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**Understanding Supramolecular Interactions Provide Clues for Building
Molecules into Minerals and Materials: A Retrosynthetic Analysis of
Copper Based Solids**

Monika Singh, Jency Thomas and Arunachalam Ramanan*

Department of Chemistry, Indian Institute of Technology, New Delhi 110016, India

Fax: +91 11 26581102; Tel: +91 11 26591507

E-mail: aramanan@chemistry.iitd.ac.in

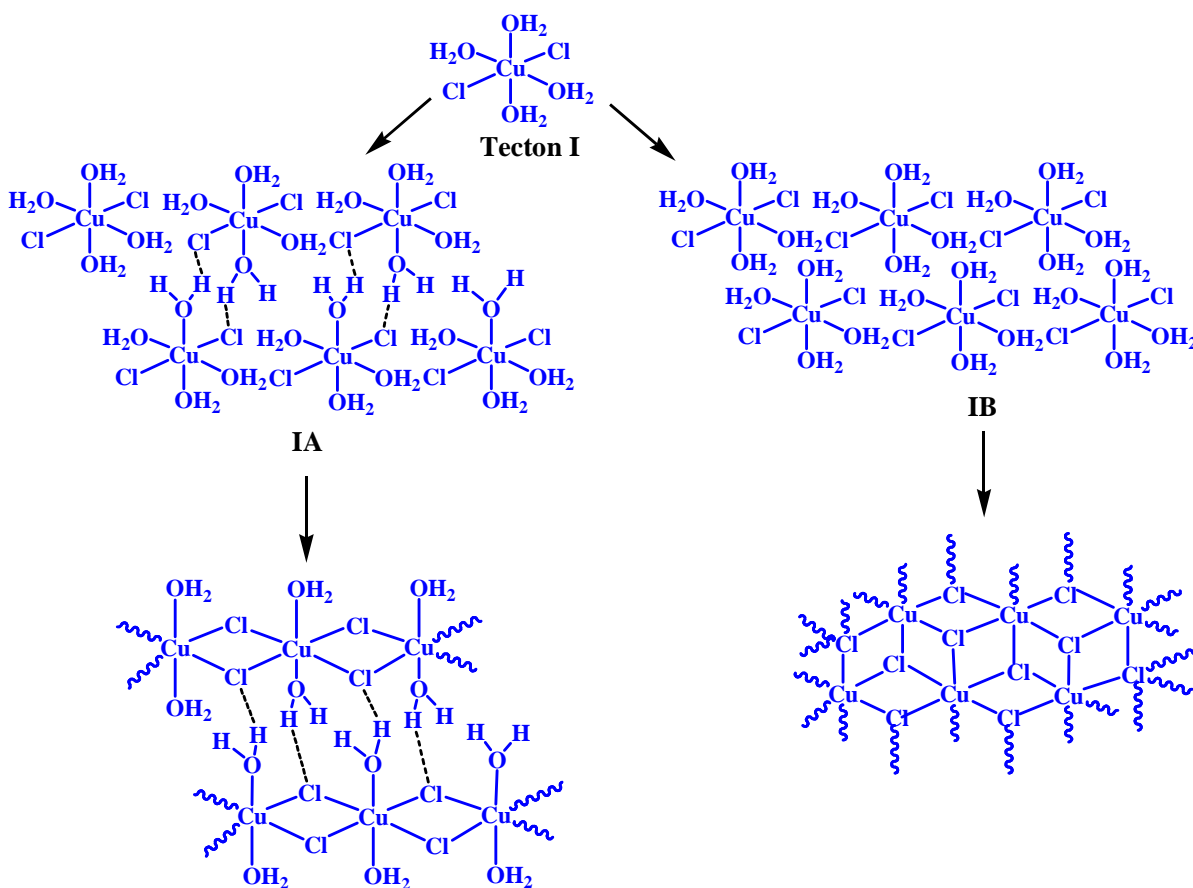


Fig. S1. During crystallization *tecton I* induces two types of crystal nuclei (**IA** and **IB**) depending on the condition – water solvent and room temperature favors **IA** while nonaqueous solvent or hydrothermal/solvothermal favors **IB**. The *supramolecular synthons F & I* favor **IA** while *G* leads to **IB** (Scheme 1). In **IA** the dominating intermolecular interactions lead to a sheet type structure with covalent bonds while adjacent sheets are held together by weak OH₂...Cl interactions. The compromised intermolecular interactions of **IA** lead to CuCl₂·2H₂O whereas **IB** favors a more close-packed three-dimensional structure for the anhydrous CuCl₂. [Structural Inorganic Chemistry, Oxford, **1962**; *J. Chem. Phys. A*, **1957**, 6, 220].

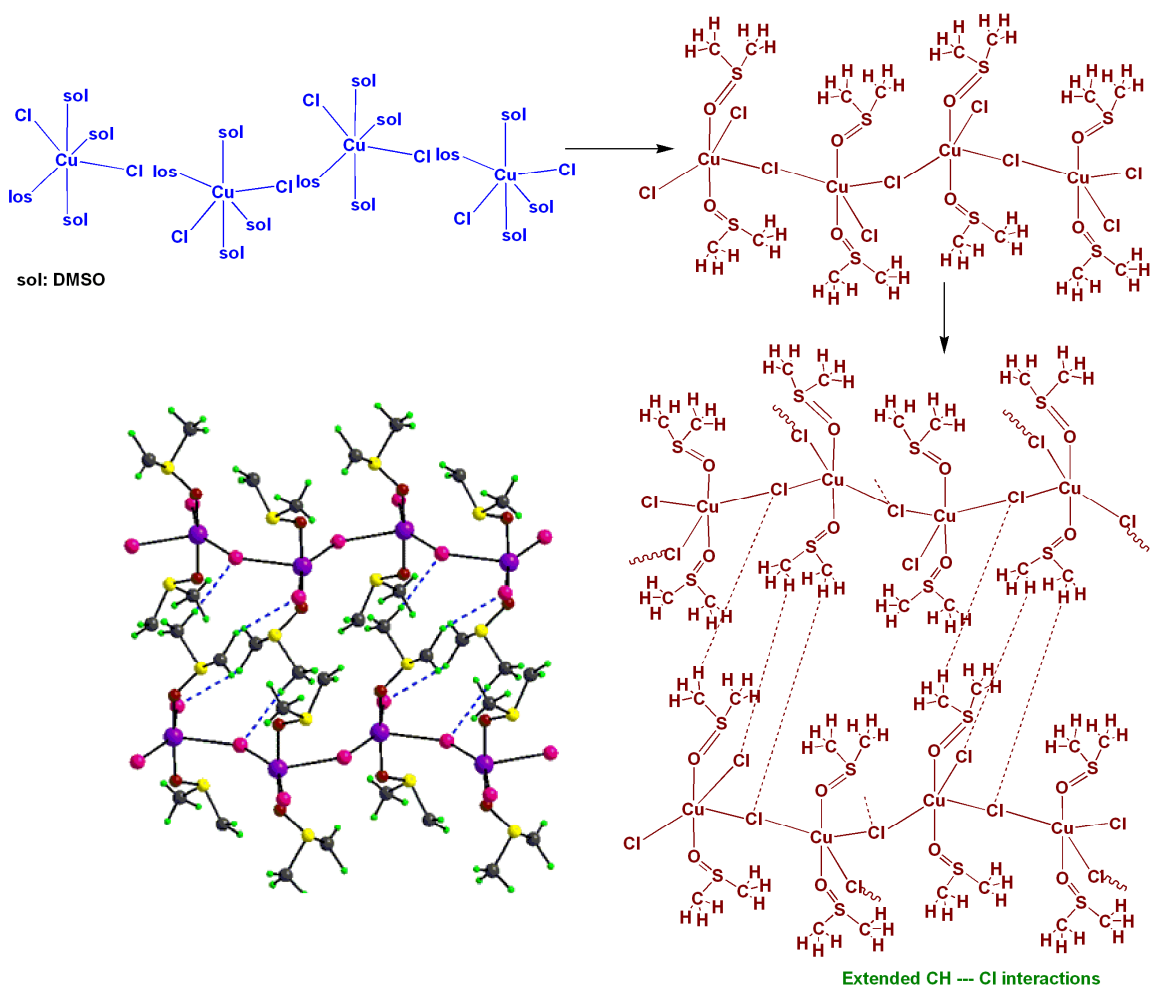


Fig. S2. When the crystallization is carried out in the presence of a strongly coordinating solvent like DMSO, a different *tecton* occurs; the major force is still the self assembling **I** favoring -Cl-Cu-Cl- interactions; condensation leads to one dimension chains. The presence of bulky DMSO groups favor hydrophobic and CH...Cl interactions on the other dimensions (different *supramolecular synthons*) and hence the final solid state structure.

[*Inorg. Chim. Acta* **1970**, 4, 447]

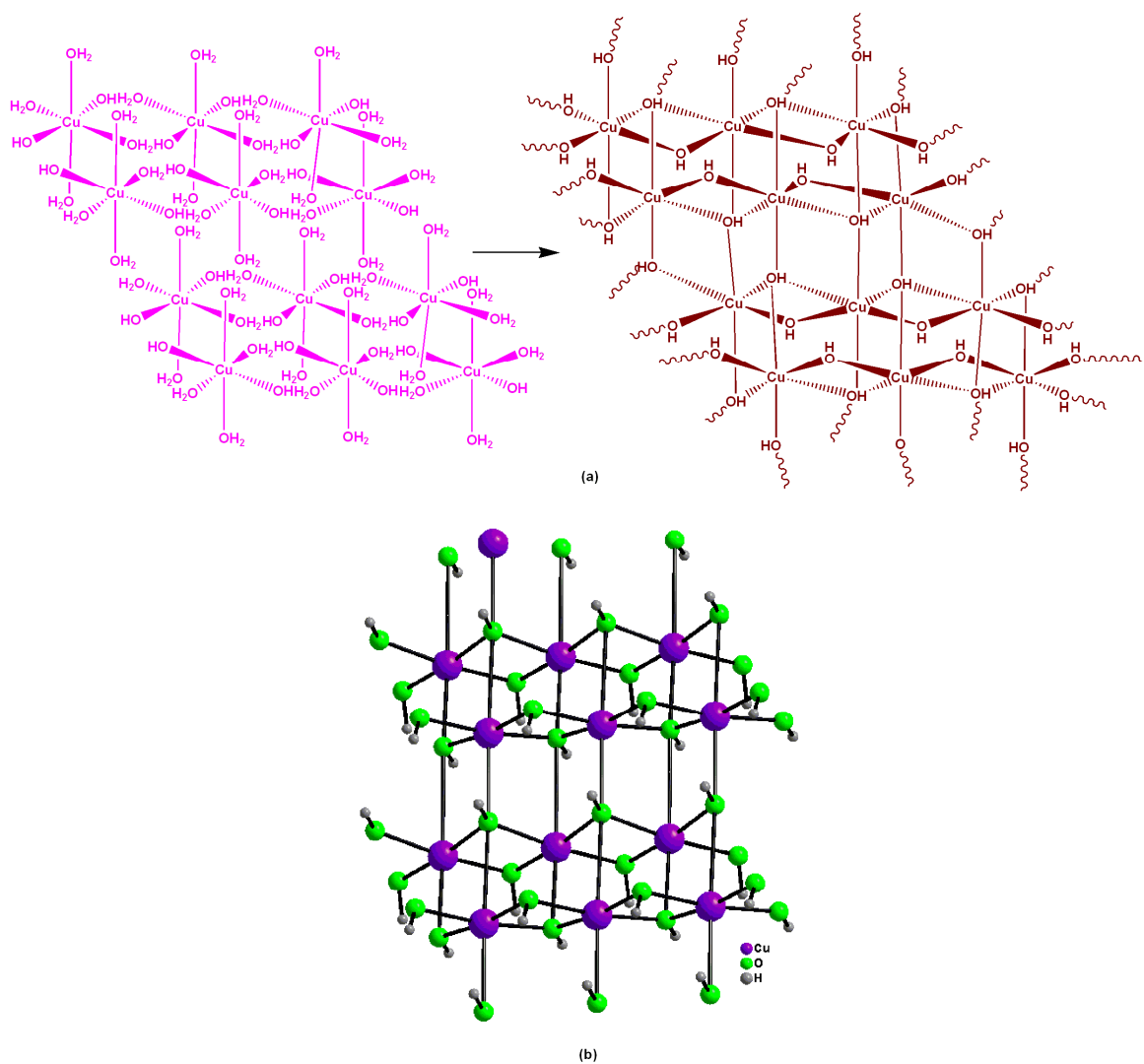


Fig. S3. Assembly of **II** through *supramolecular synthons A* and *C* lead to the crystal nucleus (a) which eventually result in $\text{Cu}(\text{OH})_2$. A matching crystal structure is shown in (b). Notice the difference in assembly between $\text{Cu}(\text{OH})_2$ with that of CuCl_2 (Fig. S1). In the former two synthons are involved while in the latter only one is involved. [*Acta Cryst.* **1990**, *C46*, 2279].

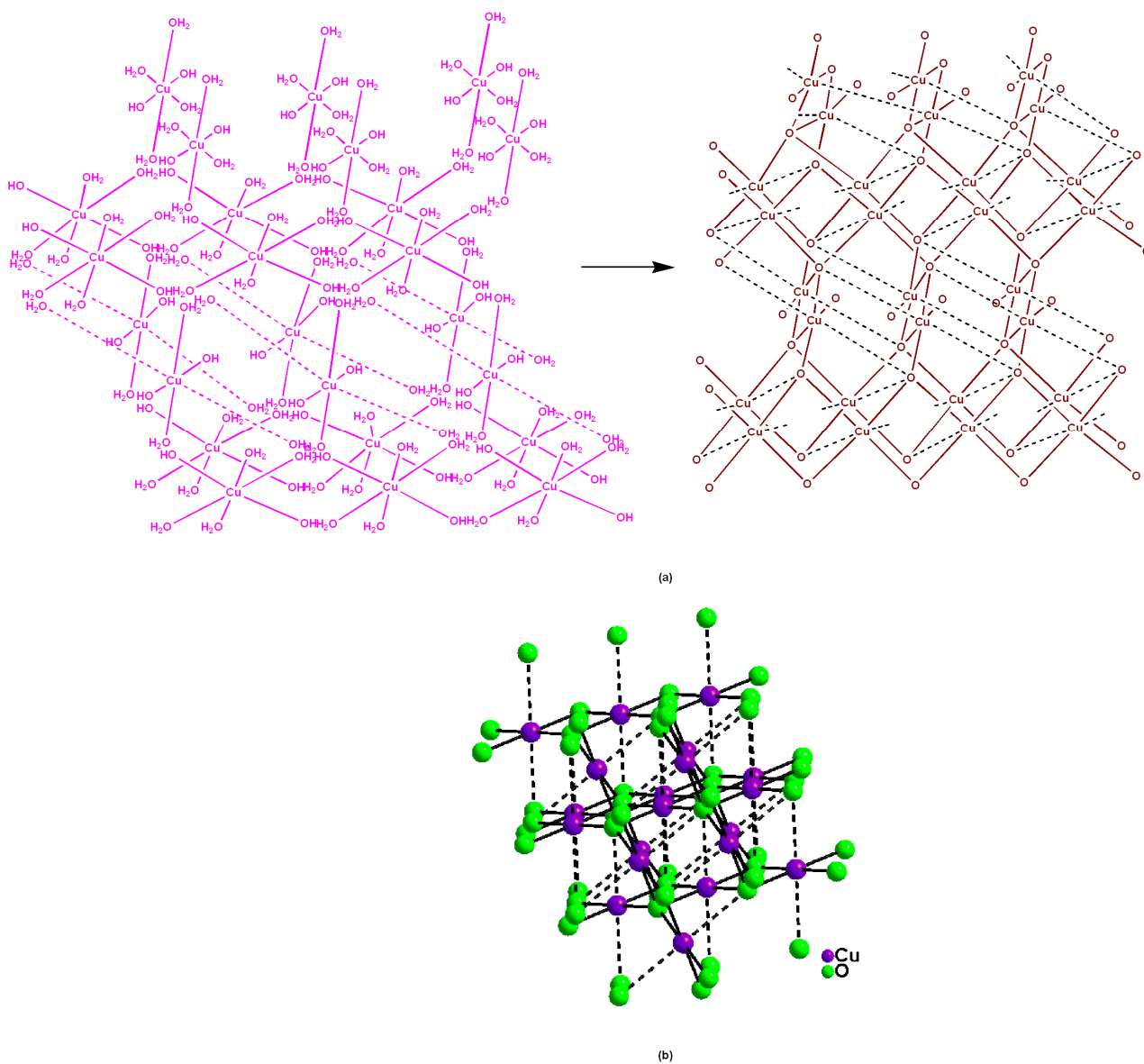


Fig. S4. Assembly of **II** through a new *supramolecular synthon E* lead to the crystal nucleus (a) which eventually form CuO. Crystal structure is shown in (b). [*Mineral. Mag.* **1989**, *53*, 557]

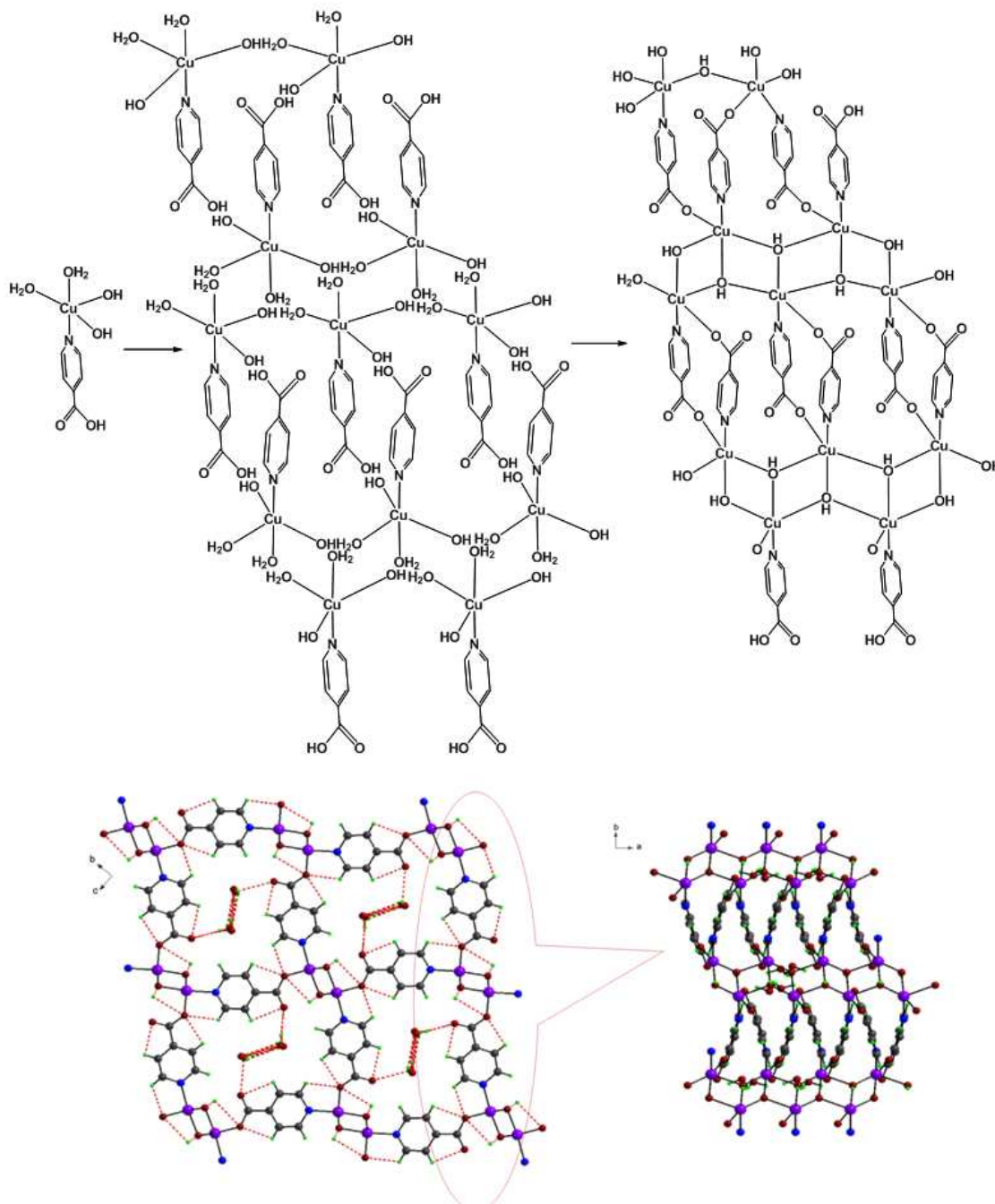


Fig. S5 Presence of pyridine-4-carboxylic acid (*py4c*) leads to a new *tecton*, $[\text{Cu}(\text{py4c})(\text{OH})_2(\text{OH}_2)_2]$. The crystal nucleus arises as a result of strong self assembling *supramolecular synthon B* favoring a ladder-like cupric hydroxide chains and the adjacent chains are bridged by bidentating pyridine-4-carboxylate. Two water *tectons* mediate the two free carboxylate oxygens.

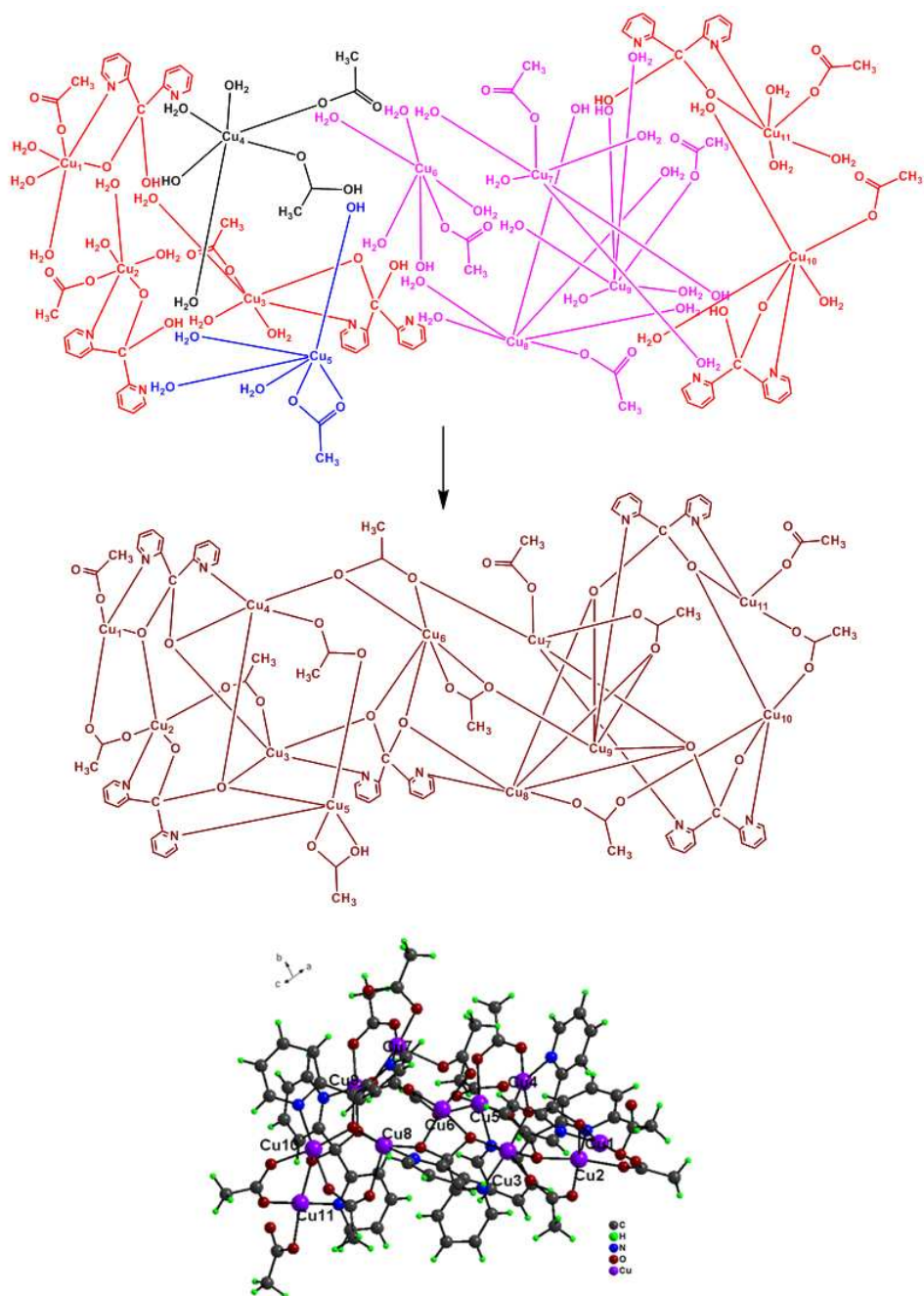


Fig. S6 The presence of aliphatic and aromatic groups on the periphery forces the aggregation of the four *tectons* $\{\text{Cu}(\text{py}_2(\text{CO}))(\text{CH}_3\text{COO})(\text{OH}_2)_3\}$, $\{\text{Cu}(\text{CH}_3\text{COO})_2(\text{OH})(\text{OH}_2)_3\}$, $\{\text{Cu}(\text{CH}_3\text{COO})(\text{OH})(\text{OH}_2)_3\}$ and $\{\text{Cu}(\text{CH}_3\text{COO})(\text{OH})(\text{OH}_2)_4\}$ to result in a high nuclear copper Cu_{11} cluster. [*Inorg. Chem. Commun.* **2008**, *11*, 418]

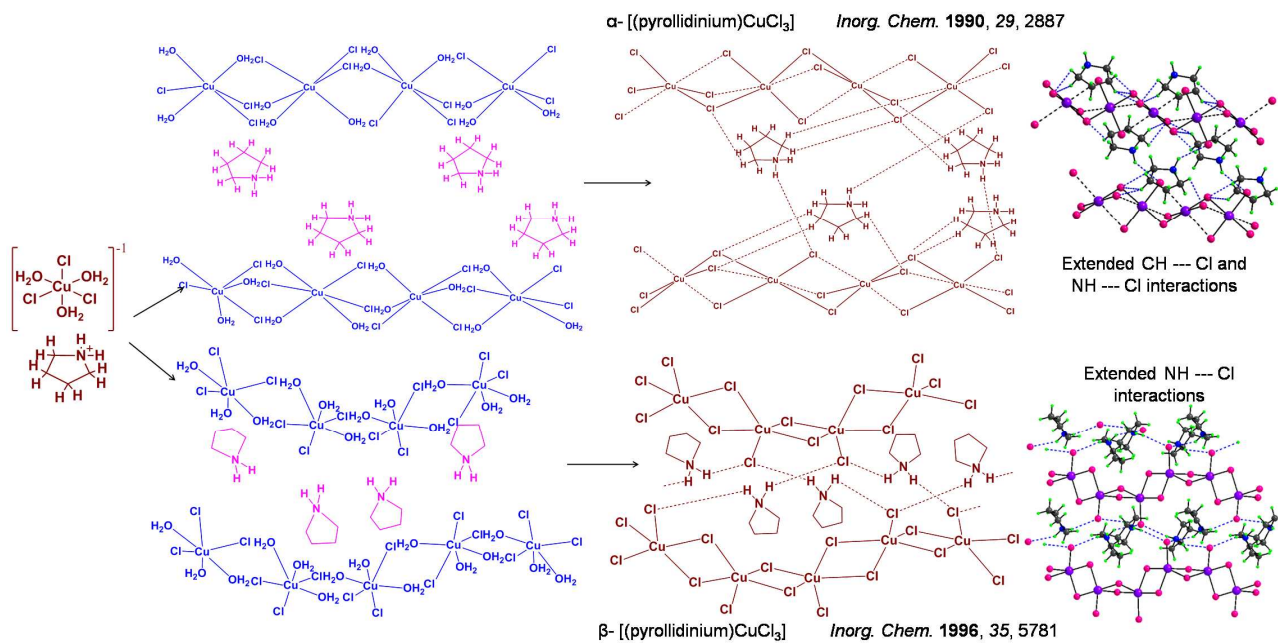


Fig. S7. Mechanistic path for the structural organization of pyrrolidinium chloride polymorphs based on the *tecton III*, $[\text{Cu}(\text{H}_2\text{O})_3\text{Cl}_3]^-$. [*Inorg. Chem.* **1990**, *29*, 2887; *Inorg. Chem.* **1996**, *35*, 5781].

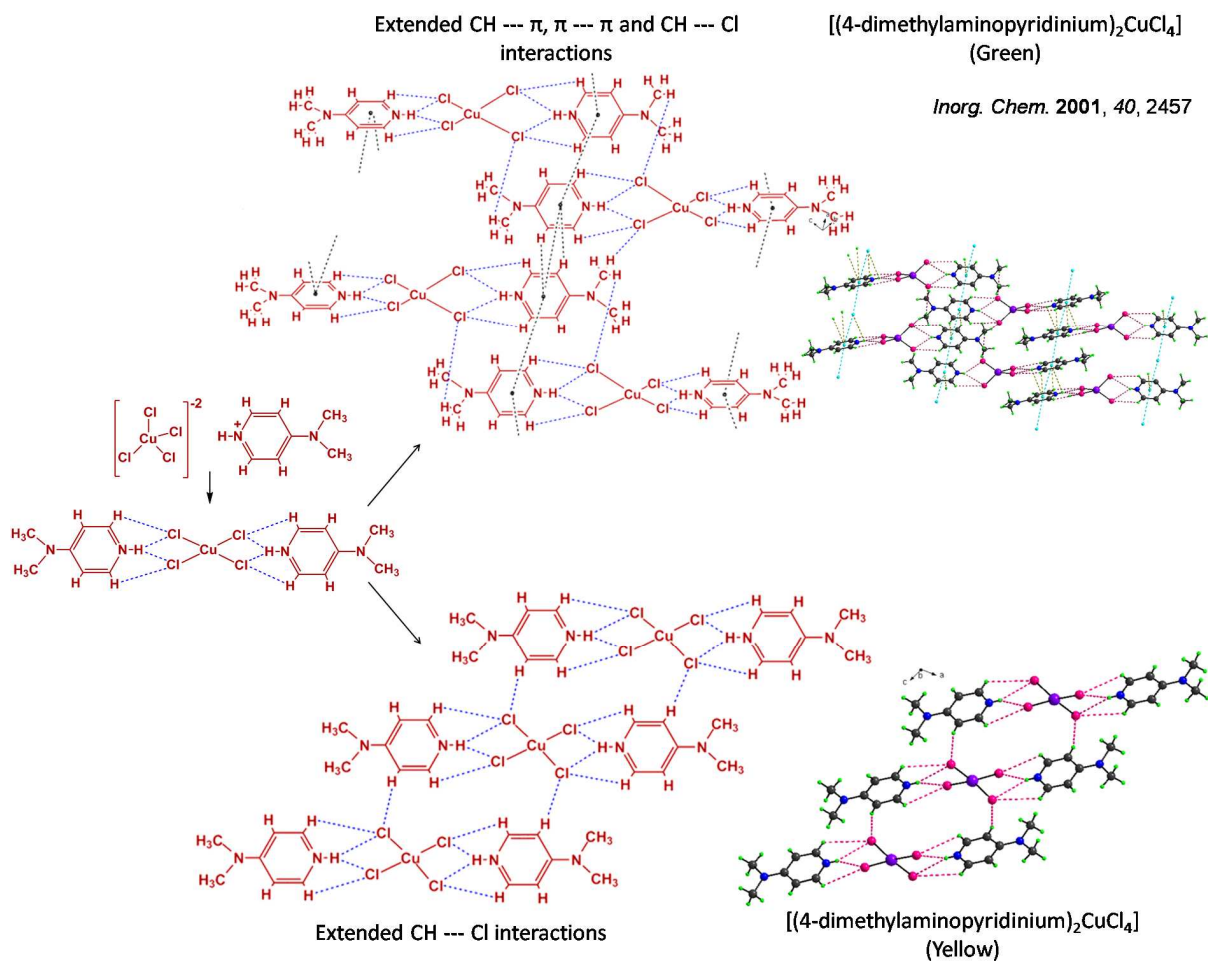


Fig. S8. The *tecton* IV, $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_4]^{2-}$ is dianionic and hence occurs with two cationic *tectons* (4-dimethylaminopyridinium). The strongly H-bonded aggregate interact through two competing *supramolecular synthons* ($\pi \cdots \pi$) and CH...Cl leads two polymorphs. [*Inorg. Chem.* **2001**, *40*, 2457]

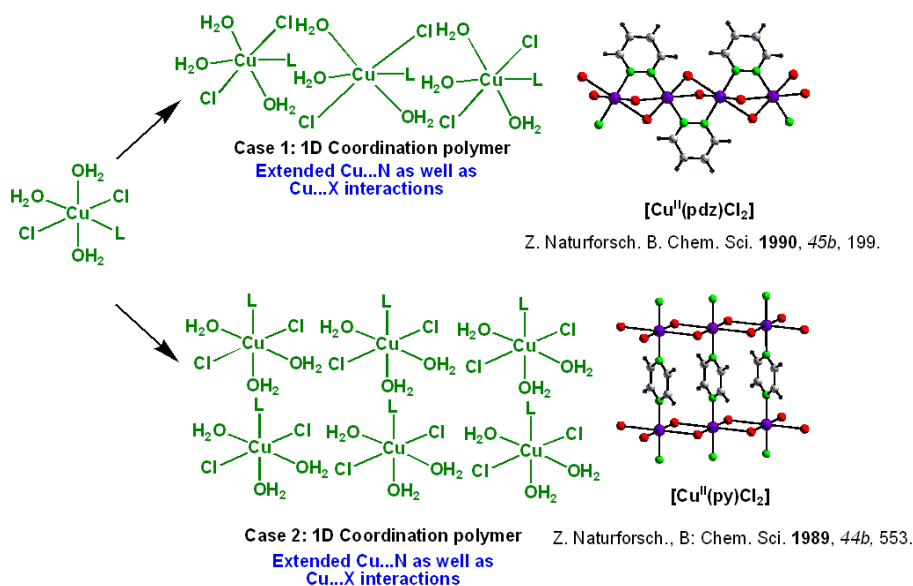


Fig. S9. Here the *tecton* is a copper complex with the appropriate ligand (pyridazine or pyrazine). The *tecton* induces nucleation to favour the formation of bridging –Cu-Cl-Cu- interactions as well as coordination through the second N resulting in 1D coordination polymer. [Z. Naturforsch. B. Chem. Sci. 1990, 45b, 199; Z. Naturforsch. B. Chem. Sci. 1989, 44b, 553].

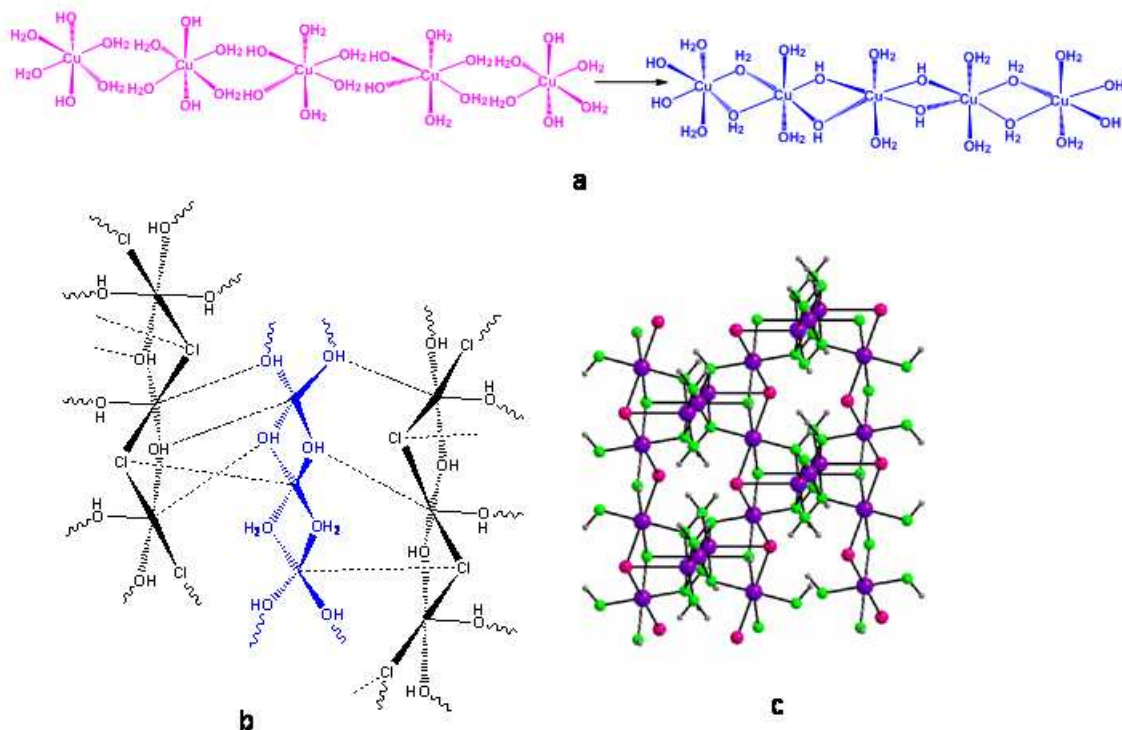


Fig. S10. Retrosynthetic analysis of the crystal structure of Bobkingite, $[\text{Cu}_5(\text{OH})_8\text{Cl}_2(\text{H}_2\text{O})_2]$ shows that the black chains are identical to that of atacamite and its polymorphs (Fig. 3). However, a new chain (blue) perpendicular to the black chains are assembled from *teuton* II but the interaction leads to a chain wherein a repeating trimeric unit (the bridging units are H_2O , OH and OH) is observed. [*Mineral. Mag.* **2002**, *66*, 301].

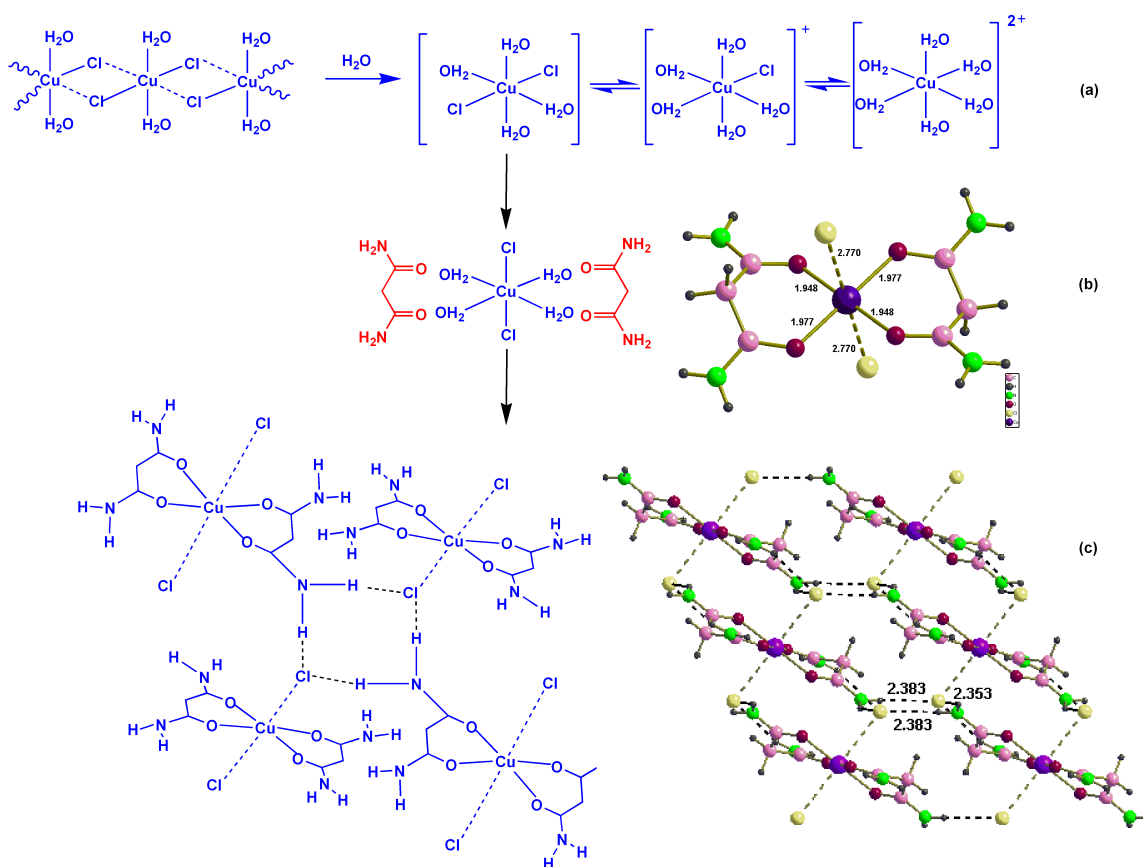


Fig. S11. Self assembly of $[\text{CuCl}_2\text{L}_2]$, L: melonamide

(a) In aqueous solution, the tecton **I**, $[\text{CuCl}_2(\text{H}_2\text{O})_4]$ is directed towards the melonamide through H-bonding. (b) Notice the increase in the bond distances of $\text{Cu}\cdots\text{Cl}$. This is due to the extra stabilization provided by the bidentate ligands. (c) Driving force for the solid state structure is molecular recognition occurring between four copper complexes (reacting molecular unit) such that two Cl atoms from one pair interacts with two NH_2 groups from another pair forming an octameric H-bonded cluster through $\text{N}\cdots\text{H}\cdots\text{Cl}$ [*Acta Cryst. E* **2006**, E62, m3076].

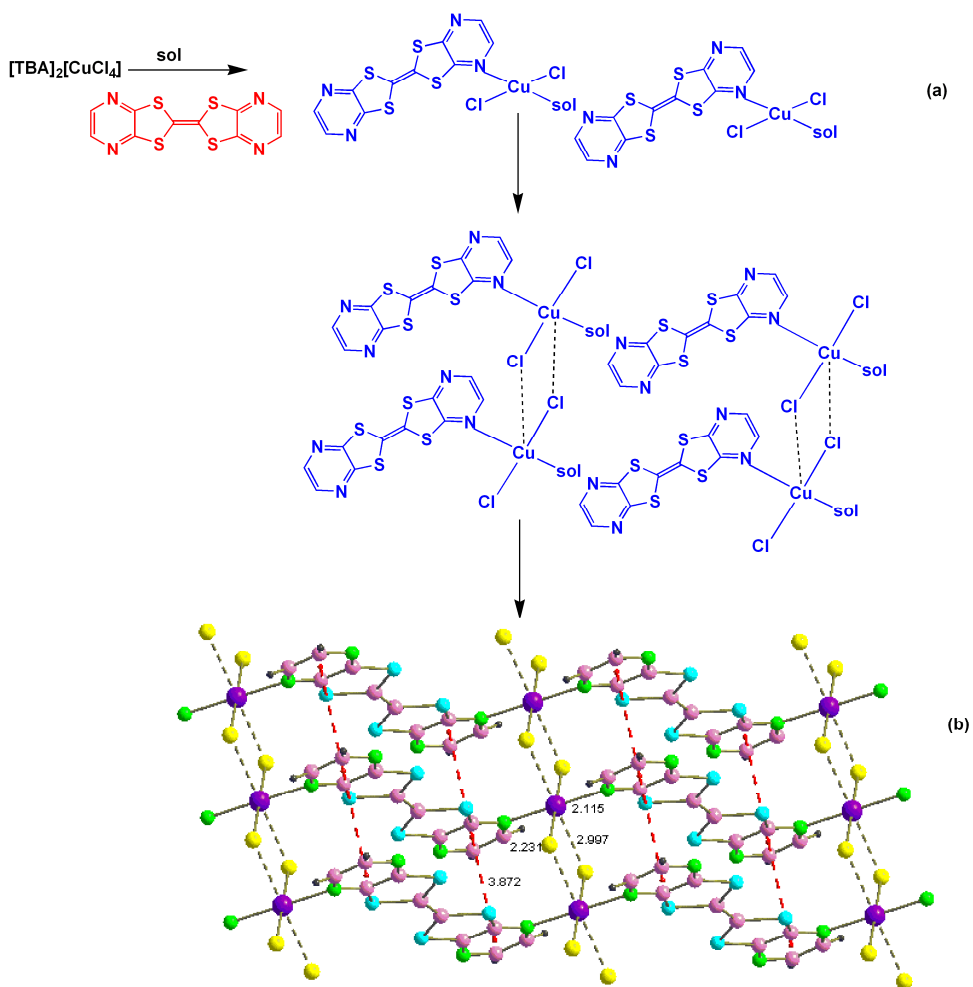


Fig. S12. Self assembly of $[\text{CuCl}_2\text{L}]$, L: [bis(pyrazino)-Tetrathiafulvalene]

(a) Here, chelation leads to $[\text{CuCl}_2\text{L}(\text{sol})]$; the assembly of such units are strongly influenced by the possibility of extended Cu-N linkages to form chains; also it favors Cu..Cl and $\pi.. \pi$ interactions such that the ligands lie one over the other. (b) Crystal structure to match our scheme [*Inorg. Chem.* **2006**, *45*, 7575].

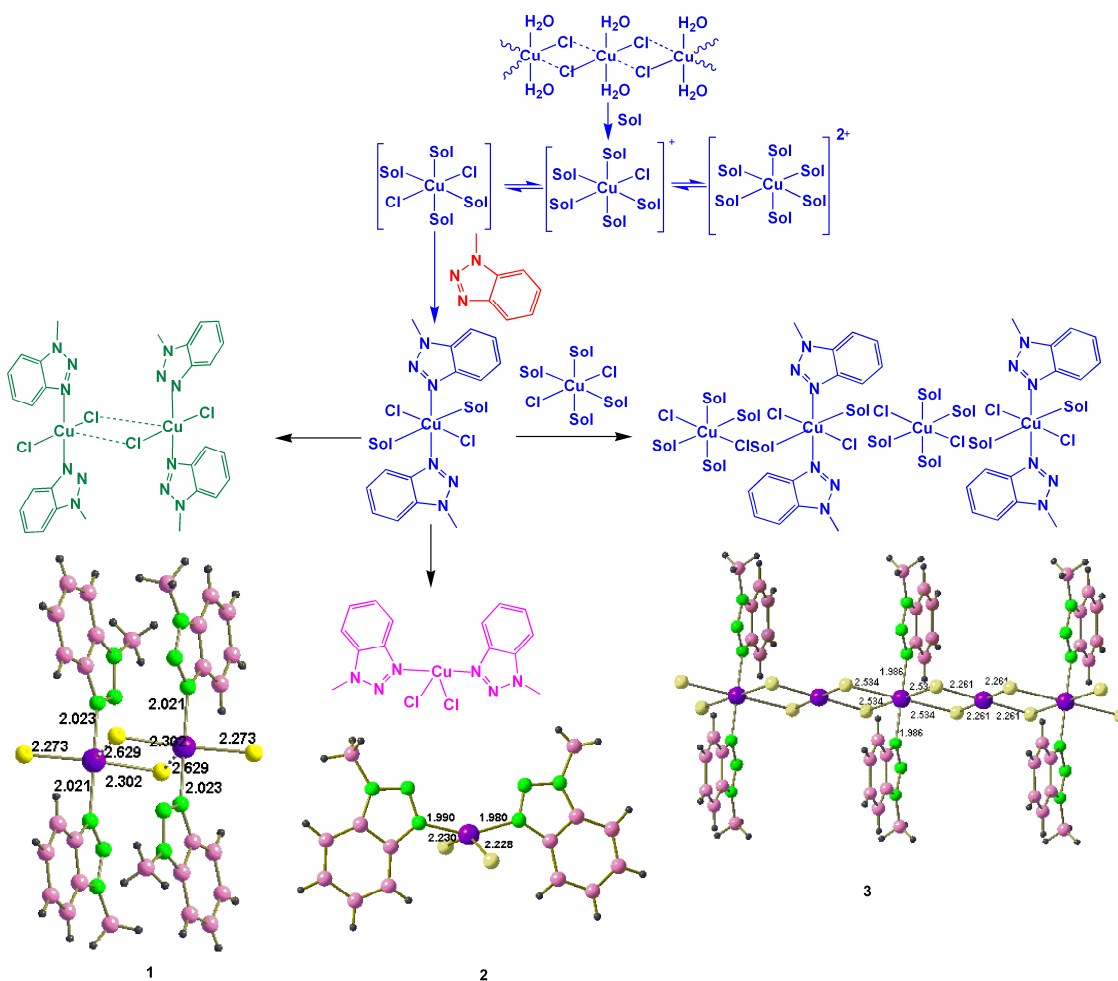


Fig. S13. Self assembly of $[\text{Cu}_2\text{Cl}_4\text{L}_4]$ and $[\text{CuCl}_2\text{L}_2]$, L: Methylbenzotriazole

Copper forms the *bis* complex with ligand, $[\text{CuCl}_2\text{L}_2(\text{sol})_2]$. The three crystals **1**, **2** and **3** are essentially manifestations of these *tectons* primarily through $\text{Cu}\dots\text{Cl}$ and subsequently other non bonding interactions. In **1**, the dimeric unit is formed due to strong $\text{Cu}\dots\text{Cl}$ bond (both Cl interact strongly with the other copper) and further assembles through $\text{CH}\dots\text{Cl}$. **2** contains only monomeric units and aggregate through $\text{CH}\dots\text{Cl}$. In **3**, the assembly occurs between two different copper *tectons*, i.e., $[\text{CuCl}_2\text{L}_2(\text{sol})_2]$ and $[\text{CuCl}_2(\text{sol})_4]$. Here again, $\text{Cu}\dots\text{Cl}$ is responsible for the assembly. In **3**, the solvent does not appear in the final solid as it does not provide additional stability to the system [*Inorg. Chim. Acta* **2005**, 358, 565].

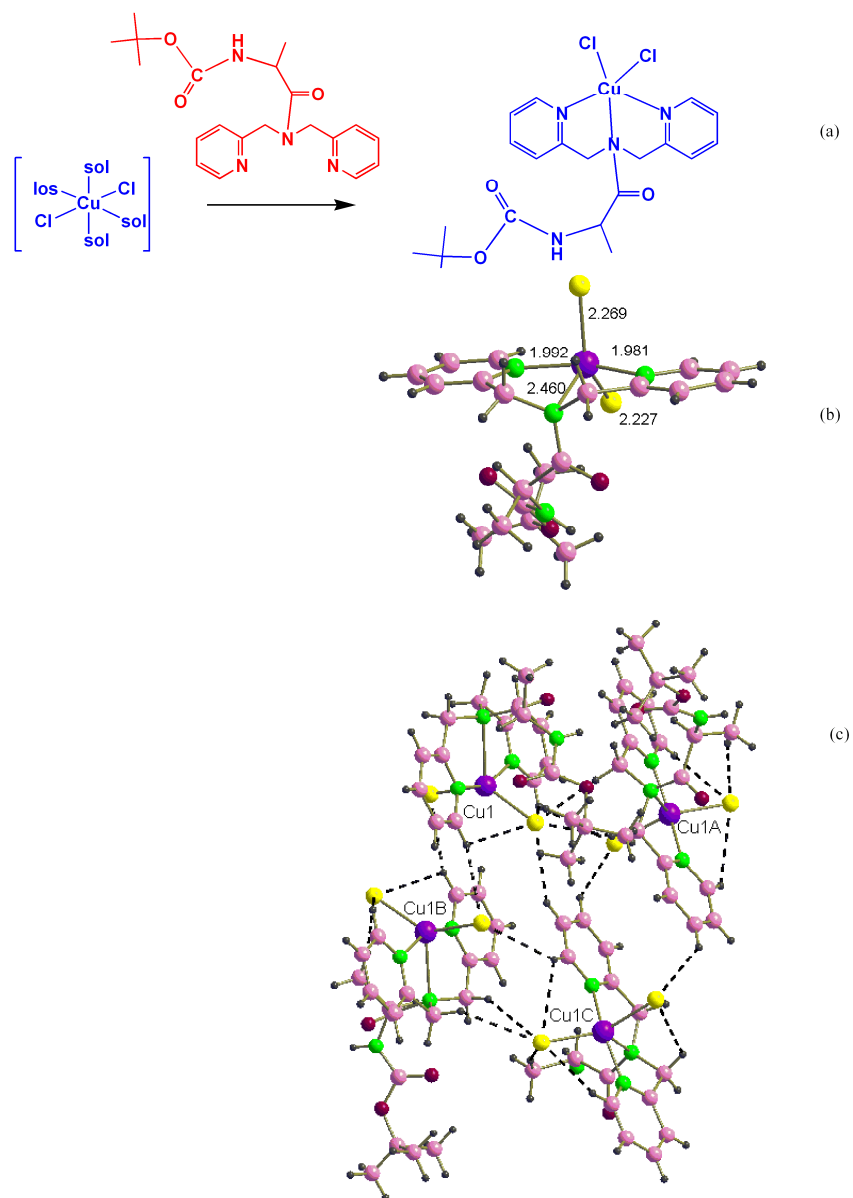


Fig. S14. Self assembly of $[\text{CuCl}_2\text{L}]$, **L**: (Boc-Ala-bpa); Boc = t-butyloxycarbonyl, Ala: Alanine, bpa = N,N-bis(pyridin-2-ylmethyl) amine).

(a) The *tecton* is a tridentate complex of copper. (b) A structure of the discrete complex. (c) CH...Cl interactions are the main forces in the assembly of the molecules in the solid state but the complexity of the ligand makes the interaction and hence geometry around the four asymmetrical copper very different. Here, the solvent molecules occur as space filling units [*Angew. Chem. Int. Ed.* **2002**, *41*, 3386].