High T bistability in SCO

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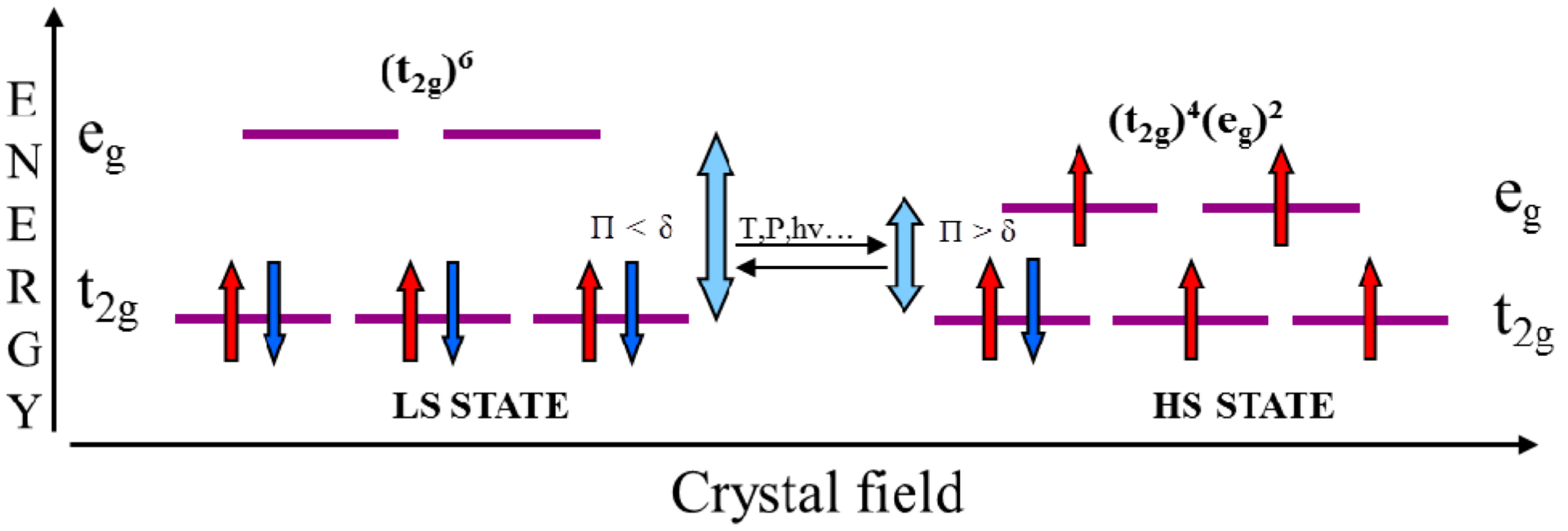
What is SCO?

spin crossover : a metal ion switches between different electronic spin states that can be induced by multiple external inputs, such as temperature, pressure, guest or light irradiation. This phenomenon can be explained by **electron–phonon coupling and elastic properties of the crystal lattice.**

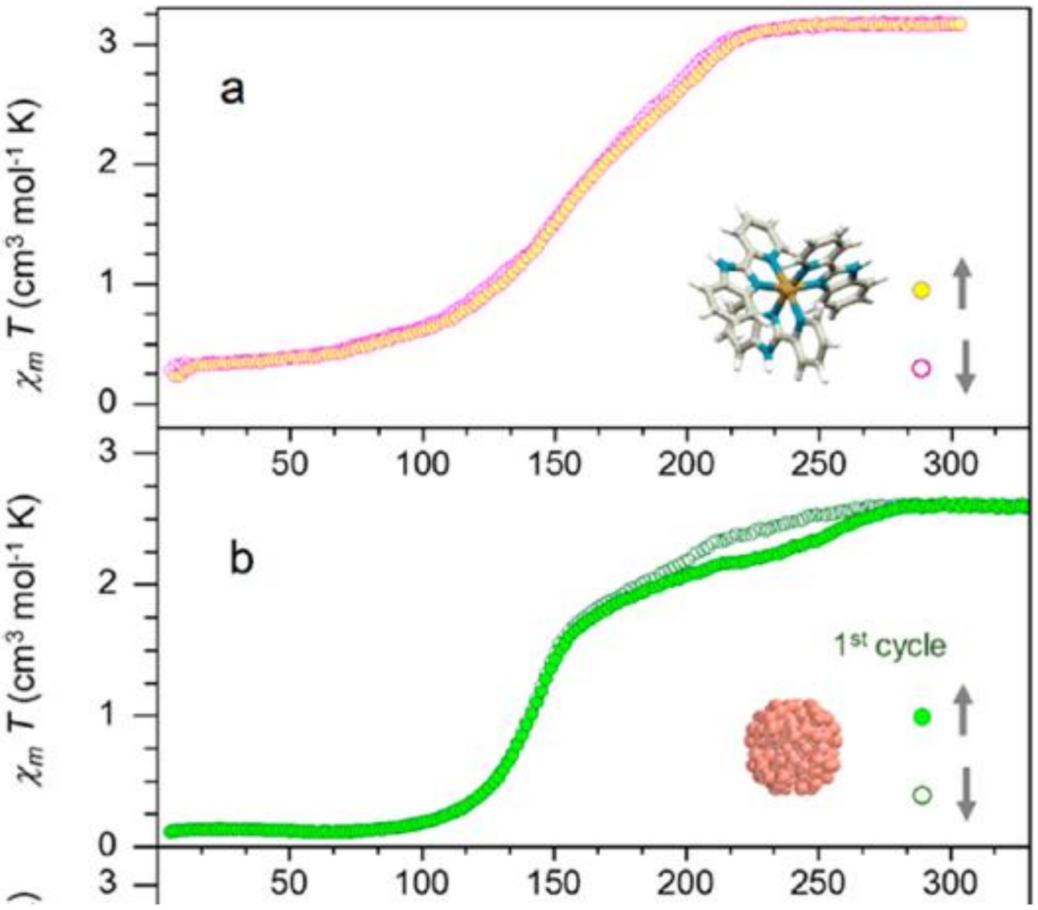
It can be used in memories, switching devices and sensors if HS and LS are both stable at room temperature.

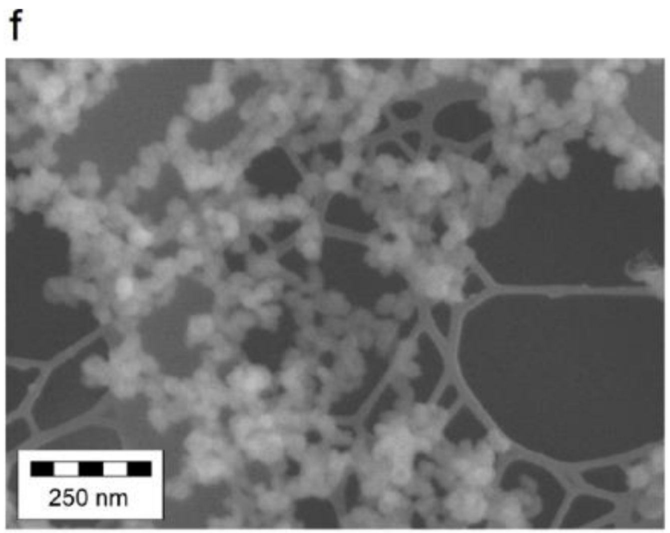


How to get high T HS and LS states?

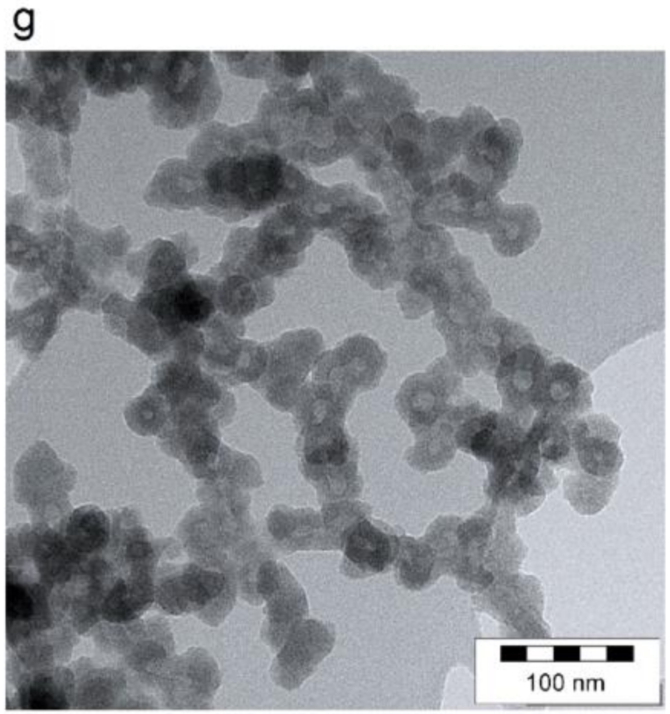
- 1. Different matrix in nanoparticle.
- 2. Substrate locking in thin film.
- 3. Hydrogen bonds between molecules.
- 4. Dipolar moment interacts with Polarization.

Nanopariticle





SEM

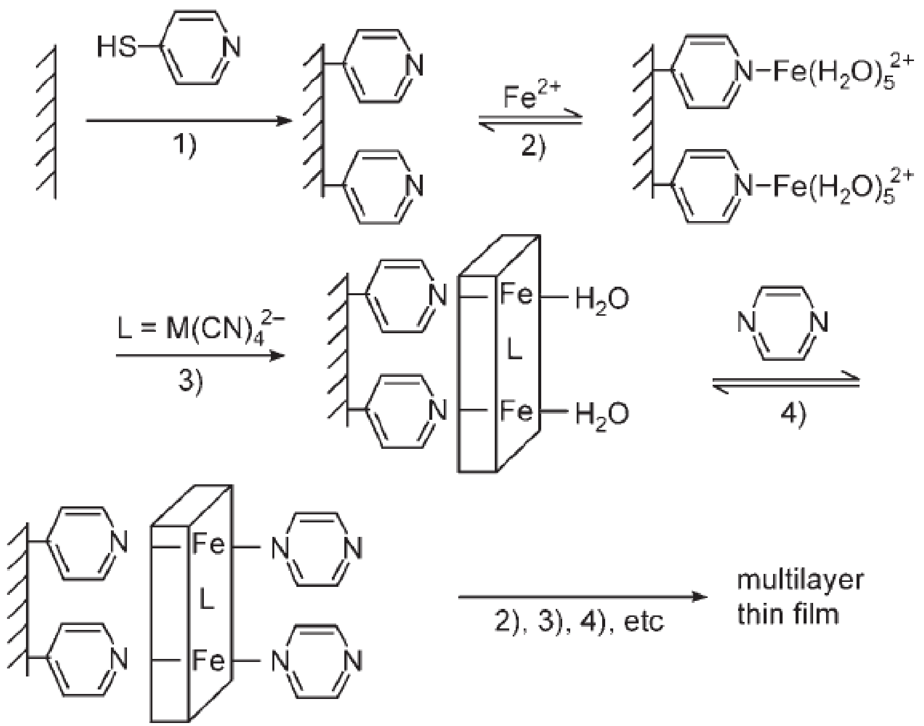


TEM

1. Core molecules vs P123 micelle contacted molecules. Different surface rigidity leads to diff Tc.
2. Size constraint by matrix boundary gives plasticity for core molecules.

Chem. Mater. 2017, 29, 8875-8883

Thin film



Scheme 1. Sequential assembly of [Fe(pyrazine){M(CN)$_4$}] (M = Ni, Pd, or Pt) films.

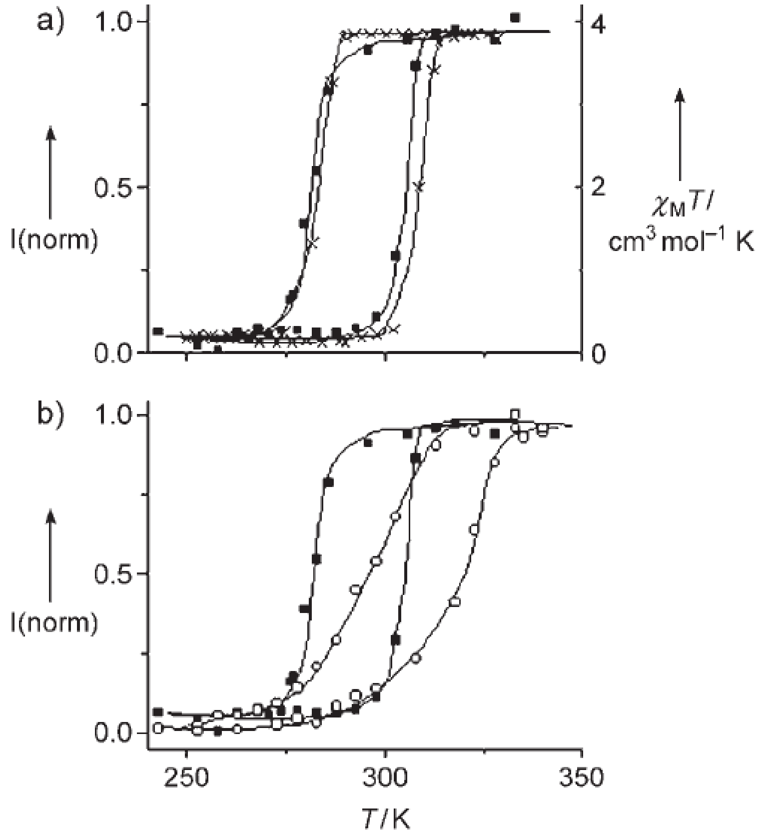


Figure 3. a) Temperature dependence of the $\chi_M T$ product (×; χ_M is the molar magnetic susceptibility) and the normalized Raman intensity ratio (■; I(norm) = I(1025 cm^{-1})/I(1230 cm^{-1})) for [Fe(pyrazine){Pt(CN)$_4$}] powder upon cooling and heating. b) Temperature dependence of the normalized Raman intensity ratio (I(norm) = I(1025 cm^{-1})/I(1230 cm^{-1})) for [Fe(pyrazine){Pt(CN)$_4$}] powder (■) and film samples (○) upon cooling and heating.

Spin state can be locked by substrate.

Angew. Chem. Int. Ed. 2006, 45, 5786 –5789

Intermolecule bonding

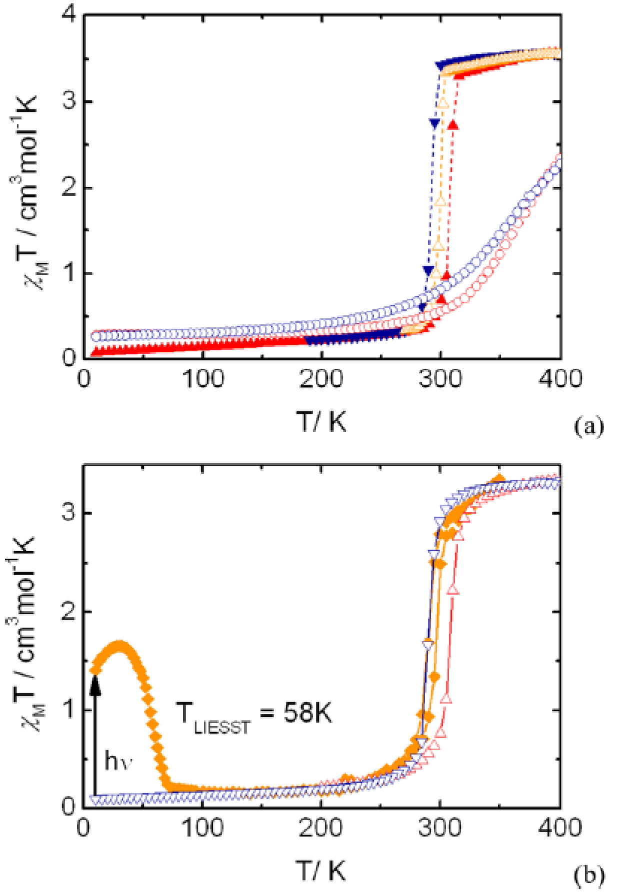
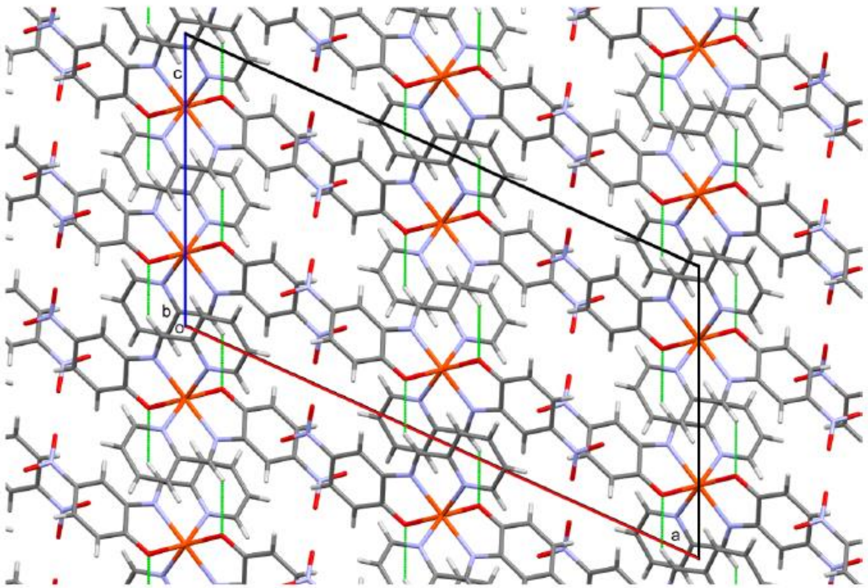


Figure 4. (a) Thermal variation of $\chi_M T$ vs T plots of polycrystalline samples **1** and **2·Solv**: upon heating (**1**, red ▲; **2·Solv**, red ○), then upon cooling (**1**, blue ▼; **2·Solv**, blue ○), and again upon heating (**1**, orange △) (sweeping rate = 2 K min^{-1}). (b) Thermal variation of $\chi_M T$ vs T plots of **1** recorded after reaching the photostationary state at 10 K with λ = 750 nm, first on heating in darkness (orange ◆), and then on cooling (orange ◆) (sweeping rate = 0.3 K min^{-1}). These curves were superimposed with the thermal behavior (red △ or blue ▽) determined for the same sample.



The hydrogen-bonded sites form infinite chains (green lines) interconnected via a three-dimensional network of intermolecular van der Waals contacts and π–π interactions. Therefore, the spin transition involves the synergetic influence of electrostatic and elastic interactions, which cause the enhancement of cooperativity and result in the bistability at room temperature.

Inorg. Chem. 2015, 54, 1791-1799

Dipole in E field

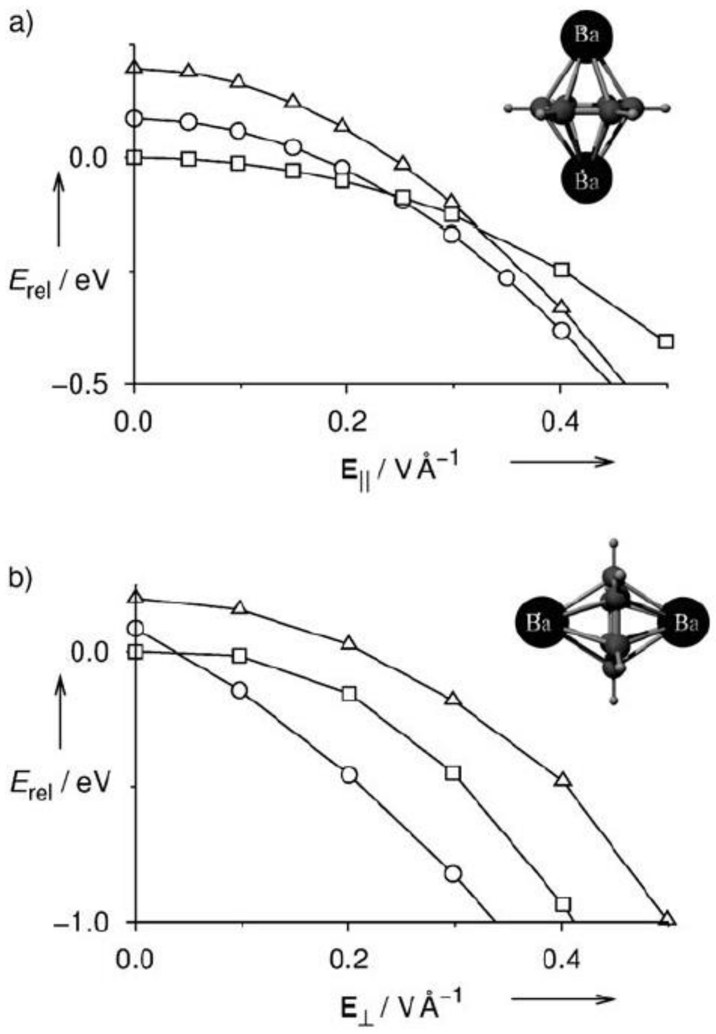
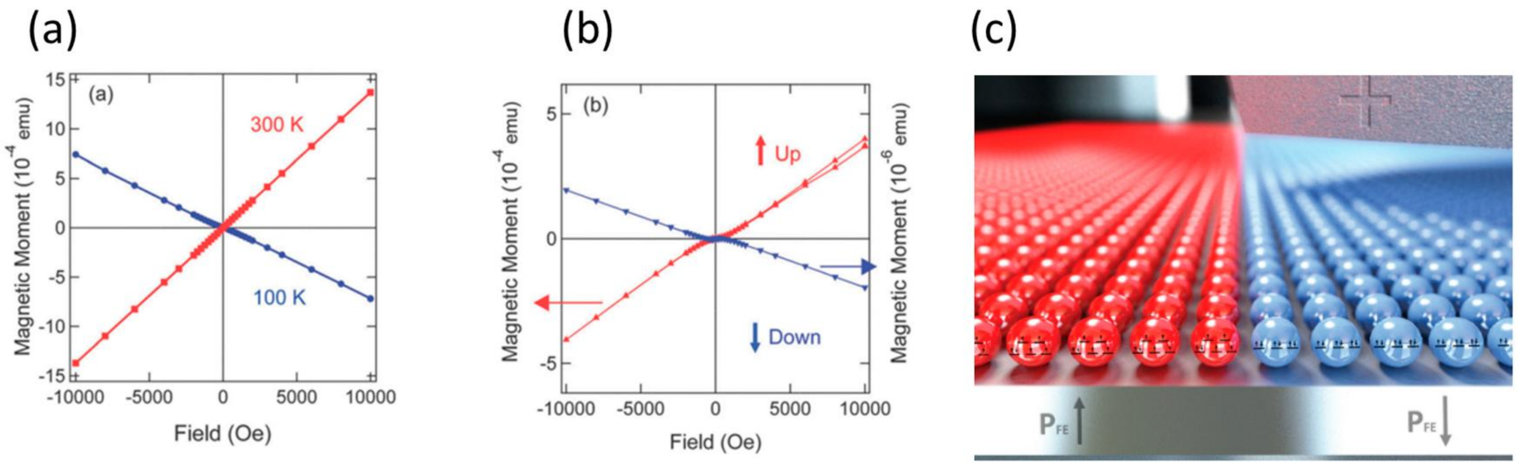


Figure 1. Stark effect on the relative energies of the singlet (□), triplet (○), and quintet (△) electronic spin states in high-electron-density benzene. a) The electric field $\mathbf{E}_{||}$ is applied parallel to the benzene ring plane. b) The electric field $\mathbf{E}_{\perp}$ is applied perpendicular to the benzene ring plane.



Electric field induced by polarization in ferroelectric substrate changes the order of energetic favor of spin state. So E field can lock spin state at room temperature.

Angew. Chem. Int. Ed. 2007, 46, 7640 –7643