process, and the observation of LITH hysteresis loops under constant irradiation, demonstrate the cooperative nature of the spin-transitions undergone by these materials. All the compounds in this study follow a previously proposed linear relation between T(LIESST) and their thermal spin-transition temperatures $T_{1/2}$: $T(\text{LIESST}) = T_0 - 0.3T_{1/2}$. T_0 for these compounds is identical to that found previously for another family of iron(II) complexes of a related tridentate ligand, the first time such a comparison has been made. Crystallographic characterisation of the high- and low-spin forms of **5** and **6**, the light-induced high-spin state of **5**, and the low-spin complex $[Fe(L^4)_2][BF_4]_2$ (**7**), are described.

Electronic Supplementary Information

Fig. S1 View of the complex dication in the crystal structure of $[Fe(L^4)_2][BF_4]_2{\cdot}xH_2O$ (**7**·$x$$H_2O$, $x \approx 0.2$), with selected bond distances and angles.

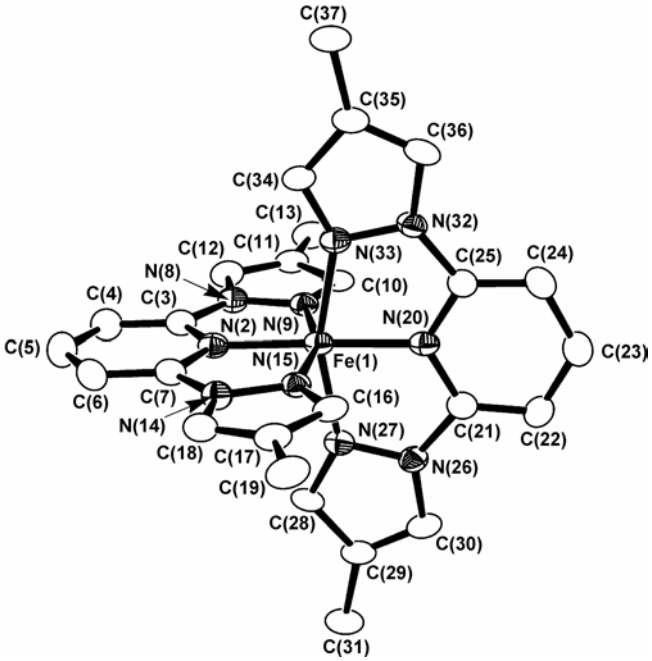

Fig. S1 View of the complex dication in the crystal structure of $[Fe(L^4)_2][BF_4]_2 \cdot xH_2O$ (**7**·xH_2O, $x \approx 0.2$). Thermal ellipsoids are at the 35% probability level, and all H atoms have been removed for clarity. Selected bond distances and angles (Å, °): Fe(1)–N(2) 1.892(3), Fe(1)–N(9) 1.964(3), Fe(1)–N(15) 1.968(3), Fe(1)–N(20) 1.888(3), Fe(1)–N(27) 1.972(2), Fe(1)–N(33) 1.971(3), N(2)–Fe(1)–N(9) 80.24(12), N(2)–Fe(1)–N(15) 80.51(11), N(2)–Fe(1)–N(20) 177.95(11), N(2)–Fe(1)–N(27) 98.99(11), N(2)–Fe(1)–N(33) 100.62(11), N(9)–Fe(1)–N(15) 160.74(12), N(9)–Fe(1)–N(20) 101.63(11), N(9)–Fe(1)–N(27) 91.84(10), N(9)–Fe(1)–N(33) 91.68(10), N(15)–Fe(1)–N(20) 97.63(11), N(15)–Fe(1)–N(27) 91.84(10), N(15)–Fe(1)–N(33) 91.16(10), N(20)–Fe(1)–N(27) 80.17(11), N(20)–Fe(1)–N(33) 80.22(11), N(27)–Fe(1)–N(33) 160.39(12).