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

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The photomagnetic properties of the following iron(II) complexes have been investigated: [Fe(L1)2][BF4]2 (1), [Fe(L2)2][BF4]2 (2), [Fe(L3)2][ClO4]2 (3), [Fe(L3)2][BF4]2 (4), [Fe(L4)2][ClO4]2 (5) and [Fe(L4)2][ClO4]2 (6) (L1 = 2,6-di{pyrazol-1-yl}pyridine; L2 = 2,6-di{pyrazol-1-yl}pyrazine; L3 = 2,6-di{pyrazol-1-yl}pyridine; and L4 = 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 T1/2: T(LIESST) = T0 − 0.3T1/2. T0 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(L4)2][BF4]2 (7), are described.

Electronic Supplementary Information

Fig. S1 View of the complex dication in the crystal structure of [Fe(L4)2][BF4]2·xH2O (7·xH2O, x ≈ 0.2), with selected bond distances and angles.
Fig. S1 View of the complex dication in the crystal structure of [Fe(L^3)₂][BF₄]₂·xH₂O (7·xH₂O, x ≈ 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).