Electronic Supporting Information (ESI)

Unprecedented 1D alternate Co_5 chain and discrete Co_3 unit embedded in a 3D framework exhibiting slow magnetic relaxation behavior

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Materials and Measurements: All reagents were purchased from commercial sources and used as received. Infrared spectra were obtained in KBr discs on a Nicolet Avatar 360 FTIR spectrometer in the range of 400−4000 cm^{-1}. Elemental analyses of C, H and N were determined with a Perkin-Elmer 2400C Elemental Analyzer. Thermogravimetric analyses (TGA) were carried out in nitrogen stream using a Seiko Extar 6000 TG/DTA equipment with heating rate of 5°C min^{-1}. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (CuKα, 1.5418 Å). Magnetism measurements were performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).[1]

Synthesis of $[Co_4(\mu_3\text{-}OH)_2(L)_2(bpe)_2]$ (1): A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (0.0586 g, 0.2 mmol), L (0.0260 g, 0.1 mmol), bpe (0.0182 g, 0.1 mmol), NaOH (0.016 g, 0.4 mmol) and deionized water (10 mL) was stirred for 30 min in the air, then transferred and sealed in a 25 mL Teflon reactor, which was heated at 140 °C for 72 h. The autoclave was cooled to room temperature at a rate of 5 °C h^{-1}, and red crystals of **1** were isolated by washing with water, and dried in air (final yield: 87% based on L). Elem anal. Calcd for **1**: C, 53.97; H, 2.83; N, 4.66. Found: C, 53.92; H, 2.76; N, 4.63. IR data (KBr, cm^{-1}): 3516m, 1600vs, 1558s, 1498s, 1392vs, 1365m, 1250m, 1012m, 962m, 824m, 775m, 696m, 555m, 494w.

X-Ray Crystallography: Single-crystal X-ray diffraction analysis of **1** were carried out on a Bruker SMART APEX II CCD area detector diffractometer at 296(2) K using ω rotation scans with a scan width of 0.3° and Mo Kα radiation (λ = 0.71073 Å). Empirical absorption corrections were carried out utilizing SADABS routine.[2] All of the structures were solved by the direct methods and refined by full-matrix least-squares refinements based on F^2.[3] All non-hydrogen

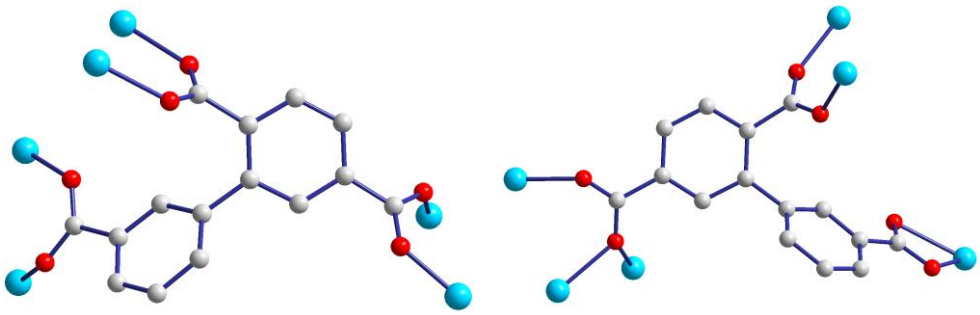
atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Crystal data of **1**: $C_{54}H_{36}Co_4N_4O_{14}$, M = 1200.63, 296(2) K, triclinic, P-1, a = 8.1571(10) Å, b = 14.7919(18) Å, c = 20.877(3) Å, β = 95.964(2) Å, V = 2328.5(5) Å^3, Z = 2, D_c = 1.709 mg cm^{-3}, F(000) = 1212, R_{int} = 0.0378, final R_1 = 0.0537, wR_2 = 0.1325 for 8511 unique reflections ($I \geq 2\sigma$), S = 0.99. CCDC–883424 contains the crystallographic data for **1**, and the selected bond distances and angles are listed in Table S1.

References

1 Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993.

2 Bruker. *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconson, USA, 2002.

3 Sheldrick, G. M. SHELXL-97, program for the refinement of the crystal structures. University of Göttingen, Germany, 1997.



Scheme S1 Two coordination modes of L in **1**: μ_2-η^1:η^1 (left) and μ_1-η^1:η^1, μ_2-η^1:η^1 and μ_3-η^1:η^2 (right)

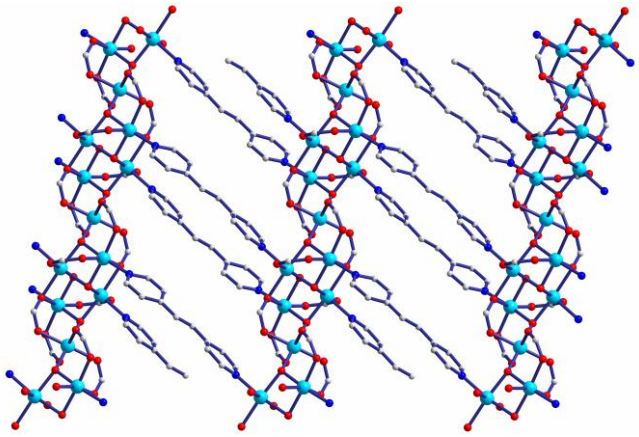


Fig. S1 The 2D layer constructed by 1D Co_5-chains and bpe linkers.

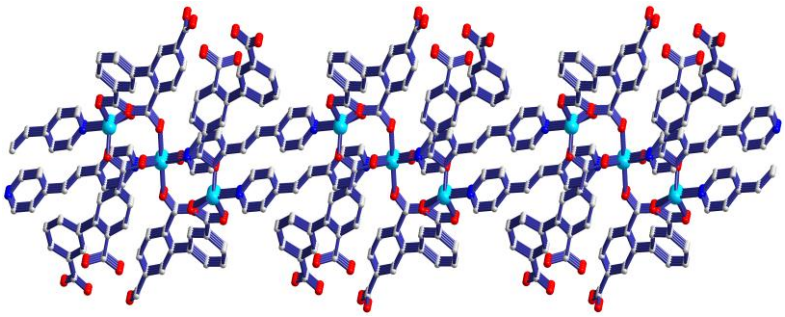


Fig. S2 The 2D layer constructed by Co_3 units, bpe and L ligands.

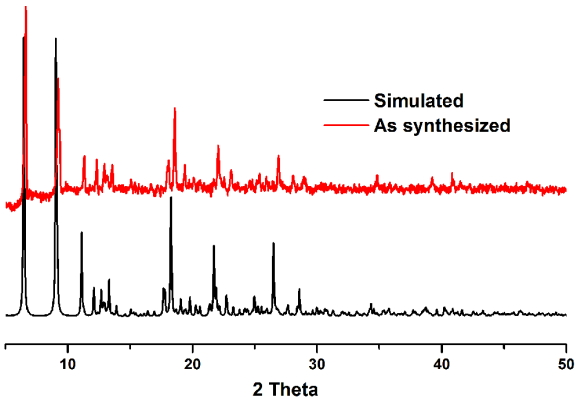


Fig. S3 X-ray diffraction patterns of **1** measured at 298 K are in good agreement with theirs corresponding simulated patterns, indicating phase purities of the samples.

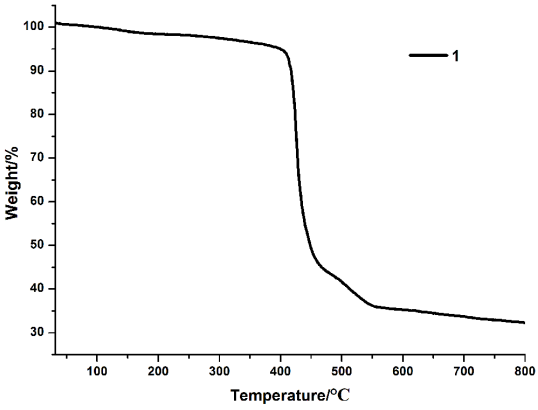


Fig. S4 TGA curve of **1** under N_2. The curve shows that **1** can be stable up to 420 °C, indicating high thermal stability of the framework.

The χ_M expression for **1** is provided in the following Eq:

$$\chi_{Co} = \frac{8N\beta^2}{k(T-\theta)x} \frac{\begin{array}{l} \dfrac{7(3-A)^2x}{5} + \dfrac{12(A+2)^2}{25A} + \left\{ \dfrac{2(11-2A)^2x}{45} + \dfrac{176(A+2)^2}{675A} \right\} \exp(-5Ax/2) \\ + \left\{ \dfrac{(A+5)^2x}{9} - \dfrac{20(A+2)^2}{27A} \right\} x\exp(-4Ax) \end{array}}{3+2\exp(-5Ax/2)+\exp(-4Ax)}$$

Where $x = \lambda / kT$, and A is a measure of the crystal field strength.

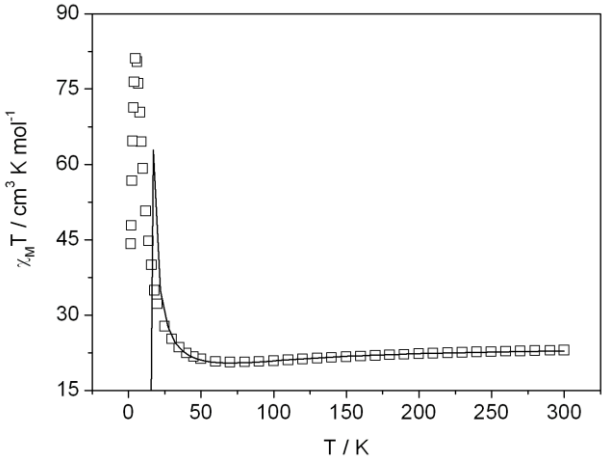


Fig. S5 The fits of the data accounting to the spin-orbit coupling λ for the $^4T_{1g}$ state of Co^{2+}.

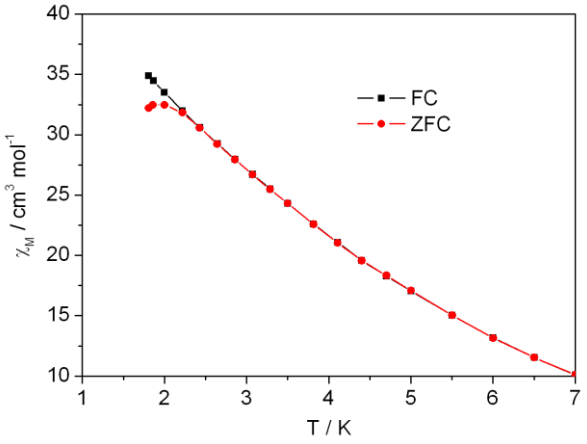


Fig. S6 Zero field cooled magnetization (ZFC) and field cooled magnetization (FC) versus T measured at 30 Oe for **1**.

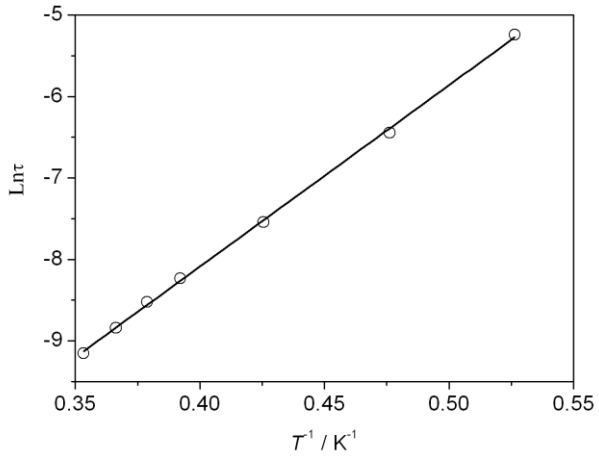


Fig. S7 The ln(τ) versus 1/T plot of **1**, the solid line representing the fit to the Arrhenius law.

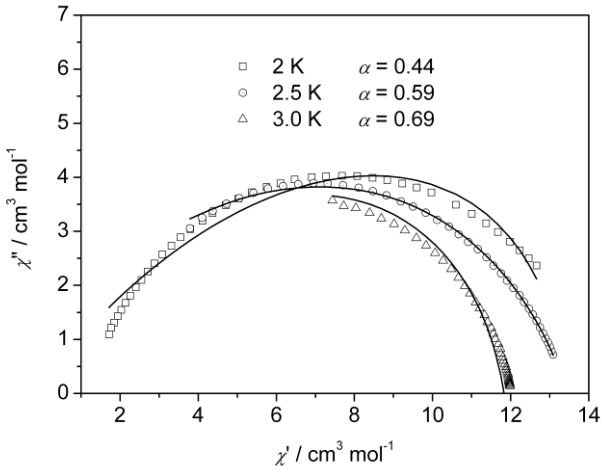
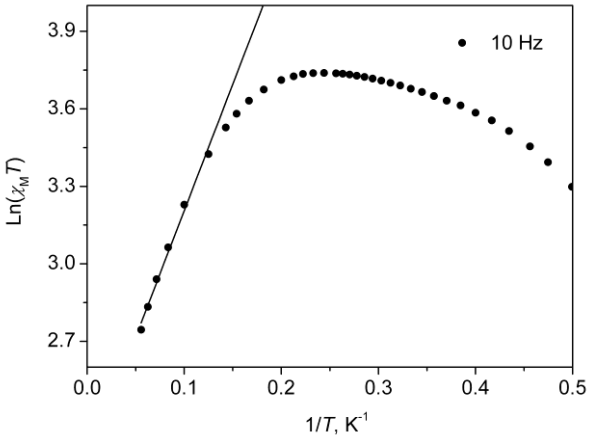


Fig. S8 Cole-Cole plots of χ″ vs χ′ at 2.0 K, 2.5 K and 3 K for **1**. The solid lines represent the least-squares fit by a generalized Debye model. References: Cole, K. S.; Cole, R. H. *J. Chem. Phys*. **1941**, *9*, 341. (b) Boettcher, C. J. F.; *Theory of Electric Polarisation*, Elsevier, Amsterdam, 1952. (c) 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.

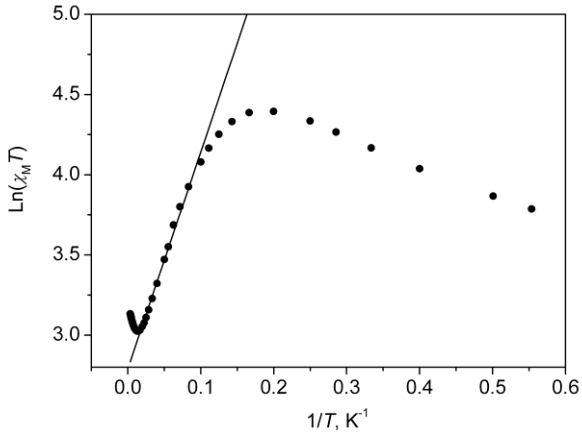
Extended Debye model:

$$x' = x_S + (x_T - x_S)\frac{1+(w\tau)^{1-\alpha}\sin\left(\alpha\frac{\pi}{2}\right)}{1+2(w\tau)^{1-\alpha}\sin\left(\alpha\frac{\pi}{2}\right)+(w\tau)^{2-2\alpha}}$$

$$x'' = (x_T - x_S)\frac{(w\tau)^{1-\alpha}\cos\left(\alpha\frac{\pi}{2}\right)}{1+2(w\tau)^{1-\alpha}\sin\left(\alpha\frac{\pi}{2}\right)+(w\tau)^{2-2\alpha}}$$



(a)



(b)

Fig. S9 (a) The logarithm of Ln(χ'T) vs. 1/T of **1**. The susceptibility was obtained in an applied ac field of 3.5 Oe and frequency of 10 Hz. The solid line is the result of a fit between 6 and 18 K (above), giving the creation energy for domain wall (Δ_ζ) 9.8 K. (b) The logarithm of Ln($\chi_M T$) vs. 1/T. The susceptibility was obtained in an applied dc field of 1 kOe. The solid line is the result of a fit between 8.0 and 60 K (down). The best fitting gives the Δ_ζ = 13.5 K.

Table S1. Selected bond lengths [Å] and angles [°] for **1**

Co(1)-O(5)	2.060(3)	Co(1)-O(6)	2.092(3)
Co(1)-O(2)#1	2.094(4)	Co(1)-O(4)	2.114(4)
Co(1)-N(2)#2	2.146(4)	Co(1)-O(7)#3	2.233(3)
Co(2)-O(6)#4	2.003(3)	Co(2)-O(3)	2.054(3)
Co(2)-O(5)	2.086(3)	Co(2)-N(1)	2.186(4)
Co(2)-O(6)	2.187(3)	Co(2)-O(7)#5	2.234(3)
Co(3)-O(5)	2.043(3)	Co(3)-O(14)	2.094(3)
Co(3)-O(1)#4	2.150(3)	Co(4)-O(12)	2.097(4)
Co(4)-O(8)#5	2.123(4)	Co(4)-N(3)	2.137(4)
Co(5)-O(13)	1.947(4)	Co(5)-O(9)#7	1.928(4)
Co(5)-O(11)#8	1.980(4)	Co(5)-O(10)#8	2.369(4)
Co(5)-N(4)#9	2.080(5)		
O(5)-Co(1)-O(6)	86.97(13)	O(5)-Co(1)-O(2)#1	91.13(14)
O(6)-Co(1)-O(4)	86.70(14)	O(5)-Co(1)-O(4)	91.40(14)
O(2)#1-Co(1)-O(7)#3	107.36(14)	O(2)#1-Co(1)-O(4)	88.48(15)
O(5)-Co(1)-O(7)#3	86.33(13)	O(6)-Co(1)-O(7)#3	77.39(13)
O(5)-Co(2)-O(6)	83.92(13)	O(3)-Co(2)-O(5)	87.69(14)
O(6)-Co(2)-O(7)#5	93.31(13)	O(6)#4-Co(2)-O(6)	81.67(14)
O(3)-Co(2)-O(6)	88.85(13)	O(3)-Co(2)-O(7)#5	98.87(14)
O(5)-Co(3)-O(14)	83.05(13)	O(14)-Co(3)-O(1)#4	98.97(14)
O(5)-Co(3)-O(1)#1	86.76(13)	O(12)-Co(4)-O(8)#7	93.71(15)
O(9)#7-Co(5)-O(11)#8	110.65(19)	O(13)-Co(5)-O(11)#8	114.90(19)

Symmetry codes: #1 x-1,y,z; #2 x+1,y+1,z; #3 -x,-y+2,-z+1; #4 -x+1,-y+2,-z+1; #5 x+1,y,z; #6 -x+1,-y+1,-z; #7 -x,-y+1,-z; #8 -x-1,-y+1,-z; #9 -x+2,-y+2,-z.