Electronic Supplementary Information for CrystEngComm

Electronic Supplementary Information (ESI)

Self-assembly of $[Cu_3I_2]$- or $[CuI]_n$-based (n = 2, 4, and ∞) coordination polymers from unsymmetrical bis(pyridyl) and in situ ligands: synthesis, structures, and properties

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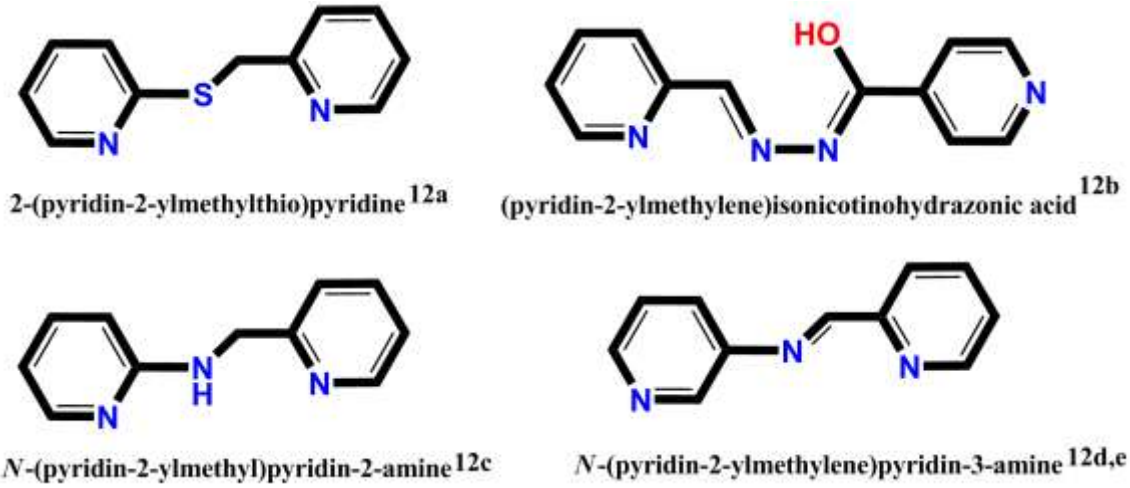
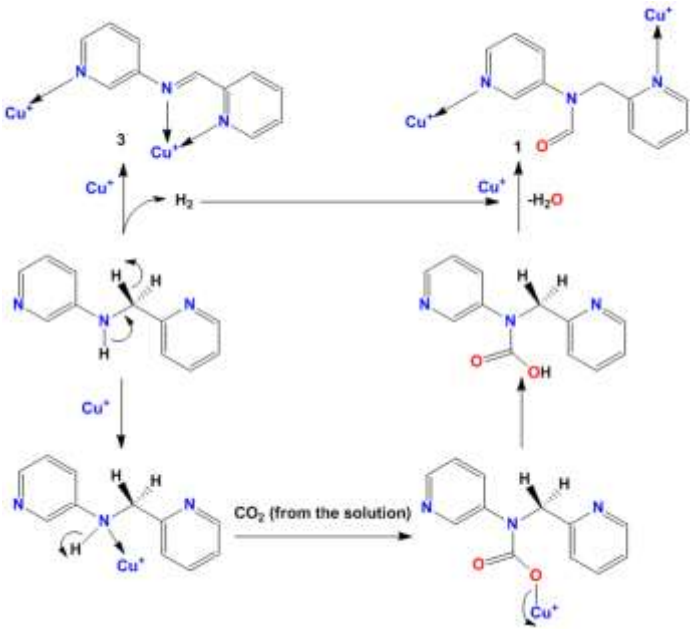


Scheme S1 Schematic representation of the unsymmetrical bis(pyridyl) ligands in reported Cu(I) complexes.



Scheme S2 Proposed mechanism for the formation of complexes **1** and **3**.[S1]

References

S1 (*a*) J. Liu, C. Guo, Z. Zhang, T. Jiang, H. Liu, J. Song, H. Fan and B. Han, *Chem. Commun.*, 2010, **46**, 5770-5772; (*b*) B. Xu, R. J. Madix and C. M. Friend, *Chem. Eur. J.*, 2012, **18**, 2313-2318.

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Disorder of complexes 2, 4 and 5

The acetonitrile of complex **2** is eliminated with SQUEEZE during resolution of the structure but added to total atom count. The free water molecule in complex **4** is disordered over two positions with the ratio of 0.55:0.45. In complex **5**, the ligand **L3** is disordered about the center of the aliphatic C-N bond. Meanwhile, the C and N atom in this aliphatic C-N bond have the same chance to occupy the two positions. Therefore, during the refinement, the C and N atom is refined with fifty percent occupancy in the two positions of aliphatic C-N bond.

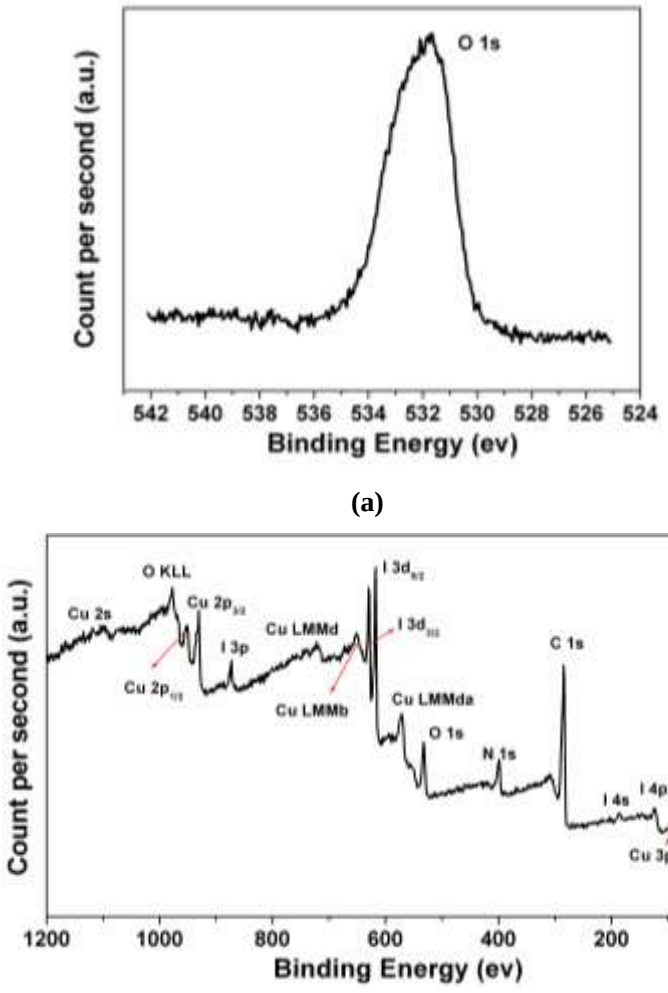

Fig. S1 (a) XPS spectrum of **1** in the range corresponding to the O1s level; (b) XPS spectrum of **1**.

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Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) patterns for solid samples of **1-5** are measured at room temperature as illustrated in Fig. S2. The patterns are highly similar to their simulated ones (based on the single-crystal X-ray diffraction data), indicating that the single-crystal structures are really representative of the bulk of the corresponding samples.

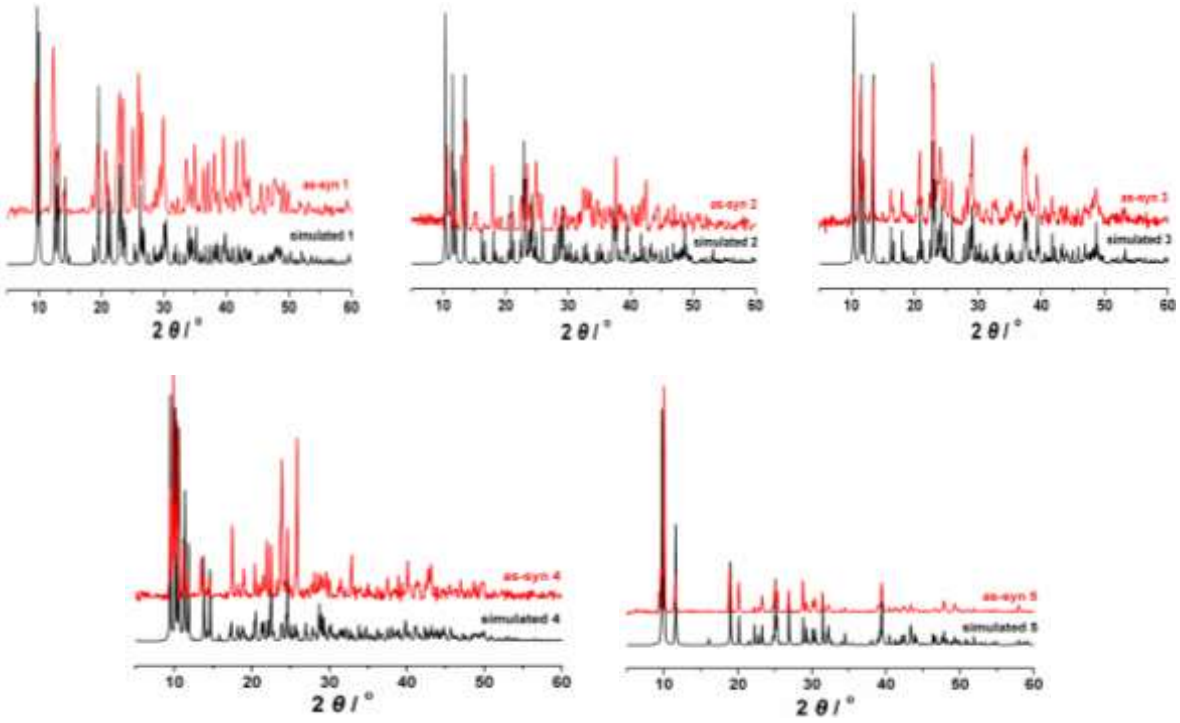

Fig. S2 PXRD patterns for **1-5**.

Thermogravimetric analysis (TGA)

The thermal stabilities of **1-5** were analyzed on crystalline samples by thermogravimetric analyses (TGA) from room temperature to 900 °C at a rate of 10 °C min^{-1} under N_2 atmosphere. As shown in Fig. S3, the TG curves indicated that **1** was stable up to ca. 120 °C and the initial weight loss in the temperature range 120-330 °C was due to the decomposition of **L1a** (obsd 52.59%, calcd 52.82%). Over the range 330-600 °C, the weight loss should correspond to the sublimation of iodine (obsd 31.48%, calcd 31.44%). The TG curve for **2** showed a minor weight loss in the temperature range 63-108 °C, which corresponded to the loss of acetonitrile molecule (obsd 3.41%, calcd 3.71%). Then, the **dmtrz**$^-$ was decomposed in the temperature range 180-375 °C, with a weight loss of 45.02% (calcd 44.64%). Further weight loss of 34.64% in the temperature range 375-610 °C was consistent with the sublimation of iodine (calcd 34.42%). The first weight loss of **3** occurred in the temperature range 204-335 °C, corresponding to the decomposition of **L1b** (obsd 32.26%, calcd 32.48%). Then, the second weight loss of 45.31% in the temperature range 335-540 °C was consistent with the sublimation of iodine (calcd 44.99%). For **4**, the minor weight loss of 1.77% in the temperature range 60-85 °C was caused by the loss of free water molecule (calcd 1.57%). After that, the **L2** was decomposed in the temperature range 130-345 °C, with a weight loss of 31.86% (calcd 32.2%). Over the range 345-484 °C, the weight loss should correspond to the sublimation of iodine (obsd 44.21%, calcd 44.13%). The initial weight loss of **5** in the temperature range 160-376 °C was due to the decomposition of **L3** (obsd 32.61%, calcd 32.72%). Over the range 376-702 °C, the weight loss should correspond to the sublimation of iodine (obsd 44.69%, calcd 44.83%).

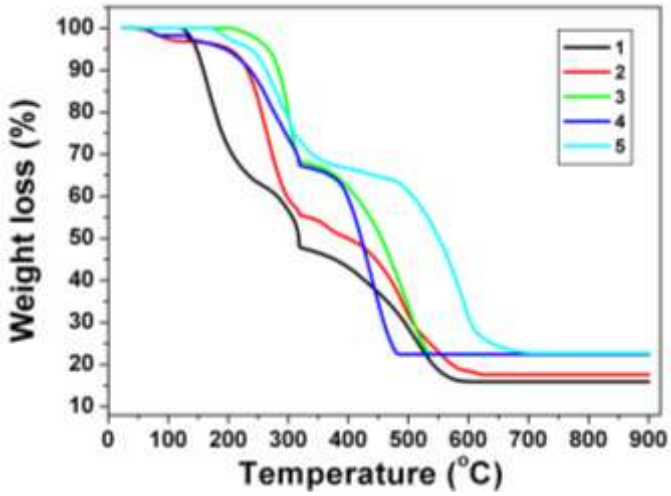

Fig. S3 TG curves of **1-5** at N_2 atmosphere.

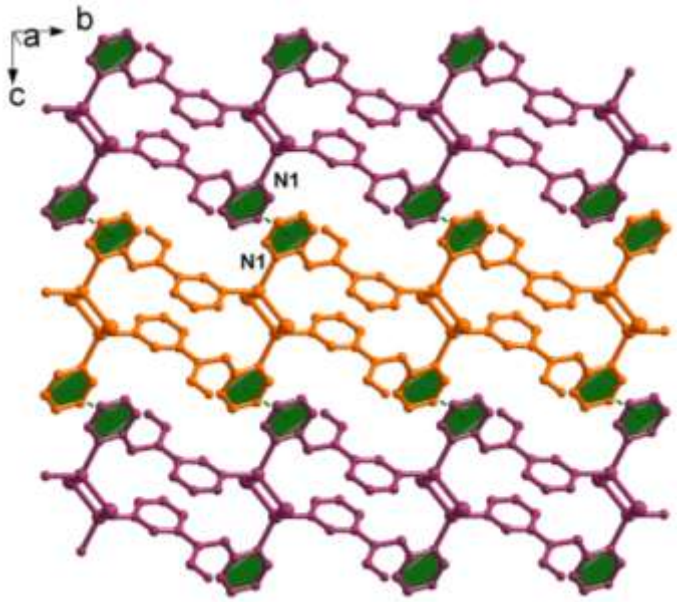

Fig. S4 Layer structure of **1** extended by the π···π interactions (green dashed lines). Orange and purple ball-and-stick modes represented different double chains.

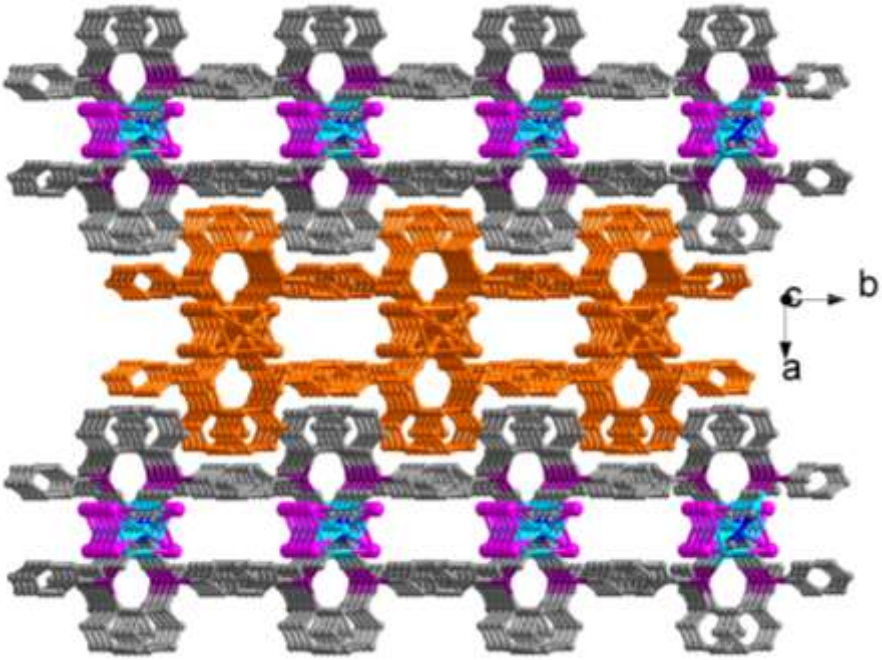

Fig. S5 Double layer structure of **2** with the acetonitrile molecules were omitted for clarity.

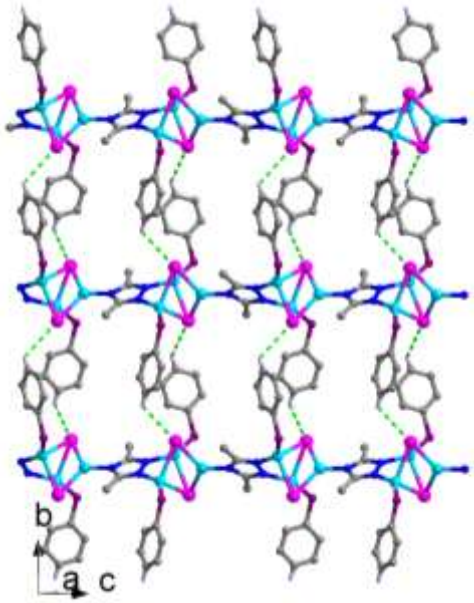

Fig. S6 Layer structure of **2** extended by the C-H···I interactions (green dashed lines). The other two phenyl rings of the PPh_3 molecules were omitted for clarity.

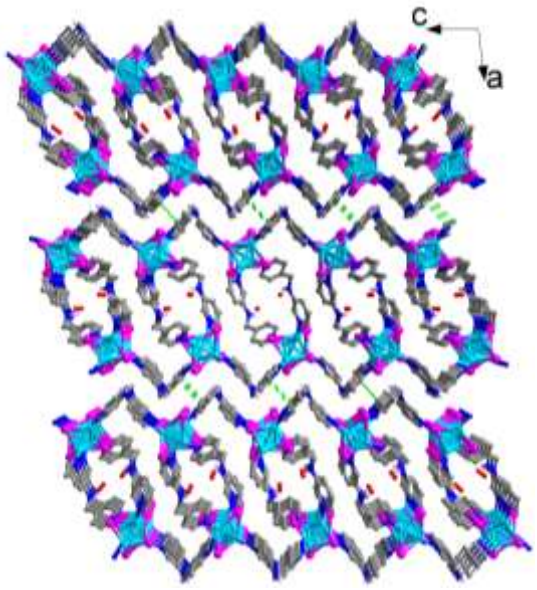

Fig. S7 3-D supramolecular architecture of **4** extended by the π···π interactions (green dashed lines) with free water molecules encapsulated in the 1-D channels.

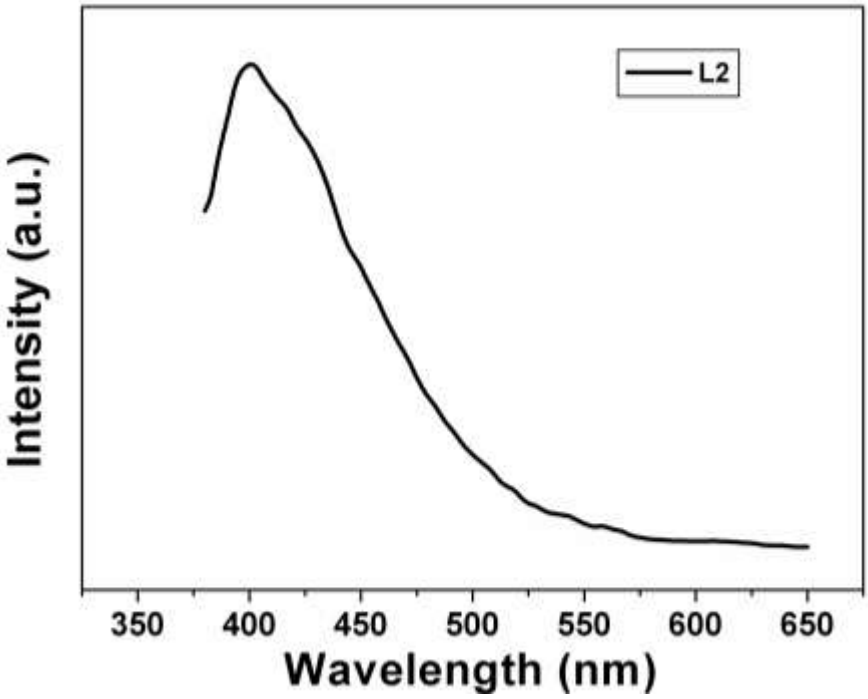

Fig. S8 Emission spectrum of free ligand **L2** in solid state.

Table S1 Selected bond lengths for **1**-**5**[a]

1			
Cu(1)-N(1)	2.078(7)	Cu(1)-I(1)^{ii}	2.6711(19)
Cu(1)-N(3)^{i}	2.083(7)	Cu(1)-Cu(1)^{ii}	2.717(3)
Cu(1)-I(1)	2.6246(17)		
2			
I(1)-Cu(1)	2.8447(9)	Cu(1)-Cu(2)	2.9027(6)
Cu(1)-N(2)^{ii}	1.958(4)	Cu(2)-N(1)	1.952(5)
Cu(1)-P(1)	2.1934(5)	Cu(2)-I(1)^{i}	2.5671(6)
Cu(1)-I(1)^{i}	2.8520(6)	I(1)-Cu(2)	2.5671(6)
3			
I(1)-Cu(1)	2.6048(13)	Cu(1)-N(2)	2.119(7)
I(1)-Cu(2)	2.6285(15)	Cu(1)-Cu(2)^{i}	2.665(2)
I(1)-Cu(2)^{i}	2.7797(18)	Cu(2)-N(3)^{ii}	2.049(7)
I(2)-Cu(1)	2.5738(15)	Cu(2)-I(2)^{i}	2.6777(15)
I(2)-Cu(2)^{i}	2.6777(15)	Cu(2)-I(1)^{i}	2.7797(18)
Cu(1)-N(1)	2.077(7)		
4			
Cu(1)-N(1)	2.030(8)	Cu(2)-I(3)	2.7261(16)
Cu(1)-Cu(3)	2.645(2)	Cu(2)-Cu(4)	2.839(2)
Cu(1)-Cu(4)	2.658(2)	Cu(3)-N(3)^{i}	2.013(9)
Cu(1)-I(3)	2.6699(16)	Cu(3)-I(2)	2.6502(16)
Cu(1)-Cu(2)	2.674(2)	Cu(3)-I(4)	2.6826(17)
Cu(1)-I(1)	2.6777(15)	Cu(3)-I(1)	2.7209(16)
Cu(1)-I(2)	2.7759(17)	Cu(3)-Cu(4)	2.818(2)
Cu(2)-N(4)	2.028(8)	Cu(4)-N(6)^{ii}	2.042(8)
Cu(2)-Cu(3)	2.618(2)	Cu(4)-I(3)	2.6497(17)
Cu(2)-I(1)	2.7002(16)	Cu(4)-I(4)	2.6592(16)
Cu(2)-I(4)	2.7193(16)	Cu(4)-I(2)	2.7516(17)
5			
I(1)-Cu(1)	2.6497(9)	Cu(1)-I(1)^{i}	2.6846(11)
Cu(1)-N(1)	1.973(7)	Cu(1)-I(1)^{iv}	2.7016(9)

Cu(1)-N(3)^{iii}	2.07(4)	Cu(1)-Cu(1)^{v}	2.751(2)

[a] Symmetry operations: **For 1**, i x,y-1,z; ii -x+1,-y,-z+1. **For 2**, i -x+3/2,-y+3/2,z; ii x,-y+3/2,z-1/2. **For 3**, i -x,-y+1,-z+1; ii x-1/2,-y+1/2,z+1/2. **For 4**, i x,-y+1,z-1/2; ii -x+1,y-1,-z+1/2. **For 5**, i -x+1,-y+1,-z+1; iii -x+1,y,-z+1/2; iv x,y-1,z; v -x+1,-y,-z+1.