The construction of Cu(I)/Cu(II) coordination polymers based on pyrazine-carboxylate: structural diversity tuned by *in situ* hydrolysis reaction

ZhenZhen Wen, SongLiang Cai, ShengRun Zheng*, Jun Fan, Wei-Guang Zhang*

School of Chemistry and Environment, South China Normal University, Guangzhou, 510006, P. R. China. E-mail: zhengsr@scnu.edu.cn, wgzhang@scnu.edu.cn; Fax:+86-20-39347768

Supporting information

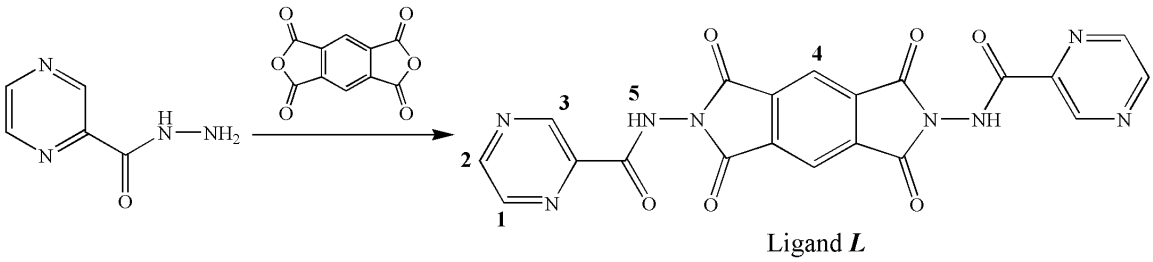
Table S**1** Selected bond lengths [Å] and angles [°] for the compounds.[a]

Compound **1**			
Cu(1)-N(1)	1.978(8)	Cu(2)-O(4)#2	1.918(6)
Cu(1)-O(1)	1.989(6)	Cu(2)-N(3)#2	2.017(8)
Cu(1)-N(4)#1	2.057(9)	Cu(2)-N(2)	2.020(9)
Cu(1)-Cl(1)	2.222(3)	Cu(2)-Cl(2)	2.235(3)
Cu(1)-O(3)	2.385(6)	Cu(2)-O(2)#3	2.436(6)
N(1)-Cu(1)-O(1)	82.4(3)	O(4)#2-Cu(2)-N(3)#2	83.2(3)
N(1)-Cu(1)-N(4)#1	169.2(3)	O(4)#2-Cu(2)-N(2)	89.8(3)
O(1)-Cu(1)-N(4)#1	86.9(3)	N(3)#2-Cu(2)-N(2)	168.8(3)
N(1)-Cu(1)-Cl(1)	95.4(2)	O(4)#2-Cu(2)-Cl(2)	174.7(2)
O(1)-Cu(1)-Cl(1)	172.3(2)	N(3)#2-Cu(2)-Cl(2)	94.2(2)
N(4)#1-Cu(1)-Cl(1)	95.4(2)	N(2)-Cu(2)-Cl(2)	92.1(2)
N(1)-Cu(1)-O(3)	82.0(3)	O(4)#2-Cu(2)-O(2)#3	90.6(2)
O(1)-Cu(1)-O(3)	86.4(2)	N(3)#2-Cu(2)-O(2)#3	106.6(3)
N(4)#1-Cu(1)-O(3)	95.9(3)	N(2)-Cu(2)-O(2)#3	82.1(3)
Cl(1)-Cu(1)-O(3)	100.63(17)	Cl(2)-Cu(2)-O(2)#3	94.56(17)
Compound **2a**			
Cu(1)-O(4)	1.932(7)	Cu(2)-N(3)#1	2.002(8)
Cu(1)-O(1)	1.935(7)	Cu(2)-N(2)	2.017(8)
Cu(1)-N(1)	1.997(8)	Cu(2)-Cl(1)	2.378(3)
Cu(1)-N(4)	2.000(8)	Cu(2)-Cl(1)#2	2.613(4)

Cu(1)-O(1W)	2.289(8)		
O(4)-Cu(1)-O(1)	173.0(3)	N(1)-Cu(1)-O(1W)	92.8(3)
O(4)-Cu(1)-N(1)	96.5(3)	N(4)-Cu(1)-O(1W)	89.0(3)
O(1)-Cu(1)-N(1)	82.6(3)	N(3)#1-Cu(2)-N(2)	142.0(3)
O(4)-Cu(1)-N(4)	82.6(3)	N(3)#1-Cu(2)-Cl(1)	96.9(2)
O(1)-Cu(1)-N(4)	98.1(3)	N(2)-Cu(2)-Cl(1)	102.5(2)
N(1)-Cu(1)-N(4)	178.0(3)	N(3)#1-Cu(2)-Cl(1)#2	97.4(3)
O(4)-Cu(1)-O(1W)	92.0(3)	N(2)-Cu(2)-Cl(1)#2	100.0(2)
O(1)-Cu(1)-O(1W)	95.0(3)	Cl(1)-Cu(2)-Cl(1)#2	121.08(9)
Compound **3**			
I(1)-Cu(2)#1	2.631(2)	Cu(2)-N(4)#3	2.096(13)
I(1)-Cu(2)	2.649(2)	Cu(3)-O(3)	1.929(12)
I(1)-Cu(1)	2.650(2)	Cu(3)-O(1)	1.961(11)
I(2)-Cu(1)#2	2.655(2)	Cu(3)-N(3)	1.999(13)
I(2)-Cu(1)	2.656(2)	Cu(3)-N(1)	2.010(13)
I(2)-Cu(2)#2	2.707(3)	Cu(3)-O(5)	2.227(14)
Cu(1)-N(2)	2.091(13)		
N(2)-Cu(1)-I(1)	105.3(4)	I(1)-Cu(2)-I(2)#2	114.68(9)
N(2)-Cu(1)-I(2)#2	108.5(4)	O(3)-Cu(3)-O(1)	171.5(6)
I(1)-Cu(1)-I(2)#2	116.45(8)	O(3)-Cu(3)-N(3)	83.2(5)
N(2)-Cu(1)-I(2)	102.9(4)	O(1)-Cu(3)-N(3)	96.4(5)
I(1)-Cu(1)-I(2)	106.88(8)	O(3)-Cu(3)-N(1)	94.9(5)
I(2)#2-Cu(1)-I(2)	115.56(9)	O(1)-Cu(3)-N(1)	83.4(5)
N(4)#3-Cu(2)-I(1)#1	107.7(3)	N(3)-Cu(3)-N(1)	165.5(6)
N(4)#3-Cu(2)-I(1)	108.9(3)	O(3)-Cu(3)-O(5)	97.4(5)
I(1)#1-Cu(2)-I(1)	119.50(8)	O(1)-Cu(3)-O(5)	91.1(5)
N(4)#3-Cu(2)-I(2)#2	99.8(4)	N(3)-Cu(3)-O(5)	99.4(6)
I(1)#1-Cu(2)-I(2)#2	104.29(8)	N(1)-Cu(3)-O(5)	95.1(6)

[a]Symmetry transformations used to generate equivalentatoms: #1 x+1,y,z #2 x,y,z+1 #3 x,-y+1,z+1/2 for compound **1**; #1 x+1,-y+3/2,z+1/2 #2 -x+1,y-1/2,-z+3/2 for compound **2a**; #1 -x,-y+1,-z+1 #2 -x,y,-z+1/2 for compound **3**.

Scheme S**1.** Synthetic route of the ligand ***L***



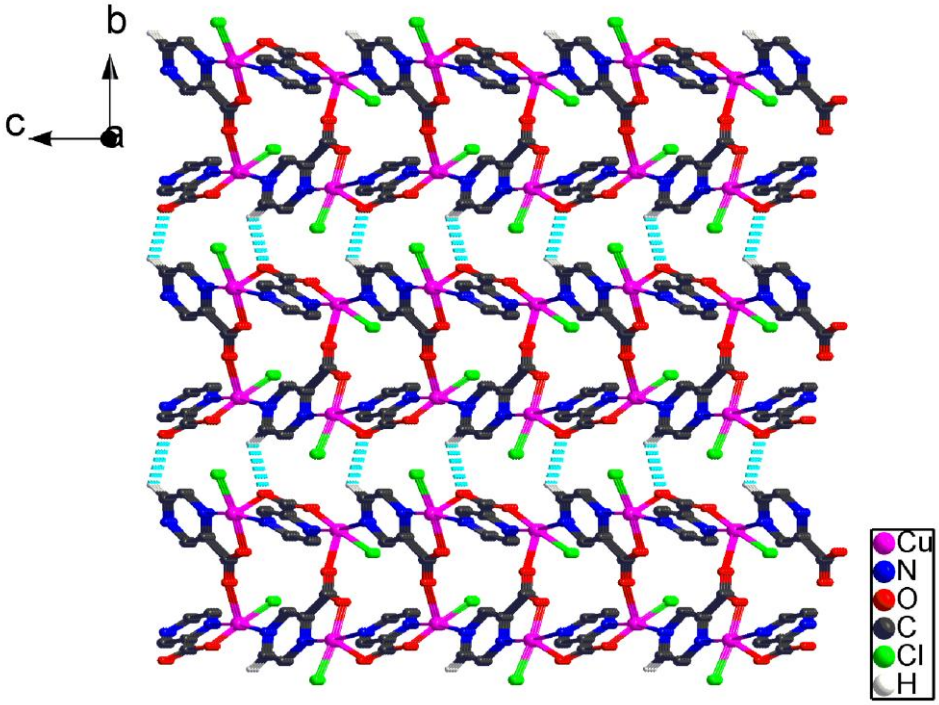


Figure S**1.** The 3D supramolecular framework of compound **1** assembled through interlayer hydrogen bonding interactions between the 2D double-layer (hydrogen bonds shown as dashed lines)