

## ***Electronic Supplementary Information***

### **Unique 3D Co<sup>II</sup>/Zn<sup>II</sup> -coordination polymers with (3,4,5)-connected self-penetrating topology: Syntheses, topological structures, luminescent and magnetic properties**

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## Materials and General Methods

All the solvents and reagents for syntheses were commercially available and used as received. The infrared spectra ( $400\text{--}4000\text{ cm}^{-1}$ ) were recorded as KBr pellets a FTIR Nexus spectrophotometer. Elemental analyses were performed on a Perkin-Elmer 2400 Series II analyzer. Powder X-ray diffraction (PXRD) patterns were taken on a Rigaku Ultima IV diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.5406\text{ \AA}$ ), with a scan speed of  $8^\circ/\text{min}$  and a step size of  $0.02^\circ$  in  $2\theta$ . The calculated PXRD patterns were simulated by using the single-crystal X-ray diffraction data. Thermogravimetric (TG) curves were recorded on a NETZSCH STA 449C microanalyzer in air atmosphere at a heating rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$ . the fluorescent property and fluorescence lifetime were recorded on a EDINBURGH INSTRUMENTS-FLS920. Variable-temperature magnetic susceptibility measurements (2-300 K) were carried out on a Quantum Design PPMS60000 in a magnetic field of 1KOe, and the diamagnetic corrections were evaluated by using Pascal's constants.

## Crystallographic data collection and refinement

The data collections were performed at 293(2)K on a Bruker SMART APEX CCD diffractometer using graphite-monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). Absorption corrections were made with the program SADABS [1], and the crystallographic package SHELXTL [2] was used for all calculations. Metal atoms in complex 1 were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses, which were refined with anisotropic thermal parameters on  $F^2$ . The H atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The H atoms of the water molecules were located using the difference Fourier method and constrained refinement. CCDC 847910 and 873469 contain the supplementary crystallographic data for this paper.

## References

- [1] G. M. Sheldrick, SADABS, Program for area detector adsorption correction, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.
- [2] G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997; SHELXTL Reference Manual, Version 5.1, Bruker AXS, Analytical X-Ray Systems, Inc., Madison, WI, USA, 1997.

**Table S1.** Selected bond lengths (Å) and bond angles(°) for **1** and **2**

| <b>1<sup>a</sup></b> |            |                     |            |                      |            |
|----------------------|------------|---------------------|------------|----------------------|------------|
| Co(1)-O(7)#1         | 1.999(4)   | Co(2)-O(2)#4        | 2.013(4)   | Co(3)-O(9)           | 2.043(4)   |
| Co(1)-N(3)           | 2.040(5)   | Co(2)-O(1)          | 2.031(4)   | Co(3)-O(8)#5         | 2.047(4)   |
| Co(1)-O(3)#2         | 2.080(4)   | Co(2)-N(7)          | 2.157(4)   | Co(3)-N(11)          | 2.052(4)   |
| Co(1)-N(1)#3         | 2.099(5)   | Co(2)-O(6)          | 2.160(4)   | Co(3)-N(12)#6        | 2.082(4)   |
| Co(1)-N(5)           | 2.226(4)   | Co(2)-O(5)          | 2.180(4)   | Co(3)-N(8)           | 2.187(4)   |
| Co(1)-O(4)#2         | 2.275(5)   | Co(2)-N(6)          | 2.191(4)   |                      |            |
| O(7)#1-Co(1)-N(3)    | 106.48(2)  | N(1)#3-Co(1)-O(4)#2 | 93.80(2)   | O(2)#4-Co(2)-O(1)    | 116.12(2)  |
| O(7)#1-Co(1)-O(3)#2  | 101.33(2)  | O(5)-Co(2)-N(6)     | 96.00(2)   | O(2)#4-Co(2)-N(7)    | 91.25(2)   |
| N(3)-Co(1)-O(3)#2    | 146.02(2)  | O(1)-Co(2)-N(7)     | 91.14(2)   | O(6)-Co(2)-N(6)      | 91.41(2)   |
| O(7)#1-Co(1)-N(1)#3  | 90.8(2)    | O(2)#4-Co(2)-O(6)   | 90.16(2)   | O(9)-Co(3)-N(11)     | 97.47(2)   |
| N(3)-Co(1)-N(1)#3    | 102.27(2)  | O(1)-Co(2)-O(6)     | 153.49(2)  | O(8)#5-Co(3)-N(11)   | 158.17(2)  |
| O(3)#2-Co(1)-N(1)#3  | 96.39(2)   | N(7)-Co(2)-O(6)     | 91.80(2)   | O(9)-Co(3)-N(12)#6   | 100.66(2)  |
| O(7)#1-Co(1)-N(5)    | 84.59(2)   | O(2)#4-Co(2)-O(5)   | 150.13(2)  | O(8)#5-Co(3)-N(12)#6 | 93.87(2)   |
| N(3)-Co(1)-N(5)      | 76.90(2)   | O(1)-Co(2)-O(5)     | 93.75(2)   | N(11)-Co(3)-N(12)#6  | 101.92(2)  |
| O(3)#2-Co(1)-N(5)    | 86.82(2)   | N(7)-Co(2)-O(5)     | 87.90(2)   | O(9)-Co(3)-N(8)      | 86.13(2)   |
| N(1)#3-Co(1)-N(5)    | 174.86(2)  | O(6)-Co(2)-O(5)     | 60.05(1)   | O(8)#5-Co(3)-N(8)    | 85.94(2)   |
| O(7)#1-Co(1)-O(4)#2  | 161.18(2)  | O(2)#4-Co(2)-N(6)   | 86.09(2)   | N(11)-Co(3)-N(8)     | 76.59(2)   |
| N(3)-Co(1)-O(4)#2    | 90.34(2)   | O(1)-Co(2)-N(6)     | 87.17(2)   | N(12)#6-Co(3)-N(8)   | 173.19(2)  |
| O(3)#2-Co(1)-O(4)#2  | 60.05(2)   | N(7)-Co(2)-N(6)     | 175.85(2)  | O(9)-Co(3)-O(8)#5    | 94.25(2)   |
| N(5)-Co(1)-O(4)#2    | 91.28(2)   |                     |            |                      |            |
| <b>2<sup>b</sup></b> |            |                     |            |                      |            |
| Zn(1)-O(7)#1         | 2.028(3)   | Zn(2)-O(3)#1        | 2.015(3)   | Zn(3)-O(4)#3         | 2.005(3)   |
| Zn(1)-N(5)           | 2.303(3)   | Zn(2)-O(2)          | 2.041(3)   | Zn(3)-N(10)          | 2.013(3)   |
| Zn(1)-N(1)#2         | 2.068(3)   | Zn(2)-O(9)#3        | 2.156(3)   | Zn(3)-O(6)           | 2.016(3)   |
| Zn(1)-N(3)           | 2.043(3)   | Zn(2)-N(6)          | 2.191(3)   | Zn(3)-N(7)#4         | 2.078(4)   |
| Zn(1)-O(1)           | 2.048(3)   | Zn(2)-N(12)         | 2.215(3)   | Zn(3)-O(5)#3         | 2.422(4)   |
| O(7)#1-Zn(1)-N(3)    | 154.65(14) | Zn(2)-O(8)#3        | 2.232(3)   | Zn(3)-N(11)          | 2.489(4)   |
| N(1)#2-Zn(1)-N(5)    | 170.24(14) | O(3)#1-Zn(2)-O(2)   | 118.20(13) | O(4)#3-Zn(3)-N(10)   | 137.90(14) |
| O(1)-Zn(1)-N(5)      | 87.93(13)  | O(3)#1-Zn(2)-N(12)  | 87.75(12)  | O(5)#3-Zn(3)-N(11)   | 90.33(16)  |
| N(3)-Zn(1)-N(5)      | 74.61(12)  | O(9)#3-Zn(2)-N(6)   | 88.14(13)  | N(7)#4-Zn(3)-N(11)   | 172.48(14) |
| O(7)#1-Zn(1)-N(5)    | 83.32(12)  | O(2)-Zn(2)-N(6)     | 89.71(13)  | O(6)-Zn(3)-N(11)     | 80.41(14)  |
| O(1)-Zn(1)-N(1)#2    | 101.83(13) | O(3)#1-Zn(2)-N(6)   | 91.96(12)  | N(10)-Zn(3)-N(11)    | 72.95(13)  |
| N(3)-Zn(1)-N(1)#2    | 103.63(13) | O(2)-Zn(2)-O(9)#3   | 146.55(12) | O(4)#3-Zn(3)-N(11)   | 83.03(13)  |
| O(7)#1-Zn(1)-N(1)#2  | 95.98(12)  | N(12)-Zn(2)-O(8)#3  | 90.71(13)  | N(7)#4-Zn(3)-O(5)#3  | 97.18(16)  |
| N(3)-Zn(1)-O(1)      | 98.15(14)  | N(6)-Zn(2)-O(8)#3   | 92.20(13)  | O(6)-Zn(3)-O(5)#3    | 163.27(13) |

|                     |            |                    |            |                     |            |
|---------------------|------------|--------------------|------------|---------------------|------------|
| O(7)#1-Zn(1)-O(1)   | 93.30(13)  | O(9)#3-Zn(2)-O(8)3 | 59.38(11)  | N(10)-Zn(3)-O(5)#3  | 87.61(14)  |
| N(6)-Zn(2)-N(12)    | 173.90(13) | O(2)-Zn(2)-O(8)#3  | 87.37(12)  | O(4)#3-Zn(3)-O(5)#3 | 57.93(12)  |
| O(3)#1-Zn(2)-O(9)#3 | 95.23(12)  | O(3)#1-Zn(2)-O(8)3 | 154.10(12) | O(6)-Zn(3)-N(7)#4   | 92.37(15)  |
| O(2)-Zn(2)-N(12)    | 85.07(13)  | O(4)#3-Zn(3)-O(6)  | 106.77(14) | N(10)-Zn(3)-N(7)#4  | 106.92(14) |
| O(9)#3-Zn(2)-N(12)  | 97.95(13)  | N(10)-Zn(3)-O(6)   | 102.74(15) | O(4)#3-Zn(3)-N(7)#4 | 101.21(14) |

<sup>a</sup> Symmetry codes for **1**: #1 -x+1, -y, -z+2; #2 x, y, z+1, z+1/2; #3 x-1/2, -y+1/2; #4 -x+1, -y, -z+1; #5 x, y, z-1; #6 x+1/2, -y-1/2, z-1/2;

<sup>b</sup> Symmetry codes for **2**: #1 -x+1, -y+1, -z+1; #2 x+1/2, -y+3/2, z-1/2; #3 -x+1, -y+1, -z+2; #4 x-1/2, -y+1/2, z+1/2.

**Table S2** Summary of the linking modes of the 10- and 12-membered shortest ring within 3D net

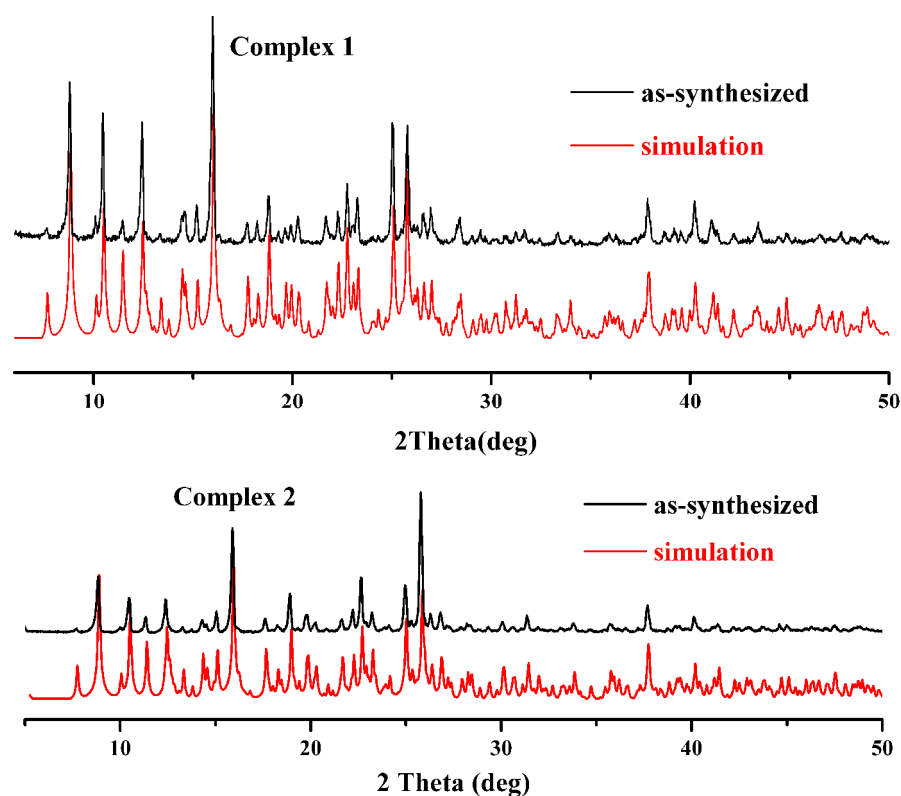
| Cycle 1 | Cycle 2 | Chain <sup>a</sup> | Cross <sup>b</sup> | Mult <sup>c</sup> |
|---------|---------|--------------------|--------------------|-------------------|
| 10a     | 10g     | 1                  | 1                  | 2                 |
| 10a     | 12a     | 1                  | 1                  | 2                 |
| 10a     | 12f     | 1                  | 1                  | 2                 |
| 10a     | 12g     | 1                  | 1                  | 1                 |
| 10a     | 12h     | 1                  | 1                  | 1                 |
| 10a     | 12i     | 1                  | 1                  | 1                 |
| 10a     | 12j     | 1                  | 1                  | 1                 |
| 10g     | 10a     | 1                  | 1                  | 2                 |
| 10g     | 12a     | 1                  | 1                  | 2                 |
| 10g     | 12b     | 1                  | 1                  | 2                 |
| 12a     | 8c      | 1                  | 2                  | 1                 |
| 12a     | 10a     | 1                  | 1                  | 2                 |
| 12a     | 12b     | 1                  | 1                  | 2                 |
| 12a     | 12f     | 1                  | 1                  | 2                 |
| 12b     | 10g     | 1                  | 1                  | 2                 |
| 12b     | 12a     | 1                  | 1                  | 2                 |
| 12b     | 12f     | 1                  | 1                  | 2                 |
| 12b     | 12g     | 1                  | 1                  | 2                 |
| 12b     | 12h     | 1                  | 1                  | 1                 |
| 12b     | 12i     | 1                  | 1                  | 1                 |
| 12b     | 12j     | 1                  | 1                  | 1                 |
| 12f     | 10a     | 1                  | 1                  | 1                 |
| 12f     | 10a     | 1                  | 2                  | 2                 |
| 12f     | 12a     | 1                  | 1                  | 1                 |
| 12f     | 12b     | 1                  | 1                  | 2                 |
| 12f     | 12f     | 1                  | 2                  | 1                 |
| 12g     | 10a     | 1                  | 1                  | 1                 |
| 12g     | 12b     | 1                  | 1                  | 1                 |

|     |     |   |   |   |
|-----|-----|---|---|---|
| 12h | 10a | 1 | 1 | 1 |
| 12h | 12b | 1 | 1 | 1 |
| 12i | 10a | 1 | 1 | 1 |
| 12i | 12b | 1 | 1 | 1 |
| 12j | 10a | 1 | 1 | 1 |
| 12j | 12b | 1 | 1 | 1 |

<sup>a</sup> Chain: the bond amount of the shortest chain that interconnected two rings.

<sup>b</sup> Cross: the times of each ring crossing another ring.

<sup>c</sup> Mult: the ring numbers of each ring crossed by other on



**Fig. S1.** The PXRD patterns of **1** and **2**. ( the red curve for the simulated from the single-crystal, the black curve for experimental data )

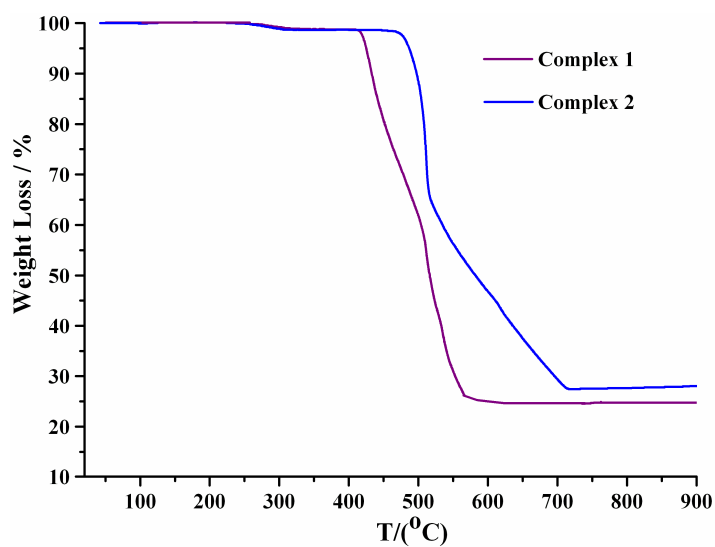


Fig. S2 TGA curves of complexes **1** and **2**.

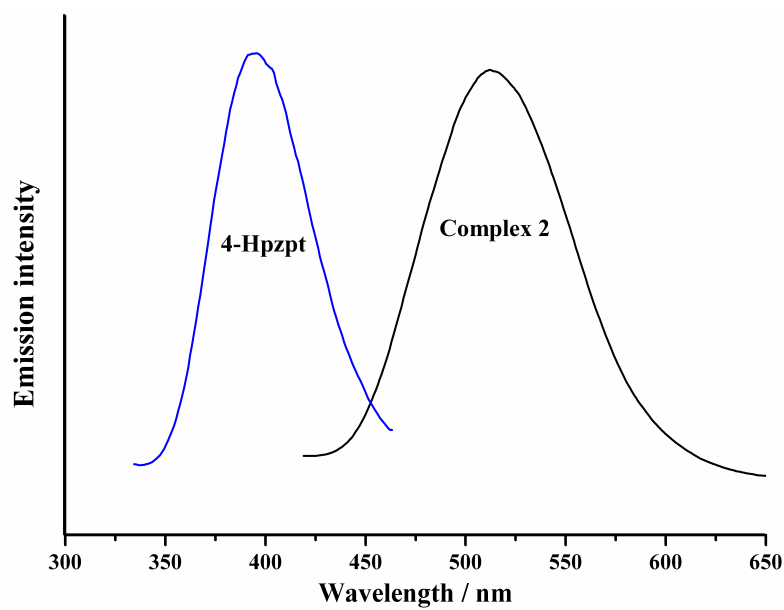
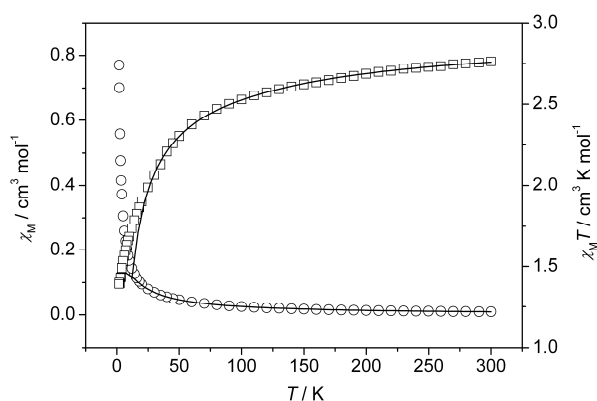


Fig. S3 Solid-state fluorescence emission recorded at room temperature for compound **2** (black) and 4-Hpzpt (blue).



**Fig. S4** Plots of  $\chi_M T$  vs  $T$  ( $\square$ ) and  $\chi_M$  vs  $T$  ( $\circ$ ) for **1**. Solid lines represent the fit through simple phenomenological equation

$$\chi_M T = A \exp(-E_1/kT) + B \exp(-E_2/kT)$$

Here,  $A + B$  equals the Curie constant, and  $E_1$ ,  $E_2$  represent the “activation energies” corresponding to the spin-orbit coupling and the antiferromagnetic exchange interaction. This equation adequately describes the spin-orbit coupling, which results in a splitting between discrete levels, and the exponential low-temperature divergence of the susceptibility [ $\chi_M T \propto \exp(aJ/2kT)$ ]. Moreover, it is in excellent agreement with the experimental data obtained in the present work (Figure 4). The obtained values of  $A + B = 2.93 \text{ cm}^3 \text{ K mol}^{-1}$  and  $E_1/k = 151 \text{ K}$  (using a least-squares fitting method) are consistent with those given in the literature for the Curie constant and for the effect of spin-orbit coupling and site distortion. As for the value found for the antiferromagnetic exchange interaction, it is very weak indeed ( $-E_2/k = -0.28 \text{ K}$ ), corresponding to  $J = -0.56 \text{ K}$  according to the Ising chain approximation [see above;  $\chi T \sim \exp(+J/2kT)$ ].