

Supplemental Material for:

**Assembly of Copper–Tetrazole Frameworks with Role-Changeable Keggin Clusters: Syntheses, Structures, Solvent-Dependent Luminescence and Electrochemistry Properties**

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**Scheme S1** View of the coordination modes of HL ligands in compound **2**.

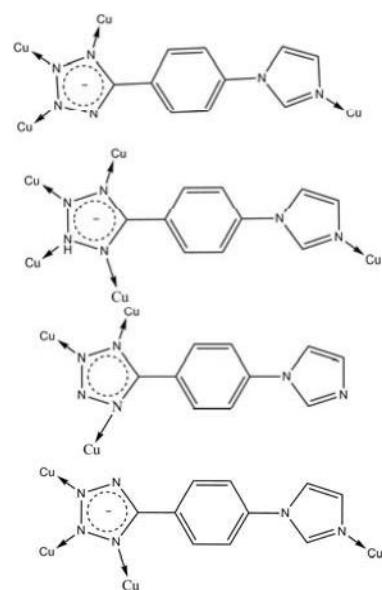


Fig. S1 (a) View of the 2D layers linked into a 3D framework through supramolecular interactions.  
(b) View of the compacted aromatic stacking interactions in compound **1**. All hydrogen atoms are omitted for clarity.

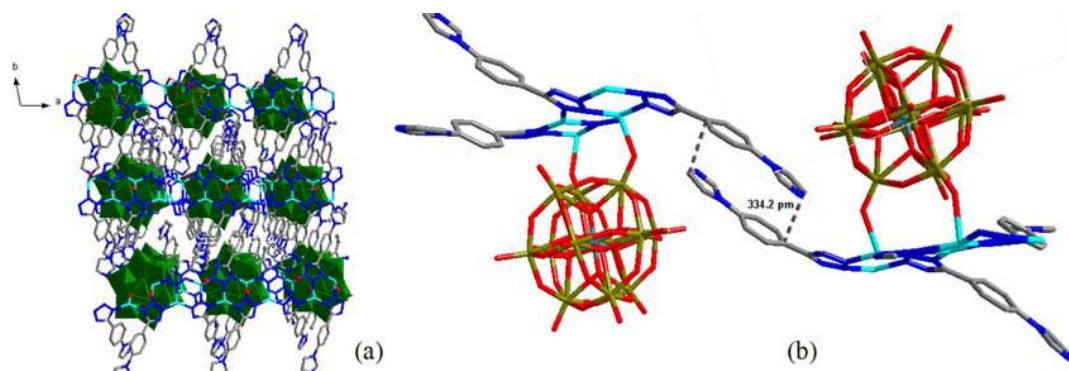


Fig. S2 View of the variable coordination modes of HL ligands in compound **2**.

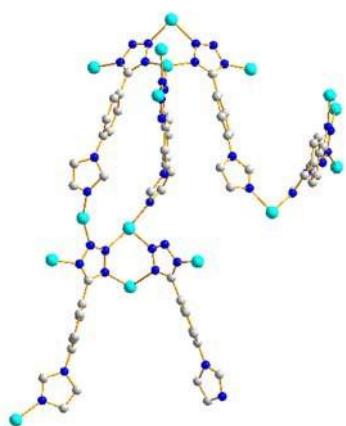


Fig. S3 View of  $\{\text{Cu}_4\}^{4+}$  cluster in compound **2**.

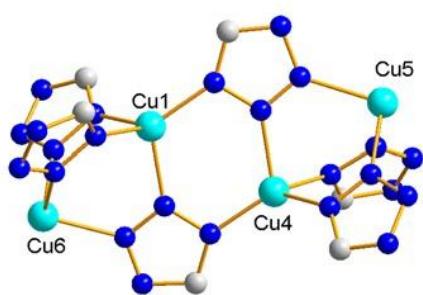


Fig. S4 IR spectra of compounds **1** and **2**.

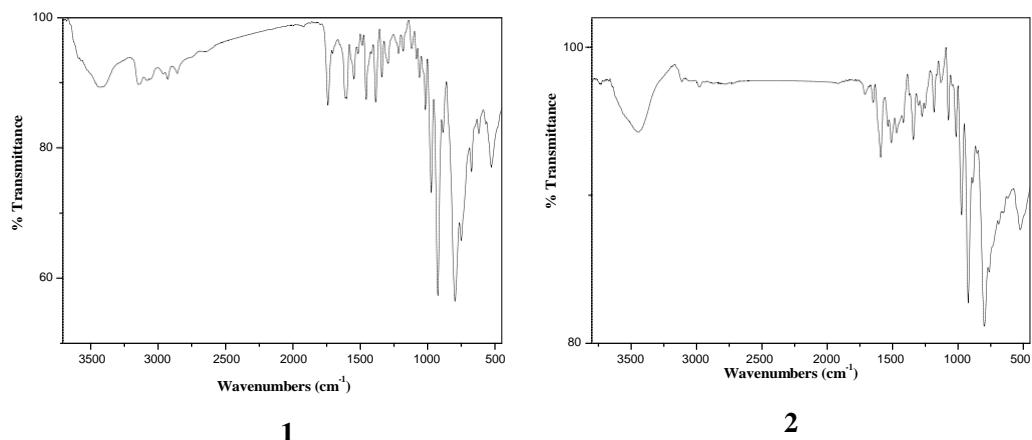


Fig. S5 TG curves of compounds **1** and **2**.

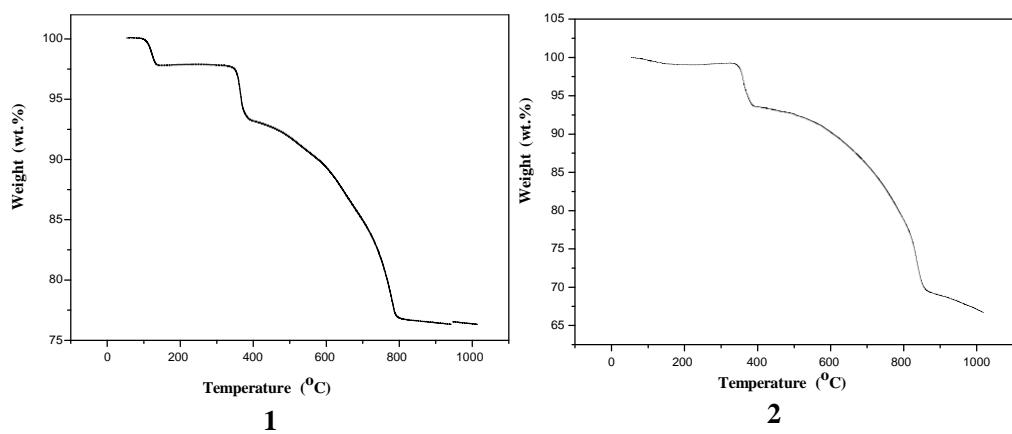


Fig. S6 PXRD patterns of compounds **1** and **2**: a) simulated from single-crystal data, b) as-synthesized sample, (c) heated at 180 °C for 12 h.

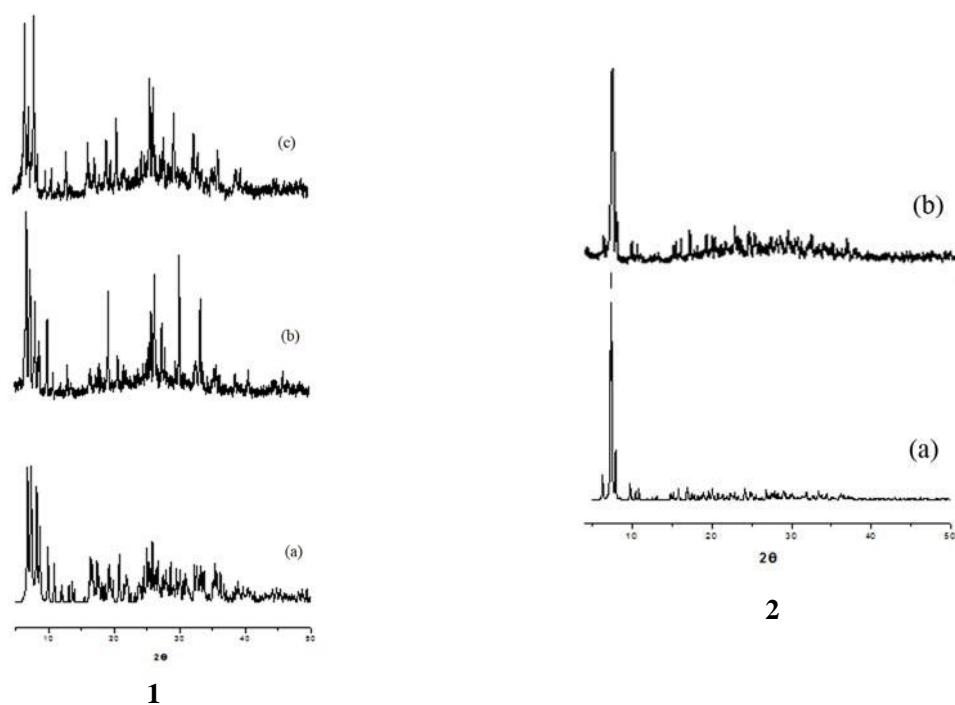


Fig. S7 Solid-state emission spectra of HL ligand, compounds **1** and **2**.

