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Electronic Supplementary Information
Magnetic chains of Fe_3 clusters in the Fe_3YO_2 butterfly molecular compound

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1. Notes on the Blume-Capel model

The original Blume-Capel model is an Ising-type model for $S = 1$ ($S_z = 0, \pm 1$) and axial crystal field[1]. It can be generalized to any spin-S[2, 3]. In the 1-dimensional case, the Hamiltonian for a chain of N identical spins S is written

$$\mathcal{H} = \sum_{j=1}^{N} \left[-2JS_{z,j}S_{z,j+1} + D\left(S_{z,j}\right)^2 \right] \tag{1}$$

where $S_z = -S, -S+1, \ldots, S-1, S$.

Thermodynamic magnitudes can be obtained from the canonical partition function $\mathcal{Z}$, which is calculated by the transfer matrix method. In the S_z representation and assuming a ring of N spins ($S_{z,N+1} = S_{z,1}$) with large N, the partition function, $\mathcal{Z}_N$, can be expressed as

$$\mathcal{Z}_N = \mathrm{Tr} \prod_{j=1}^{N} \mathbf{T}_j = \mathrm{Tr}\left[\mathbf{T}^N\right] \tag{2}$$

where $\mathbf{T} = \mathbf{T}_j \; \forall j$, *i.e.*, all $\mathbf{T}_j$ are identical hermitian matrices. This is the transfer matrix, which has the form $\mathbf{T} = e^{-\beta\mathcal{H}}$ with $\beta = 1/k_{\mathrm{B}}T$ and matrix elements

$$\langle S_z|\mathbf{T}|S'_z\rangle = e^{2\beta J S_z S'_z - (\beta D/2)\left[(S_z)^2 - (S'_z)^2\right)]} \tag{3}$$

Then, the calculation procedure will include diagonalizing $\mathbf{T}$ to obtain its eigenvalues λ_i, in order to use $\mathrm{Tr}\left[\mathbf{T}^N\right] = \sum_{i=1}^{N} \lambda_i^N$. Since the transfer matrix is real square with positive elements, there exist a non-degenerate largest real eigenvalue λ_1 (the *principal* eigenvalue). For large N, $\mathcal{Z}_N \approx \lambda_1^N$, and in the thermodynamic limit $N \to \infty$ the ring is equivalent to an infinite chain.

The specific heat is calculated from the partition function as

$$C_V = -\frac{1}{\mathcal{Z}_N}\frac{\partial \mathcal{Z}_N}{\partial \beta} \tag{4}$$

in the thermodynamic limit $N \to \infty$.

The equilibrium susceptibility is calculated from spin correlation functions. For a general spin at position K, its correlation function with spin at position $K+l$ is

$$\begin{aligned}\langle S_K S_{K+l}\rangle &= \lim_{N\to\infty}\frac{1}{\mathcal{Z}_N}\sum_{\{S\}} S_K S_{K+l}\exp\left(-\beta\mathcal{H}\right)\\ &= \lim_{N\to\infty}\frac{1}{\mathcal{Z}_N}\sum_{i,j=1}^{n}\lambda_i^l\lambda_j^{N-l}\left\langle\phi_i|\mathbf{S}|\phi_j\right\rangle\left\langle\phi_j|\mathbf{S}|\phi_i\right\rangle \\ &\approx \sum_{i=1}^{n}\left(\frac{\lambda_i}{\lambda_1}\right)^l\langle\phi_i|\mathbf{S}|\phi_1\rangle\langle\phi_1|\mathbf{S}|\phi_i\rangle\end{aligned} \tag{5}$$

where $\mathbf{S}$ is the spin matrix, $n = 2S+1$ is its dimension and ϕ_i are the eigenfunctions of the transfer matrix. Then the (parallel) molar susceptibility is

$$\chi = \frac{N_A\mu_B^2 g^2}{k_B T}\sum_{l=-\infty}^{+\infty}\langle S_{z,K}S_{z,K+l}\rangle \tag{6}$$

We note that in the infinite chain, for a given spin K the interaction is symmetric with respect to spins at either side of K, *i.e*, $\langle\sigma_K\sigma_{K+l}\rangle = \langle\sigma_K\sigma_{K-l}\rangle$, $|l| > 0$. Therefore, eq. (6) can be writen

$$\chi = \frac{N_A\mu_B^2 g^2}{k_B T}\left[\langle S_{z,K}S_{z,K}\rangle + 2\sum_{l=1}^{+\infty}\langle S_{z,K}S_{z,K+l}\rangle\right] \tag{7}$$

The cases of $S = 1$ and $3/2$ can be solved analytically, while for larger spin numerical calculations are performed [3]. For both specific heat and susceptibility, the calculation procedure includes diagonalization of the transfer matrix and obtaining a limit numerically. In the latter, the influence of the principal eigenvalue is of the utmost importance. Although the principal value is non-degenerate, next lower eigenvalues can be close, and therefore convergence of the calculations for increasing N has to be checked, which can be an issue for very low or very large temperatures in comparison with the interaction energies involved (J and D).

2. Specific heat under external magnetic field

Fig. S.1 shows the experimental specific heat of the $\{\mathrm{Fe_3YO_2}\}$ compound under external magnetic field with values H = 10, 20 and 40 kOe. Note that a magnetic field of 10 kOe produces maximum Zeeman splittings in a powder sample of $\sim gS\mu_\mathrm{B}H/k_\mathrm{B} \sim 1\,\mathrm{K}$, *i.e.*, of the order of the temperatures where the effect of the single ion anisotropy and intercluster interactions a show up. We have calculated this specific heat using a quantum Monte Carlo simulation (from ALPS project libraries [4]) on a chain of 20 spin $S = 5/2$ clusters with intercluster Heisenberg interaction $J = -40\,\mathrm{mK}$ and magnetocrystalline anisotropy parameter $D = -0.56\,\mathrm{K}$ as obtained from the zero field measurements. The fig. S.1 includes the calculations for $H = 10\,\mathrm{kOe}$ after a powder average carried out with simulations for angles between the anisotropy axis (quantization axis) and applied field direction, θ, in steps of 5°. The agreement supports the proposed model of an antiferromagnetic chain with single ion anisotropy.

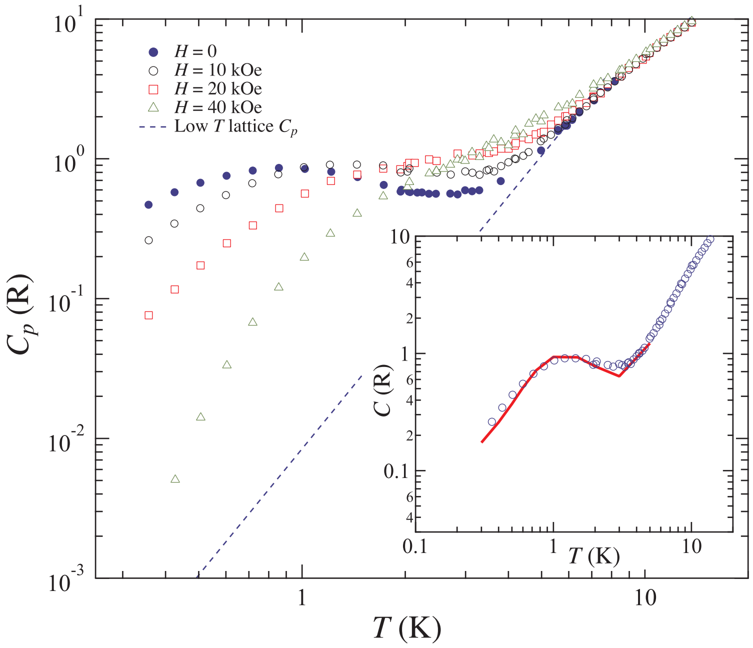

Figure S.1: Experimental specific heat of the $\{Fe_3YO_2\}$ compound under various external magnetic fields H. Inset: experimental data for $H = 10\,\mathrm{kOe}$ and quantum Monte Carlo simulation of the specific heat for a isotropic Heisenberg chain of 20 $S = 5/2$ cluster spins with axial magnetocrystalline anisotropy $D = -0.56\,\mathrm{K}$, intercluster interaction constant $J = -40\,\mathrm{mK}$ and external applied field $H = 10\,\mathrm{kOe}$ (the lattice contribution has been added to the calculation).

3. Equilibrium magnetic susceptibility

In the main text we have shown the calculation of the equilibrium susceptibility for an antiferromagnetic chain including axial magnetic anisotropy. This has been done using the general spin Blume-Capel model and a classical Monte Carlo simulation of Heisenberg chain. In order to assess the effect of the anisotropy, here we have added the results for the Ising and classical Heisenberg $S = 5/2$ chain without anisotropy (Fig. S.2). The major contribution of the anisotropy is a fast drop of χT with decreasing temperature. However, in every studied model, the very low temperature trend to a non zero value of χT is not predicted. As explained in the text, such a trend could be produced by a small ferromagnetic component, a finite chain length or a not random powder sample.

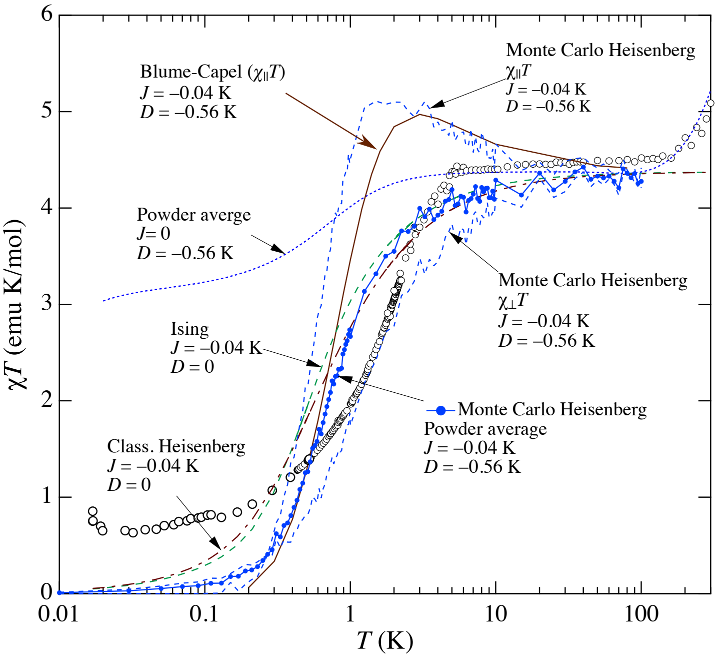

Figure S.2: Experimental (large circles) and calculated χT of the $\{Fe_3YO_2\}$ compound for several chain interaction models and with or without single molecule magnetic anisotropy.

4. Magnetic relaxation under external *dc* field

At zero magnetic field, spin-phonon processes are forbidden in Kramers-conjugate states (van Vleck cancellation). This is the present case of the $S = 5/2$ Fe_3 clusters. However, the phonon-driven processes can be made observable by applying an external magnetic field. When an external static magnetic field $\vec{H}_0$ is applied and a parallel *ac* magnetic field $\vec{h} = \vec{h}_0 \cos \omega t$ is used to measure the *ac* susceptibility, this frequency-dependent susceptibility can be written as [5]

$$\chi(\omega, T, H) = \sum_k \frac{\Delta\chi_k(T, H)}{1 + (i\omega\tau_k)} + \chi_{\mathrm{VV}} \tag{8}$$

where χ_{VV} is the van Vleck susceptibility which includes quantum processes, as quantum tunnelling. The first term includes phonon-induced jumps between energy levels characterized by relaxation times τ_k and susceptibility amplitudes $\Delta\chi_k$. Each spin transition from a state n to a state n' will produce a Debye-like function $\chi''(\omega)$ that peaks at $\tau = 1/\omega$ and is symmetric in a logarithm scale.

For $H_0 \gg h_0$, the static field produces Zeeman splitting of the spin energy levels which are modulated by the *ac* field. We searched for relaxation modes triggered by external magnetic applied fields at 2 K in the frequency range 0.1 Hz – 1 kHz (Fig. S.3). A process was observed for a frequency around 1 Hz, which is assigned to a direct process under phonon-bottleneck effect. The magnetic field dependence of the amplitude of the out-of-phase susceptibility χ''_{max} (or $\Delta\chi$) shows a maximum at ≈ 8 kOe. For the measurements of the *ac* susceptibility as a function of temperature in the frequency range 0.1 Hz – 10 kHz the applied field value 6.5 kOe was chosen, which showed a phonon-induced process with characteristic time $\sim 10^{-5}$ s and an Arrhenius type temperature dependence (see main text).

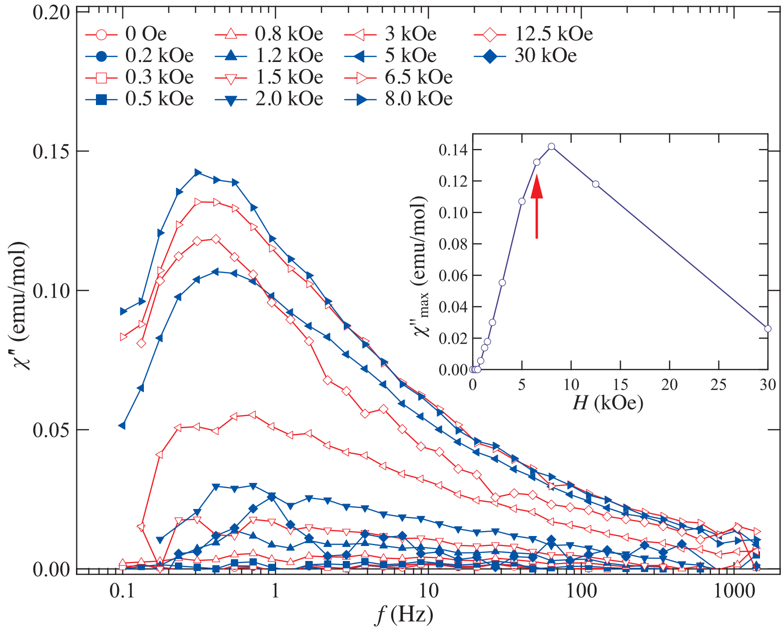

Figure S.3: $\chi''(f)$ at $T = 2\,\mathrm{K}$ at applied magnetic fields $0 \leq H \leq 30\,\mathrm{kOe}$ for the $\{\mathrm{Fe_3YO_2}\}$ compound. Inset: magnetic field dependence of the maximum of χ''; the vertical arrow indicates the field value used for subsequent $\chi(f)$ measurements at higher temperatures.

5. Transition probability models

Thermal relaxation processes have been described by stochastic models, which assume single spin flips [6]. The relaxation times can be calculated from a master equation and transition probabilities $W_i(\sigma_i)$ to flip spin i from σ_i to $-\sigma_i$ ($\sigma_i = \pm 1$) under a local field $E_i = 2JS^2(\sigma_{i-1} + \sigma_{i+1})$. Thermal equilibrium requires that $W_i(\sigma_i)$ have the general form

$$W_i(\sigma_i) = f\left(\frac{E_i}{k_\mathrm{B}T}\right)\left[1 - \sigma_i \tanh\left(\frac{E_i}{k_\mathrm{B}T}\right)\right] \tag{9}$$

where f is an even function of the local field. Then, the relaxation times are calculated from the master equation

$$\frac{dp(\sigma_1, \cdots, \sigma_N, t)}{dt} = -\sum_i W_i(\sigma_i)p(\sigma_1, \cdots, \sigma_i, \cdots, \sigma_N, t) + \sum_i W_i(-\sigma_i)p(\sigma_1, \cdots, -\sigma_i, \cdots, \sigma_N, t) \tag{10}$$

which considers the change with time of the probability a particular spin configuration $p(\sigma_1, \cdots, \sigma_N, t)$ through its destruction by flipping of any spin σ_i or creation from spins $-\sigma_i$.

Two models for $W_i(\sigma_i)$ will be considered:

i. Glauber's model [6]. The function f is taken as $f = 1/2\tau_0$, where τ_0 is the spin flip time in absence of interspin interactions. This is the simplest model. Then,

$$W_i(\sigma_i) = \frac{1}{2\tau_0}\left[1 - \sigma_i \tanh\left(\frac{E_i}{k_\mathrm{B}T}\right)\right] \tag{11}$$

ii. Arrhenius law. The main advantage of Glauber's models is that the master equation is solvable analytically. However, a more physical probability law can be chosen through an Arrhenius law

$$W_i(\sigma_i) = \frac{1}{2\tau_0} \exp\left(-\frac{E_i\sigma_i}{k_\mathrm{B}T}\right) \tag{12}$$

which comes out from Eq. 9 when the choice $f(E_i/k_\mathrm{B}T) = \cosh(E_i/k_\mathrm{B}T)/2\tau_0$ is made.

When an external magnetic field H is applied, the models can be modified as follows:

i. Glauber's model. The transition probability is

$$W_i(\sigma_i) = \frac{1}{2\tau_0}\left[1 - \tanh\left(\frac{\mu H}{k_{\mathrm{B}}T}\right)\right]\left[1 - \sigma_i \tanh\left(\frac{E_i}{k_{\mathrm{B}}T}\right)\right] \tag{13}$$

where $\mu = g\mu_B S$. This choice of $W_i(\sigma_i)$ was used by Glauber for small values of H [6].

ii. Arrhenius law:

$$W_i(\sigma_i) = \frac{1}{2\tau_0}\exp\left(-\frac{E_i + \mu H}{k_{\mathrm{B}}T}\sigma_i\right) \tag{14}$$

iii. Suzuki-Kubo model [7]. An alternative to Glauber's choice is

$$W_i(\sigma_i) = \frac{1}{2\tau_0}\left[1 - \sigma_i \tanh\left(\frac{E_i + \mu H}{k_{\mathrm{B}}T}\right)\right] \tag{15}$$

Note that τ_0 is also expected to follow an Arrhenius law $\tau_0 = \tau_i \exp\left(-\Delta_{\mathrm{A}}/k_{\mathrm{B}}T\right)$. Coulon *et al.* [8] have calculated the dependence of the activation energy of the normalized relaxation time Δ_{τ/τ_0} as a function of the inverse of the reduced applied field $\mu H/k_{\mathrm{B}}T$ for the three transition probability functions above (see Fig. 13 in ref. [8]). The main results are:

i. Δ_{τ/τ_0} is almost independent of the reduced applied field for Glauber's model.
ii. For the Suzuki-Kubo probability law, Δ_{τ/τ_0} decreases monotonously with the applied field until $\mu H/k_{\mathrm{B}}T \approx 0.5$, when it stabilized at $\Delta_{\tau/\tau_0} = 0$. Then, for $h \gtrsim 0.5$ the activation energy obtained from the measured relaxation time τ is $\Delta_\tau = \Delta_{\mathrm{A}}$.
iii. For the Arrhenius probability law, Δ_{τ/τ_0} decreases monotonously and it drops below zero for $\mu H/k_{\mathrm{B}}T \approx 0.5$. In this case, the observed activation energy is smaller than Δ_{A} for $h \gtrsim 0.5$.

6. Additional figures of supramolecular magnetic chains

In addition to Fig. 8 in the main text, three further figures are included in order to help visualize the chain formation of $S = 5/2$ $\mathrm{Fe_3}$ spin clusters in the $\{\mathrm{Fe_3YO_2}\}$ compound. The chains are represented in a simplified structure with only Fe and Y atoms shown and the proposed orientation of magnetic moments. Chains are viewed along the **a** (left figure), **b** (centre figure), and **c** (right figure) crystallographic axes. In each figure, a plane containing the centres of the $\mathrm{Fe_3}$ clusters of a single chain is also depicted.

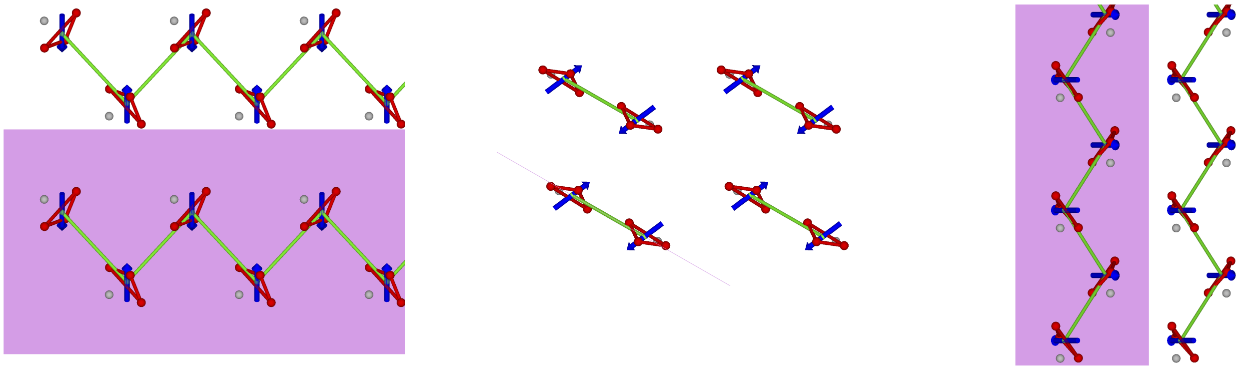

Figure S.4: $S = 5/2$ $\mathrm{Fe_3}$ spin clusters chains

References

[1] H. W. Capel, On the possibility of first-order phase transitions in Ising systems of triplet ionss, Physyca 32 (1966) 966–988.

[2] M. Lines, Temperature-dependent single-ion excitations in anisotropic paramagnets, Phys. Rev. Lett. 42 (1979) 533–536.

[3] I. Chatterjee, Crsytal field effect in an Ising model, J. Math. Phys. 25 (1985) 2339–2344.

[4] B. Bauer, L. D. Carr, H. G. Evertz, A. Feiguin, J. Freire, S. Fuchs, L. Gamper, J. Gukelberger, E. Gull, S. Guertler, A. Hehn, R. Igarashi, S. V. Isakov, D. Koop, P. N. Ma, P. Mates, H. Matsuo, O. Parcollet, G. Pawłowski, J. D. Picon, L. Pollet, E. Santos, V. W. Scarola, U. Schollwöck, C. Silva, B. Surer, S. Todo, S. Trebst, M. Troyer, M. L. Wall, P. Werner, S. Wessel, The ALPS project release 2.0: open source software for strongly correlated systems, J. Stat. Mech. (2011) P05001.

[5] S. Gómez-Coca, A. Urtizberea, E. Cremades, P. J. Alonso, A. Camón, E. Ruiz, F. Luis, Origin of slow magnetic relaxation in Kramers ions with non-uniaxial anisotropy, Nature Comm. 5 (2014) 5300.

[6] R. Glauber, Time dependent statistics of the Ising model, J. Math. Phys. 4 (1963) 294–307.

[7] M. Suzuki, R. Kubo, Dynamics of the Ising model near the critical point. I, J. Phys. Soc. Jpn. 24 (1968) 51–60.

[8] C. Coulon, V. Pianet, M. Urdampilleta, R. Clérac, Single-chain magnets and related phenomena, in: S. Gao (Ed.), Molecular Nanomagnets and Related Phenomena, Vol. 164 of Structure and Bonding, Springer-Verlag, Berlin Heidelberg, 2015, pp. 143–184.