Supporting Information

Linear Trinuclear Cobalt(II) Single-Molecule Magnets

Yuan-Zhu Zhang,[a,*] Andrew J Brown,[b] Yin-Shan Meng,[a] Hao-Ling Sun,[c] Song Gao*,[a]

[a] *Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, 100871 Beijing, China. Fax: (+86)-10-62751708; Tel: (+86)-10-62756320; E-mail: yuanzhuzhang@gmail.com; gaosong@pku.edu.cn.*

[b] *Department of Chemistry, Texas A & M University, College Station, TX 77842-3012 (USA).*

[b] *Department of Chemistry, Beijing Normal University, Beijing 100875, P. R. China*

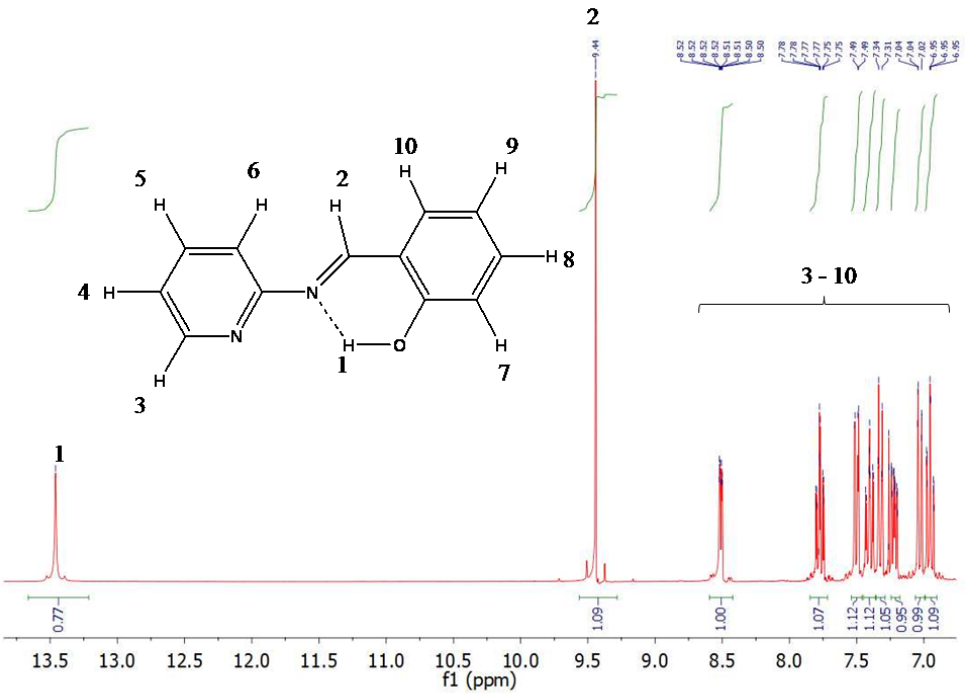

Fig. S1 NMR spectra of HPymp in $CDCl_3$.

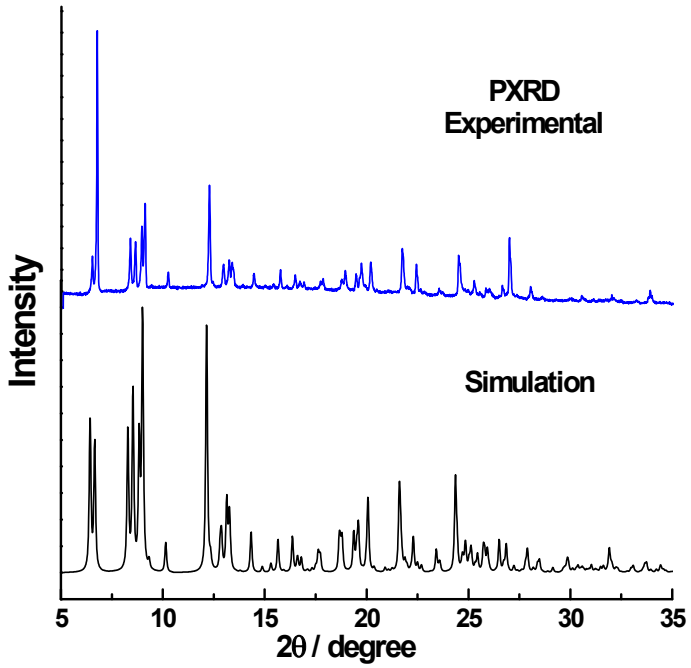

Fig. S2 Experimental and simulated powder x-ray diffraction patterns of **1**.

The powder X-ray diffraction (PXRD) data of ground fine powder was collected on a Rigaku Multiplex powder X-ray diffractometer with Cu Kα radiation (40 kV, 40 mA) between 5.0 and 35° (2θ) at ambient temperature.(Fig. S1) The PXRD data at room temperature on the sample **1** well matched with the calculated one from single crystal data.

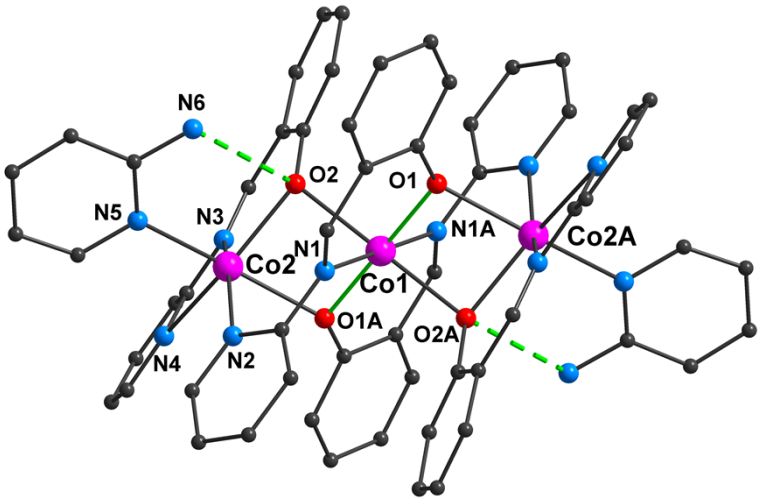

Fig. S3. Ball-and-stick view of X-ray structure of **2**. All anions and hydrogen atoms are eliminated for clarity.

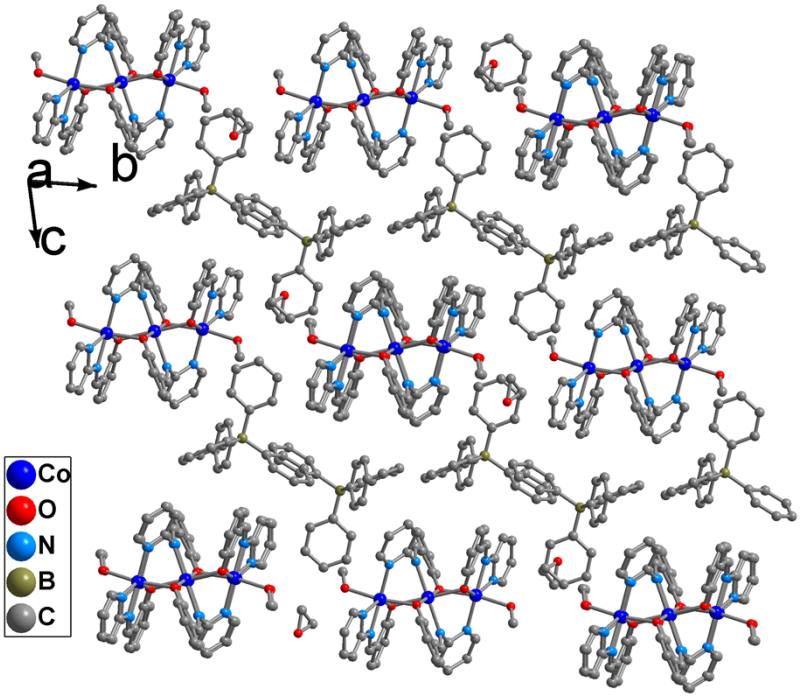

Fig. S4 Packing view of **1** showing a 3D structure, where the linear $[Co^{II}_3]^{2+}$ cations are well isolated by the large counter anions of $[BPh_4]^-$.

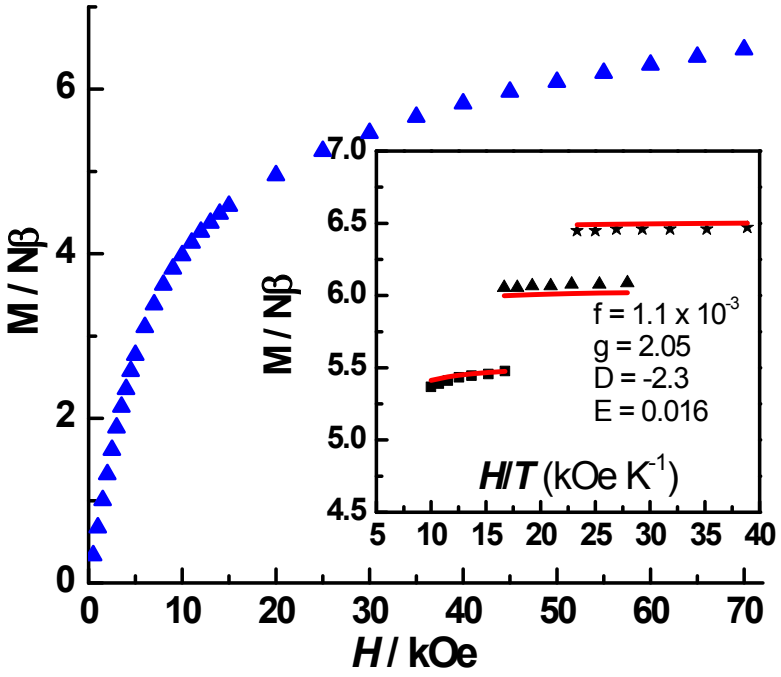

Fig. S5. *M* vs. *H* plot at 1.8 K for **2**. Inset: Reduced magnetization data in applied fields (30, 50 and 70 kOe) at temperatures between 1.8 and 3.0 K; the solid lines represent the best fitting via ANISOFIT$^{2.0}$ with D = -2.3 cm^{-1}, E = 0.016 cm^{-1}, and g = 2.05 for a S_T = 9/2 spin model.

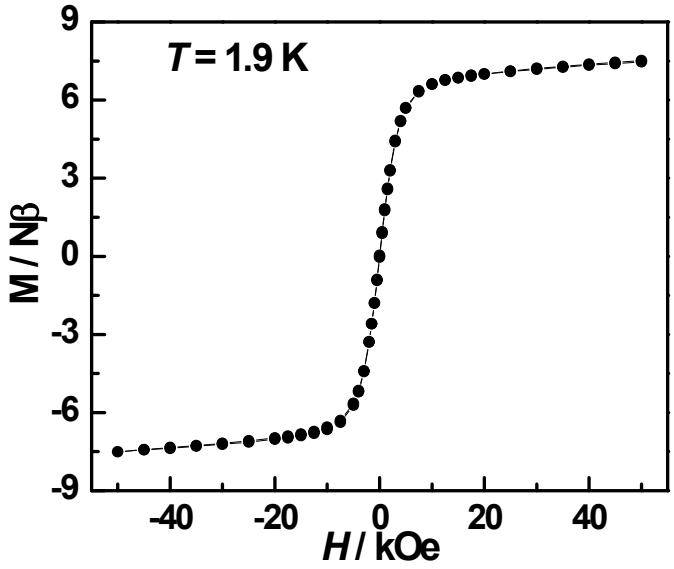

Fig. S6. Magnetic hysteresis loop at 1.9 K for **1**. Solid line is guide for eyes.

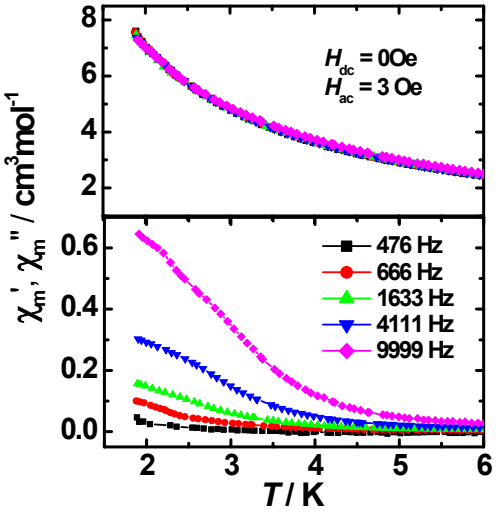

Fig. S7 In-phase ((χ_m') and out-of-phase (χ_m'') ac susceptibilities under zero applied *dc* field and an *ac* field of 3 Oe at different frequencies for **1.**

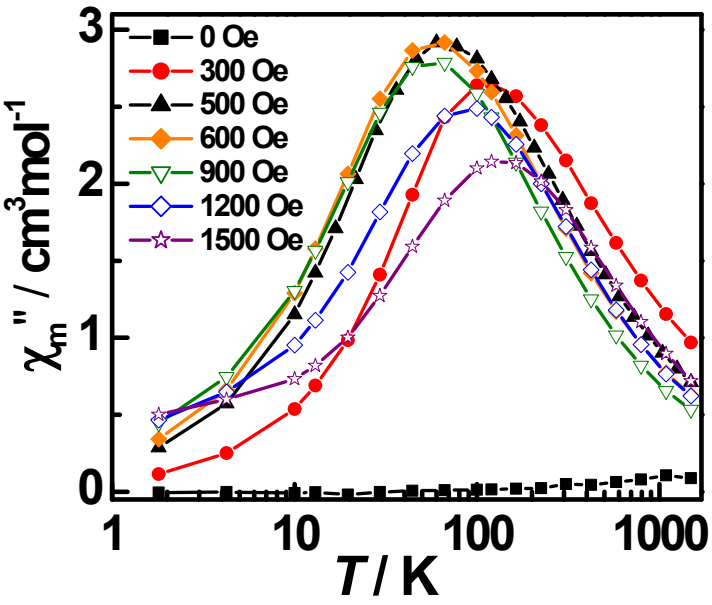

Fig. S8 Variable-frequency out-of-phase (χ_m'') components of the ac magnetic susceptibility data for **1**, collected at temperatures of 1.80 K with an ac filed of 3 Oe and 0-1500 Oe dc applied fields.

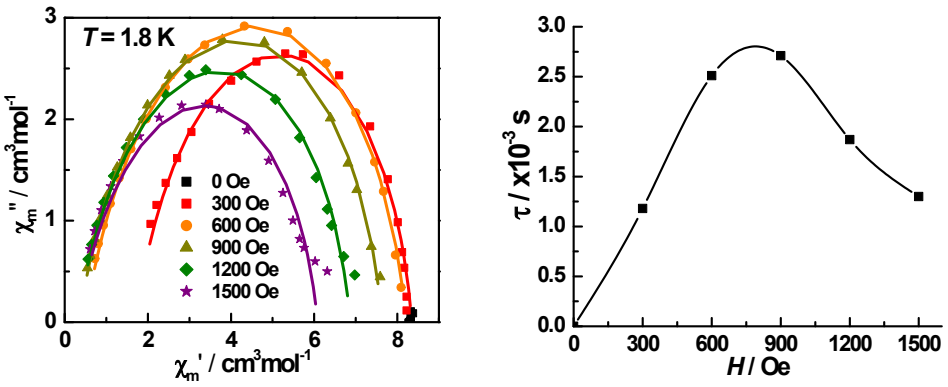

Fig. S9. (left) Cole-Cole diagrams of **1** at 1.80 K with applied dc fields of 0-1500 Oe and ac field of 3 Oe. The solid lines are least-square fittings of the data to a distribution of single relaxation processes with a generalized Debye model.[a,b] (right) the plot of the pre-exponential time (τ) vs. applied dc fields.

Refs: (a) Cole, K. S.; Cole, R. H. *J. Chem. Phys.* **1941**, 9, 341. (b) Aubin, S. M.; Sun, Z.; Pardi, L.; Krzysteck, J.; Folting, K.; Brunel, L.-J.; Rheingold, A. L.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **1999**, 38, 5329.

Table S1. Fittings of Cole-Cole plots of the variable-frequency ac data, collected at 1.8 K under different dc fields (0-1500 Oe), based on a generalized Debye model.

H / Oe	χ_s ($cm^3\ mol^{-1}$)	χ_t ($cm^3\ mol^{-1}$)	τ (S)	α	R
300	1.72426	8.34446	0.00118	0.14442	4.32×10^{-4}
600	0.49137	8.20729	0.00251	0.17532	2.72×10^{-4}
900	0.34342	7.63448	0.00271	0.17051	1.65×10^{-4}
1200	0.30042	6.86897	0.00187	0.17673	3.86×10^{-4}
1500	0.30021	6.08291	0.00130	0.19045	1.12×10^{-3}

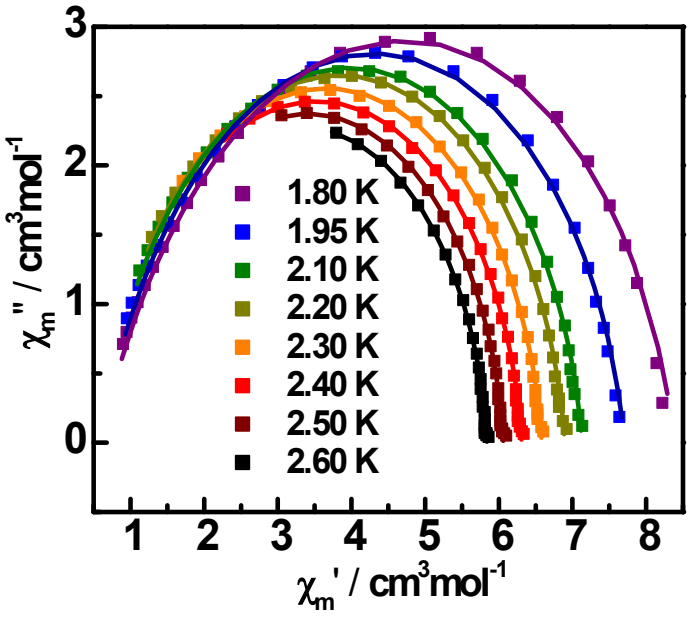

Fig. S10 Cole-Cole diagrams of **1** at 1.80 to 2.60 K with an applied dc field of 500 Oe and ac field of 3 Oe. The solid lines are least-square fittings of the data to a distribution of single relaxation processes with a generalized Debye model.

T / K	χ_s (cm^3 mol^{-1})	χ_t (cm^3 mol^{-1})	τ (S)	α	R
1.80	0.60296	8.38488	0.00218	0.18453	3.43×10^{-4}
1.95	0.60761	7.70748	0.00127	0.14832	2.39×10^{-4}
2.10	0.59273	7.13226	0.00067	0.11995	1.19×10^{-4}
2.20	0.57666	6.89795	0.00049	0.11111	8.62×10^{-5}
2.30	0.56791	6.58369	0.00030	0.10246	4.79×10^{-5}
2.40	0.60278	6.31127	0.00019	0.09268	3.21×10^{-5}
2.50	0.63322	6.06312	0.00013	0.08485	1.93×10^{-5}
2.60	0.69169	5.83851	0.00009	0.07783	1.56×10^{-5}

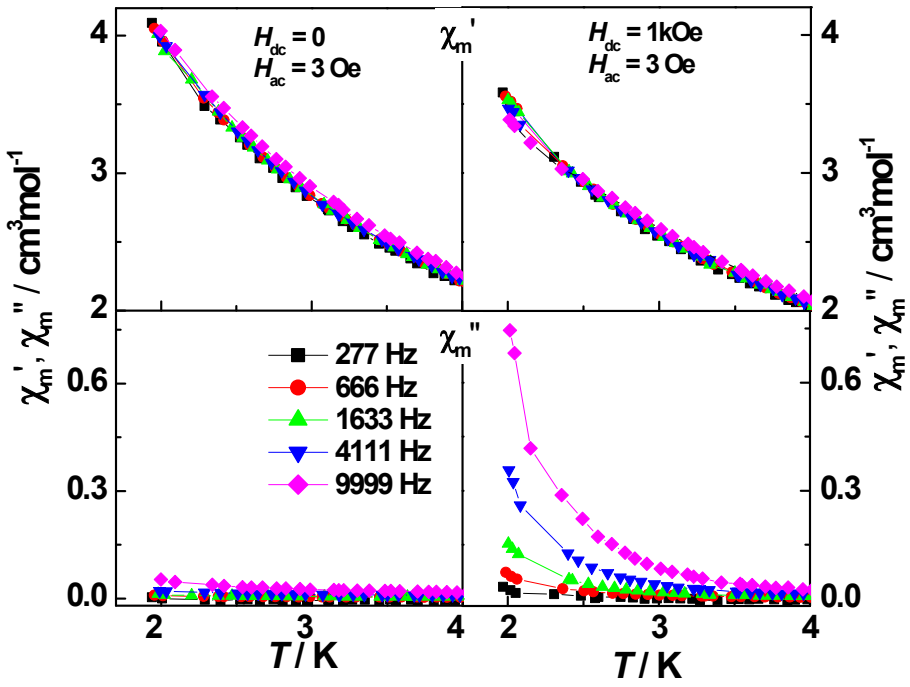

Fig. S11 In-phase ((χ_m') and out-of-phase (χ_m'') ac susceptibilities in zero (left) and 1 kOe (right) applied *dc* field and an *ac* field of 3 Oe at different frequencies for **2.**

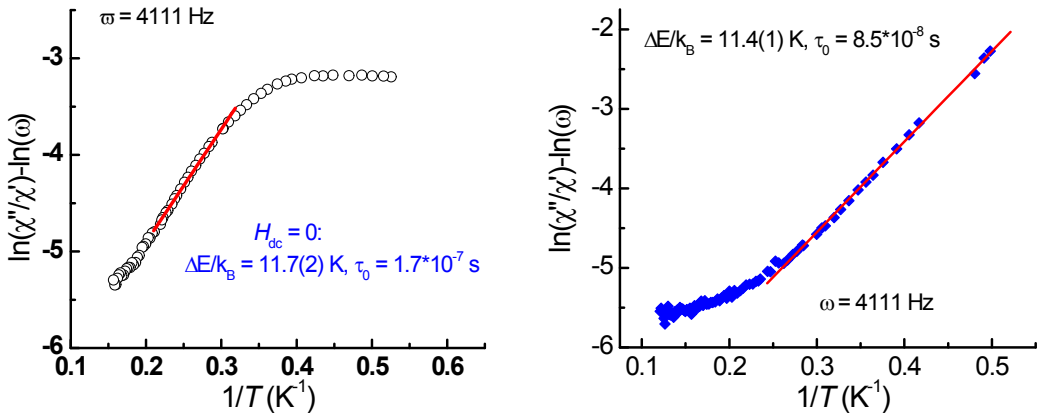

Fig. S12 Estimations of the U_{eff} and τ_0 for both **1** and **2** by fitting the experimental data at 4111 Hz based on a relative expression: $\ln(\chi''/\chi') = \ln(\omega\tau_0)+Ea/(K_BT)$ gave: (left) for **1**, U_{eff} (zero) = 11.7(2) K and τ_0(zero) = 1.7 × 10^{-7} S; (Right) for **2**, U_{eff} (1kOe) = 11.4(1) K and τ_0(1kOe) = 8.5 × 10^{-8} S.

Ref: Bartolomé, J.; Filoti, G.; Kuncser, V.; Schinteie, G.; Mereacre, V.; Anson, C.E.; Powell, A. K.; Prodius, D.; and Turta, C.; *Phys. Rev. B*, **2009**, *80*, 014430.