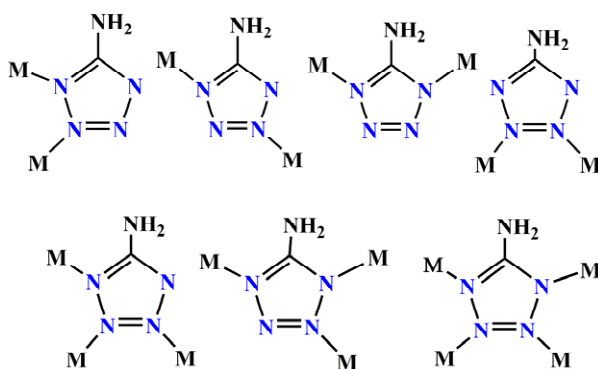


Electronic supplementary information

Co^{II} , Mn^{II} and Cu^{II} -directed coordination polymers with mixed tetrazolate-dicarboxylate heterobridges exhibiting spin-canted, spin-frustrated antiferromagnetism and a slight spin-flop transition

En-Cui Yang*, Zhong-Yi Liu, Xiao-Yun Wu, Hong Chang, En-Chan Wang and Xiao-Jun Zhao*



Scheme S1 Possible binding modes of anionic atz⁻ ligand.

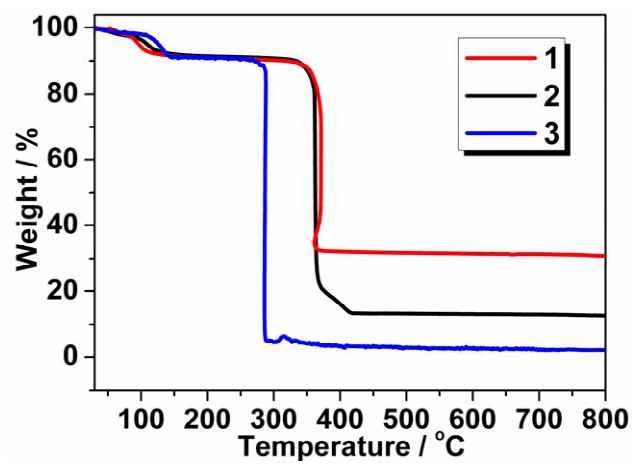


Fig. S1 TG curves for 1 – 3.

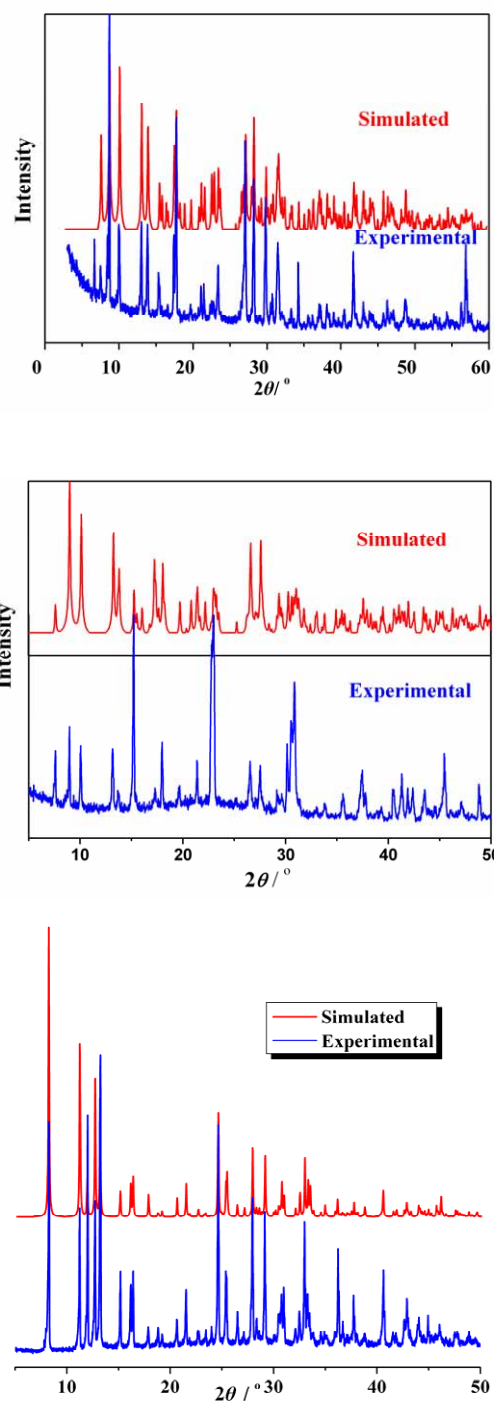


Fig. S2 Simulated (red) and experimental (blue) X-ray powder diffraction patterns for **1 – 3**.

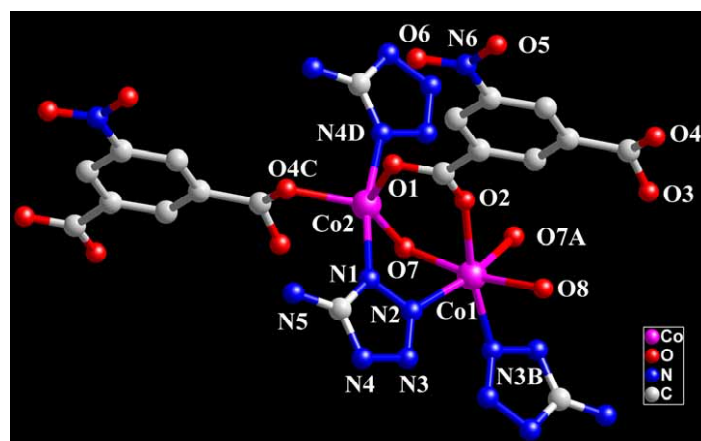


Fig. S3 Local coordination environments of Co^{II} atoms in **1** (Hydrogen atoms were omitted for clarity. Symmetry codes: A = 1 - x, 2 - y, 2 - z; B = 2 - x, 2 - y, 2 - z; C = x, 1 + y, z; D = x - 1, y, z).

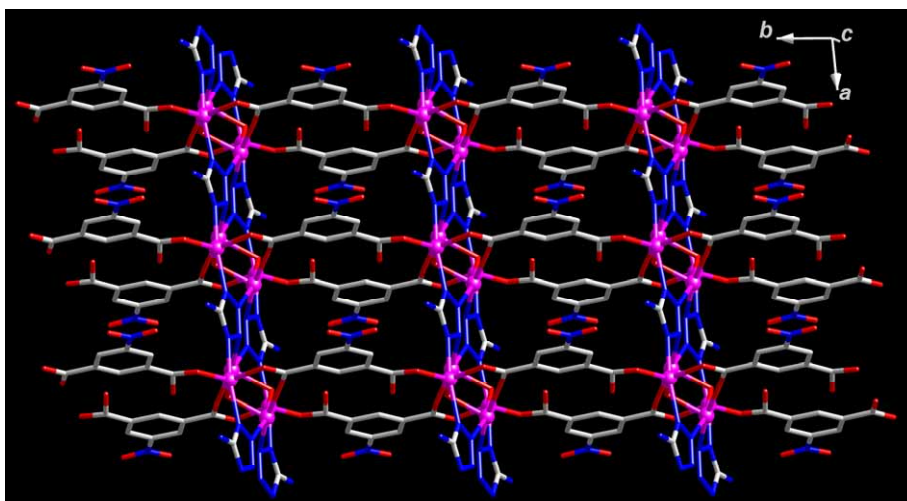


Fig. S4 2D covalent layer of **1** jointly extended by atz^- and nip^{2-} connectors (Terminal aqua ligands were omitted for clarity).

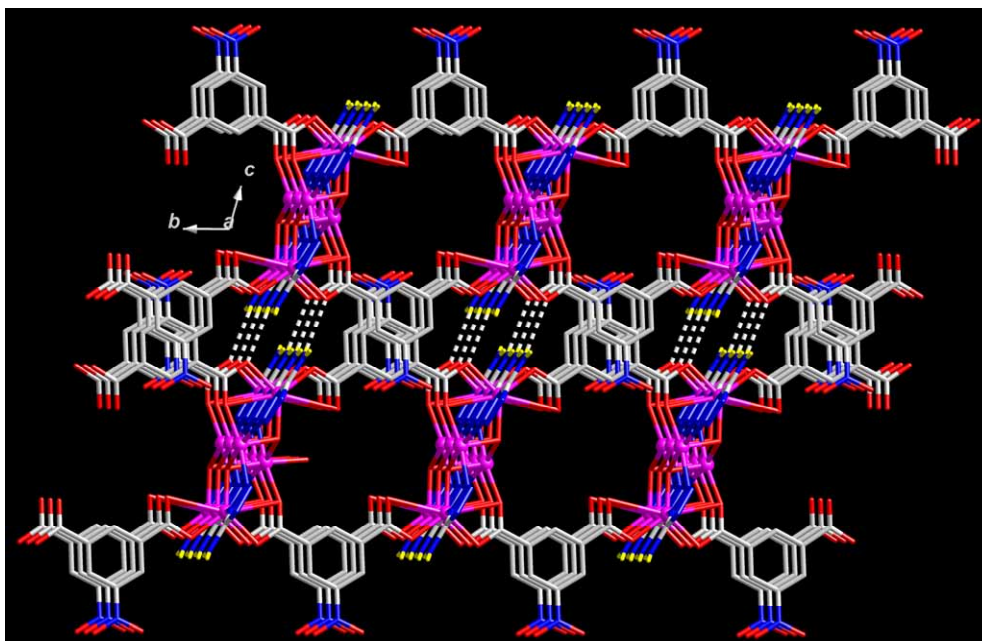


Fig. S5 3D supramolecular network of **1** formed by interlayer N–H...O hydrogen-bonding interactions.

Table S1 Hydrogen-bonds distances (Å) and angles (°) for **1**^a

Donor – H···Acceptor	D – H	H ··· A	D···A	D – H···A
N(5)–H(5B)···O(1) ^{#1}	0.86	2.41	2.947(3)	121

^a Symmetry code: ^{#1} 1 – x, 2 – y, 1 – z.

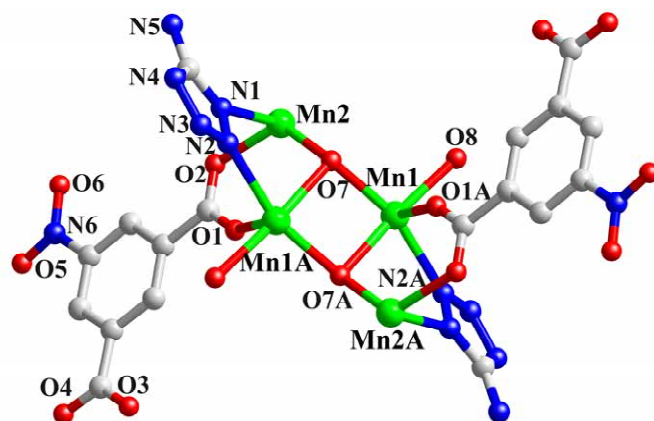


Fig. S6 The SBU of **2** with atom-numbering scheme in the asymmetric unit (H atoms were omitted for clarity).
Symmetry code: A = 1 - x, 1 - y, 1 - z).

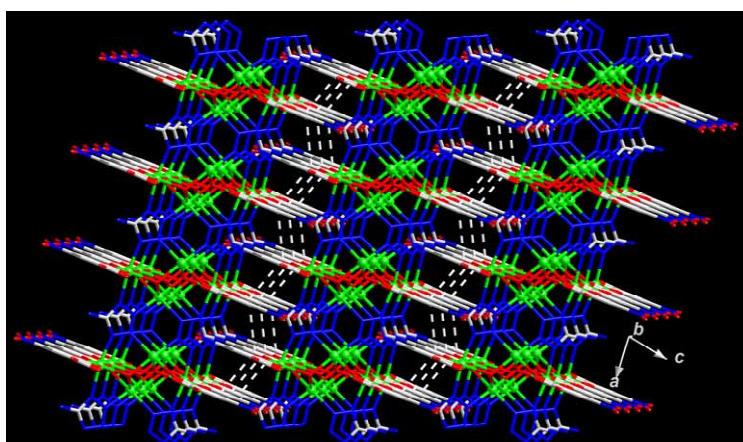


Fig. S7 3D supramolecular network of **2** formed by interlayer $\pi \cdots \pi$ stacking interactions.

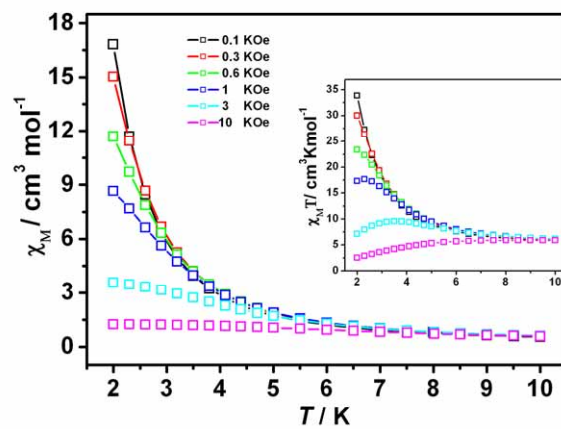


Fig. S8 Plots of χ_M and $\chi_M T$ vs T at different fields for **1**.

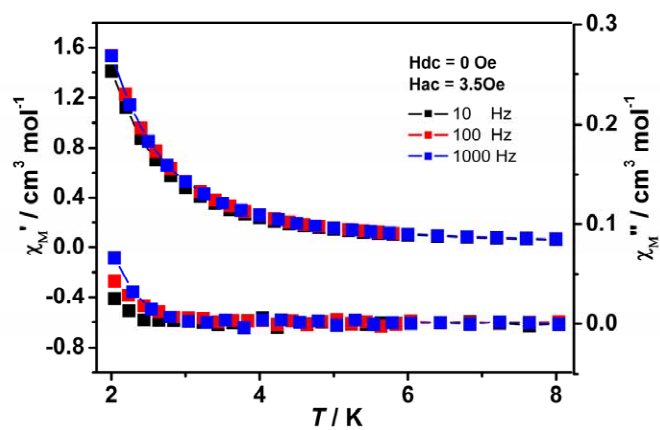


Fig. S9 Real (χ') and imaginary (χ'') *ac* magnetic susceptibilities in zero applied dc field and an ac field of 3.5 Oe at different frequencies for **1**.

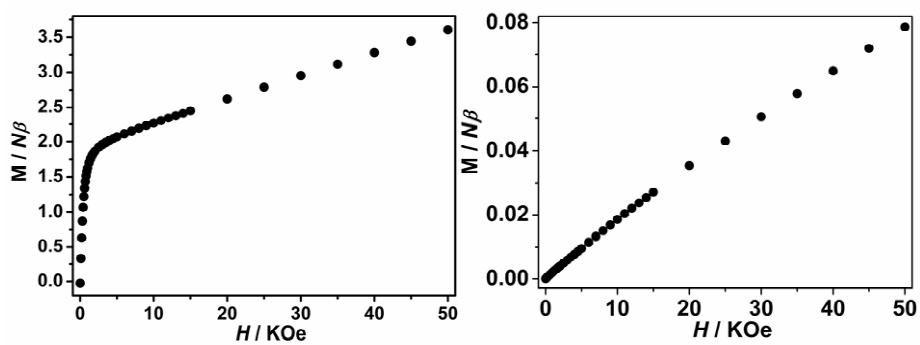


Fig. S10 Field dependence of magnetization at 2 K for **1** (left) and **3** (right), respectively.

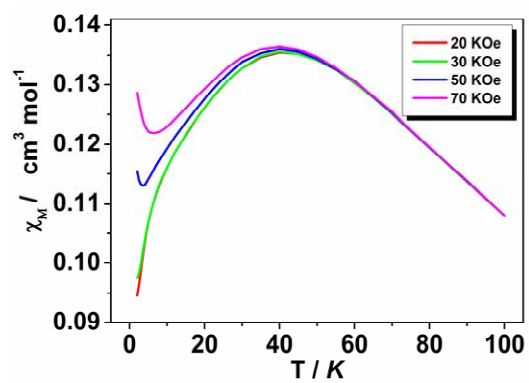


Fig. S11 Temperature dependence of χ_M for **2** under different dc fields.