Electronic Supplementary Information (ESI)

Coordination Polymers Based on Copper Carboxylates and Angular 2,5-bis(imidazol-1-yl)thiophene ($thim_2$) Ligand: Sequential Structural Transformations

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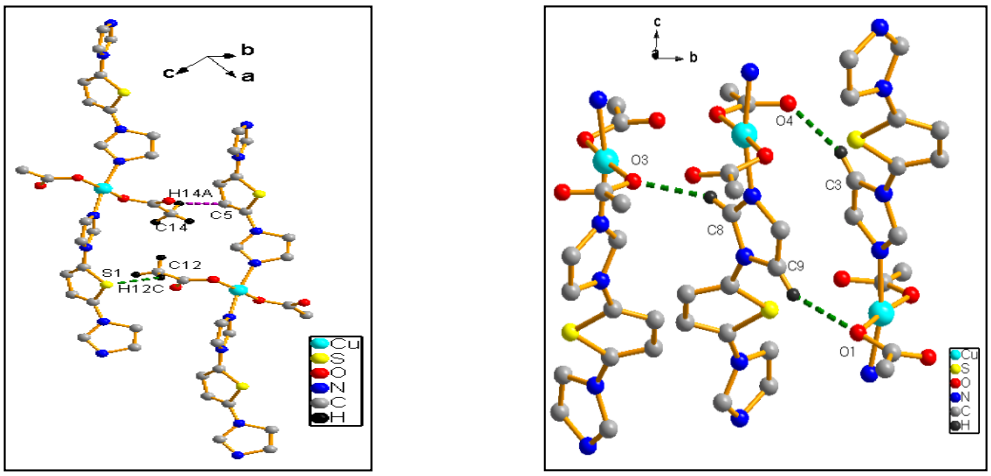
Table S1: Selected bond distances and angles for CPs **1-4**

1					
Cu(1)-O(3)	1.946(3)	Cu(1)-N(4)#1	1.979(4)	Cu(1)-N(1)	1.998(4)
Cu(1)-O(1)	1.969(3)				
O(3)-Cu(1)-O(1)	173.55(13)	O(1)-Cu(1)-N(4)#1	90.54(14)	O(1)-Cu(1)-N(1)	87.67(14)
O(3)-Cu(1)-N(4)#1	90.50(14)	O(3)-Cu(1)-N(1)	92.54(14)	N(4)#1-Cu(1)-N(1)	168.53(15)
2					
Cu(1)-O(2)	1.967(5)	Cu(1)-N(1)	2.120(5)	Cu(2)-O(8)	1.994(8)
Cu(1)-O(1)	1.974(5)	Cu(2)-O(5)	1.958(5)	Cu(2)-N(4)	2.125(7)
Cu(1)-O(4)	1.974(5)	Cu(2)-O(6)	1.972(6)	Cu(1)-Cu(1)#1	2.6597(19)
Cu(1)-O(3)	1.991(5)	Cu(2)-O(7)	1.981(6)	Cu(2)-Cu(2)#2	2.641(2)
O(2)-Cu(1)-O(1)	167.6(2)	O(2)-Cu(1)-Cu(1)#1	86.36(15)	O(7)-Cu(2)-O(8)	167.9(3)
O(2)-Cu(1)-O(4)	87.7(2)	O(1)-Cu(1)-Cu(1)#1	81.35(15)	O(5)-Cu(2)-N(4)	95.1(2)
O(1)-Cu(1)-O(4)	90.3(2)	O(4)-Cu(1)-Cu(1)#1	86.85(16)	O(6)-Cu(2)-N(4)	96.6(3)
O(2)-Cu(1)-O(3)	90.2(2)	O(3)-Cu(1)-Cu(1)#1	80.86(16)	O(7)-Cu(2)-N(4)	96.6(3)
O(1)-Cu(1)-O(3)	89.1(2)	N(1)-Cu(1)-Cu(1)#1	170.46(16)	O(8)-Cu(2)-N(4)	95.3(3)
O(4)-Cu(1)-O(3)	167.7(2)	O(5)-Cu(2)-O(6)	168.1(2)	O(5)-Cu(2)-Cu(2)#2	81.87(16)
O(2)-Cu(1)-N(1)	100.0(2)	O(5)-Cu(2)-O(7)	89.8(2)	O(6)-Cu(2)-Cu(2)#2	86.35(17)
O(1)-Cu(1)-N(1)	92.4(2)	O(6)-Cu(2)-O(7)	90.8(3)	O(7)-Cu(2)-Cu(2)#2	84.12(18)
O(4)-Cu(1)-N(1)	100.4(2)	O(5)-Cu(2)-O(8)	87.2(3)	O(8)-Cu(2)-Cu(2)#2	83.8(2)
O(3)-Cu(1)-N(1)	91.9(2)	O(6)-Cu(2)-O(8)	89.7(3)	N(4)-Cu(2)-Cu(2)#2	176.9(2)
3					
Cu(1)-O(2)	1.957(4)	Cu(1)-N(3)	2.003(4)	Cu(1)-O(1)#1	2.311(4)
Cu(1)-O(3)	1.979(4)	Cu(1)-N(1)	2.007(4)		
O(2)-Cu(1)-O(3)	158.95(16)	O(3)-Cu(1)-N(1)	90.16(16)	O(3)-Cu(1)-O(1)#1	87.52(14)
O(2)-Cu(1)-N(3)	94.20(16)	N(3)-Cu(1)-N(1)	175.99(18)	N(3)-Cu(1)-O(1)#1	91.04(16)
O(3)-Cu(1)-N(3)	89.79(16)	O(2)-Cu(1)-O(1)#1	113.01(15)	N(1)-Cu(1)-O(1)#1	84.96(16)
O(2)-Cu(1)-N(1)	87.27(16)				
4					
Cu(1)-N(1)	1.990(6)	Cu(2)-N(5)	1.982(6)	Cu(2)-O(7)	1.955(6)
Cu(1)-N(8)#1	1.974(6)	Cu(2)-N(4)#2	1.989(6)	Cu(1)-O(9W)	2.399(5)
Cu(1)-O(1)	1.968(5)	Cu(2)-O(5)	1.952(5)	Cu(2)-O(9W)	2.330(5)
Cu(1)-O(3)	1.978(5)				

O(1)-Cu(1)-N(8)#1	88.4(2)	N(8)#1-Cu(1)-N(1)	171.6(3)	O(7)-Cu(2)-N(4)#2	86.3(2)
O(1)-Cu(1)-N(1)	90.7(2)	O(1)-Cu(1)-O(9W)	93.79(19)	N(5)-Cu(2)-N(4)#2	168.9(3)
O(1)-Cu(1)-O(3)	175.2(2)	N(1)-Cu(1)-O(9W)	95.1(2)	O(5)-Cu(2)-O(9W)	89.1(2)
O(3)-Cu(1)-N(1)	90.6(2)	O(5)-Cu(2)-O(7)	173.1(2)	O(7)-Cu(2)-O(9W)	96.6(2)
N(8)#1-Cu(1)-O(3)	89.5(2)	O(5)-Cu(2)-N(5)	92.7(2)	N(5)-Cu(2)-O(9W)	91.3(2)
N(8)#1-Cu(1)-O(9W)	93.3(2)	O(7)-Cu(2)-N(5)	91.1(3)	N(4)#2-Cu(2)-O(9W)	99.8(2)
O(3)-Cu(1)-O(9W)	90.7(2)	O(5)-Cu(2)-N(4)#2	88.9(2)	Cu2 O9W Cu1	153.3(2)

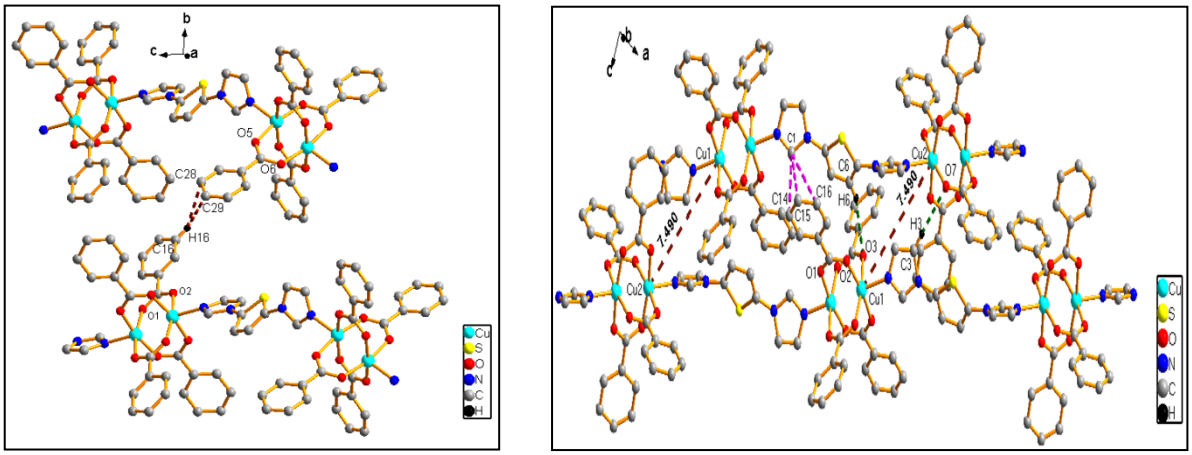
Table S2. Supra-molecular interactions present in **1-4**

Compound no.	***D***–H····***A***	H····***A*** Å	***D***····***A*** Å	***D***–H····***A*** (°)
1	C12–H12···S1	2.964(3)	3.619(6)	125.26(2)
	C14–H14A···π	2.892(1)	3.641(1)	133.97(2)
	C3–H3···O4	2.281(1)	3.120(7)	147.04(1)
	C8–H8···O3	2.421(8)	3.275(6)	149.29(8)
	C9–H9···O1	2.618(8)	3.348(9)	133.91(9)
2	C15–H15···π	2.964(6)	3.802(5)	150.41(5)
	C16–H16···π	2.914(5)	3.699(3)	147.11(3)
	C3–H3···O7	2.691(1)	3.633(1)	171.72(1)
	C6–H6···O3	2.670(4)	3.567(5)	157.82(1)
3	C5–H5···O4	2.400(4)	3.201(5)	144.19(7)
	C9–H9···O4	2.255(2)	3.140(4)	158.71(2)
	C2–H2···π	3.018(9)	3.840(4)	148.20(1)
4	C3–H3···O1	2.507(2)	3.257(2)	140.02(1)

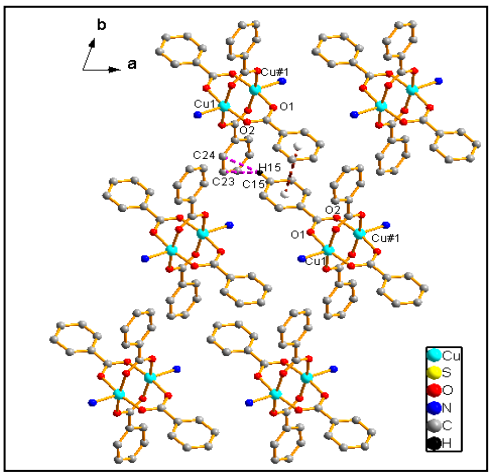


(a) (b)

Figure S1: (a) Supra-molecular interactions between 1D chains along *a* direction (b) C–H···O interactions between 1D chain in *bc* plane

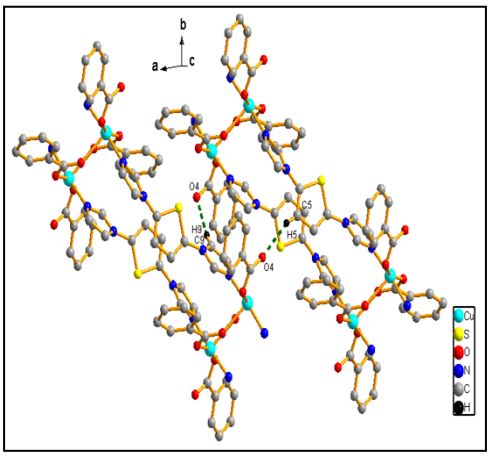


(a) (b)

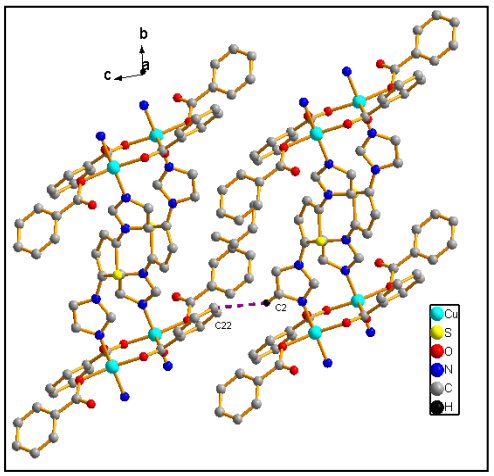


(c)

Figure S2: (a) C–H···π interactions between 1D chains in *bc* plane (b) Supra-molecular interactions between 1D chains along *a* direction, π···π = 3.830(6) Å (c) Supra-molecular interactions between 1D chains in *ab* plane, π···π= 4.369 Å

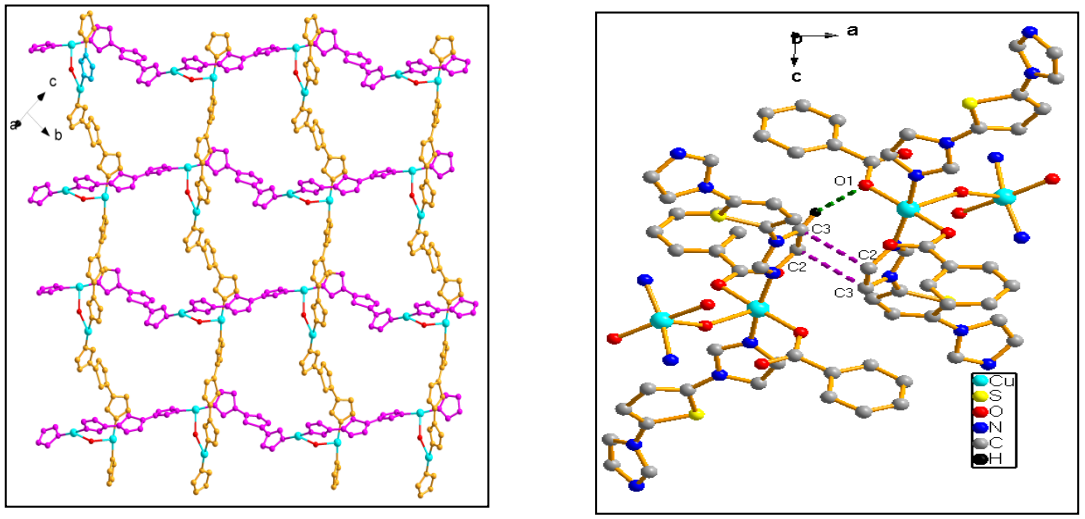


(a)



(b)

Figure S3: (a) C–H···O interactions between 1D chains along *a* direction, (b) C–H···π interactions between 1D chains in *bc* plane



(a) (b)

Figure S4: (a) View of the perpendicular helical chains making 2D plain weave like pattern (benzoate molecules are omitted for clarity) (b) supra-molecular interactions between 2D layer along *b* direction, π···π= 3.252(7) Å

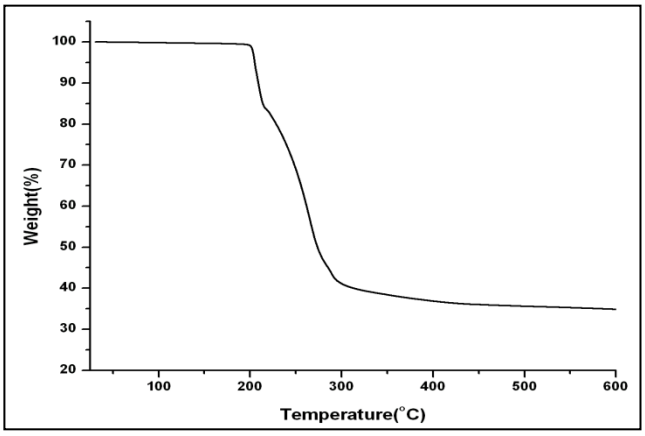


Figure S5. Thermogravimetric analysis of **1**

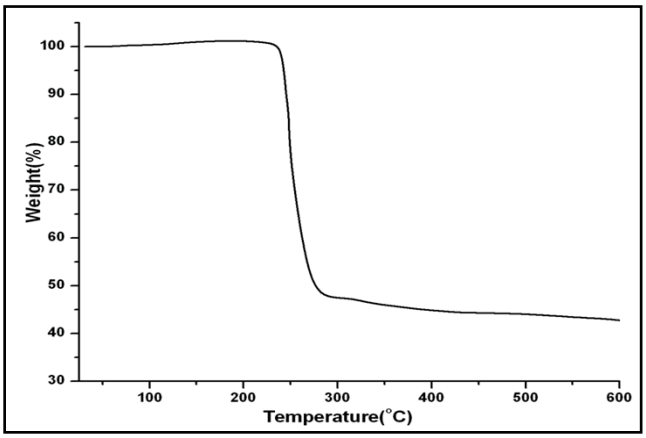


Figure S6. Thermogravimetric analysis of **2**

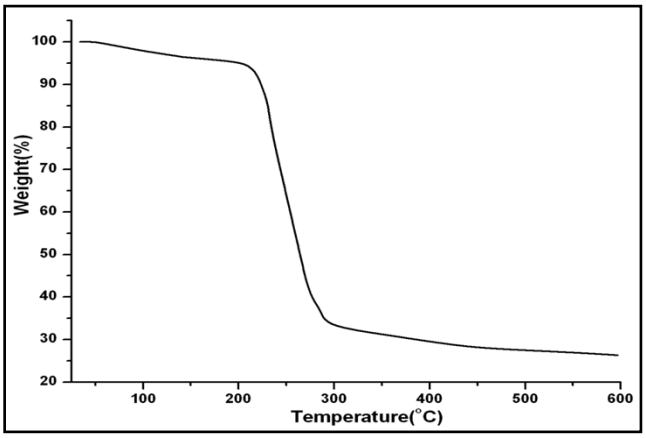


Figure S7. Thermogravimetric analysis of **3**

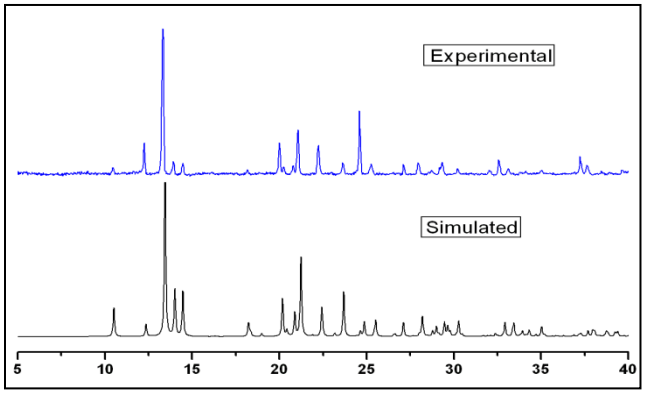


Figure S8. PXRD of **1**

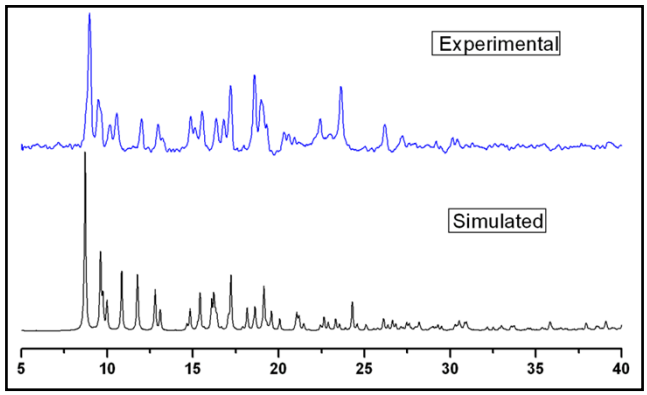


Figure S9. PXRD of **2**

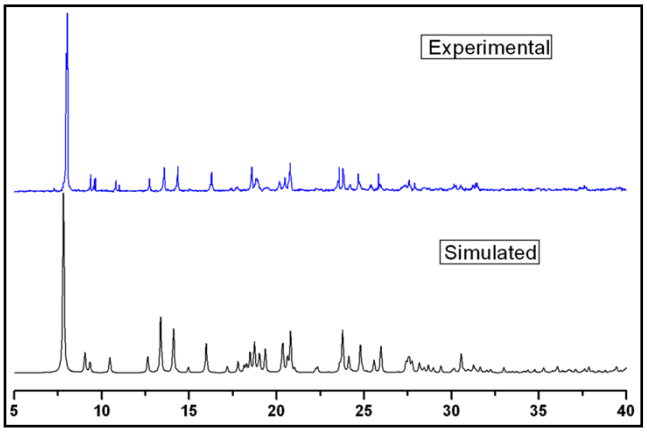


Figure S10. PXRD of **3**