

MULTI-FUNCTIONAL FRAMEWORK MATERIALS: NANOPOROSITY AND SPIN-CROSSOVER

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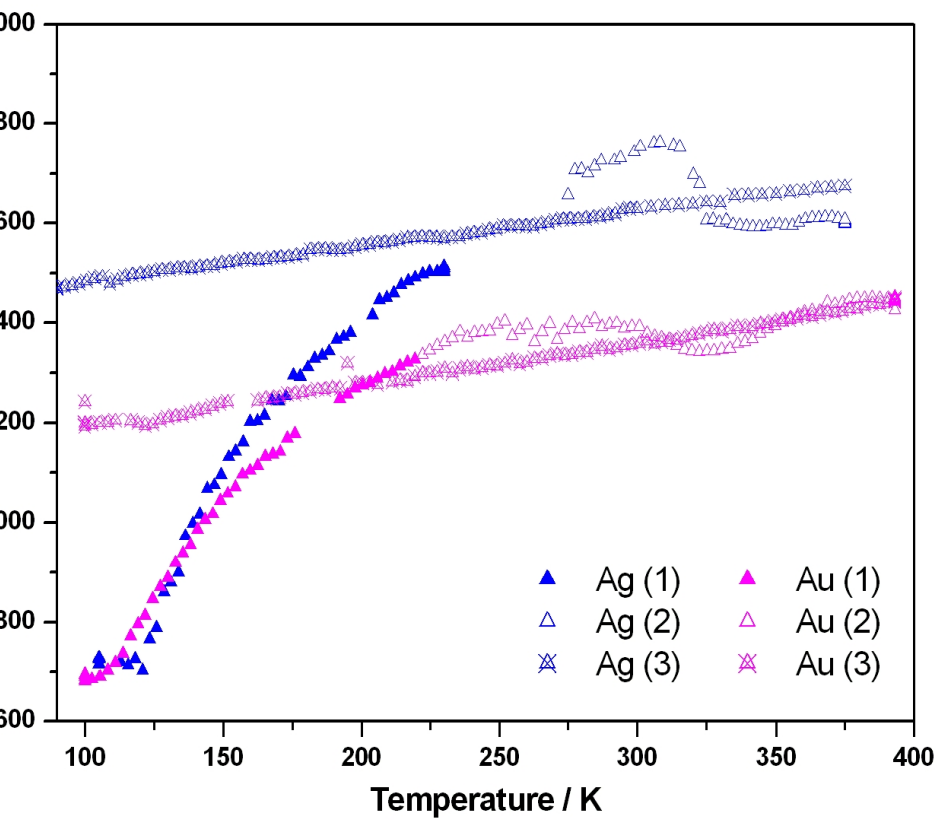
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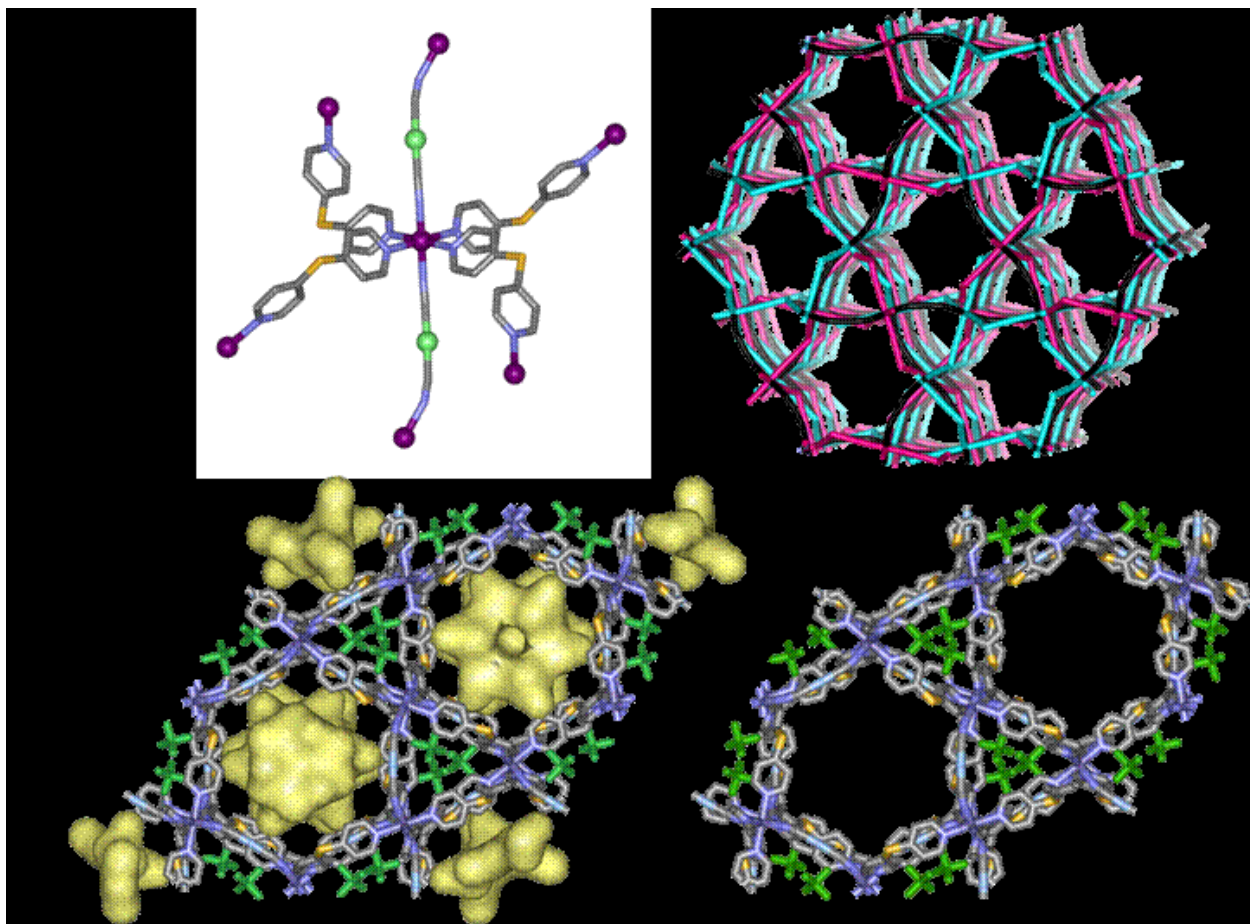
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The design of multifunctional coordination materials has become a dynamic and important area of advanced research in contemporary chemistry, whereby traditionally independent properties can be incorporated into the same material. Spin-crossover (electronic spin-state switching) and permanent nanoporosity describe two highly desirable and traditionally independent properties concerning the design, synthesis and characterisation of functional materials. The integration and synergism of these properties offer a new opportunity to develop novel materials capable of a dynamical response to their environment and with additional prospects for commercial potential beyond that of mass data storage devices or molecular storage and separation materials. For example, sensor capabilities become realized when chromic, electronic and magnetic properties characteristic to spin-crossover materials can be reversibly and selectively altered by specific guest-interactions.

Interplay between spin-crossover and guest-exchange presents new means to systematically investigate ligand field, structural, electronic and dynamic effects imposed by different guest influences. In particular, diffraction techniques provide an invaluable tool. Variable-temperature single-crystal X-ray diffraction (SCXRD) techniques are employed to monitor the structural consequences of a reversible high- \uparrow spin to low- \downarrow spin transition and to observe the implications of framework desolvation on structural integrity and spin crossover functionality. Furthermore, SCXRD and PXRD methods combined with *in-situ* guest exchange processes can be utilised to observe the dynamic host-guest interactions that influence the structure and multi-functionality demonstrated by these materials.





Left: VT-SCXRD data for the novel 3D-Spin-crossover and porous coordination framework (A) : $\text{Fe}^{\text{II}}(\text{dps})_2(\text{M}(\text{CN})_2)(\text{ClO}_4) \cdot x\text{EtOH}$, $\text{M}=\text{Ag}$, $\text{M}=\text{Au}$. (1) Single Crystals of $\text{M} = \text{Ag}$ and $\text{M} = \text{Au}$ were quench-cooled to ~ 90 K under a nitrogen cryostream, then heated *in-situ* up to 230 K. Thermal spin transition is observed here; (2) Desolvation of both crystals achieved by further heating to 375 or 395 K respectively, exhibiting robust nanoporosity; (3) Subsequent cooling of the crystals to 90 K. Spin-crossover has been inhibited, demonstrating functionality and sensitivity to guest species.

Right: Representation of the novel framework A . Top: Coordination sphere and the novel topology of the system; and Bottom: highlights the reversible guest exchange properties exhibited by this robust material.