An azido-bridged disc-like heptanuclear cobalt(II) cluster: towards single-molecule magnet

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Supporting Materials

§ [Magnetic Analysis]

The exchange Hamiltonian for a S_6 symmetric heptanuclear model is

$$H = -2J_{intra}(\sum_{i=2}^{7} S_1 \cdot S_i + \sum_{j=2}^{6} S_j \cdot S_{j+1} + S_2 \cdot S_7) + g_0\mu_B H_0 \sum_{i=1}^{7} S_i^z \quad \text{(S1)}$$

where J_{intra} is the exchange integral between adjacent Co atoms. Then, based on the Kambe's method,

$$H = -2J_{intra}\{\frac{1}{2}\sum_{i=2}^{7}(S_{1i}^2 - S_1^2 - S_i^2) + \frac{1}{2}\sum_{j=2}^{6}(S'^2 - S_j^2 - S_{j+1}^2) + \frac{1}{2}(S_{27}^2 - S_2^2 - S_7^2)\} + g_0\mu_B H_0 \sum_{i=1}^{7} S_i^z \quad \text{(S2)}$$

where each S_i is 1/2, $S_{1i} = S_1+S_i$, $S' = S_j+S_{j+1}$, $S_{27} = S_2+S_7$. Thus, the energy expression is easy to get:

$$E = -J_{intra}\{\sum_{i=2}^{7} S_{1i}(S_{1i}+1) + S_{23}(S_{23}+1) + \mathrm{L} + S_{72}(S_{72}+1)\} \quad \text{(S3)}$$

where $S_{ij} = S_i+S_j, S_i+S_j-1, \ldots, |S_i-S_j|$, here $S_{ij} = 1$ or 0. By solving the exchange matrix, the molecular magnetic susceptibility expression in the van Vleck equation was shown in eq S4:

$$\chi_m = (\frac{Ng^2\beta^2}{3kT})(\frac{A}{B}) \quad \text{(S4)}$$

Here N is Avogadro's number, g the Landé g factor, β the electron Bohr magneton, k the Boltzmann constant, T the temperature, and,

$$A = 126\exp(24y) + 315\exp(18y) + 90\exp(14y) + 187.5\exp(12y) + 12\exp(10y) + 108\exp(8y) + 12\exp(6y) + 13.5\exp(4y);$$

$$B = 8\exp(24y) + 36\exp(18y) + 24\exp(14y) + 42\exp(12y) + 12\exp(10y) + 48\exp(8y) + 16\exp(6y) + 18\exp(4y)$$

with $y = \frac{J_{intra}}{kT}$;

If intermolecular interaction (J_{inter}) are considered by mean field approximation, then:

$$\chi_m T = \frac{\chi_m T}{1 - 2J_{inter}\chi_m/(N\beta^2 g^2)} \quad \text{(S5)}$$

The experimental data (2–30 K) were fitted to eq 4, and the best fitting of the data gave: J_1 = 10.4 cm^{-1}, J_2 = –0.05 cm^{-1}, g = 5.9, with R = 1.5 × 10^{-5}; {R = $\Sigma[(\chi_M T)_{obs}-(\chi_M T)_{calc}]^2/\Sigma(\chi_M T)_{obs}^2$}.

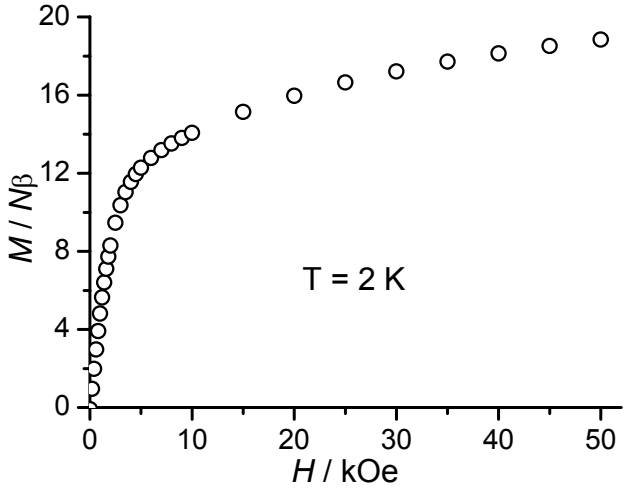


Figure S1 *dc* field-dependence of magnetization of **1** at 2 K..

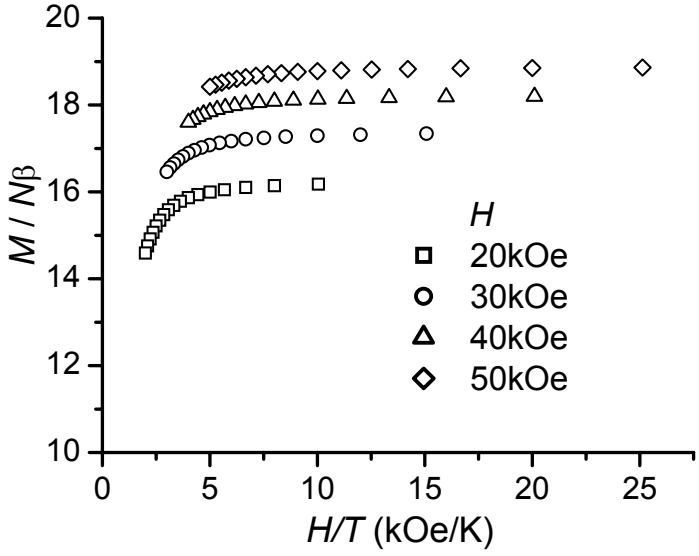


Figure S2 Magnetization data in applied fields from 20 to 50 kOe at temperatures between 2 and 10K.

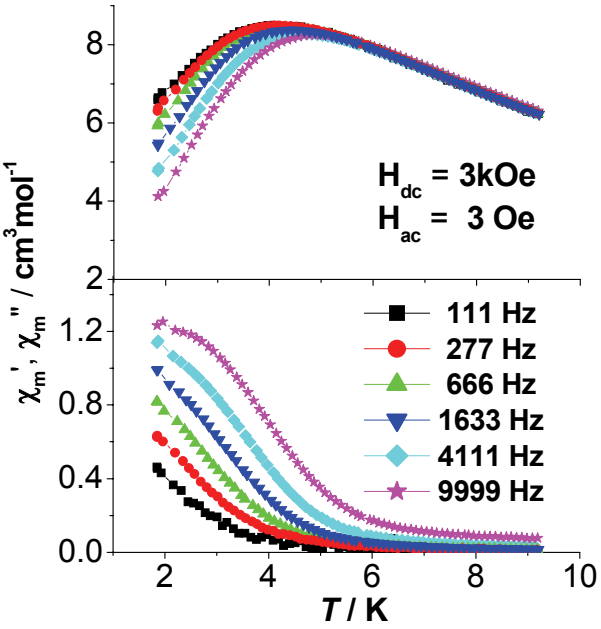


Figure S3 Temperature dependence of the real (top) and imaginary (bottom) components of the *ac* susceptibility for **1** with an oscillating field 3 Oe in frequency of 111-9999 Hz in an applied static field of 3 kOe.

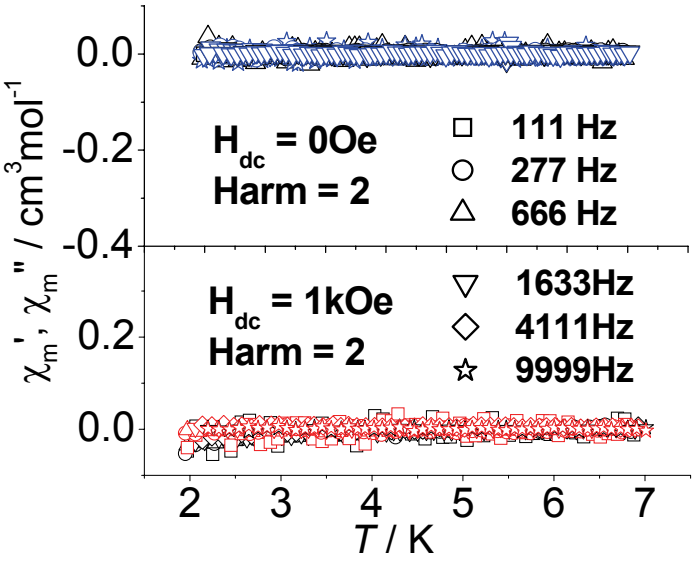
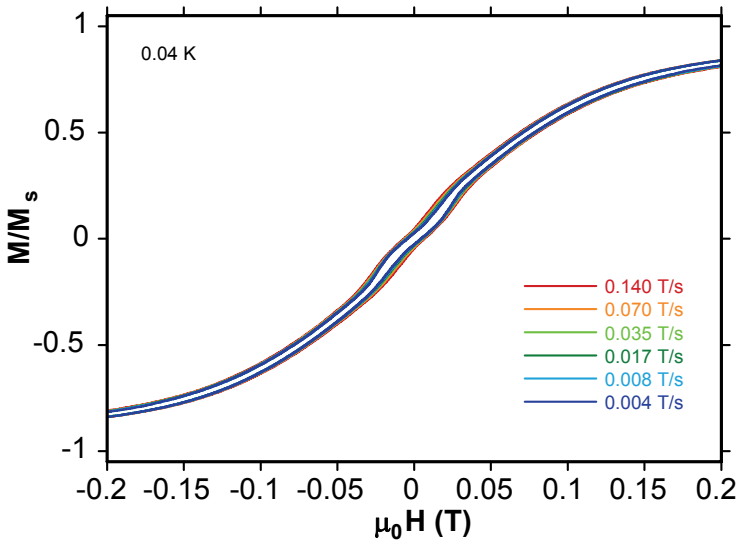


Figure S4 Temperature dependence of the real and imaginary components of the nonlinear second harmonic *ac* susceptibility for **1** in zero applied static field (up) and 1kOe (down) with an oscillating field 5 Oe in frequency of 111-9999 Hz.



(b)

Figure S5 Single crystal magnetization (M) versus field (H) hysteresis loops for **1** at the indicated field sweep rates and temperatures. The small features at low fields (0.03 T) are probably due to tiny antiferromagnetic interactions between molecules.