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Electronic Supporting Information (ESI) for the manuscript:

## Spin-crossover complex encapsulation within a magnetic metal-organic framework

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## **Experimental Section**

**Materials.** Na<sub>4</sub>[Cu<sub>2</sub>(Me<sub>3</sub>mpba)<sub>2</sub>]  $\cdot$  4H<sub>2</sub>O (1) and [Fe<sup>III</sup>(sal<sub>2</sub>-trien)]NO<sub>3</sub>  $\cdot$  H<sub>2</sub>O were synthesized according to literature methods.<sup>1</sup> All chemicals were of reagent grade quality, and they were purchased from commercial sources and used as received.

**Preparation of [Fe<sup>III</sup>(sal2-trien)]Nas{Mn4[Cu2(Me3mpba)2]3}** · **43H2O [Fe(sal2-trien)@1]:** Well-formed dark green prisms of **Fe(sal2-trien)@1** were obtained by immersing *ca*. 50 mg of crystals of **1** in a water solution containing 35 mg of [Fe<sup>III</sup>(sal2-trien)]NO<sub>3</sub> · H<sub>2</sub>O<sup>1b</sup> for six days and then, gently washed with water to remove any trace of the mononuclear complex. The exchange of Na<sup>+</sup> cations by the cationic [Fe<sup>III</sup>(sal2-trien)]<sup>+</sup> complexes was monitored through SEM every 24 hours to ensure the maximum loading. Unfortunately, crystals of **Fe(sal2-trien)@1** were not suitable for X-ray diffraction but they were characterized by SEM microscopy, Elemental Analysis, IR, ICP-AES and TGA and PXRD studies. Elemental analysis calculated (%) for C<sub>98</sub>H<sub>170</sub>Cu<sub>6</sub>FeMn<sub>4</sub>N<sub>16</sub>Na<sub>3</sub>O<sub>81</sub> (3589.2): C 32.76, H 4.77, N 6.24; found: C 32.75, H 4.62, N 6.31. IR (KBr) 3319 cm<sup>-1</sup> (NH from Fe(sal2-trien)), 1622 cm<sup>-1</sup> (CN from Fe(sal2-trien)) and 1591 cm<sup>-1</sup> (CO from 1).

**Physical Techniques.** Elemental (C, H, N) and Inductively coupled plasma–atomic emission spectroscopy (ICP-AES) analyses were performed at the Microanalytical Service of the Universitat de València. The thermogravimetric analysis was performed on crystalline samples under a dry  $N_2$  atmosphere with a Mettler Toledo TGA/STDA 851<sup>e</sup> thermobalance operating at a heating rate of 10 °C min<sup>-1</sup>. Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM/EDX) was carried out with a XL 30 ESEM (PHILIPS) microscope equipped with a home-made EDX energy dispersive x-ray detector.

**X-ray Powder Diffraction Measurements.** Solid polycrystalline samples as well as water suspended polycrystalline samples of **1** and **Fe(sal2-trien)@1** were introduced into 0.5 mm borosilicate capillaries prior to being mounted and aligned on a Empyrean PANalytical powder diffractometer, using Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å).

<sup>&</sup>lt;sup>1</sup> (a) J. Ferrando-Soria, P. Serra-Crespo, M. de Lange, J. Gascon, F. Kapteijn, M. Julve, J. Cano, F. Lloret, J. Pasán, C. Ruiz-Pérez, Y. Journaux and E. Pardo, *J. Am. Chem. Soc.*, 2012, **134**, 15301–4. (b) E. Sinn, G. Sim, E. V. Dose, M. F. Tweedle and L. J. Wilson, *J. Am. Chem. Soc.*, 1978, **100**, 3375–3390.

For each sample, five repeated measurements were collected at room temperature ( $2\theta = 2-40^{\circ}$ ) and merged in a single diffractogram. The spinning option was disabled for the water suspended samples due to the presence of water solvent within the capillaries which accounts for the slight asymmetry observed in some of the peaks.

**Magnetic Measurements.** Variable-temperature (2.0–400 K) direct current (*dc*) magnetic susceptibility measurements under an applied field of 100 G (T < 30 K) and 5.0 kG ( $T \ge 30$  K), and magnetization measurements at 2.0 K were carried out with a Quantum Design SQUID magnetometer. Variable-temperature (2.0–30 K) alternating current (ac) magnetic susceptibility measurements under ±5.0 G oscillating field at frequencies in the range of 1–10.0 kHz were carried out under different applied static fields in the range of 0–5.0 kG with a Quantum Design Physical Property Measurement System (PPMS). The magnetic susceptibility data were corrected for the diamagnetism of the constituent atoms and the sample holder. *Dc* and *ac* magnetic measurements were performed on powdered microcrystals and restraining the sample with *n*-eicosane in order to avoid any field induced torqueing as well as to prevent any solvent loss.

Mössbauer spectra were collected between 300 and 50 K in transmission mode using a conventional constant-acceleration spectrometer and a 25 mCi <sup>57</sup>Co source in a Rh matrix. The velocity scale was calibrated using  $\alpha$ -Fe foil. Isomer shifts, IS, are given relative to this standard at room temperature. The absorbers were obtained by packing the powdered samples (approximately 2 mg of natural Fe/cm<sup>2</sup>) into a perspex holder. Absorber thicknesses were calculated on the basis of the corresponding electronic massabsorption coefficients for the 14.4 keV radiation, according to Long *et al.*<sup>2</sup> Lowtemperature measurements were performed with the sample in He exchange gas in a bath cryostat. The spectra were fitted to Lorentzian lines using a non-linear leastsquares method.

<sup>&</sup>lt;sup>2</sup> G. J. Long, T. E.Cranshaw, G. Longworth, Mossb. Effect. Ref. Data J. 1983, 6, 42-49.

Table S1. Selected data from the ICP-AES and SEM/EDX analyses.

Compound	% mass <sup>a</sup>	% atomic <sup>a</sup>	Cu/M ratio <sup>b</sup>	% mass <sup>b</sup>	% atomic <sup>b</sup>	Cu/M ratio <sup>b</sup>
Cu	10.517	1.583	1.000	10.43	1.57	1.00
Mn	6.123	1.051	1.506	6.03	1.04	1.51
Fe	1.553	0.264	5.996	1.53	0.26	6.04
Na	1.902	0.789	2.001	-	-	-

<sup>a</sup> ICP-AES analyses. <sup>b</sup> SEM/EDX analyses.



**Fig. S1.** IR spectra of  $[Fe^{III}(sal_2-trien)]NO_3 \cdot H_2O$  (blue), **1** (green) and **Fe(sal\_2-trien)@1** (red) in the range 400-4000 cm<sup>-1</sup>.



Fig. S2. TGA of 1 (blue) and  $Fe(sal_2-trien)@1$  (red) under dry  $N_2$  atmosphere.



**Fig. S3.** Field dependence of the magnetization (*M*) of **1** (blue) and **Fe**(**sal**<sub>2</sub>-**trien**)@**1** (red) at T = 2.0 K.

The Mössbauer spectrum taken at 300 K (Fig. 4) of a sample prepared at room temperature (not pre-heated to 400 K) show four absorption peaks corresponding to two doublets. The estimated parameters (Table S2) of the most intense doublet, isomer shift IS = 0.36 mm/s, quadrupole splitting QS = 0.71 mm/s, are consistent with HS Fe<sup>III</sup>, S=5/2. The other doublet (IS = 0.14 mm/s, QS = 2.53 mm/s) is consistent with LS Fe<sup>III</sup>, S = 1/2.<sup>3</sup> The estimated relative areas clearly show that Fe<sup>III</sup> in the HS state is predominant. Assuming that the recoilless factors for HS and LS Fe<sup>III</sup> are not very different, as in the case of related Fe<sup>III</sup> complexes with sal<sub>2</sub>trien or R-sal<sub>2</sub>trien (R acetylacetonate, salicylate) ligands<sup>3</sup> the fraction of Fe<sup>III</sup> in the HS state is approximately equal to 80% at 300 K.

The spectrum taken at 50 K also shows four absorption peaks corresponding to a HS and a LS Fe<sup>III</sup>. The IS are higher due to the second order Doppler shift, the QS of HS Fe<sup>III</sup> is equal within experimental error to the value at 300 K and the QS of LS Fe<sup>III</sup> increases with decreasing temperature, as explained in detail in ref.3. It is obvious that at 50 K the fraction of Fe<sup>III</sup> in the LS state is predominant, the fraction of HS Fe<sup>III</sup> having decreased down to approximately 29 %, evidencing a spin transition of the Fe complex.

<sup>&</sup>lt;sup>3</sup> (a) S. Floquet, S. Salunke, M. Boillot, R. Clément, F. Varret, K. Boukheddaden and E. Rivière, *Chem. Mater.*, 2002, **14**, 4164–4171. (b) M. Clemente-León, E. Coronado, M. C. Giménez-López, A. Soriano-Portillo, J. C. Waerenborgh, F.S. Delgado, C. Ruiz-Pérez, *Inorg. Chem.* 2008, **47**, 9111-9120. (c) M. Clemente-León, E. Coronado, M. López-Jordà, G. Mínguez Espallargas, A. Soriano-Portillo and J. C. Waerenborgh, *Chem. Eur. J.*, 2010, **16**, 2207–2219.

**Table S2.** Estimated parameters from the Mössbauer spectra taken at different temperatures T of a **Fe(sal<sub>2</sub>-trien)@1** sample prepared at 300 K, not pre-heated to 400 K.

	LS	Fe <sup>III</sup>		HS Fe <sup>Ⅲ</sup>		
Т	IS	QS	Ι	IS	QS	Ι
300 K	0.14	2.53	20 %	0.36	0.71	80 %
50 K	0.21	2.74	71 %	0.45	0.70	29 %

HS and LS, high-spin and low-spin Fe<sup>III</sup>, respectively. IS (mm/s) isomer shift relative to metallic  $\alpha$ -Fe at room temperature; QS (mm/s) quadrupole splitting; I relative area. Estimated errors  $\leq 0.02$  mm/s for IS, QS, and <2% for I.