Table S1 Selected bond distances (Å) and angles (°) for complexes 1-5

Compound 1

Co(1)-O(7)	2.0655(19)	Co(1)-N(3)#1	2.073(2)	Co(1)-N(1)	2.112(2)
Co(1)-O(3)#2	2.1182(16)	Co(1)-O(1)	2.1475(17)	Co(1)-O(2)	2.3249(17)
O(7)-Co(1)-N(3)#1	106.63(9)	O(7)-Co(1)-N(1)	91.32(7)	N(3)#1-Co(1)-N(1)	90.99(8)
O(7)-Co(1)-O(3)#2	87.24(7)	N(3)#1-Co(1)-O(3)#2	88.58(7)	N(1)-Co(1)-O(3)#2	178.31(7)
O(7)-Co(1)-O(1)	96.51(7)	N(3)#1-Co(1)-O(1)	156.12(8)	N(1)-Co(1)-O(1)	94.33(7)
O(3)#2-Co(1)-O(1)	86.71(6)	O(7)-Co(1)-O(2)	154.96(7)	N(3)#1-Co(1)-O(2)	98.38(8)
O(3)#2-Co(1)-O(2)	92.33(6)	O(1)-Co(1)-O(2)	58.49(6)		

Compound 2

Co(1)-N(7)	2.062(2)	Co(1)-N(12)#1	2.080(3)	Co(1)-N(4)	2.104(2)
Co(1)-O(4)#2	2.103(2)	Co(1)-O(10)	2.131(2)	Co(1)-O(2)	2.1421(18)
Co(2)-N(10)	2.067(2)	Co(2)-N(11)#3	2.075(2)	Co(2)-O(5)#4	2.0919(18)
Co(2)-N(1)	2.112(3)	Co(2)-O(9)	2.117(2)	Co(2)-O(8)	2.125(2)
N(7)-Co(1)-N(12)#1	94.14(10)	N(7)-Co(1)-N(4)	90.19(9)	N(12)#1-Co(1)-N(4)	91.68(9)
N(7)-Co(1)-O(4)#2	87.26(9)	N(12)#1-Co(1)-O(4)#2	178.53(9)	N(4)-Co(1)-O(4)#2	87.87(8)
N(7)-Co(1)-O(10)	176.38(9)	N(12)#1-Co(1)-O(10)	89.30(9)	N(4)-Co(1)-O(10)	88.46(8)
O(4)#2-Co(1)-O(10)	89.29(8)	N(7)-Co(1)-O(2)	90.38(8)	N(12)#1-Co(1)-O(2)	89.81(9)
N(4)-Co(1)-O(2)	178.37(9)	O(4)#2-Co(1)-O(2)	90.62(7)	O(10)-Co(1)-O(2)	90.78(7)
N(10)-Co(2)-N(11)#3	89.42(9)	N(10)-Co(2)-O(5)#4	92.65(8)	N(11)#3-Co(2)-O(5)#4	176.22(9)
N(10)-Co(2)-N(1)	94.11(10)	N(11)#3-Co(2)-N(1)	90.32(10)	O(5)#4-Co(2)-N(1)	86.38(9)
N(10)-Co(2)-O(9)	173.37(9)	N(11)#3-Co(2)-O(9)	87.66(9)	O(5)#4-Co(2)-O(9)	90.60(7)
N(1)-Co(2)-O(9)	91.87(9)	N(10)-Co(2)-O(8)	84.78(9)	N(11)#3-Co(2)-O(8)	91.16(9)
O(5)#4-Co(2)-O(8)	92.18(8)	N(1)-Co(2)-O(8)	178.14(9)	O(9)-Co(2)-O(8)	89.32(8)

Compound 3

Co(1)-O(3)#1	1.9375(14)	Co(1)-O(2)	2.0161(14)	Co(1)-N(1)	2.0389(17)
Co(1)-N(4)#2	2.0472(16)	Co(1)-O(1)	2.3812(16)		
O(3)#1-Co(1)-O(2)	117.07(6)	O(3)#1-Co(1)-N(1)	102.87(7)	O(2)-Co(1)-N(1)	126.33(7)
O(3)#1-Co(1)-N(4)#2	108.12(7)	O(2)-Co(1)-N(4)#2	93.99(6)	N(1)-Co(1)-N(4)#2	106.57(7)

O(3)#1-Co(1)-O(1)	91.21(6)	O(2)-Co(1)-O(1)	58.67(5)	N(1)-Co(1)-O(1)	87.82(6)
N(4)#2-Co(1)-O(1)	152.04(6)				

Compound 4

Co(1)-O(2)#2	1.971(3)	Co(1)-O(3)#3	1.973(3)	Co(1)-O(1)	1.983(3)
Co(1)-N(1)	1.997(4)				
O(2)#2-Co(1)-O(3)#3	101.42(15)	O(2)#2-Co(1)-O(1)	102.10(13)	O(3)#3-Co(1)-O(1)	118.66(14)
O(2)#2-Co(1)-N(1)	107.19(15)	O(3)#3-Co(1)-N(1)	126.09(16)	O(1)-Co(1)-N(1)	98.80(14)

Compound 5

Co(1)-O(2)#3	1.938(2)	Co(1)-N(3)	2.006(2)	Co(1)-N(1)	2.030(2)
Co(1)-O(3)	1.9534(18)				
O(2)#3-Co(1)-O(3)	112.18(9)	O(3)-Co(1)-N(3)	112.54(8)	O(3)-Co(1)-N(1)	98.65(9)
O(2)#3-Co(1)-N(3)	114.22(9)	O(2)#3-Co(1)-N(1)	118.41(9)	N(3)-Co(1)-N(1)	99.39(9)

Symmetry transformations used to generate equivalent atoms: for **1**: #1 –x-1/2, y+1/2, z-1/2; #2: x-1/2, -y+5/2, z; for **2**: #1 –x+1, -y+1, -z+1; #2 -x+1,y+1/2,-z+3/2; #3 -x,-y+1,-z+2; #4 -x,y+1/2,-z+3/2; for **3**: #1 -x+1,y-1/2,-z+1/2; #2 x+1,-y-1/2,z+1/2; for **4**: #2 -x+1/2,y+1/2,z; #3 -x,y+1/2,-z+1/2; for **5**: #3 -x+1,-y+1,-z+2

Table S2 The bond lengths (Å) and angles (°) of C-H···π in compound 1

	$d_{(H\cdots\pi)}$	$d_{(C\cdots\pi)}$	∠(CHπ)
C16-H16···π	2.663	3.393	148.55
C22-H22···π	2.665	3.769	158.83

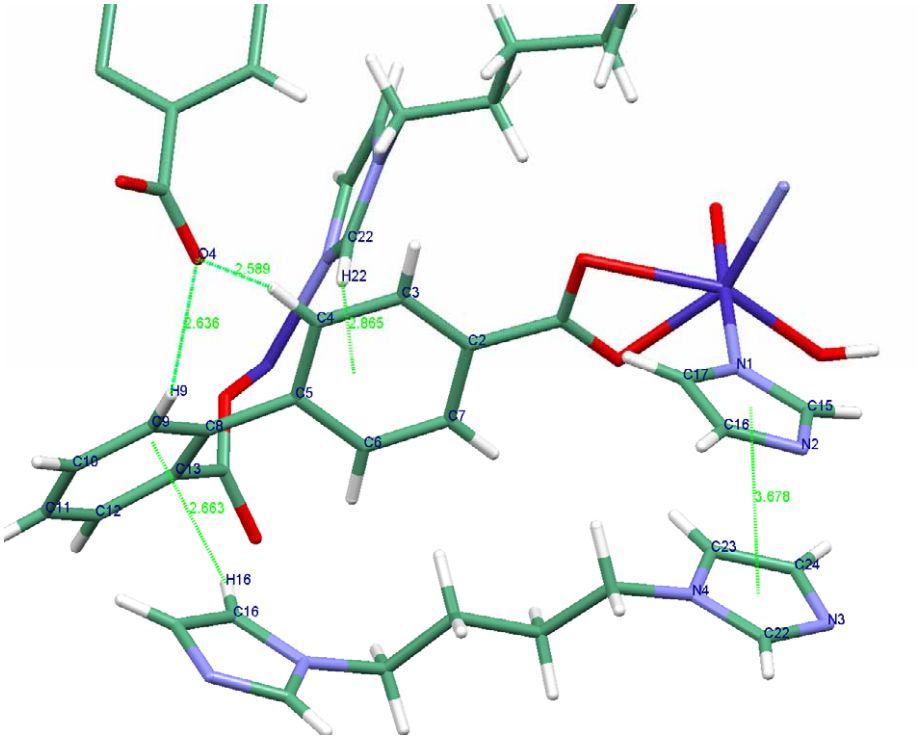


Figure S1 View of C-H···π, π···π interactions in fragment of compound 1

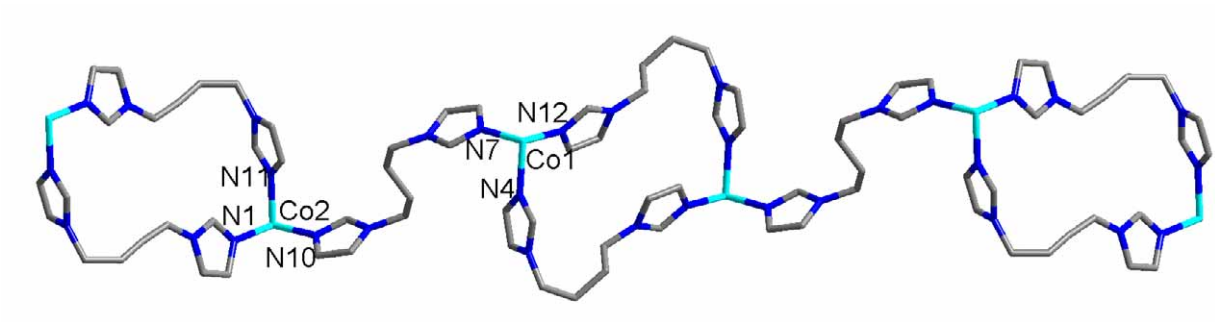
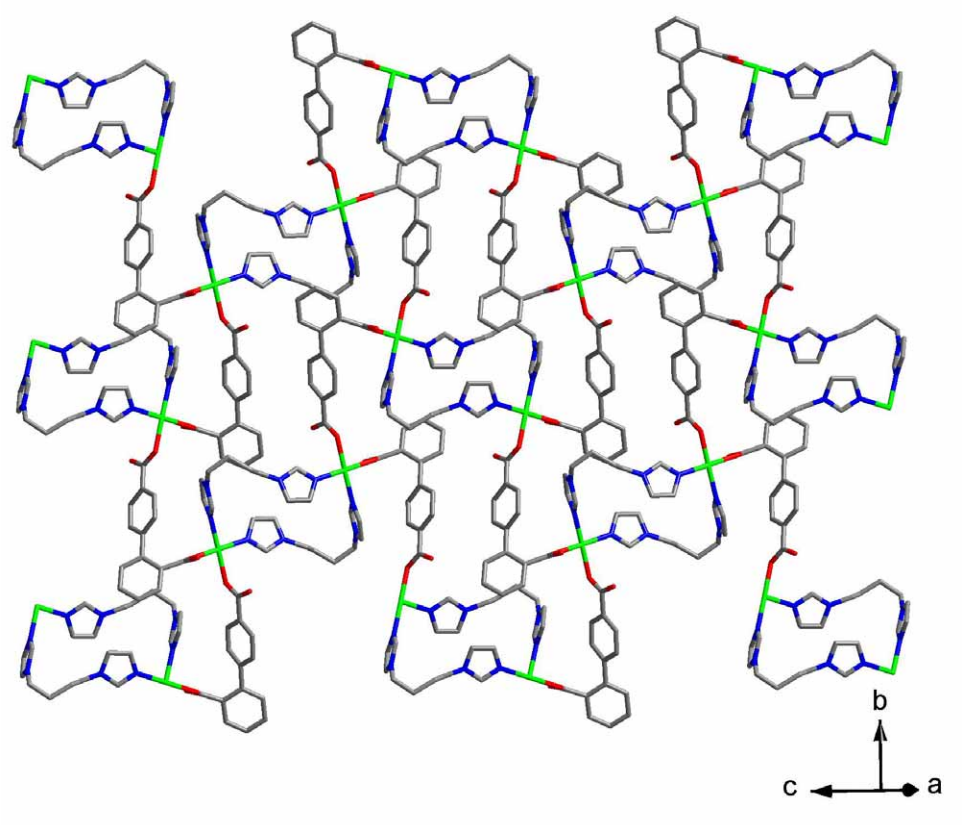


Figure S2 View of 1D chain connected by bimb ligands.



FigureS3 View of Co1 layer

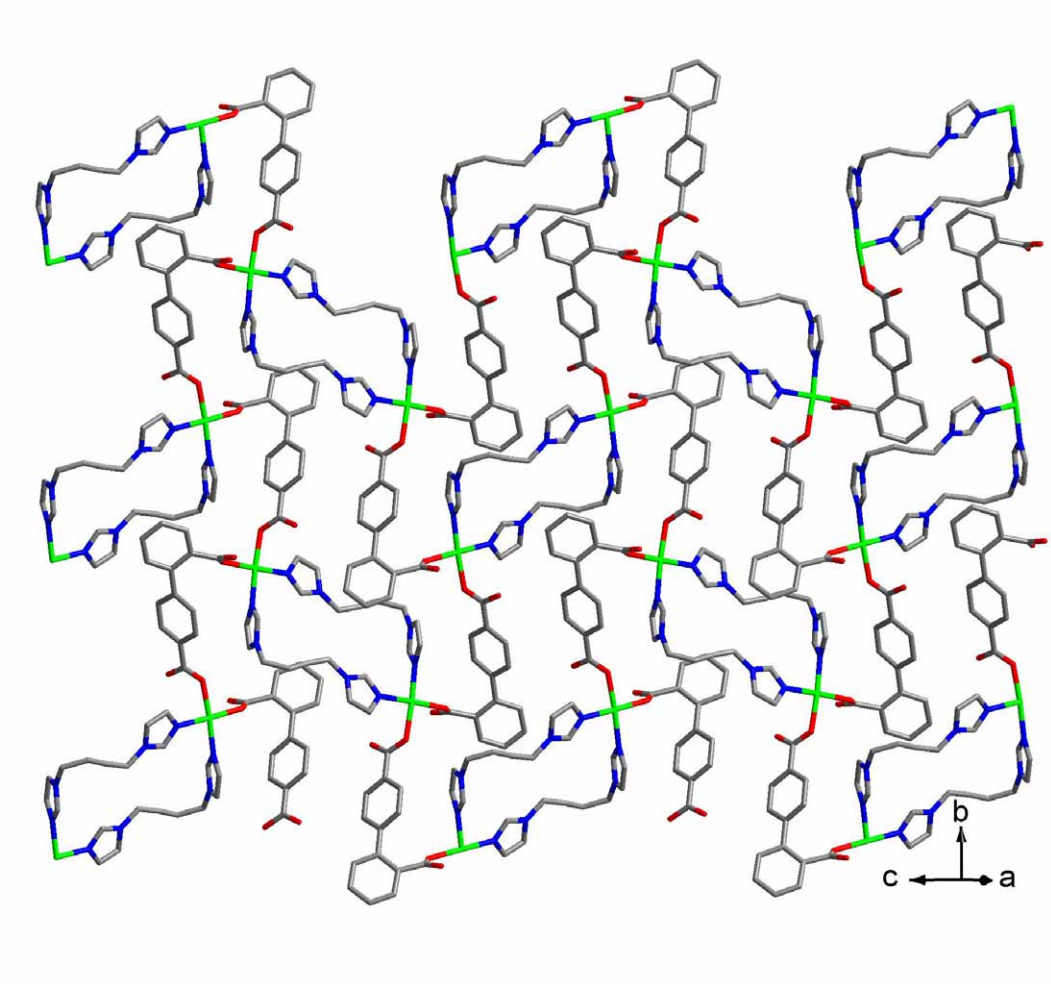


Figure S4 View of Co2 layer.

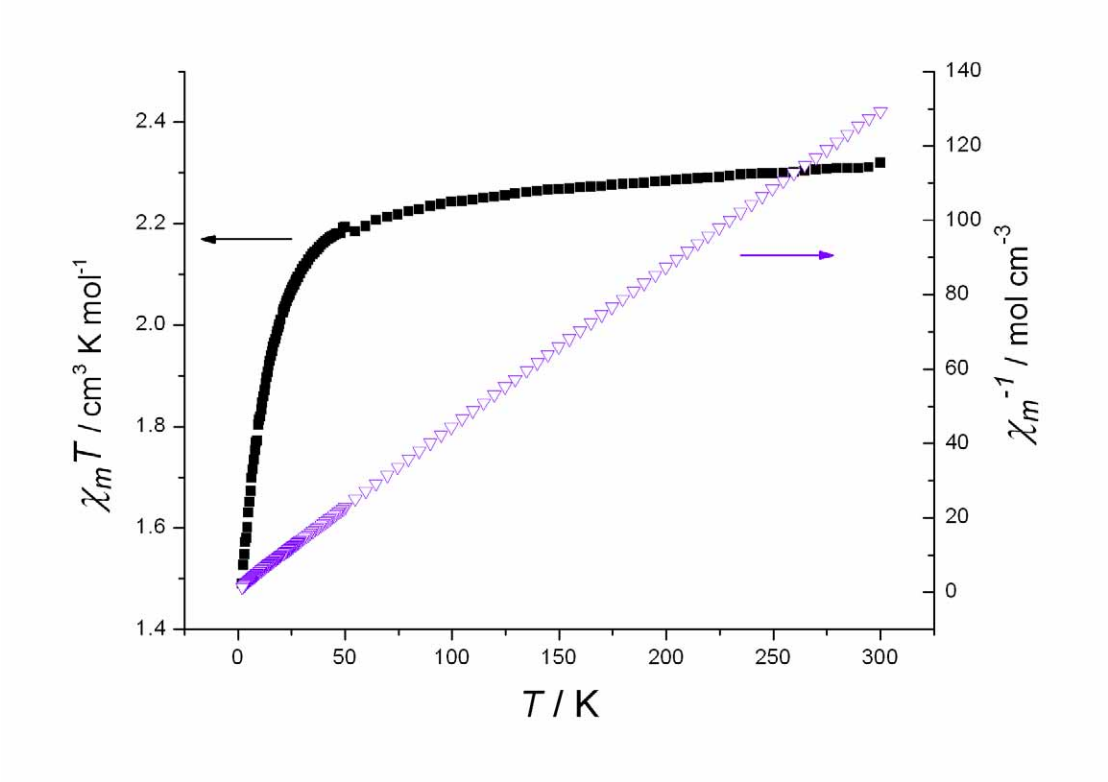


Figure S5 Plots of $\chi_M T$ verse T and $1/\chi_M$ verse T in a 1000 Oe field in compound 4