

Electronic Supplementary Information

**Cluster-based copper(II) coordination polymers with azido bridges
and chiral magnets**

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Table S1 Selected bond lengths (Å) and angles (deg) for **1**

Cu(1)-N(1)	2.001(5)	Cu(1)-N(3)	2.016(7)
Cu(1)-N(2)	2.017(5)	Cu(1)-N(6)	2.053(7)
Cu(2)-N(12)	1.937(6)	Cu(2)-N(9)	2.033(6)
Cu(2)-N(12A)	1.985(6)	Cu(2)-N(9A)	2.011(6)
Cu(3)-N(15)	1.995(6)	Cu(3)-N(18)	1.994(7)
Cu(3)-N(15C)	1.982(6)	Cu(3)-N(18C)	2.008(7)
N(1)-Cu(1)-N(3)	89.4(3)	N(1)-Cu(1)-N(2)	174.3(3)
N(3)-Cu(1)-N(2)	96.3(3)	N(1)-Cu(1)-N(6)	90.0(2)
N(3)-Cu(1)-N(6)	173.5(3)	N(2)-Cu(1)-N(6)	84.4(2)
N(12)-Cu(2)-N(12A)	169.29(7)	N(12)-Cu(2)-N(9A)	97.9(2)
N(12A)-Cu(2)-N(9A)	79.4(2)	N(12)-Cu(2)-N(9)	80.0(2)
N(12A)-Cu(2)-N(9)	100.7(2)	N(9A)-Cu(2)-N(9)	169.43(8)
N(15C)-Cu(3)-N(18)	98.8(2)	N(15C)-Cu(3)-N(15)	173.90(7)
N(18)-Cu(3)-N(15)	80.6(3)	N(15C)-Cu(3)-N(18C)	80.6(3)
N(18)-Cu(3)-N(18C)	174.02(6)	N(15)-Cu(3)-N(18C)	99.3(2)
Cu(2B)-N(9)-Cu(2)	97.8(2)	Cu(2)-N(12)-Cu(2B)	101.9(2)
Cu(3D)-N(15)-Cu(3)	99.3(2)	Cu(3)-N(18)-Cu(3D)	98.5(3)
Symmetry codes: A $-x + 2, y + 1/2, -z + 1$; B $-x + 2, y - 1/2, -z + 1$; C $-x + 2, y - 1/2, -z$; D $-x + 2, y + 1/2, -z$			

Table S2 Selected bond lengths (Å) and angles (deg) for **3**

Cu(1)-N(18)	2.008(5)	Cu(1)-N(2)	2.016(5)
Cu(1)-N(1)	2.021(5)	Cu(1)-N(3)	2.063(5)
Cu(2)-N(9)	1.958(5)	Cu(2)-N(15A)	1.987(6)
Cu(2)-N(6)	2.043(6)	Cu(2)-N(12A)	2.059(5)
Cu(3)-N(6)	1.890(5)	Cu(3)-N(15)	1.935(6)
Cu(3)-N(9)	2.040(6)	Cu(3)-N(12)	2.093(5)
Cu(3)-N(18)	2.458(4)		
N(18)-Cu(1)-N(2)	84.4(2)	N(18)-Cu(1)-N(1)	91.4(2)
N(2)-Cu(1)-N(1)	172.0(2)	N(18)-Cu(1)-N(3)	174.0(2)
N(2)-Cu(1)-N(3)	93.3(2)	N(1)-Cu(1)-N(3)	91.5(2)
N(9)-Cu(2)-N(15A)	98.2(2)	N(9)-Cu(2)-N(6)	79.4(2)
N(15A)-Cu(2)-N(6)	166.2(2)	N(9)-Cu(2)-N(12A)	177.1(2)
N(15A)-Cu(2)-N(12A)	80.5(2)	N(6)-Cu(2)-N(12A)	101.34(18)
N(6)-Cu(3)-N(15)	176.3(2)	N(6)-Cu(3)-N(9)	81.0(2)
N(15)-Cu(3)-N(9)	101.2(2)	N(6)-Cu(3)-N(12)	96.3(2)
N(15)-Cu(3)-N(12)	80.9(2)	N(9)-Cu(3)-N(12)	165.84(19)
N(6)-Cu(3)-N(18)	91.2(2)	N(15)-Cu(3)-N(18)	91.4(2)
N(9)-Cu(3)-N(18)	99.65(18)	N(12)-Cu(3)-N(18)	94.29(18)
Cu(3)-N(6)-Cu(2)	100.2(2)	Cu(2)-N(9)-Cu(3)	98.0(2)
Cu(2B)-N(12)-Cu(3)	94.83(18)	Cu(3)-N(15)-Cu(2B)	102.4(2)
Cu(1)-N(18)-Cu(3)	137.6(2)		

Symmetry codes: A $x - 1, y, z$; B $x + 1, y, z$

Table S3 Selected bond lengths (Å) and angles (deg) for **4**

Cu(1)-N(7)	1.958(4)	Cu(1)-N(10)	1.959(4)
Cu(1)-N(1)	2.018(4)	Cu(1)-N(4)	2.034(4)
Cu(2)-N(16)	1.925(5)	Cu(2)-N(13)	1.921(5)
Cu(2)-N(4)	2.007(4)	Cu(2)-N(1)	2.036(4)
Cu(3)-N(19)	1.998(4)	Cu(3)-N(19A)	1.998(4)
Cu(3)-N(20)	1.999(4)	Cu(3)-N(20A)	1.999(4)
Cu(4)-N(21)	2.012(5)	Cu(4)-N(21B)	2.012(5)
Cu(4)-N(22B)	2.018(4)	Cu(4)-N(22)	2.018(4)
N(7)-Cu(1)-N(10)	97.89(19)	N(7)-Cu(1)-N(1)	90.81(17)
N(10)-Cu(1)-N(1)	170.34(19)	N(7)-Cu(1)-N(4)	168.58(18)
N(10)-Cu(1)-N(4)	93.22(18)	N(1)-Cu(1)-N(4)	77.92(17)
N(16)-Cu(2)-N(13)	102.8(2)	N(16)-Cu(2)-N(4)	165.21(19)
N(13)-Cu(2)-N(4)	91.8(2)	N(16)-Cu(2)-N(1)	88.72(18)
N(13)-Cu(2)-N(1)	158.6(2)	N(4)-Cu(2)-N(1)	78.12(17)
N(19)-Cu(3)-N(19A)	180.000(1)	N(19)-Cu(3)-N(20)	84.34(18)
N(19A)-Cu(3)-N(20)	95.66(18)	N(19)-Cu(3)-N(20A)	95.66(18)
N(19A)-Cu(3)-N(20A)	84.34(18)	N(20)-Cu(3)-N(20A)	180.0
N(21)-Cu(4)-N(21B)	180.000(1)	N(21)-Cu(4)-N(22B)	95.96(18)
N(21B)-Cu(4)-N(22B)	84.04(18)	N(21)-Cu(4)-N(22)	84.04(18)
N(21B)-Cu(4)-N(22)	95.96(18)	N(22B)-Cu(4)-N(22)	180.000(1)
Cu(1)-N(1)-Cu(2)	101.74(19)	Cu(2)-N(4)-Cu(1)	102.22(19)

Symmetry codes: A $-x + 1, -y + 1, -z + 1$; B $-x, -y + 2, -z$

Table S4 Selected bond lengths (Å) and angles (deg) for **5**

Cu(1)-N(4)	1.929(5)	Cu(1)-N(1)	1.949(4)
Cu(1)-N(7)	1.984(4)	Cu(1)-N(10)	2.036(4)
Cu(2)-N(16)	1.963(4)	Cu(2)-N(7)	1.959(4)
Cu(2)-N(13)	2.011(4)	Cu(2)-N(10)	2.017(4)
Cu(3)-N(22)	1.921(6)	Cu(3)-N(19)	1.964(5)
Cu(3)-N(16A)	2.019(4)	Cu(3)-N(13A)	2.104(4)
Cu(3)-N(4)	2.368(5)	Cu(4)-N(25)	2.003(5)
Cu(4)-N(25B)	2.003(5)	Cu(4)-N(26B)	2.027(5)
Cu(4)-N(26)	2.027(5)	Cu(5)-N(27)	2.027(5)
Cu(5)-N(27C)	2.027(5)	Cu(5)-N(28C)	2.016(6)
Cu(5)-N(28)	2.016(6)		
N(4)-Cu(1)-N(1)	96.02(19)	N(4)-Cu(1)-N(7)	95.09(19)
N(1)-Cu(1)-N(7)	168.57(18)	N(4)-Cu(1)-N(10)	169.32(19)
N(1)-Cu(1)-N(10)	91.25(18)	N(7)-Cu(1)-N(10)	78.12(17)
N(16)-Cu(2)-N(7)	169.92(19)	N(16)-Cu(2)-N(13)	80.14(18)
N(7)-Cu(2)-N(13)	102.39(18)	N(16)-Cu(2)-N(10)	96.77(18)
N(7)-Cu(2)-N(10)	79.15(17)	N(13)-Cu(2)-N(10)	170.50(19)
N(22)-Cu(3)-N(19)	94.5(2)	N(22)-Cu(3)-N(16A)	97.7(2)
N(19)-Cu(3)-N(16A)	151.9(2)	N(22)-Cu(3)-N(13A)	174.1(2)
N(19)-Cu(3)-N(13)	89.74(19)	N(16A)-Cu(3)-N(13A)	76.69
N(22)-Cu(3)-N(4)	95.6(2)	N(19)-Cu(3)-N(4)	113.30(19)
N(16A)-Cu(3)-N(4)	90.67(18)	N(13A)-Cu(3)-N(4)	86.54(17)
N(25)-Cu(4)-N(25B)	180.00(14)	N(25B)-Cu(4)-N(26)	94.0(2)
N(25)-Cu(4)-N(26)	86.0(2)	N(25B)-Cu(4)-N(26B)	86.0(2)
N(25)-Cu(4)-N(26B)	94.0(2)	N(26)-Cu(4)-N(26B)	180.0
N(27)-Cu(5)-N(27C)	180.0(3)	N(27)-Cu(5)-N(28C)	96.1(2)
N(27C)-Cu(5)-N(28C)	83.9(2)	N(27)-Cu(5)-N(28)	83.9(2)
N(27C)-Cu(5)-N(28)	96.1(2)	N(28C)-Cu(5)-N(28)	180.0(3)

Cu(1)-N(4)-Cu(3)	104.5(2)	Cu(2)-N(7)-Cu(1)	102.9(2)
Cu(2)-N(10)-Cu(1)	99.04(19)	Cu(2)-N(13)-Cu(3A)	99.29(19)
Cu(2)-N(16)-Cu(3A)	103.9(2)		

Symmetry codes: A $-x + 1, -y + 2, -z$; B $-x + 2, -y + 1, -z$; C $-x + 1, -y + 2, -z + 1$

Table S5 Selected bond lengths (Å) and angles (deg) for **6**

Cu(1)-N(1)	1.994(5)	Cu(1)-N(13A)	1.997(5)
Cu(1)-N(4)	2.017(5)	Cu(1)-N(12B)	2.355(6)
Cu(1)-N(7)	1.991(5)	Cu(2)-N(13)	2.432(5)
Cu(2)-N(10)	1.967(6)	Cu(2)-N(16)	1.994(5)
Cu(2)-N(7)	2.008(5)	Cu(2)-N(4)	2.018(5)
Cu(3)-N(16)	2.034(5)	Cu(3)-N(19)	1.995(5)
Cu(3)-N(1A)	2.002(5)	Cu(3)-N(20)	2.032(6)
N(7)-Cu(1)-N(1)	170.4(2)	N(7)-Cu(1)-N(13A)	95.0(2)
N(1)-Cu(1)-N(13A)	86.0(2)	N(7)-Cu(1)-N(4)	79.7(2)
N(1)-Cu(1)-N(4)	97.6(2)	N(13A)-Cu(1)-N(4)	169.2(2)
N(7)-Cu(1)-N(12B)	95.7(2)	N(1)-Cu(1)-N(12B)	93.7(2)
N(13A)-Cu(1)-N(12B)	96.1(2)	N(4)-Cu(1)-N(12B)	93.8(2)
N(10)-Cu(2)-N(16)	92.8(2)	N(10)-Cu(2)-N(7)	176.0(2)
N(16)-Cu(2)-N(7)	91.0(2)	N(10)-Cu(2)-N(4)	97.0(2)
N(16)-Cu(2)-N(4)	169.6(2)	N(7)-Cu(2)-N(4)	79.3(2)
N(10)-Cu(2)-N(13)	90.8(2)	N(16)-Cu(2)-N(13)	84.71(19)
N(7)-Cu(2)-N(13)	90.7(2)	N(4)-Cu(2)-N(13)	91.7(2)
N(19)-Cu(3)-N(1A)	168.5(2)	N(19)-Cu(3)-N(20)	85.4(2)
N(1A)-Cu(3)-N(20)	92.3(2)	N(19)-Cu(3)-N(16)	90.6(2)
N(1A)-Cu(3)-N(16)	90.2(2)	N(20)-Cu(3)-N(16)	171.3(2)
Cu(1)-N(1)-Cu(3A)	108.0(2)	Cu(1)-N(4)-Cu(2)	99.9(2)
Cu(1)-N(7)-Cu(2)	101.1(2)	Cu(1A)-N(13)-Cu(2)	100.5(2)
Cu(2)-N(16)-Cu(3)	108.5(2)		

Symmetry codes: A $-x + 2, -y + 1, -z + 1$; B $-x + 3, -y + 1, -z + 1$

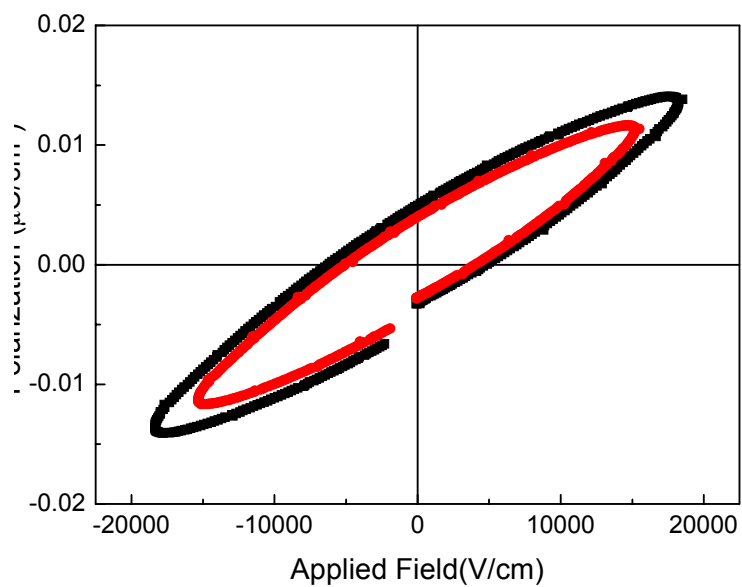


Fig. S1 Electric hysteresis loop of a pellet obtained from a powdered sample of **1** observed by Virtual Ground Mode using an RT6000 ferroelectric tester at room temperature.

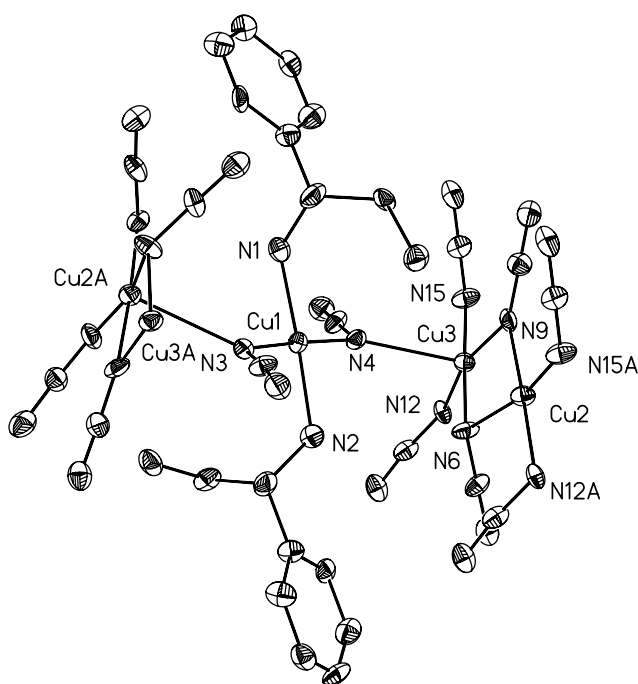


Fig. S2 View of the coordination environment of copper(II) ions in **3** with the thermal ellipsoids drawn at the 30% probability level.

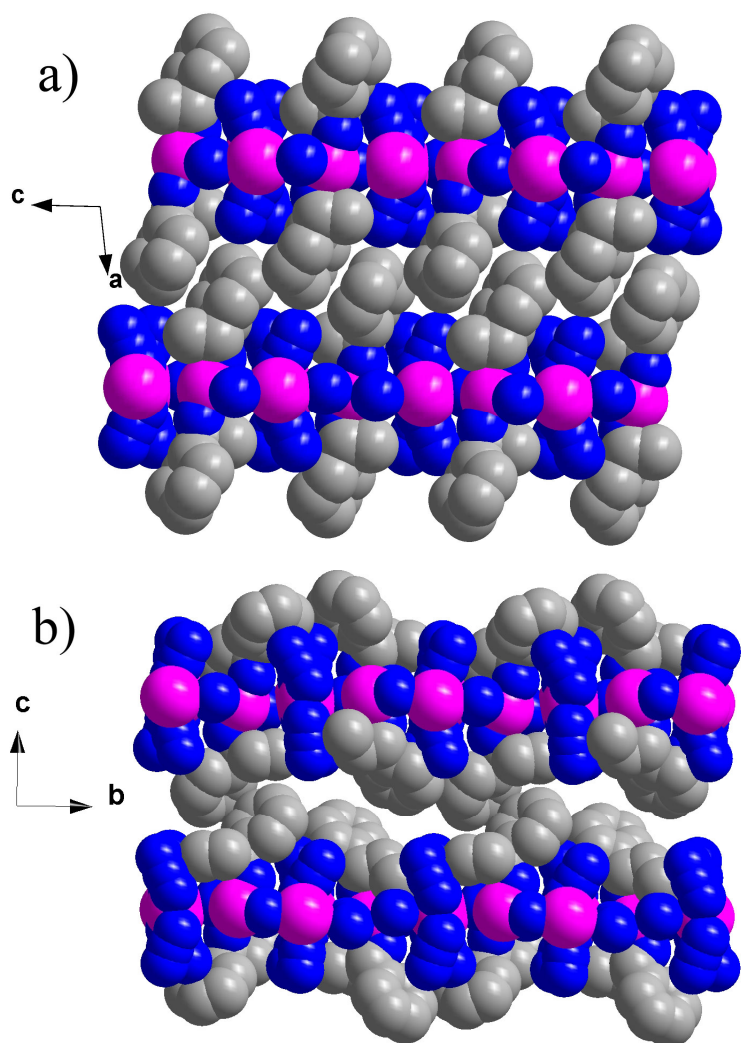


Fig. S3 Side view of the two layers of complexes **1** and **3** along the *b* and *a* axes, respectively.

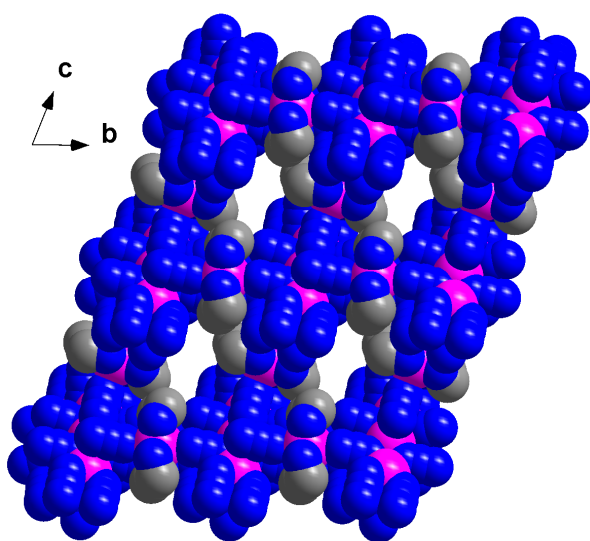
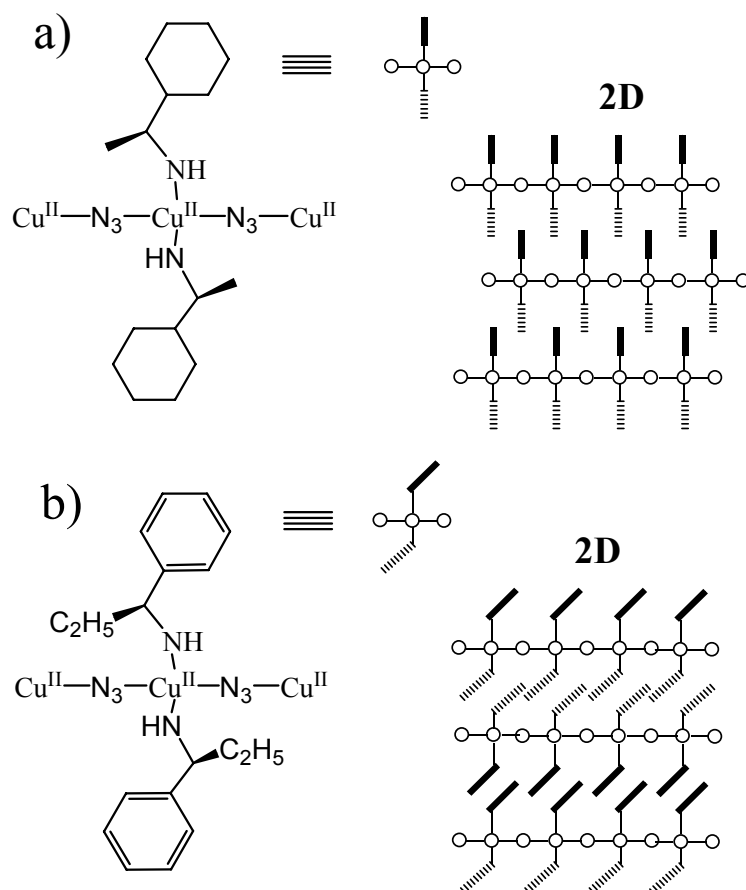


Fig. S4 Drawing of the crystal packing along the *a* axis showing the filling of the square pores of the open-framework structure of **5**.



Scheme S1. Schematic show the stacking mode of the organic amine molecules between 2D layers for **1 a)** and **3 b)**.