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# Control of Interchain Antiferromagnetic Coupling in Porous Co(II)-Based Metal–Organic Frameworks by Tuning the Aromatic Linker Length: How Far Does Magnetic Interaction Propagate?

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**Supporting Information** 

**ABSTRACT:** Three MOF-74-type Co(II) frameworks with one-dimensional hexagonal channels have been prepared. Co(II) spins in a chain are ferromagnetically coupled through carboxylate and phenoxide bridges. Interchain antiferromagnetic couplings via aromatic ring pathways operate over a Co–Co length shorter than ~10.9 Å, resulting in a field-induced metamagnetic transition, while being absent over lengths longer than ~14.7 Å.



# INTRODUCTION

Molecule-based magnetic materials have been one of the hot research topics in pursuing a fundamental understanding of intriguing magnetic features and in seeking potential applications in magnetic devices.<sup>1–3</sup> In these systems, the magnetic ordering behavior depends on the exchange strength between spin centers and the number of magnetic neighbors. Because the magnetic interactions between paramagnetic ions are mediated via the bridging groups, the critical temperature directly correlates with the number and type of constituent atoms in the linker. In fact, the ordering temperatures for one-, two-, three-, and four-atom-bridged three-dimensional materials do not surpass 900, 350, 50, and 2 K, respectively.<sup>4</sup>

When it comes to one-dimensional Heisenberg magnetic systems, magnetic ordering is theoretically not feasible. Nonetheless, long-range ordering often occurs in the chain compounds if there are substantial interchain magnetic interactions through space, noncovalent contacts, or covalent bonds.<sup>5–11</sup> An important consideration is the potential for spin-exchange anisotropy as one would expect for a non-Heisenberg ion such as Co(II). This could give rise to long-range order at low temperature as well. In comparison, when the interchain couplings in one-dimensional anisotropic systems are negligible relative to intrachain interactions, slow magnetic relaxation, characteristic of single-chain magnets, may be anticipated.<sup>12–14</sup> Thus, the extent of interchain interactions over the lattice plays

a pivotal role in controlling and tuning the spin alignment or magnetic dynamics of chain compounds. Controlling the chain-chain magnetic coupling is a formidable task because it is difficult to design one-dimensional model compounds with identical chain structures and different interchain metal-metal distances.

Metal–organic frameworks (MOFs) are a new class of porous crystalline materials and have potential applications in gas storage and separation, sensing, catalysis, and magnetism and other useful purposes.<sup>13–17</sup> They have strong merits of predesigning and adjusting structural entities in isoreticular framework families. More importantly, from a magnetic point of view, it is possible to locate the spin centers at the lattice sites of a framework structure, thereby controlling the metal–metal distances and magnetic interaction in a systematic fashion. Hence, it is envisioned that interchain metal–metal distances could be modulated by altering the organic ligand length in a predesigned MOF series with identical structural motifs and coupling strengths could be evaluated as a function of the linker length.

In this work, we realize this strategy with Co-MOF-74-type structures with various aromatic linkers. This series is characterized by one-dimensional chains of Co(II), bridged

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Figure 1. Synthetic scheme of 1-3.

by carboxylates and phenoxides, which are separated by different spacer benzene rings. Intrachain ferromagnetic coupling happens along the chain direction, while interchain antiferromagnetic interactions are mediated through the aromatic rings. We first demonstrate that the interchain magnetic coupling turns on at a Co–Co distance below 10.9 Å and turns off at a distance above 14.7 Å.

# EXPERIMENTAL SECTION

**Preparation.** All starting materials and solvents were purchased from commercial suppliers and were utilized without further purification. All chemicals and solvents in the synthesis were of reagent grade and were used as received. 4,4'-Dihydroxy-[1,1'-biphenyl]-3,3'-dicarboxylic acid (H<sub>4</sub>dobpdc) was prepared according to literature procedures.<sup>18</sup>

**Dimethyl** 4,4"-Dihydroxy-[1,1':4',1"-terphenyl]-3,3"-dicarboxylate (Me<sub>2</sub>H<sub>2</sub>dotpdc). A mixture of methyl-5-bromosalicylate (9.52 mmol, 2.20 g), 1,4-benzenediboronic acid (3.81 mmol, 631 mg), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.610 mmol, 704 mg) was added to tetrahydrofuran (75 mL) and heated to 65–70 °C. After the addition of an aqueous K<sub>2</sub>CO<sub>3</sub> (22.9 mmol, 3.16 g) solution (25 mL), the mixture was stirred at reflux for 24 h. The resulting solution was evaporated to provide a powder. The powder was portioned between chloroform and H<sub>2</sub>O. The organic layer was dried over magnesium sulfate, filtered, and evaporated to give a crude product, which was purified by silica gel column chromatography (EA:Hex = 1:3). The product was obtained as a white powder. Yield: 35% (132 mg). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  10.81 (s, 2H), 8.11 (d, 2H, *J* = 2.3 Hz), 7.73 (q, 2H, *J* = 11.0 Hz), 7.62 (s, 4H), 7.08 (d, 2H, *J* = 8.7 Hz). Anal. Calcd for C<sub>22</sub>H<sub>18</sub>O<sub>4</sub>: C, 69.83; H, 4.79. Found: C, 70.19; H, 5.01.

**4,4**<sup>*w*</sup>-**Dihydroxy-[1,1**':**4**',1"-**terphenyl]-3,3**"-**dicarboxylic Acid** (**H**<sub>4</sub>**dotpdc**). Me<sub>2</sub>H<sub>2</sub>dotpdc (200 mg) was dissolved in ethanol (EtOH; 100 mL). The solution was heated up to 130 °C. A saturated KOH solution (10 mL) and H<sub>2</sub>O (50 mL) were added to it and then heated for 1 h. The resulting solution was heated to remove EtOH, and the remaining aqueous solution was filtered by a Celite. The resulting solution was acidified to pH = 1 with HCl, and a white powder was generated. The powder was collected and washed with H<sub>2</sub>O. Yield: 91% (337 mg). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ 11.11–11.46 (br, 2H), 8.07 (d, 2H, *J* = 2.4 Hz), 7.87 (q, 2H, *J* = 11.1 Hz), 7.70 (s, 4H), 7.05 (d, 2H, J = 8.6 Hz). Anal. Calcd for  $C_{20}H_{14}O_6$ · 1.1H<sub>2</sub>O: C, 64.90; H, 4.41. Found: C, 64.93; H, 4.44.

 $[Co_2(dobdc)(DMF)_{1.5}(H_2O)_{0.5}]\cdot 0.4H_2O$  (1). A mixture of cobalt(II) bromide (328 mg, 1.50 mmol) and H<sub>4</sub>dobdc (147 mg, 0.750 mmol) was dissolved in a mixed solvent of *N*,*N*-dimethylformamide (DMF; 8 mL) and EtOH (8 mL). The resulting solution was transferred into each of the 35 mL Pyrex cells and sealed with poly-(tetrafluoroethylene) caps. The mixture was irradiated in a microwave reactor (CEM Discover, 100 W, 150 psi) at 130 °C for 20 min. The light-brown powder was collected by filtration and washed with DMF and EtOH. The product was dried in vacuum conditions. Anal. Calcd for  $C_{12.5}H_{14.3}Co_2N_{1.5}O_{8.4}$ : C, 34.29; H, 3.29; N, 4.80. Found: C, 33.98; H, 3.61; N, 4.66. This compound was soaked in MeOH for 3 days and refreshed every day. The MeOH-exchanged sample was evacuated at 360 °C for 90 min to generate the activated solid of  $[Co_2(dobdc)]$ (activated 1).

 $[Co_2(dobpdc)(DMF)_2] \cdot 1.7H_2O$  (2). Compound 2 was obtained by the same procedure as that for compound 1, except that H<sub>4</sub>dobpdc (206 mg, 0.750 mmol) was used instead of H<sub>4</sub>dobdc. Anal. Calcd for  $C_{20}H_{23.4}Co_2N_2O_{9.7}$ : C, 42.53; H, 4.18; N, 4.96. Found: C, 42.18; H, 4.33; N, 4.71. For the adsorption experiments, we synthesized a sample in *N*,*N*-dibutylformamide (DBF) instead of DMF because DBF was easy to remove from the framework. The phase of  $[Co_2(dobpdc)(DBF)_2]$  was confirmed by powder X-ray diffraction (PXRD). This compound was soaked in methanol (MeOH) for 3 days and refreshed every day. The MeOH-exchanged sample was evacuated at 350 °C for 90 min to generate the activated solid of  $[Co_2(dobpdc)]$ (activated 2).

 $[Co_2(dotpdc)(DMF)_2]\cdot 2.4H_2O$  (3). Compound 3 was obtained by the same procedure as that for compound 1, except that H<sub>4</sub>dotpdc (263 mg, 0.750 mmol) was used instead of H<sub>4</sub>dobdc. Anal. Calcd for  $C_{26}H_{28.8}Co_2N_2O_{10.4}$ : C, 47.78; H, 4.44; N, 4.29. Found: C, 48.03; H, 4.11; N, 4.61. For the adsorption experiments, we synthesized a sample using DBF instead of DMF because the DBF solvent was easy to remove. The phase of  $[Co_2(dotpdc))(DBF)_2]$  was confirmed by PXRD. This compound was soaked in MeOH for 3 days and refreshed every day. The MeOH-exchanged sample was evacuated at 300 °C for 60 min to generate the activated solid of  $[Co_2(dotpdc)]$  (activated 3).

**PXRD.** The synchrotron PXRD data were collected at 298 K with a detector distance of 240 mm in 2400 s exposure with synchrotron radiation ( $\lambda = 1.09998$  Å) using a two-dimensional SMC ADSC Quantum 210 detector with a silicon (111) double-crystal

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monochromator at the Pohang Accelerator Laboratory. The *ADX* program<sup>19</sup> was used for data collection, and the *Fit2D* program<sup>20</sup> was used for converting a two-dimensional diffraction image to a one-dimensional diffraction pattern.

**Other Physical Measurements.** Gas sorption isotherms were measured using a BEL Belsorp mini II gas adsorption instrument up to 1 atm of gas pressure. The highly pure  $N_2$  (99.999%) was used in the sorption experiments. The  $N_2$  gas isotherm was measured at 77 K. Thermogravimetric analysis (TGA) was carried out at a ramp rate of 20 °C min<sup>-1</sup> for all samples or 5 °C min<sup>-1</sup> for the others in an Ar (99.999%) flow using a Scinco TGA N-1000 instrument. IR spectra were obtained using a Thermo Nicolet 380 spectrometer. Elemental analyses for C, H, and N atoms were performed at the Elemental Analysis Service Center of Sogang University. Magnetic susceptibilities for all compounds were carried out using a Quantum Design SQUID susceptometer (Korea Basic Science Institute) and a PPMS magnetometer. Diamagnetic corrections of all samples were estimated from Pascal's tables.

# RESULTS AND DISCUSSION

Structures and Characterization. We prepared three Co(II)-based frameworks,  $[Co_2(L)(DMF)_x(H_2O)_y] \cdot zH_2O$  with different linker lengths, in a microwave-assisted solvothermal reaction where L<sup>4-</sup> represents 2,5-dihydroxybenzene-1,4dicarboxylic acid (H<sub>4</sub>dobdc; 1), 4,4'-dihydroxy-[1,1'-biphenyl]-3,3'-dicarboxylic acid (H<sub>4</sub>dobpdc; 2), and 4,4"-dihydroxy-[1,1':4',1''-terphenyl]-3,3''-dicarboxylic acid (H<sub>4</sub>dotpdc; 3). To confirm the phases of the prepared solid frameworks, we performed synchrotron PXRD measurements and analyzed the data using a Pawley refinement. Our results showed that all compounds adopted MOF-74 or extended MOF-74-type structures (Figures 1 and S1). The hexagonal channels are developed along the *c* axis, and each corner of the hexagon consists of a one-dimensional Co(II) chain formed by bridging carboxylates and phenoxides of the organic ligand, leading to the intrachain Co-Co distances of 2.81 Å for 1, 2.78 Å for 2, and 2.70 Å for 3. The chains in the structures are separated by the aromatic parts of the organic linkers, and the Co-Co distances between the chains are 8.1 Å for 1, 10.9 Å for 2, and 14.7 Å for 3. The internal metric parameters reveal that Co atoms within a chain are linked together by similar bond distances, but they are significantly separated by different spacings between chains.

The as-prepared samples were soaked in MeOH for 3 days to allow exchange of DMF with MeOH because the DMF molecules with high boiling temperatures are not easily removed from the pores. The MeOH-exchanged solids were fully activated at 300-380 °C for 60-90 min under vacuum. We performed IR spectroscopy to examine the complete removal of guest molecules from the pores of the frameworks. The C=O stretching vibration of DMF and the HOH bending mode of H<sub>2</sub>O are evident at 1650-1660 and 1690 cm<sup>-1</sup> respectively (Figure S2). These characteristic peaks disappeared after MeOH exchange and subsequent activation processes, implying that the lattice molecules were unoccupied in the pores of the frameworks. The structural integrity of the MeOHexchanged and activated samples was maintained, as confirmed by PXRD patterns (Figure S3). The thermal stabilities of 1-3were investigated by using TGA (Figure S4). The guest solvents of 1-3 were eliminated between 300 and 400 °C, and the structures started to decompose at ~500  $^{\circ}$ C. The N<sub>2</sub> isotherms of the activated samples of 1-3 were recorded at 77 K to probe the basic gas adsorption behavior (Figure 2). The Brunauer-Emmett-Teller surface areas are 750 m<sup>2</sup> g<sup>-1</sup> for 1,

2072 m<sup>2</sup> g<sup>-1</sup> for 2, and 2523 m<sup>2</sup> g<sup>-1</sup> for 3, which are dependent on the ligand linker length.



Figure 2.  $\rm N_2$  adsorption isotherms in activated samples of 1–3 at 77 K.

Magnetic Properties. We collected the molar magnetic susceptibility data of 1-3 at T = 2-300 K and H = 1000 G (Figure 3). The  $\chi_m T$  values at room temperature are equal to  $6.41 \text{ cm}^3 \text{ K mol}^{-1}$  for 1, 6.30 cm<sup>3</sup> K mol<sup>-1</sup> for 2, and 6.23 cm<sup>3</sup> K  $mol^{-1}$  for 3, which are much larger than the theoretical value  $(3.75 \text{ cm}^3 \text{ K mol}^{-1})$  expected for two Co(II) ions with  $S = \frac{3}{2}$ . The observed values are different from the theoretical one because of the substantial orbital contribution of a high-spin Co(II) ion in an octahedral ligand field. As the temperature decreases,  $\chi_m T$  undergoes a gradual reduction and reaches a minimum around  $T_{min}$  = 25 K for 2 and 3, while no minimum is visible in 1. The slow downturn in  $\gamma_m T$  is associated with the thermal depopulation of the low-lying excited-state levels created by spin-orbit coupling. It is not manifest which magnetic character is operative with the steady decrease in  $\chi_m T$ for 1. However,  $\chi_m T$  for 2 and 3 increases below  $T_{\min}$ , which undoubtedly supports ferromagnetic coupling between Co spins along a metal oxide chain. Hence, the overall feature in the  $\chi_m T$  product can be described by not only spin-orbit coupling but also ferromagnetic exchange interaction.

To take into account both effects, we attempted to simulate the magnetic data of 1-3 using the simple phenomenological equation  $\chi_m T = A \exp(-E_1/k_B T) + B \exp(-E_2/k_B T)$ , where A + B,  $E_1$ , and  $E_2$  stand for the Curie constant, the spin–orbit coupling, and the magnetic coupling, respectively.<sup>21–24</sup> The best fit gives  $A + B = 6.86 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$ ,  $E_1 = 28.9 \text{ cm}^{-1}$ , and  $E_2$  $= -2.98 \text{ cm}^{-1}$  for 1,  $A + B = 6.61 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$ ,  $E_1 = 30.9 \text{ cm}^{-1}$ , and  $E_2 = -4.83 \text{ cm}^{-1}$  for 2, and  $A + B = 6.59 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$ ,  $E_1 = 32.0 \text{ cm}^{-1}$ , and  $E_2 = -2.90 \text{ cm}^{-1}$  for 3. The A + B parameter lies in the range ( $5.6-6.8 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$ ) of the Curie constant for two high-spin Co(II) ions in an octahedral field, and the  $E_1$ value is similar to that observed for Co(II) systems.<sup>4</sup> The negative  $E_2$  component implies that Co(II) spins ferromagnetically interact within a chain on the basis of the Ising chain model  $\chi_m T \propto \exp(\beta J/k_B T)$ .

To extract the magnetic contribution only from the susceptibility curve, we used the modified formula, given as  $\chi_m T_{mag} = \chi_m T_{exp} - A \exp(-E_1/k_B T)$ , by removing the spin-orbit coupling term. The extracted magnetic part was plotted in the  $\chi_m T$  versus T frame and fitted based on an infinite-chain model with the Hamiltonian  $H = -J\Sigma_i S_i \cdot S_{i+1}$ .<sup>25</sup> The best-fit parameters for the S = 3/2 Co(II) chain system result in g =



**Figure 3.** Plot of  $\chi_m T$  versus *T* for (a) **1**, (b) **2**, and (c) **3**. The open squares show raw experimental data, which were fitted using the Rueff expression (solid line). The dotted line shows the spin-orbit coupling effect contributed from  $A \exp(-E_1/k_BT)$ . The subtraction of the dotted line from the raw data results in the open circles. The solid line is the result fitted with the Fisher model.

2.80 and J = 0.77 cm<sup>-1</sup> for 1, g = 2.83 and J = 1.61 cm<sup>-1</sup> for 2, and g = 2.89 and J = 1.10 cm<sup>-1</sup> for 3. The positive values corroborate that ferromagnetic interaction in a Co(II) chain is communicated via carboxylates and phenoxides of the bridging ligands. The sharp drop in  $\chi_m T$  is appreciable for 1 and 2, which is responsible for the existence of interchain antiferromagnetic interactions as well as the possible involvement of zero-field splitting. In contrast, a continuous  $\chi_m T$  rise is observed in 3, revealing that the interchain antiferromagnetic coupling is negligible.

The M(H) data of 1-3 were collected at T = 2 K and H = 0-7 T (Figure 4). Compounds 1 and 2 exhibit a sigmoidal shape, typical of metamagnetic behavior, whereas the magnetization curve of 3 does not show such a characteristic. The metamagnetic transition is characterized by a critical field that



**Figure 4.** Plots of *M* versus *H* for 1-3 at 2 K. The inset gives the derivatives of *M* against *H*.

can be calculated from the peak in the dM/dH versus H plot. The critical field  $(H_{cr})$ , which implies Ising-like anisotropy of the Co(II) ion, is estimated to be 25 kG for 1 and 2 kG for 2. Below this critical field, interchain antiferromagnetic interactions are mediated through the aromatic linkers. This feature is confirmed by the presence of the cusp temperature in the  $\chi_{\rm m}(T)$  plot at fields below  $H_{\rm cr}$  (Figure S5). The application of an external field causes the weak antiferromagnetic coupling to be overcome, which promotes a magnetic phase transition from the antiferromagnetic state to the ferromagnetic state. In comparison, a maximum peak in the  $\chi_m(T)$  plot is not observed in 3, suggesting that antiferromagnetic interactions between chains are absent (Figure S6). The phase diagrams of 1 and 2 are plotted in Figure S7 on the basis of the peak field in dM/dHand the cusp temperature in field-cooled  $\chi_m(T)$ . At low temperatures, Co(II) can be evaluated as an effective spin S' = $^{1}/_{2}$ . The Brillouin functions at 2 K allow for the g values being 4.55 for 1, 4.40 for 2, and 4.17 for 3 at 7 T (Figure S8), which are usually higher than 4 for a high-spin Co(II) system in an octahedral field.<sup>26</sup> The large g value is associated with the formation of a Kramers' doublet at low temperature.

To check the dynamic magnetic behavior, we performed ac susceptibility measurements at  $H_{ac} = 3$  G and  $H_{dc} = 0$  G with several frequencies in the temperature range of 2–30 K (Figure S9). The in-phase part  $(\chi_m')$  gradually increases below 10 K and shows a frequency-independent maximum at 6.6 K for 1 and 3.8 K for 2, while the out-of-phase component  $(\chi_m'')$  is invisible in the same temperature region. The peak temperature in  $\chi_m'(T)$  is indicative of the occurrence of an antiferromagnetic ordering, which is in good agreement with the critical points in the phase diagrams of 1 and 2 (Figure S7).

From the MOF-74-type structures, we demonstrated that Co(II) spin centers are positioned to generate identical chains along the *c* direction and the chain—chain distances are systematically altered using ligands containing one, two, and three phenyl rings. Therefore, the Co–Co distance between chains changes from 8.1 Å for 1 to 10.9 Å for 2 and to 14.7 Å for 3. The magnetic data reveal that interchain antiferromagnetic coupling survives within a distance of 10.9 Å but becomes nullified at 14.7 Å. This is a clear first demonstration of the distance limit of the interchain antiferromagnetic coupling range in magnetic MOF-74-type families, although super-

exchange coupling between Co spins could be slightly mediated through  $\pi$  systems of the benzene rings.

# CONCLUSIONS

We prepared a series of three Co(II) MOF-74 analogues, formed by bridging groups with benzene (1; dobdc<sup>4–</sup>), biphenyl (2; dobpdc<sup>4–</sup>), and *p*-terphenyl (3; dotpdc<sup>4–</sup>) rings, which have carboxylate/phenoxide-bridged one-dimensional Co(II) chains, and the distance between chains varies with the aromatic linker length. The ferromagnetic Co(II) chains in 1 and 2 interact antiferromagnetically through the phenyl rings, resulting in field-induced metamagnetic transitions, whereas 3 does not show antiferromagnetic interactions between chains. These results indicate that the interchain interaction is systematically controllable by the ligand length and disappears if the Co–Co distance is above ~14.7 Å in the current series.

# ASSOCIATED CONTENT

#### **S** Supporting Information

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Additional structural and magnetic data for the compounds (PDF)

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#### Notes

The authors declare no competing financial interest.

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