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Cooperative thermal and optical switching of spin states in a new two-dimensional coordination polymer

Virginie Niel,[a] Ana Galet,[ab] Ana B. Gaspar,[a] M. Carmen Muñoz[b] and José A. Real*[a]
[a] Institut de Ciencia Molecular/Departament de Química Inorgánica, Universitat de València, Doctor Moliner 50, Burjassot, Spain. E-mail: jose.a.real@uv.es
[b] Departament de Física Aplicada, Universitat Politècnica de València, Camino de Vera s/n, 46071, Valencia, Spain

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{Fe(pmd)$_2$[Cu(CN)$_2$]$_2$} (pmd = pyrimidine) displays a rigid two-dimensional structure and undergoes thermal- and optical-driven spin crossover behaviour; cooperative elastic coupling between iron(II) ions in the framework induces thermal hysteresis in the HS $\leftrightarrow$ LS conversion and sigmoidal HS $\rightarrow$ LS relaxation of the photo-induced HS state at low temperatures.

The search for coordination polymers having specific network topologies and potential properties is a current source of inspiration in crystal engineering. The challenge being the construction of efficient crystalline materials with switch functions and memory transduction.[1] Incorporation of electronically active iron(II) spin crossover (SCO) building blocks in such framework systems is particularly suitable for these purposes as their labile electronic configurations may be switched reversibly between the high- (HS) and low-spin (LS) states involving magnetic, optical and structural changes, usually stimulated by a variation of temperature and/or pressure and by light irradiation.[2] Strong signal generation and hysteresis (memory effect) may be achieved when rigid linkers, communicating the SCO centres, propagate the structural changes cooperatively to the whole framework. A number of interesting one-, two- and three-dimensional (1–3D) SCO networks have been synthesised from bridging ligands of the 4,4′-bipyridine, azole, and bisazole type. Most of these polymers, however, display moderate or poor cooperative SCO; the resulting frameworks are not sufficiently rigid to transmit efficiently the structural changes upon SCO.[3–6]

The chemistry of Hofmann-like clathrates applied to the synthesis of new iron(II) SCO networks has been proposed as an alternative route to explore the cooperative nature of the SCO as the coordination geometry of iron(II) may be propagated into infinite architectures of varying topology and dimensionality by varying the organic ligand and metal-cyanide anion. This strategy has afforded the synthesis of the systems {Fe(pyridine)$_2$[M(CN)$_4$]},[7,8] {Fe(pyrazine)[M(CN)$_4$]}·2H$_2$O[8] (M = Ni, Pd, Pt) and {Fe(bpe)$_2$[Ag(CN)$_2$]$_2$} (bpe = bispyridylethylene)[9] a new class of 2D and 3D frameworks with magnetic and chromatic bistability. Following this research, herein we report the synthesis,† structure, magnetic and photomagnetic properties of {Fe(pmd)$_2$[Cu(CN)$_2$]$_2$} (pmd = pyrimidine) a 2D iron(II)-copper(I) cyanide-bridged SCO framework.

The crystal structure has been studied at 293 K.‡ It is constituted by extended 2D layers with iron(II) and copper(I) ions defining the knots of the networks. The iron atoms lie in the inversion centre of an elongated octahedron whose equatorial and axial positions of the [FeN$_6$] site are occupied by the [Cu(CN)$_2$]$^-$ and pmd groups, respectively. Axial [Fe–N(1) = 2.261(3) Å] and equatorial [Fe–N(2) = 2.123(4) and Fe–N(3) = 2.178(5) Å] bond distances are consistent with the HS state of the iron(II) ion. The pmd ligand binds the copper(I) ion through the N(4) atom [Cu–N(4) = 2.074(3) Å] (Fig. 1). This fact causes strong deviation from linearity of the [Cu(CN)$_2$]$^-$ group [C(5)–Cu–C(6) = 118.46(18)°]. So, the copper atom defines a distorted trigonal site and is 0.434(2) Å out of the trigonal plane defined by N(4), C(5) and C(6). As a result of the strong deviation from linearity, the [Cu(CN)$_2$]$^-$ groups connect two adjacent iron atoms, which define {Fe[Cu(CN)$_2$]$_2$}$_n$ chains running along the *c* axis. Each pmd ligand links one copper and one iron atom of adjacent chains defining layers parallel to the *bc* plane, which eclipse along the *a* axis. Topologically the layers represent an expanded version of the archetypal structure CdCl$_2$ where the iron(II) and copper(I) ions play the role of cadmium and chloride ions, respectively (Fig. 2).

The magnetic susceptibility, χ_M, was determined over the 2–300 K range. The $\chi_M T$ *versus* T plot is shown in Fig. 3. In the high temperature region the $\chi_M T$ value is close to 3.7 cm^3 K mol^{-1}. This value is consistent with the S = 2 HS state of an iron(II) atom. Upon cooling, $\chi_M T$ remains almost constant up to a temperature value which undergoes a sharp decrease characteristic of a first order spin transition. The warming mode reveals the occurrence of thermal hysteresis. The critical temperatures are T_c^{down} = 132 K and T_c^{up} = 142 K for the cooling and warming modes, respectively. The conversion to

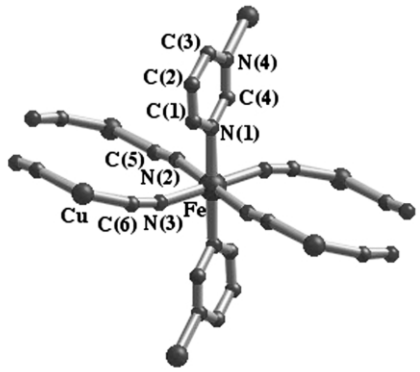

Fig. 1 Perspective view of a representative fragment of {Fe(pmd)$_2$[Cu(CN)$_2$]$_2$}including the non-hydrogen atom numbering.

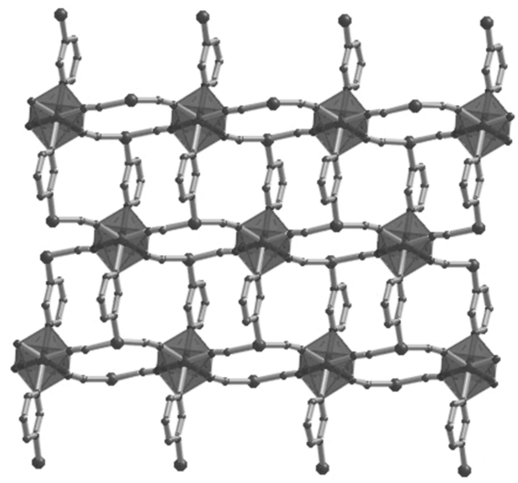

Fig. 2 View of the fragment of a layer displaying the structure of CdCl$_2$.

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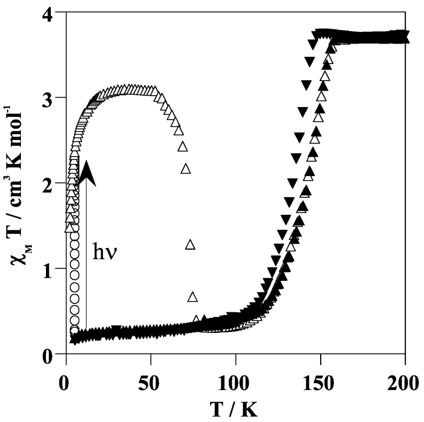

Fig. 3 $\chi_M T$ *versus* T plots. Normal cooling (▼) and warming (▲) modes before irradiation. Irradiation at 5 K (○) (λ = 550 nm). Warming mode (0.3 K min^{-1}) from 2 to 150 K after light irradiation was turned off (Δ).

the LS state is virtually complete ($\chi_M T \approx 0.2$ cm^3 K mol^{-1} at 5 K).

Light induced excited high spin state trapping (LIESST)[10] was carried out irradiating the sample with a Xe lamp coupled through an optical fiber to the SQUID susceptometer (filter 550 nm, 2 mW cm^{-2}) at 5 K for 150 min, the time required to reach the photo-stationary state. $\chi_M T$ attained a value of 2.3 cm^3 K mol^{-1}, which apparently indicates *ca*. 60% of LS → HS conversion. Then the temperature was set at 2 K and χ_M recorded (0.3 K min^{-1}) without irradiation. In the 2–25 K region the increase of $\chi_M T$ is consistent with thermal population of the different microstates arising from zero-field splitting of the S = 2 state. In the temperature range 25–50 K, $\chi_M T$ is almost constant with a value around 3.1 cm^3 K mol^{-1} suggesting that *ca*. 100% of molecules have been converted to the metastable HS state. At temperatures greater than 50 K, $\chi_M T$ drops rapidly to reach a value close to 0.2 cm^3 K mol^{-1} at 76 K, indicating the occurrence of a complete HS → LS relaxation. The characteristic temperature corresponding to the maximum variation of $\chi_M T$ in the HS → LS relaxation after LIESST, T_{LIESST},[11] is *ca*. 73 K.

The kinetics of the relaxation was investigated from 30 up to 60 K (Fig. 4). Below 30 K, the relaxation is very slow, $\chi_M T$ does not vary appreciably in 17 h, which requires relaxation rates, k_{HL}, smaller than 10^{-6} s^{-1}. The decays of the HS molar fraction, γ_{HS}, *versus* time, at various temperatures, are represented in Fig. 4; γ_{HS} has been deduced from

$$\frac{[(\chi_M T)-(\chi_M T)_{LS}]}{[(\chi_M T)_{HS}-(\chi_M T)_{LS}]}$$

where $(\chi_M T)$ represents $\chi_M T$ at any temperature, $(\chi_M T)_{LS} \approx 0.2$ cm^3 K mol^{-1} and $(\chi_M T)_{HS} \approx 3.7$ cm^3 K mol^{-1}. The sigmoidal shape of the relaxation curves reflect the cooperative nature of the HS → LS process.[10] A rough estimate of k_{HL} has been obtained from simulation of the data using Avrami's equation ($k_{HL} = \exp(k_{HL}t)^{\alpha}$).[10] The plot of ln k_{HL} *versus* $1/T$ matches the theory of HS → LS relaxation proposed by Buhks *et al.*,[12] which predicts a temperature-independent rate (tunnelling region) at low temperature and a thermally activated relaxation process at higher temperatures. However, the activation energy, E_a = 1250 cm^{-1} and in particular the pre-exponential factor, A = 766 s^{-1}, obtained from the Arrhenius plot at temperatures higher than 50 K clearly indicate that in this temperature range tunnelling is still the dominant mechanism.

In summary, this communication reports the first example of an iron(II)-copper(I) bimetallic cyanide based spin crossover coordination polymer, which displays a 2D layered structure with $CdCl_2$ connectivity. The magnetic measurements have shown the occurrence of a thermally induced cooperative spin transition with a 10 K wide hysteresis loop and quantitative LS → HS optical switching at temperatures below 50 K.

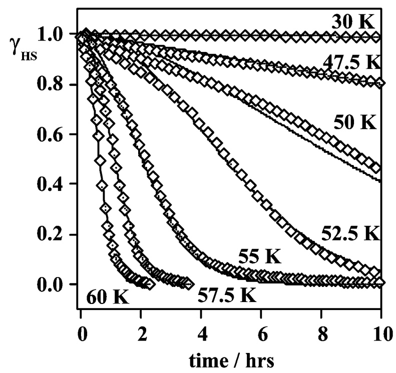

Fig. 4 Time dependence at various temperatures of the HS molar fraction generated by light irradiation at 5 K.

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Notes and references

† *Synthesis*: Orange crystals of $\{Fe(pmd)_2[Cu(CN)_2]_2\}$ were obtained by slow diffusion in water/methanol under an argon atmosphere, with H-double-tube glass vessels. One side contained an aqueous solution (2 ml) of $Fe(BF_4)_2 \cdot 6H_2O$ and pmd (1 : 1, 2.49 × 10^{-2} mol). The other side contained 2 ml of a methanolic solution of (TBA)[Cu(CN)$_2$] (4.99 × 10^{-4} mol). The H vessel was filled with methanol (*ca.* 80 ml). After 3–4 weeks crystals appeared as dendritic agglomerations (10%). CHN analysis: C (calc.) 32.23 (found) 32.52, H (calc.) 1.80 (found) 2.01, N (calc.) 25.60 (found) 25.24%.

‡ *Crystal data*: $C_6H_4N_4Cu_1Fe_{0.5}$, M_r = 223.6, triclinic, $P\bar{1}$ (no. 2), Z = 2, a = 6.8020(4), b = 8.0470(3), c = 8.0650(4) Å, α = 110.214(2), β = 99.134(2), γ = 108.733(2)°, V = 373.81(3) Å^3, D_c = 1.987 Mg m^{-3}, μ = 3.785 mm^{-1}, λ(Mo-Kα) = 0.71073 Å, T = 293 K. 4004 reflections measured, 1692 independent (R_{int} = 0.0618), final residuals $R1$ = 0.0408 [with $I > 2\sigma(I)$], $wR2$ = 0.1069 (all data). Structure solution and refinement were perfomed using SHELXS97 and SHELX97 programs, respectively.[13] CCDC reference number 203741. See http://www.rsc.org/suppdata/cc/b3/b301806g/ for crystallographic data in CIF or other electronic format.

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