Spin-Crossover and Nanoporosity: Magnetic, Structural and Guest-Exchange Studies

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Spin-crossover and permanent nanoporosity describe two highly desirable and traditionally independent properties concerning the design, synthesis and characterisation of functional coordination framework materials. By integrating these properties, we are developing a new series of *smart* materials capable of a physical response to their environment. Such capabilities include guest-induced electronic, magnetic and optical switching with applications towards chemical sensors, molecular switches and data storage materials.

The new network $[Fe(dps)_2Ag(CN)_2ClO_4]\cdot 3(C_2H_6O)$ (**1**) (dps = 4,4´-dipyridylsulfide) is the first three-dimensional framework to display a synergy of spin-crossover and nanoporosity (~46% void volume). Variable-temperature single-crystal X-ray diffraction (SCXRD) techniques were employed over the range 90 K-300 K to elucidate the structural consequences of a reversible low-spin to high-spin transition. Modified *in-situ* SCXRD techniques were used to observe the implications of guest-exchange on structural integrity and spin-crossover functionality.

Several unique properties of **1** have been demonstrated: 1) complete spin transition, incurring a 7.7% crystal volume change; 2) robustness to desorption at 375 K, with complete retention of structural integrity; and 3) sensitivity of spin-crossover to the presence of guest species. Additional guest-exchange studies also establish **1** to be a highly nanoporous framework that exhibits rapid, reversible and complete sorption/desorption of a range of small molecules.

Keywords: spin-crossover, nanoporosity, *in situ* SCXRD