

Embedding 1D or 2D cobalt-carboxylate substrates in 3D coordination polymers exhibiting slow magnetic relaxation behaviors: Crystal Structures, High-Field EPR, and Magnetic Studies

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1 Experiment section

Materials and General Methods. All starting materials were obtained commercially and were used without further purification. The IR spectra were recorded in range of 400-4000 cm^{-1} on a Nicolet 5DX spectrometer (KBr pellets). The ligand were synthesized by a literature method¹⁸. Magnetic susceptibility measurements were carried out in the temperature range of 2–300 K with a magnetic field of 1000 Oe on Quantum Design MPMS XL-7 magnetometer. The low temperature heat capacity had been measured by PPMS.

Synthesis of $\{[\text{Co}(\text{H}_2\text{O})_6] \cdot [\text{Co}_2(\text{L}_1)_2]\}_n$ (1): A mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (25 mg, 0.1 mmol), L1 (27 mg, 0.1 mmol), acetone (2 mL) and deionized water (0.5 mL) was placed in a 25 mL Teflon-lined reactor then sealed and heated at 155°C for 3 days. After the mixture was cooled to room temperature at a rate of 5 °C·h⁻¹, red plate-like crystals were obtained in 40% yield. IR (KBr, cm^{-1}): 3580(m), 3122(m), 1666(s), 1570(s), 1413(2), 1392(s), 1282(s), 1138(w), 1004(m), 781(m).

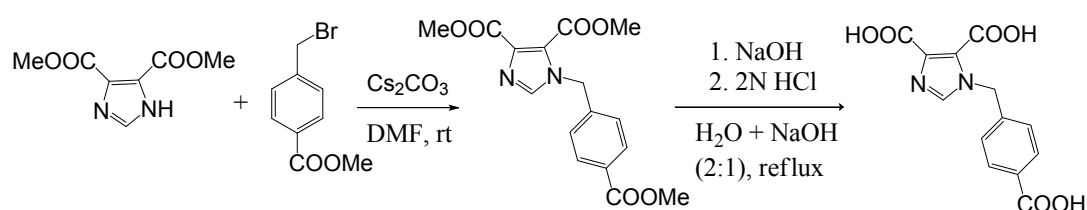
Synthesis of $\{\text{Co}(\text{H}_2\text{O})(\text{L}_3)\}_n$ (2**):** A mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (25 mg, 0.1 mmol), L2(32 mg, 0.1 mmol), DEF(4 mL) and deionized water (4 mL) was sealed in a 20 mL borosilicate screw vial and then heated at 80 °C for 24 h., red crystals were obtained in 60% yield. IR (KBr, cm^{-1}): 3364(m), 1683(m), 1577(s), 1508(m), 1375(s), 1236(m), 1134(w), 862(w), 764(m).

X-Ray Structural Determination. X-ray diffraction data of **1** ($0.2 \times 0.1 \times 0.1$ mm) and **2** ($0.1 \times 0.1 \times 0.05$ mm) were collected on Bruker diffractometer using Mo- $K\alpha$ ($\lambda = 0.71073$ Å) radiation at room temperature. The structures of complexes were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix leastsquares procedure based on F^2 values. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. CCDC-1508980 (**1**) and CCDC-1508981 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Reference:

(1) (a) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, 32, b115-119; b) G. M. Sheldrick, *SHELXL-97; Program for refinement of crystal structures*. University of Göttingen, Göttingen, Germany, **1997**.

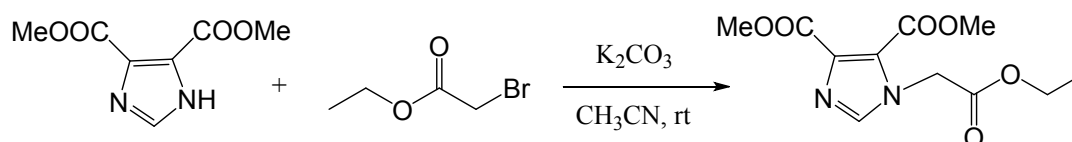
Synthesis of L1



The synthesis of **1** was similar to *CrystEngComm*, **2013**, 15, 9596–9602. 1 g (5.4 mmol) dimethyl 1H-imidazole-4,5-dicarboxylate was dissolved in 50 mL DMF and 2.1 g (6.48 mmol) Cs₂CO₃ was added to it. After 1 h stirring, to the suspension, 1.34 g (5.89 mmol) methyl-4-(bromomethyl)benzoate was added and stirred at room temperature for 24 h.

The reaction mixture was poured into 400 mL H₂O, further EtOAc was added and the mixture was stirred for 10 min, the organic layer was separated, washed with water and dried over anhydrous Na₂SO₄. Solvent was evaporated under reduced pressure, 1.6 g white solid was obtained. The product was refluxed with NaOH in a 2 : 1 (v/v) water and ethanol mixture for 24 h. The neutralization of the resulting solution by 2N HCl yielded 1.3 g white solid product (yield 87%). The NMR spectral data were consistent with the those previously reported. ¹H NMR (400 MHz, DMSO-d₆): 8.72 (H, s), 5.82 (2H, s), 7.30(2H, d), 7.88 (2H, d).

Synthesis of L2



The synthesis of 1 was similar to *Eur. J. Org. Chem.* **2015**, 188–194. A 50 mL round bottomed flask, fitted with a magnetic stirring bar, was charged with dimethyl 1H-imidazole-4,5-dicarboxylate (4 g, 21.6 mmol) in acetonitrile (30 mL). To this K₂CO₃ (3.0 g, 21.6 mmol) was added and the reaction mixture was stirred for 2 h under an argon atmosphere. Ethyl bromoacetate (4.8 mL, 53.2 mmol) was added and the reaction mixture was stirred at room temperature for 2 d. Upon completion of the reaction, the solvent was removed in vacuo and the resulting residue was extracted with dichloromethane. The extracts were combined and concentrated in vacuo giving a pale yellow solid. This solid was washed with ether after which the pure product L1 was obtained as a white solid (4.5 g, 80%). The NMR spectral data were consistent with the those previously reported. ¹H NMR (400 MHz, CDCl₃): 1.29(t, 3H), 3.90(s, 3H), 3.94(s, 3H), 4.25(s, 3H), 4.98(s, 2H), 7.61(s, 1H).

Synthesis of {[Co(H₂O)₆] • [Co₂(L₁)₂]}_n (**1**): A mixture of Co(OAc)₂·4H₂O (25 mg, 0.1 mmol), L1 (27 mg, 0.1 mmol), acetone(2 mL) and deionized water (0.5 mL) was placed in a 25 mL Teflon-lined reactor then sealed and heated at 155°C for 3 days. After the mixture was cooled to room temperature at a rate of 5 °C·h⁻¹, red plate-like crystals were obtained in 40% yield. IR (KBr, cm⁻¹): 3580(m), 3122(m), 1666(s), 1570(s),

1413(2), 1392(s), 1282(s), 1138(w), 1004(m), 781(m).

Synthesis of $\{Co(H_2O)(L_3)\}_n$ (2): A mixture of $Co(OAc)_2 \cdot 4H_2O$ (25 mg, 0.1 mmol), L2(32 mg, 0.1 mmol), DEF(4 mL) and deionized water (4 mL) was sealed in a 20 mL borosilicate screw vial and then heated at 80 °C for 24 h., red crystals were obtained in 60% yield. IR (KBr, cm^{-1}): 3364(m), 1683(m), 1577(s), 1508(m), 1375(s), 1236(m), 1134(w), 862(w), 764(m),

2 QMC simulation detail

Simulation Method: Quantum Monte Carlo calculations were performed by our fitting program, which call LOOP[1] sub-program of ALPS[2]. Specifically, four parameters (J , g , zJ and TIP) were further used to fit M-T curve by use of exhaustive-iterative method. The corresponding formulas were shown in Eq(1)-Eq(4). The running procedure of our program is presented as follows: In the beginning, the range of four parameters (J , g , TIP , zJ) were respectively set to that: $[J_1: J_2]$, $[g_1: g_2]$, $[TIP_1: TIP_2]$, $[zJ_1: zJ_2]$, and the step sizes were set to ΔJ , Δg , ΔTIP and ΔzJ . Until the running is over, the best parameters (R_b , J_b , g_b , TIP_b , zJ_b) were obtained.

$$\chi_u = \frac{1}{NT} \left\langle \left(\sum_{i=1}^N S_i^z \right)^2 \right\rangle \quad \text{Eq(1)}$$

where uniform magnetic susceptibility χ_u is dimensionless.

Convert uniform magnetic susceptibility to χ_T ($cm^3 mol^{-1}$)

$$\chi_T (cm^3 mol^{-1}) = Ag^2 \chi_u \quad \text{Eq(2)}$$

where g is Landé-factor and A is unit constant.

Import zJ and TIP factor to χ_T , as bellows:

$$\chi_T (cm^3 mol^{-1}) = \frac{(\chi_T + TIP)}{1 + \frac{zJ(\chi_T + TIP)}{0.1303g^2}} \quad \text{Eq(3)}$$

The reliability factor R is obtained by

$$R = \frac{\sum (\chi_T^I - \chi_{obs}^I)^2}{\sum (\chi_{obs}^I)^2} \quad \text{Eq(4)}$$

Simulation Parameters: For each site, 2×10^6 Monte Carlo steps and 2×10^5 Monte Carlo sweeps for thermalization were performed. The spins sample of 20×20 for **1** is large enough to prevent any finite size effects. Moreover, periodic boundary conditions (PBC) were applied in order to avoid perturbation from the edge of the sample and speed up convergence toward the infinite lattice limit. The Hamiltonian operator was presented as following Eq(5).

$$H = - \sum_{i=i+2}^W \sum_{j=j+2}^L [J_1(S_{ij}S_{ij+1} + S_{i+1,j+1}S_{i+1,j+2}) + J_2(S_{ij}S_{i+1,j} + S_{i+1,j}S_{i+2,j})] + \sum_{i=i+1}^W \sum_{j=j+1}^L D(S_{ij})_z$$

Eq(5)

3. DFT computational detail

3.1 The computation of U_{eff} value of **2**

The U_{eff} of Co(II) ion in compound **2** was calculated using the linear response approach introduced by Cococcioni et.al[3]. Computation was performed by using of PWSCF package[4]. In this calculation, based on the projector augmented wave (PAW) [5] method, Perdew, Burke and Ernzerhof (PBE) [6] exchange-correlation functional was used to described the exchange-correlation interaction. And Vanderbilt ultrasoft pseudopotentials with the plane-wave energy cutoff of 35 Ryd were adopted. The sampling of Brillouin zone involves $4 \times 2 \times 4$ Monkhorst-Pack grid. By invariant formulation, the total energy of DFT+U can be described as follow:

$$E_{\text{DFT+U}}[n(r)] = E_{\text{DFT}}[n(r)] + E_{\text{U}}[\{n_{\text{mm}}^{I\sigma}\}]$$

Where, E_{DFT} is a total energy from noninteraction Kohn-Sham algorithm; E_{U} is Hubbard correction.

Furthermore, if neglecting higher-multipolar terms of Coulomb interaction, E_{U} is written as:

$$E_{\text{U}}[\{n_{\text{mm}}^{I\sigma}\}] = \frac{U-J}{2} \sum_{I,\sigma} \text{Tr}[n^{I\sigma}(1-n^{I\sigma})] = \frac{U_{\text{eff}}}{2} \sum_{I,\sigma} \text{Tr}[n^{I\sigma}(1-n^{I\sigma})]$$

By linear-response approach U method, the linear response function is defined as

$$\chi = \frac{\partial n}{\partial \alpha}$$

In this method, the interacting (χ) and noninteracting density response functions with respect to localized perturbations were firstly calculated. Thus U can be obtained by following formula:

$$U_{eff} = \chi_0^{-1} - \chi^{-1}$$

By changing the rigid potential shifts α , we obtain the bare and self-consistent occupation regression response functions. The interacting (χ) and the noninteracting (χ_0) are the slopes of bare and self-consistent regression response functions, respectively. Therefore, the obtained U_{eff} are 2.14 eV for **1**, as shown in Fig.S1.

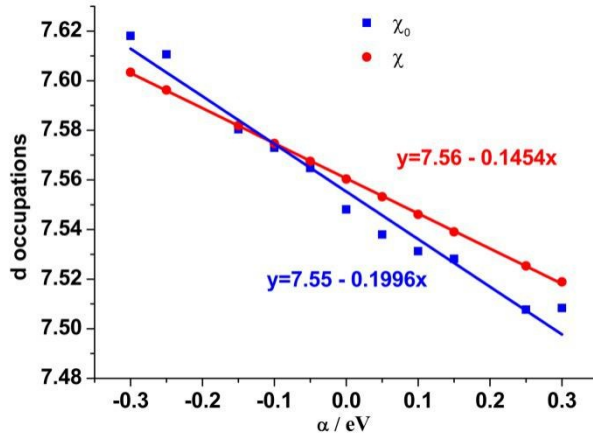


Fig. S1 A curve of interacting (χ) and noninteracting density response functions of **2**.

3.2 Electronic structure and Magnetic property calculation

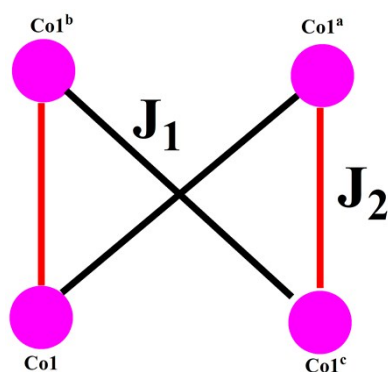
Spin-polarized DFT calculation, including geometry optimization, electronic structure and magnetic properties, were performed by using VASP program[7]. Projector-augmented wave (PAW) [5] method of Blöchl, featuring the accuracy of augmented plane-wave methods as well as the efficiency of the pseudopotential approach, was used to treat wave function. Based on generalized gradient approximation (GGA), Perdew Burke Ernzerhof (PBE)[6] functional was used to deal with the exchange-correlation (XC) effects. The 3d electrons of Co, 2s and 2p electrons of C, N and O, and 1s electrons of H were explicitly regarded as valence electrons. The electron wave function is expanded in plane waves up to a cutoff energy of 450 eV. For the Brillouin zone integration, the Γ centered $4 \times 2 \times 4$ grids were adopted. One non-local

correlation vdW-DF based on opt88 functional [8] was applied to correct the dispersion interaction. Meanwhile, GGA+U algorithm[9] was used to correct the strongly correlated interaction in 3d electrons of Co ion. The effective Hubbard U_{eff} values were identified by linear response method (see following details). The optimization convergence in energy and force was set to 1.0×10^{-5} eV and 2.0×10^{-3} eV/Å, and the SCF convergence was set to 1.0×10^{-6} . Partial Density of State (PDOS) was also identified following the tetrahedron method with Blöchl corrections. Spin magnetic moment $M = N(\uparrow) - N(\downarrow)$ is the difference between the number of spin-up and spin-down electrons, which can be obtained by integrating the corresponding spin-projected densities of states up to the Fermi level. Two magnetic exchange parameters (J_1 and J_2) following hamiltonian operator $H = -\sum J_i S_i S_j$ were identified by using of broken symmetry method[10-11].

Table S1: Comparison of bond length for experiment structure, optimized geometry of **2** with U and without U.

Bond	Experiment	U=2.14	U=0.00
Co1-O3	2.038	2.046	2.037
Co1-O2	2.085	2.106	2.095
Co1-O4	2.100	2.153	2.143
Co1-O1	2.139	2.157	2.159
Co1-O5	2.250	2.326	2.350
Co1-N1	2.105	2.116	2.113
Co1...Co1^a	5.411	5.410	5.414
Co1^a...Co1^b	4.518	4.508	4.494

Symmetry code: (a): 2-x, -y, 1-z; (b): -x+1/2, y+1/2, -z+1/2.



Scheme S1 connecting mode of four Co(II) ion in the cell with two syn-syn carboxylates (J_1) and one syn-anis carboxylates (J_2). Symmetry code: (a): $2-x, -y, 1-z$; (b): $-x+1/2, y+1/2, -z+1/2$; (c) $-1/2+x, -1/2-y, z+1/2$.

Table S2 Spin magnetic moment M_s (μ_B) of Co(II) ions and bridging carboxylate.

Atom	Co1 ^b	Co1 ^a	Co1	Co1 ^c	O2 ^b	C1	O1 ^a
M_s	-2.646	2.646	-2.646	2.646	0.046	0.002	-0.044
Atom	O4 ^a	C5 ^a	O3 ^a	O3	C5	O4	
M_s	-0.037	-0.004	-0.057	-0.057	-0.004	-0.037	

Symmetry code: (a): $2-x, -y, 1-z$; (b): $-x+1/2, y+1/2, -z+1/2$; (c) $-1/2+x, -1/2-y, z+1/2$.

Reference

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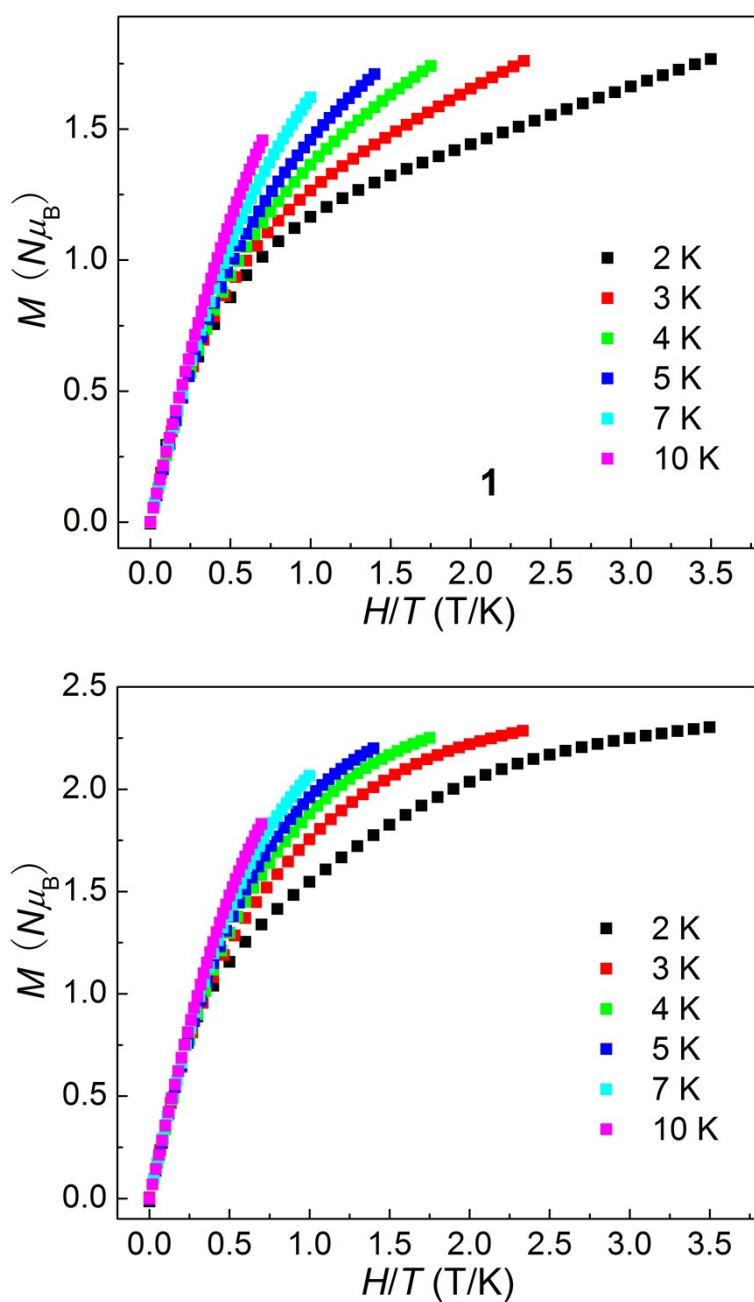


Figure S2. Isothermal magnetization curves at different temperatures for **1** (top) and **2**

(bottom).

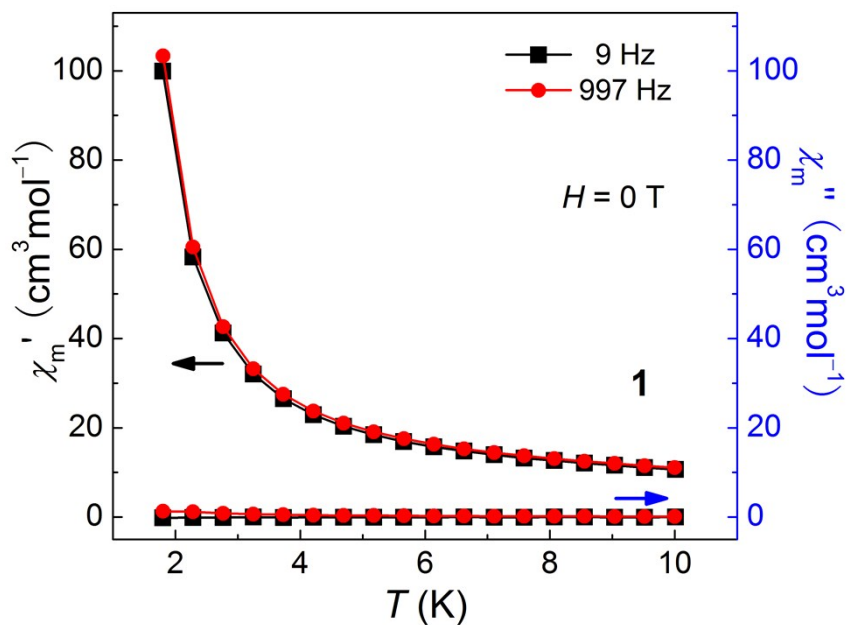


Figure S3. AC susceptibilities of **1** under zero magnetic field.

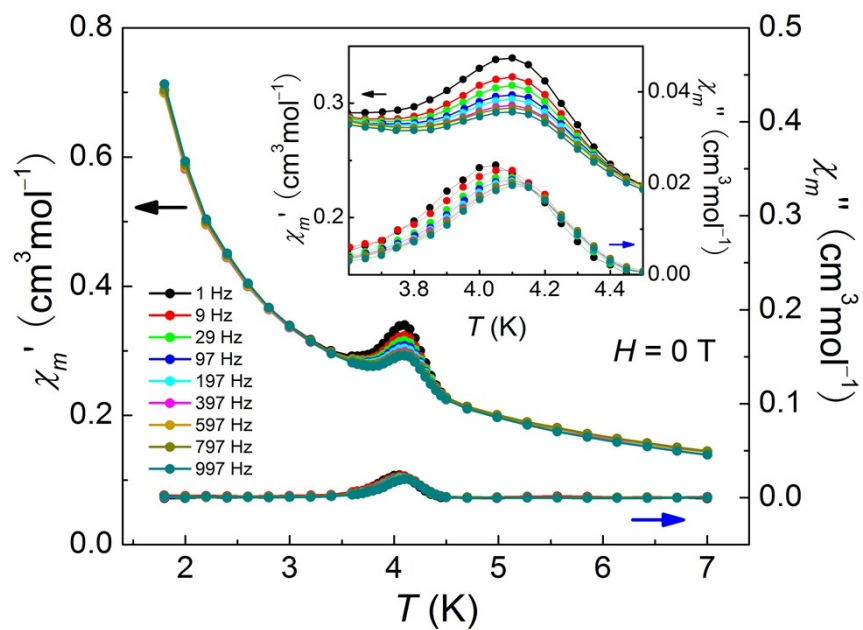


Figure S4. AC susceptibility for **2** under zero magnetic field.

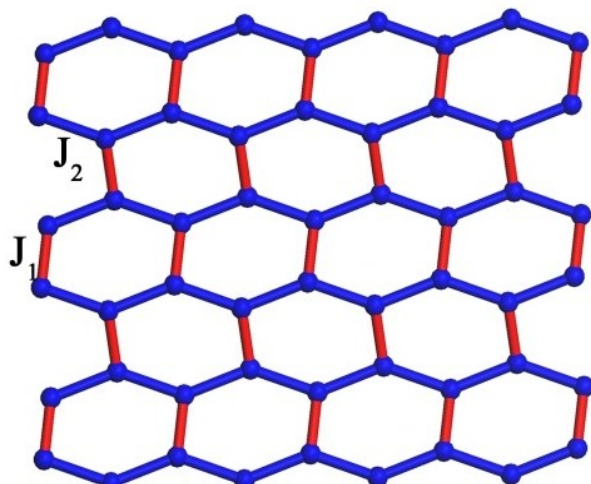


Figure S5. The coupling pathway in the two-dimensional 6³ net Co-COO layer.

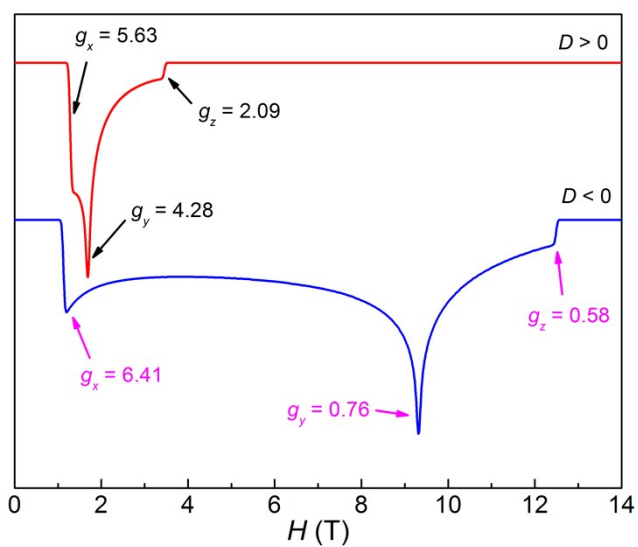


Figure S6. Simulated HF-EPR spectra of a high spin Co(II) cluster with the spin Hamiltonian parameters: $S = 3/2$, $|D| = 47.6 \text{ cm}^{-1}$, $E = 0.44 \text{ cm}^{-1}$, $g_x = g_y = 2.495$, $g_z = 2.15$ (*Angew. Chem. Int. Ed.* **2013**, 52, 9130–9134). Labeled g_x , g_y , and g_z are effective g -values which are all larger than 2.00 when $D > 0$, while g_x is larger than 2.00 but g_y and g_z are smaller than 2.00 when $D < 0$.