SUPPLEMENTARY MATERIAL

Structure, magnetic properties and DFT calculations of azido copper(II)-diamine complexes with different azido-bonding modes, nuclearity and dimensionality

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

Cu(1)-N(1)	2.096(2)	Cu(1)-N(21)	1.991(2)
Cu(1)-N(2)	2.011(2)	Cu(1)-N(11')	2.312(2)
Cu(1)-N(11)	1.995(2)	N(11)-N(12)	1.209(3)
N(12)-N(13)	1.152(3)	N(21)-N(22)	1.189(3)
N(22)-N(23)	1.168(3)		
Cu(1)-N(11)-Cu(1')	101.77(9)	N(2)-Cu(1)-N(11)	174.54(9)
N(1)-Cu(1)-N(21)	146.90(9)	Cu(1)-N(11)-N(12)	125.55(18)
Cu(1')-N(11)-N(12)	125.60(17)	Cu(1)-N(21)-N(22)	128.48(19)
N(13)-N(12)-N(11)	177.1(3)	N(23)-N(22)-N(21)	176.4(3)

Symmetry code: (') -x, -y, 2-z.

Table S2 Selected bond distances (Å) and angles (°) for **2**.

Cu(1)-N(1)	2.033(3)	Cu(2)-N(3)	2.045(3)
Cu(1)-N(2)	2.065(3)	Cu(2)-N(4)	2.056(3)
Cu(1)-N(11)	2.309(3)	Cu(2)-N(11)	2.004(2)
Cu(1)-N(21)	1.979(3)	Cu(2)-N(31)	2.237(2)
Cu(1)-N(31)	2.020(3)	Cu(2)-N(41)	2.018(2)
N(11)-N(12)	1.211(4)	N(12)-N(13)	1.150(4)
N(21)-N(22)	1.188(4)	N(22)-N(23)	1.162(4)
N(31)-N(32)	1.209(4)	N(32)-N(33)	1.137(4)
N(41)-N(42)	1.196(4)	N(42)-N(43)	1.163(4)
Cu(1)-N(11)-Cu(2)	101.77(10)	Cu(1)-N(31)-Cu(2)	102.51(10)
N(1)-Cu(1)-N(31)	174.21(10)	N(3)-Cu(2)-N(11)	177.28(10)
N(2)-Cu(1)-N(21)	162.16(11)	N(4)-Cu(2)-N(41)	142.83(10)
Cu(1)-N(11)-N(12)	134.8(2)	Cu(2)-N(11)-N(12)	120.3(2)
Cu(1)-N(21)-N(22)	123.0(2)	Cu(2)-N(31)-N(32)	132.8(2)
Cu(1)-N(31)-N(32)	120.0(2)	Cu(2)-N(41)-N(42)	120.0(2)
N(13)-N(12)-N(11)	178.4(3)	N(23)-N(22)-N(21)	178.1(3)
N(33)-N(32)-N(31)	179.1(4)	N(43)-N(42)-N(41)	179.1(3)

Table S3 Selected bond distances (Å) and angles (°) for **3**.

Cu(1)-N(1)	2.092(3)	Cu(2)-N(3)	2.067(2)
Cu(1)-N(2)	2.012(3)	Cu(2)-N(4)	2.006(3)
Cu(1)-N(11)	1.986(3)	Cu(2)-N(31)	1.983(2)
Cu(1)-N(21)	2.003(3)	Cu(2)-N(23)	2.290(3)
Cu(1)-N(13’)	2.350(3)	Cu(2)-N(33”)	1.996(3)
N(11)-N(12)	1.191(4)	N(12)-N(13)	1.163(4)
N(21)-N(22)	1.189(4)	N(22)-N(23)	1.169(4)
N(31)-N(32)	1.176(4)	N(32)-N(33)	1.174(4)
N(1)-Cu(1)-N(21)	160.57(11)	N(3)-Cu(2)-N(33’)	159.14(11)
N(2)-Cu(1)-N(11)	173.85(11)	N(4)-Cu(2)-N(31)	174.59(10)
Cu(1)-N(11)-N(12)	121.3(2)	Cu(2)-N(23)-N(22)	114.8(2)
Cu(1“)-N(13)-N(12)	136.5(2)	Cu(2)-N(31)-N(32)	127.4(2)
Cu(1)-N(21)-N(22)	129.2(2)	Cu(2’)-N(33)-N(32)	131.4(2)
N(13)-N(12)-N(11)	176.7(3)	N(23)-N(22)-N(21)	176.1(3)
N(33)-N(32)-N(31)	174.1(3)		

Symmetrie codes: (’) 1-x, 1-y, 1-z; (’’) 1-x, -y, 1-z.

Table S4 Selected bond distances (Å) and angles (°) for **4**.

Cu(1)-N(1)	2.069(3)	Cu(1)-N(21)	2.022(3)
Cu(1)-N(2)	2.010(3)	Cu(1)-N(11')	2.439(3)
Cu(1)-N(11)	2.018(3)	Cu(1)-N(13")	2.510(3)
N(11)-N(12)	1.196(4)	N(12)-N(13)	1.155(4)
N(21)-N(22)	1.212(4)	N(22)-N(23)	1.155(4)
Cu(1)-N(11)-Cu(1')	99.64(12)	N(2)-Cu(1)-N(11)	171.19(12)
N(1)-Cu(1)-N(21)	169.66(12)	N(11')-Cu(1)-N(13")	171.12(10)
Cu(1)-N(11)-N(12)	127.0(2)	Cu(1)-N(21)-N(22)	120.4(2)
Cu(1')-N(11)-N(12)	131.4(2)	N(23)-N(22)-N(21)	177.6(4)
N(13)-N(12)-N(11)	176.9(3)		

Symmetry code: (') -x, 1-y, -z; (") –x, y-1/2, -z+1/2.

Table S5 Hydrogen bond systems for compounds **1** – **4**.

D-H…A[a]	Symmetry of A	D…A (Å)	D-H…A (°)
Compound **1**			
Cu(1)-H(91)…N(23)	[-x,1-y,2-z]	3.033(4)	165(3)
Compound **2**			
N(1)-H(91)…N(43)	[3/2-x,1/2+y,1/2-z]	3.104(4)	170(3)
N(2)-H(92)…N(43)		3.182(4)	165(3)
N(3)-H(93)…N(23)	[5/2-x,-1/2+y,1/2-z]	3.034(4)	164(3)
N(4)-H(94)…N(23)		3.223(4)	150(3)
Compound **3**			
N(2)-H(91)…O(1)	[1-x,1-y,1-z]	3.131(4)	153(3)
N(4)-H(92)…O(1)		3.067(4)	168(4)
Compound **4**			
N(1)-H(90)…N(23)	[-x,1/2+y,1/2-z]	3.186(5)	153(3)
N(1)-H(91)…N(21)	[-x,1-y,-z]	3.184(4)	164(3)
N(2)-H(92)…N(21)	[-x,-y,-z]	3.058(4)	175(3)
N(2)-H(93)…N(13)	[x,-1+y,z]	3.100(5)	166(3)

[a)] D = Donor, A = Acceptor

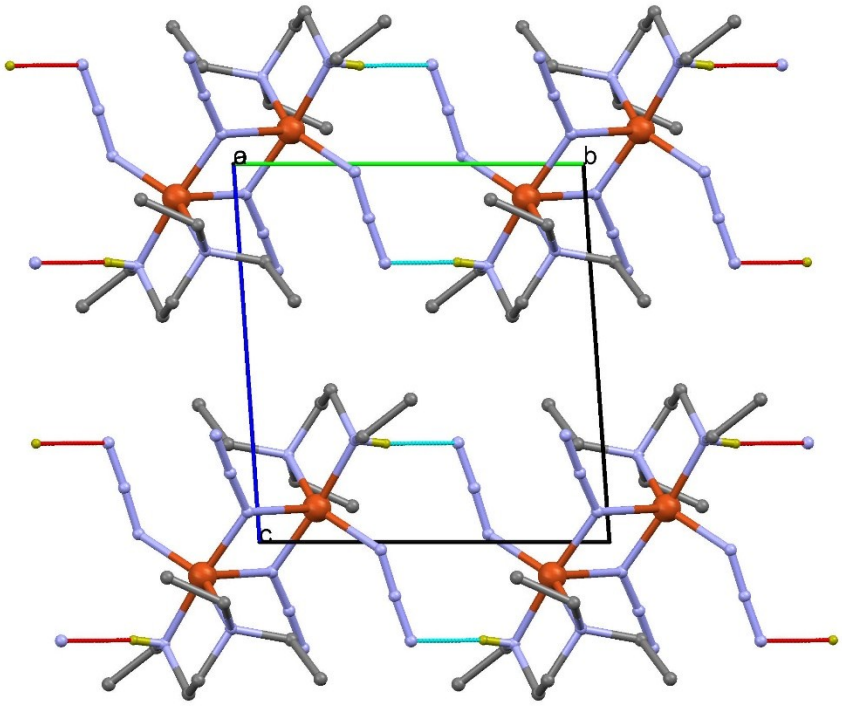

Fig. S1 Packing plot of **1.**

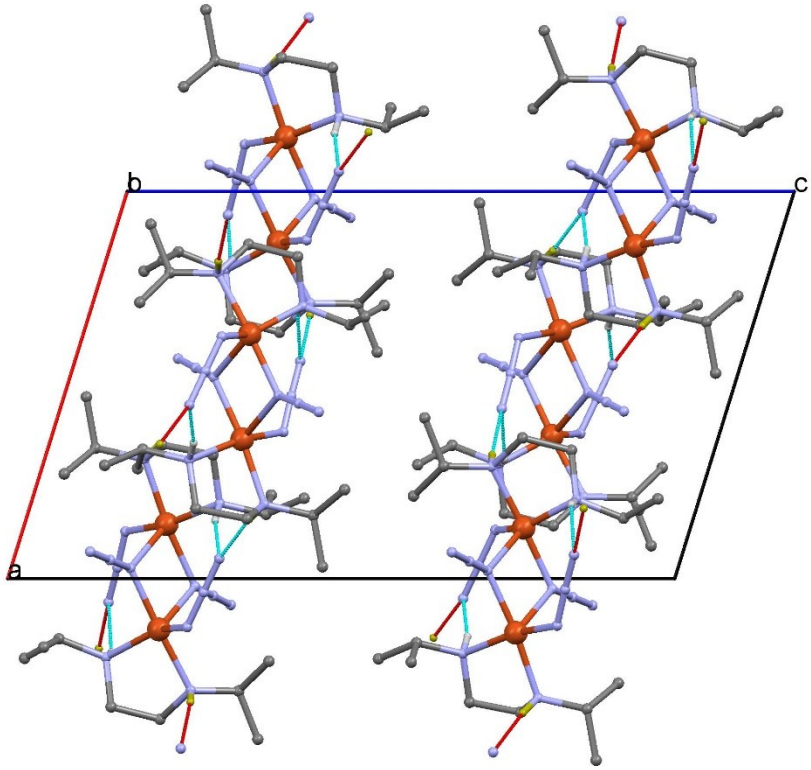

Fig. S2 Packing plot of **2**.

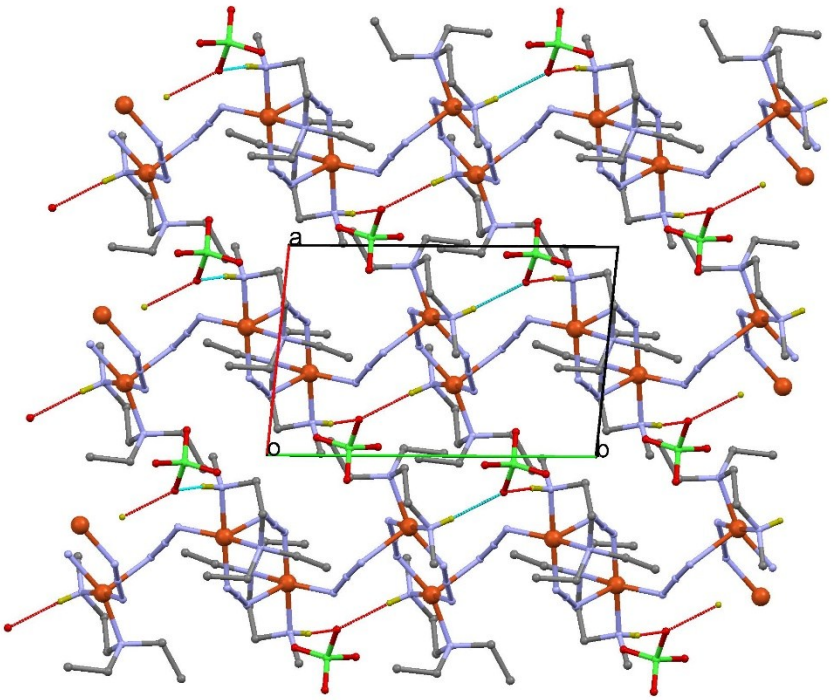

Fig. S3 Packing plot of **3**.

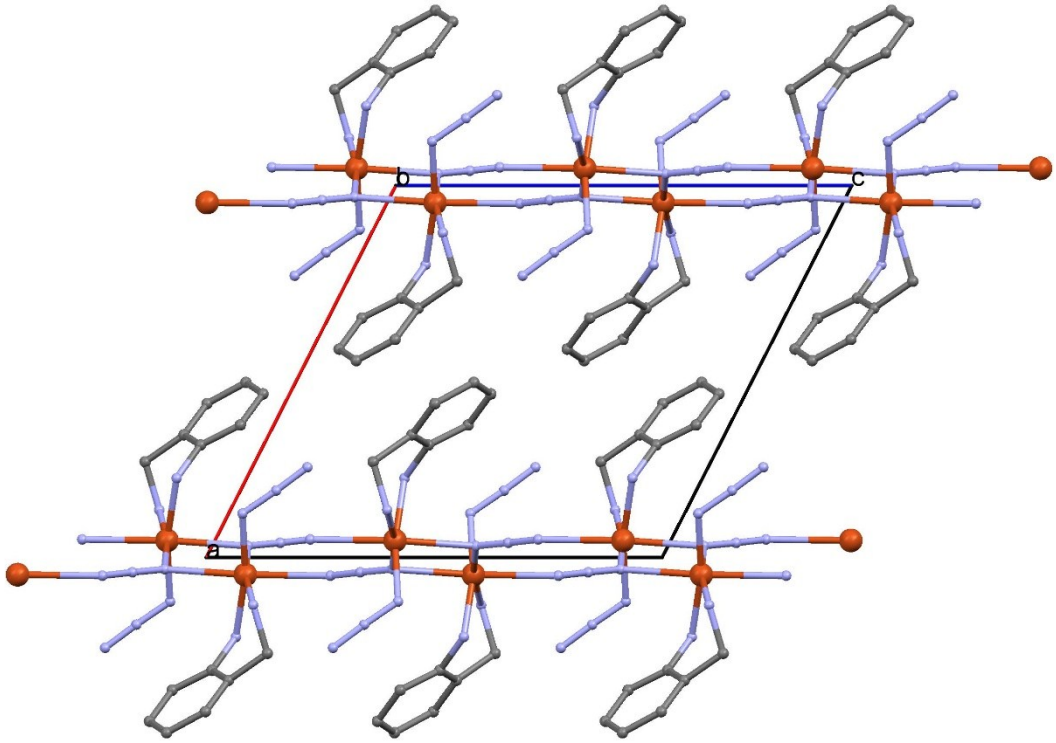

Fig. S4 Packing plot of **4**.