Electronic supplementary information

Four linear Cu^{II}_3 subunit-based coordination polymers with various inter-subunit connections, spin ground-states and intra-/inter-subunit magnetic couplings

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Table S1 Selected bond distances (Å) and angles (°) for **1** [a]

Cu1–O5	1.928(3)	Cu2–O6	1.880(3)
Cu1–O6	1.911(4)	Cu2–N2	1.986(4)
Cu1–O2	1.969(3)	Cu3–O5	1.892(3)
Cu1–N1	2.009(4)	Cu3–O1	1.973(3)
Cu1–O7W	2.341(5)		
O5–Cu1–O6	91.53(15)	O5–Cu1–O7W	95.93(19)
O6–Cu1–O1	94.99(13)	O2–Cu1–O7W	85.31(17)
O5–Cu1–O2	95.35(14)	N1–Cu1–O7	99.8(2)
O2–Cu1–N1	86.80(15)	O6–Cu2–N2	85.59(16)
O6–Cu1–O7W	101.24(19)	O5–Cu2–N2A	94.41(16)
O6–Cu1–N1	84.80(15)	O5–Cu3–O1	89.69(14)

[a] Symmetry codes: A – *x*, 1 – *y*, 2 – *z*.

Table S2 Selected bond distances (Å) and angles (°) for **2** [a]

Cu1–O8	1.901(3)	Cu2–N2	1.967(3)
Cu1–N1	2.012(3)	Cu2–O3B	2.000(3)
Cu2–O8	1.910(3)	Cu2–O3	2.361(3)
Cu2–O7	1.931(3)		
O8A–Cu1–N1A	85.78(12)	O7–Cu2–O3B	87.39(12)
O8–Cu2–N2	86.30(13)	N2–Cu2–O3B	93.73(12)
O8–Cu1–N1	85.78(12)	O8–Cu2–O3	104.87(12)
O3B–Cu2–O3	76.75(11)	O7–Cu2–O3	96.68(13)
O8–Cu2–O7	92.16(12)	N2–Cu2–O3	98.41(13)

[a] Symmetry codes: A – *x*, 1 – *y*, 1 – *z*; B – *x*, 2 – *y*, 1 – *z*.

Table S3 Selected bond distances (Å) and angles (°) for **3** [a]

Cu1–O1	1.871(4)	Cu1–N2	1.988(7)
Cu1–N6	1.990(7)	Cu1–N9	2.006(7)
Cu1–O6	2.553(7)	Cu1–N12	2.557(7)
Cu2–N12	2.362(8)	Cu2–N5	2.032(8)
Cu2–N1	1.994(7)		
O1–Cu1–N9	85.5(3)	N2–Cu1–N6	89.5(3)
N6–Cu1–N9	94.4(3)	O1–Cu1–N2	90.6(3)
N1–Cu2–N5A	91.1(3)	O1–Cu1–N2	90.6(3)
N1–Cu2–N5	88.9(3)	N1–Cu2–N12	88.4(3)
N5–Cu2–N12A	91.2(3)	N5–Cu2–N12	88.8(3)
N1A–Cu2–N12	91.6(3)	N1–Cu2–N12	88.4(3)

[a] Symmetry codes: A $-x, -y, 1-z$.

Table S4 Selected bond distances (Å) and angles (°) for **4** [a]

Cu1–O9	1.903(3)	Cu1–O8	1.920(3)
Cu1–N5	1.978(4)	Cu1–O2	1.988(3)
Cu1–O8B	2.492(5)	Cu2–O5C	2.597(8)
Cu2–O8	1.902(3)	Cu2–O10	1.910(3)
Cu2–O1	1.967(3)	Cu2–N1	2.007(4)
Cu3–O9	1.899(3)	Cu3–O10A	1.916(4)
Cu3–N6	2.009(4)	Cu3–N2A	2.021(4)
Cu3–O11	2.381(5)	N5–Cu1–O2	86.56(15)
O9–Cu1–O8	95.47(14)	O9–Cu1–N5	86.61(16)
O8–Cu1–O2	91.27(14)	O1–Cu2–N1	87.56(15)
O8–Cu2–O10	94.06(14)	O8–Cu2–O1	91.29(14)
O10–Cu2–N1	86.01(16)	N2A–Cu3–O11	99.76(18)
O10A–Cu3–N6	94.41(16)	O9–Cu3–N2A	94.33(16)
O10A–Cu3–N2A	85.38(16)	O9–Cu3–N6	85.65(16)
O9–Cu3–O11	93.83(17)	O10A–Cu3–O11	87.62(17)
N6–Cu3–O11	89.34(18)		

[a] Symmetry codes: A 1/2 – *x*, *y* + 1/2, 1/2 – *z*; B 0.5– *x*, 0.5 – *y*, 1 – *z*; C 1 – *x*, *y*, 1.5 – *z*.

Table S5 Hydrogen-bonding parameters (Å, º) for **1**–**3**

D–H···A	*d* (D–H)	*d* (H···A)	*d* (D···A)	∠DHA
1				
N4–H4A···O4[A]	0.90	2.056	2.935	165.17
N4–H4B···O3 [B]	0.90	2.140	3.040	179.17
O7–H7A···N4 [B]	0.851	2.210	3.003	155.04
2				
N(4)–H4"···O7[A]	0.90	2.52	3.2119	134
N(4)–H4"···O [B]	0.90	2.31	3.0856	144
O7–H7B···O1[C]	0.84	2.43	3.0597	133
O7–H7B···O2[C]	0.84	1.84	2.6514	162
O8–H8'···O1[C]	0.84	2.15	2.9778	169
3				
N8–H8B···N4[A]	0.900	2.390	135.00	3.092

Symmetry codes for **1**: [A] 1 – *x*, 1 – *y*, 1 – *z*; [B] – *x*, 1 – *y*, 1 – *z*. For **2**: [A] 1 + *x* , *y*, *z*; [B] 1 – *x*, 2 – *y*, 1 – *z*; [C] *x* – 1, *y*, *z*.

For **3**: [A] 1/2 – *x*, – *y*, *z* + 1/2.

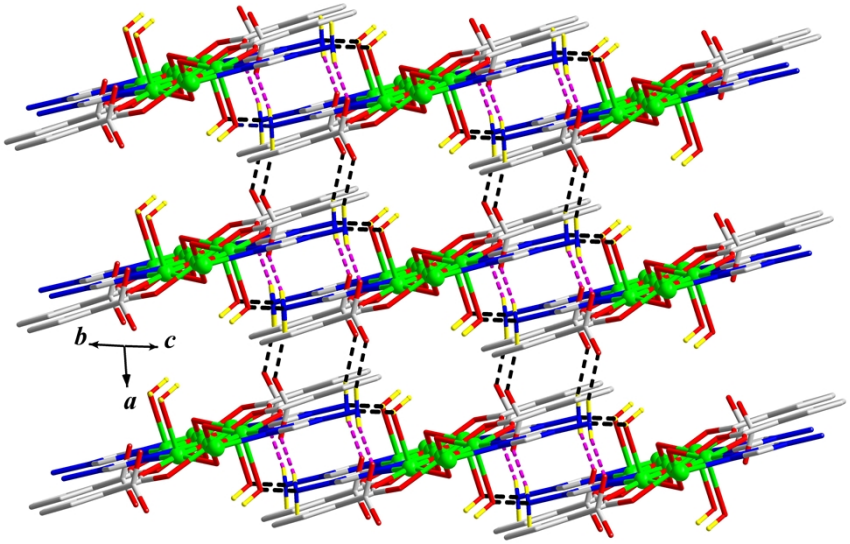

Fig. S1 3D supramolecular network of **1** by non-covalent N–H···O interactions.

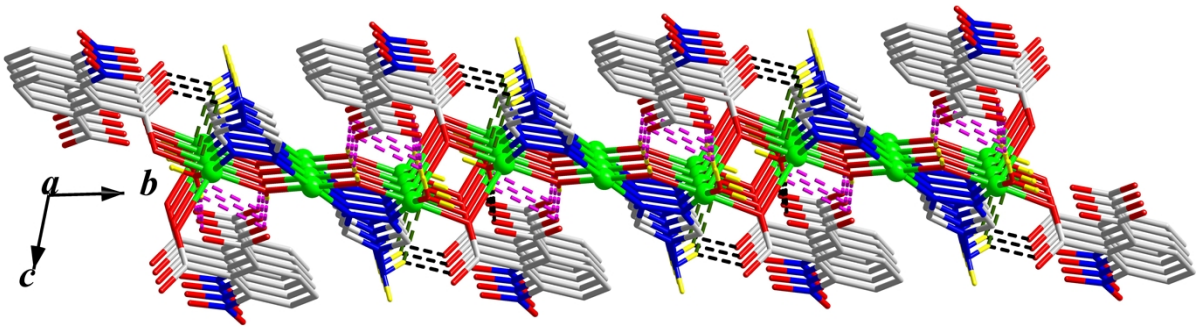

Fig. S2 2D layer of **2** by inter-chain O–H···O and N–H···O hydrogen-bonding interactions.

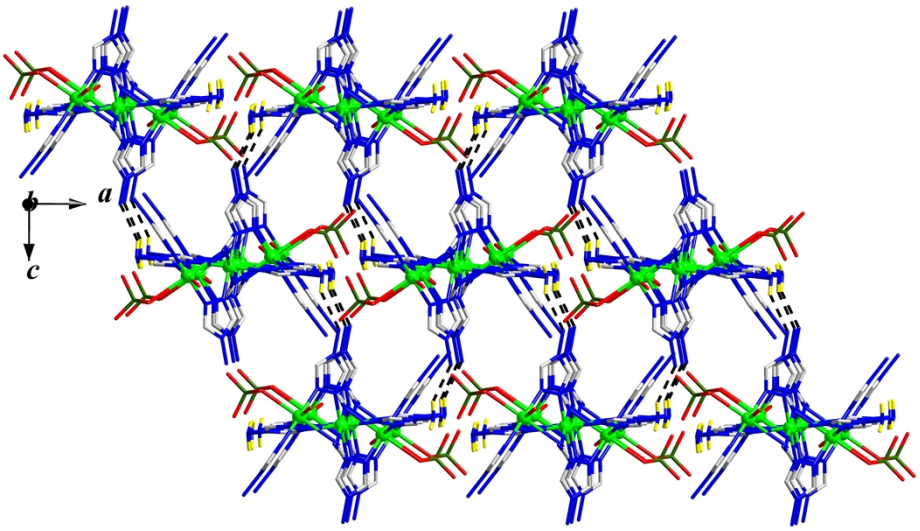

Fig. S3 3D supramolecular network of **3** generated by N–H···N hydrogen-bonding interactions.

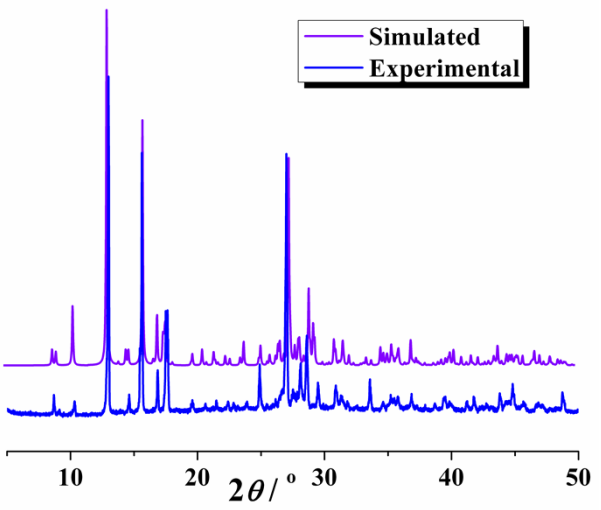

Fig. S4 Simulated (violet) and experimental (blue) X-ray powder diffraction patterns for **1**.

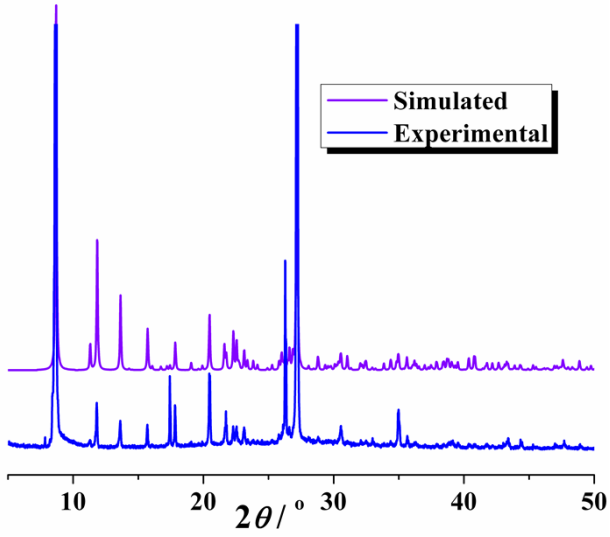

Fig. S5 Simulated (violet) and experimental (blue) X-ray powder diffraction patterns for **2**.

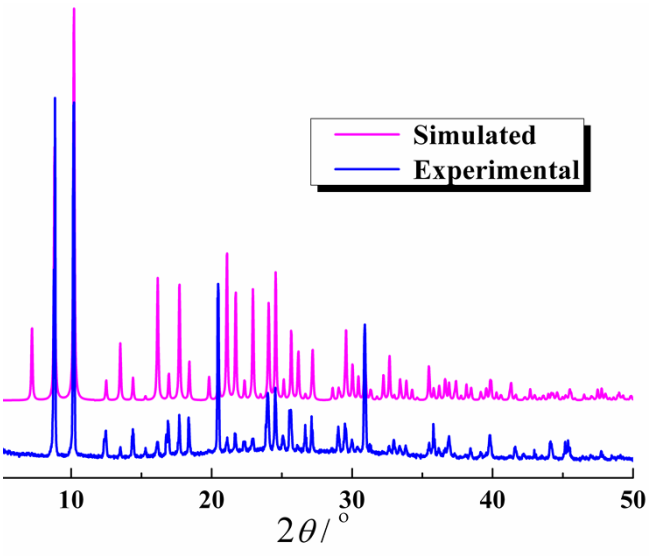

Fig. S6 Simulated (purple) and experimental (blue) X-ray powder diffraction patterns for **3**.

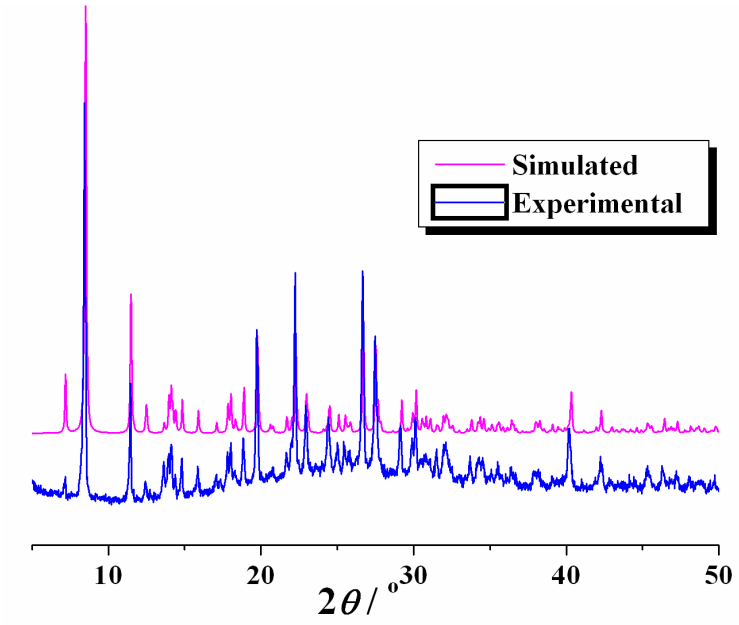

Fig. S7 Simulated (purple) and experimental (blue) X-ray powder diffraction patterns for **4**.

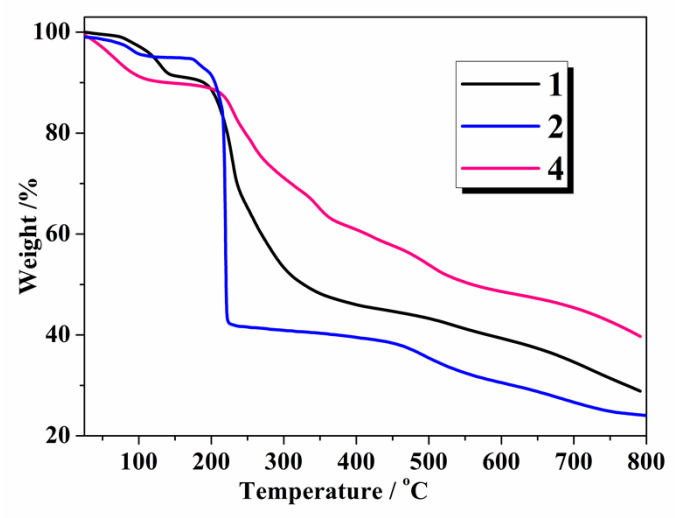

Fig. S8 TG curves for complexes **1**, **2** and **4**.

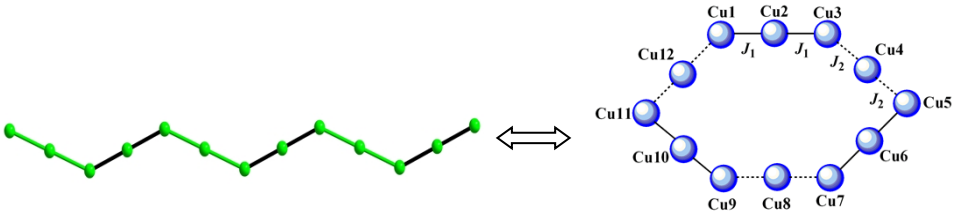

Fig. S9 Schematic diagram representing the exchange interactions in **1**.

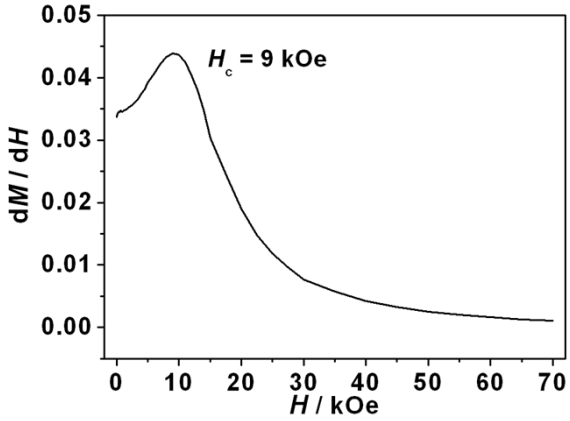

Fig. S10 The d*M*/d*H* plot for **4**.